

Vector Correlations in the Inelastic Scattering of NO(X) with Atoms and Diatoms.

A thesis submitted for the degree of Doctor of Philosophy



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Abstract

This thesis presents a joint experimental and theoretical study of the state-to-state resolved rotationally inelastic scattering of NO(X) with atoms and homonuclear diatoms. Emphasis is placed on measuring the correlations between the vectors which describe the system: $\mathbf{k}$ and $\mathbf{k}'$ the initial and final relative velocities, respectively, $\mathbf{r}$ the initial NO bond axis orientation, and j' the final rotational angular momentum of NO. Experimentally, the initial f Λ -doublet state of NO(X) is selected using a Hexapole state selector, and the scattered NO detected using $(1 + 1')$ REMPI.

In the first part of this thesis the $\mathbf{k} - \mathbf{k}'$ correlation in the scattering of NO(X) with O₂(X) is presented. A modified onion peeling algorithm is used to extract the (partially) pair correlated angular distributions from the experimental ion images, as well as the relative populations of O₂ rotational states populated during scattering. Strong similarities are observed between the scattering of NO with Ar and O₂.

The second part of this thesis focuses on steric effects (the $\mathbf{r} - \mathbf{k} - \mathbf{k}'$ correlation); the initial orientation of the NO bond axis is controlled using a static electric field, such that the collision partner approaches either the ‘ends’ or the ‘sides’ of the NO molecule. A new quantum mechanical theory is presented to describe the scattering of a symmetric top molecule in the presence of an arbitrarily directed electric field. The scattering of NO(X) with Ar at a collision energy of $E_{\text{coll}} = 651 \text{ cm}^{-1}$ is presented for ‘end-on’ and ‘side-on’ scattering on the spin-orbit changing and conserving manifolds, respectively. In both cases good agreement with full quantum mechanical calculations is observed. Scattering resulting in only weak deflection is shown to be very sensitive to the orientation of the NO bond axis prior to collision, and is maximised for collisions at the ‘side’ of the molecule. The integral steric asymmetry for scattering of NO with N₂(X) and O₂(X) is also presented, and information about the potential energy surfaces for such interactions inferred.

Publications

1. A new perspective: imaging the stereochemistry of molecular collisions.
F. J. Aoiz, M. Brouard, S. D. S. Gordon, B. Nichols, S. Stolte and V. Walpole, *Phys. Chem. Chem. Phys.*, 2015, **17**, 30210.
2. Integral steric asymmetry in the inelastic scattering of NO($X^2\Pi$).
M. Brouard, S. D. S. Gordon, A. Hackett Boyle, C. G. Heid, B. Nichols, V. Walpole, F. J. Aoiz and S. Stolte, *J. Chem. Phys.*, 2017, **146**, 14302.
3. Angular distributions for the inelastic scattering of NO($X^2\Pi$) with O₂($X^3\Sigma_g^-$).
M. Brouard, S. D. S. Gordon, B. Nichols, V. Walpole, F. J. Aoiz and S. Stolte, *J. Chem. Phys.*, 2017, **146**, 204304.

Future Publications

1. Differential steric effects in the inelastic scattering of NO($X^2\Pi$) + Ar: spin-orbit changing transitions.
M. Brouard, S. D. S. Gordon, B. Nichols, V. Walpole, F. J. Aoiz and S. Stolte
2. Side-impact collisions of Ar with NO.
C. G. Heid*, V. Walpole*, M. Brouard, F. J. Aoiz, and P. G. Jambrina
3. Diffraction oscillations in the bond orientation resolved inelastic scattering of NO(X).
M. Brouard, C. G. Heid, V. Walpole, F. J. Aoiz and P. G. Jambrina
4. Integral steric effects in the inelastic scattering of NO(X) with diatomics.
M. Brouard, S. D. S. Gordon, C. G. Heid, V. Walpole, and F. J. Aoiz

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List of Abbreviations

Many abbreviations are used throughout this thesis, they are included here for reference.

CC QM	Close coupled quantum mechanics
CCD	Charge coupled device
CIA	Collision induced alignment
CIO	Collision induced orientation
CMB	Crossed molecular beam
CoM	Center-of-mass
DCS	Differential cross section
FWHM	Full width at half maximum
HS	Hard shell
ICS	Integral cross section
LAB Frame	The laboratory frame
LIF	Laser induced fluorescence
MCP	Microchannel plate
MS	Mass spectrometry
PCS	Partial cross section
PDDCS	Polarisation dependent differential cross section
PDF	Probability density function
PEISI	Post extraction inversion slice imaging
PEM	Photoelastic modulator
PES	Potential energy surface
QCT	Quasi-classical trajectory
REMPI	Resonance enhanced multi-photon ionisation
RET	Rotational energy transfer
TOF	Time-of-flight
VMI	Velocity map imaging

Chapter 1

Introduction

Bernstein, Hershbach, and Levine once compared chemistry to an impressionist painting [1]:

“Chemistry is like an impressionist painting. If we view it from too close, all we see is puzzling detail in myriad dabs of paint. If we look from too far, all we see is a shimmering blur. At the right distance wondrous and lovely things appear.”

For the synthetic chemist, resolving the mechanism of a reaction at the level of single collisions is not particularly useful; in the bulk these processes will be averaged over many degrees of freedom and will not necessarily provide further insight into the reaction. At the laboratory scale, using suitable approximations often leads to simple intuitive models, which still accurately predict experimental observations. In such cases, knowledge of the elementary reactions and their kinetics is probably sufficient. Reaction dynamics aims to view chemical processes at just the ‘right distance’: with resolution of dynamic interactions at the molecular scale, whether in the gas phase (as in this thesis), at surfaces [2, 3] or in solution [4–6].

1.1 Molecular Collisions

Consider a bimolecular collision between two species, for which there are three possible outcomes: reactive scattering in which the reagents and products are chemically different, inelastic scattering in which the species undergo a change in internal quantum state, or elastic scattering in which the species simply recoil. Whilst reactive scattering is probably the most familiar to the chemist, both inelastic and elastic scattering are important pathways in the dynamics of many familiar processes. For example, in the atmosphere both rotationally and

vibrationally inelastic collisions compete with reactive and radiative processes, as well as electronic quenching [7–9]. Rotationally and vibrationally inelastic collisions are also major pathways for the return of non-equilibrium populations to their Boltzmann-like distributions following a reaction or photochemical event [10–12]. In this thesis the rotationally inelastic scattering of NO(X) with the rare gases and the homonuclear diatomics, N₂ and O₂, will be investigated.

To fully resolve the dynamics of scattering between two molecules, it is necessary to follow the evolution of a system from one specific state to another. This requires the selection of a single internal quantum state of each reagent, as well as a description of their initial state in terms of vector properties; measurement of a single quantum state of the products, and any vector properties which define them are then required. Whilst measurements which are not completely state-to-state resolved do not preclude inference of the dynamics of a process, observables are averaged over any undefined degrees of freedom, and extraction of meaningful mechanisms is certainly more difficult.

Whilst there is no doubt that many chemically interesting processes involve (sometimes large) polyatomic species, such systems are not ideal for studying reaction dynamics. Many such molecules possess a large number of closely spaced internal states, as well as a number of vector properties which grow with the size of the system. Consequently, complete state-to-state resolved experiments have been restricted to relatively small systems; the simplest of which is the collision between a diatom and an atom.

1.1.1 The Simplest System: Atom + Diatom

Since the focus of this thesis is rotationally inelastic scattering, discussion will focus on collisions in which the reactants and products are chemically identical (albeit in different quantum states). A similar type of discussion is of course possible for reactive scattering, however it is somewhat complicated by the chemically different reactants and products. Figure 1.1 shows a cartoon of the inelastic collision between an atom and a diatom. In a full state-to-state resolved process the diatom has a well defined initial quantum state, for example

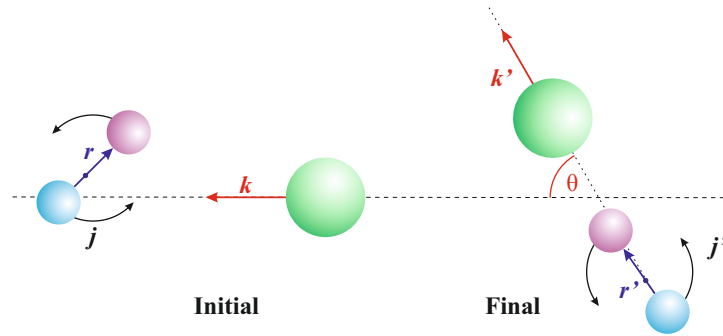


Figure 1.1: Cartoon showing the vectors used to describe a diatom-atom collision. $\mathbf{k}$ and $\mathbf{k}'$ are the initial and final relative velocity vectors (the angle, θ , between them is known as the scattering angle), $\mathbf{r}$ and $\mathbf{r}'$ are the initial and final bond axis orientations of the diatom, and $\mathbf{j}$ and $\mathbf{j}'$ are the initial and final rotational angular momenta of the diatom.

in this thesis $\text{NO}(X^2\Pi, j = 0.5, v = 0, \Omega = 0.5, \varepsilon = -1, f)$, and a well defined quantum state is resolved after the collision, $\text{NO}(X^2\Pi, j', v' = 0, \Omega', \varepsilon')$.^{*} Note that whilst the collision is rotationally inelastic, it is vibrationally and electronically elastic.

As well as these scalar quantities, a number of vector quantities describe the system: $\mathbf{k}$ and $\mathbf{k}'$ the initial and final relative velocities, $\mathbf{r}$ and $\mathbf{r}'$ the initial and final bond axis orientations, and $\mathbf{j}$ and $\mathbf{j}'$ the initial and final rotational angular momenta. The convention in which initial states are unprimed and final states are primed will be used throughout this thesis. The orientation of the bond axis and the rotational angular momentum are not independently distributed; for a well defined rotational angular momentum, which determines both the sense and plane of the diatoms rotation, the direction along which the internuclear axis may lie is also defined. Consequently, the system may be defined by four vectors, $\mathbf{k} - \mathbf{r} - \mathbf{k}' - \mathbf{r}'$ or $\mathbf{k} - \mathbf{j} - \mathbf{k}' - \mathbf{j}'$, although the choice between $\mathbf{j}/\mathbf{r}$ and $\mathbf{j}'/\mathbf{r}'$ depends on both the system of interest and the experimental apparatus used to measure observables [13].

Whilst the atom in inelastic diatom-atom scattering is typically (but not exclusively) a rare gas, a wide number of diatoms have been investigated [14–24]. Collisions of open shell species, such as $\text{NO}(\text{X})$ [25–40] and $\text{OH}(\text{X})$ [41–46], have been particularly intensely studied, due in part to their importance in atmospheric, astrophysical, and combustion chemistry.[†] The relative non-reactivity of these species, in spite of their radical nature, has meant that they are convenient

^{*}The notation used here will be outlined in Chapter 2.

[†]It is important to note that some of these studies were not resolved in the initial Λ -doublet of the diatom (*i.e.* $\varepsilon = \pm 1$).

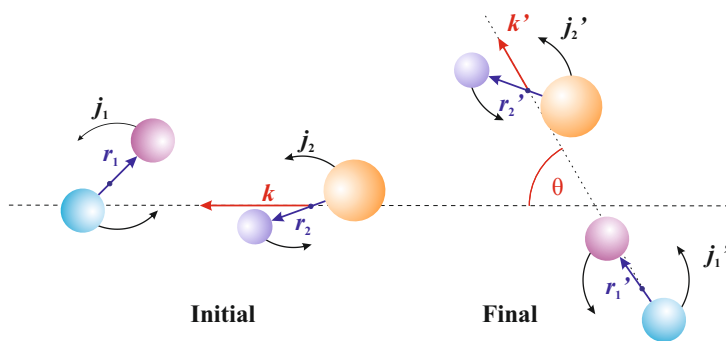


Figure 1.2: Cartoon showing the vectors used to describe a diatom-diatom collision. k and k' are the initial and final relative velocity vectors (the angle, θ , between them is known as the scattering angle), r_n and r'_n are the initial and final bond axis orientation, and j_n and j'_n are the initial and final rotational angular momenta. $n = 1, 2$ is used to differentiate between the two diatomic species.

to work with experimentally, and they have become ‘prototypes’ for the inelastic scattering of open shell molecules. It is worth noting that (electronic) excited states [47–52] and reactive [53–55] scattering have also been studied.

1.1.2 Towards Larger Systems: Diatom + Diatom

Addition of just a single atom to the diatom-atom system described in Section 1.1.1 increases the complexity of the scattering system significantly. Figure 1.2 shows a cartoon of the inelastic collision between two diatoms. To fully resolve the state-to-state scattering process there are now two initial and two final quantum states to consider, and the concept of pair-correlated scattering becomes important. There is also an additional initial and final vector to describe the direction of the second diatoms internuclear axis (or rotational angular momentum).

The majority of diatom-diatom scattering studies are state selective in only a single diatom [33, 46, 52, 56–67], and any degrees of freedom related to the second diatom are averaged across (*i.e.* no pair-correlation is recovered). There have been a few studies in which both diatoms are prepared state-selectively, although these have typically been unresolved in the co-product; for example, Kriste *et al.* reported the inelastic scattering of $\text{NO}(X^2\Pi, j = 0.5, v = 0, \Omega = 0.5, \epsilon = -1, f)$ with $\text{OH}(X^2\Pi, j = 1.5, v = 0, \Omega = 1.5, \epsilon = -1, f)$, resolved in only the final state of OH [68]. Recently, the group of van de Meeraker [69, 70] were able to completely resolve

the product pair correlations in the scattering of $\text{NO}(X^2\Pi, j_{\text{NO}} = 0.5, \Omega = 0.5, \varepsilon = -1, f)$ and $\text{O}_2(X^3\Sigma_g^-, N_{\text{O}_2} = 1)$ at collision energies of $E_{\text{coll}} = 160\text{cm}^{-1}$ and 480cm^{-1} . The (partially) pair-correlated inelastic scattering of $\text{NO}(X)$ with $\text{O}_2(X)$ at a collision energy of $E_{\text{coll}} = 550\text{cm}^{-1}$ will be investigated in Chapter 4.

1.2 Stereodynamics and Vector Correlations

Whilst a state-to-state resolved experiment allows insight into how the initial quantum state of the reagents affects the product quantum state, these properties are scalar and have only magnitude. The field of stereodynamics [1] sets out to understand the dependence of scattering processes on the polarisation of the vector properties of the system. Here, the term *polarisation* simply implies an anisotropic distribution of a vector property with respect to some axis or plane of reference [13]. We will return to detailed descriptions of these polarisations throughout this thesis; in terms of the final rotational angular momentum in Chapter 2, and the initial internuclear axis in Chapter 5. Out of necessity, the ‘language’ of stereodynamics is vector correlations [1, 71], which quantify the preferred relationships between two (or more) vector properties. In the simplest case, this corresponds to quantifying the angle between two vectors, although the situation becomes more complex as the number of correlated vectors increases [71].

For the diatom-atom system discussed in Section 1.1.1, the system is completely defined by a four vector correlation: $\mathbf{r} - \mathbf{k} - \mathbf{k}' - \mathbf{j}'$. Notice here that $\mathbf{r}$ and $\mathbf{j}'$ are used rather than $\mathbf{j}$ and $\mathbf{r}'$. This arises in part since (currently) only the $\mathbf{j}'$ vector may be directly observed, however, schemes exist that allow the specification of both $\mathbf{r}$ and $\mathbf{j}$. Whilst it is often more intuitive to consider the direction of the internuclear axis rather than the rotational angular momentum, the two vectors are not independently distributed and consequently one may, at least in principle, be inferred from the other.

Figure 1.3 shows the ‘hierarchy of vector correlations’ [72], with the complete four vector correlation at the top. Importantly, a vector whose polarisation is not observed is equivalent to

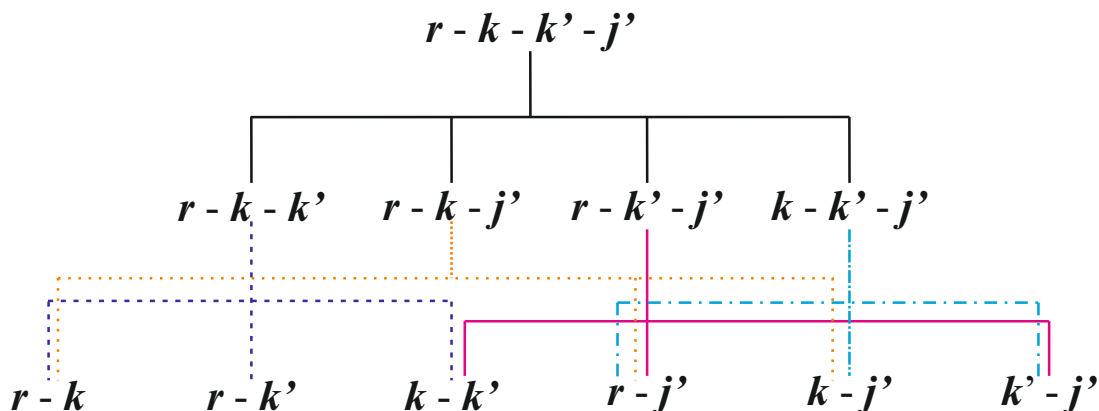


Figure 1.3: Hierarchy of vector correlations for the collision of a diatom and an atom. k and k' are the initial and final relative velocities, respectively, r describes the initial direction of the internuclear axis of the diatom, and j' is the final rotational angular momentum. The lines indicate how lower order correlations (bottom) represent special cases of higher order correlations (top). Adapted from Barnwell *et al.* [72].

a vector that is unpolarised [73, 74] and integration over all directions of the various vectors generates the lower order correlations in the middle (three vectors), and bottom (two vectors) of the hierarchy. Take, for example, the three vector $r - k - k'$ correlation, which describes the angular scattering distribution as a function of initial bond axis orientation (discussed in Chapters 6 through 8): integration over all directions of k' and r will result in the two vector $r - k$ and $k - k'$ correlations, respectively. Whilst, ultimately, all of the information is contained in the three vector correlation, it can still be insightful to consider different aspects of the collision separately, interrogating mechanisms which may (or may not) arise independently of one another.

Probably the most studied vector correlation in fully state-to-state resolved diatom-atom scattering is the two vector $k - k'$ correlation [21, 26, 39, 40, 42, 51, 75], which describes the angular dependence of the scattering cross section as a function of the angle, θ , between the two vectors. Often known as the differential cross section (DCS), this correlation provides extensive mechanistic information about the collision process. The presence or absence of certain features in the DCS may be used to infer information about different regions of the potential energy surface which governs collisions [15, 19, 76–78]: for example, ℓ -type rainbows [79, 80] interrogate the attractive part of the potential, whilst rotational (or orientational) rainbows [32, 75, 80, 81] provide information about anisotropy in the potential.

In Chapter 4, the angular scattering distributions for the collisions of NO(X) with O₂(X) will be investigated.

More recent work has focused on studies of the product rotational polarisation, the three vector $\mathbf{k} - \mathbf{k}' - \mathbf{j}'$ correlation; measuring the sense [82–84] or plane [23, 51, 52, 85–88] of rotation after the collision processes. The $\mathbf{j} - \mathbf{j}'$ correlation, sometimes referred to as the ‘rotational tilt’, has also been extensively investigated *via* collisional depolarisation studies [44, 47, 48, 50, 89].

The steric preferences of diatom-atom collisions have also been studied; that is the effect of initial bond axis or angular momentum polarisation on the product distribution. The majority of studies have focused on a quantity called the *steric asymmetry* [90–95], a measurement closely related to the two vector $\mathbf{r} - \mathbf{k}$ correlation. More recently, the $\mathbf{r} - \mathbf{k} - \mathbf{k}'$ correlation has been studied for the spin-orbit conserving scattering of NO(X) with Ar [96, 97]. Chapter 6 will discuss the spin-orbit changing collisions of NO(X) with Ar, as well as the steric asymmetry in the scattering of NO(X) with N₂(X) and O₂(X). Previous studies have focused on the ‘end-on’ steric effect, in which the collision partner approaches either ‘end’ of the diatom. Chapter 7 will present the first studies of the $\mathbf{r} - \mathbf{k} - \mathbf{k}'$ correlation in which the collision partner approaches from the ‘side’ of the molecule.

The full four vector correlation, described by Herschbach as the ‘forbidden fruit’ of stereodynamics [98], has remained elusive in diatom-atom scattering; with only a single study by Collins *et al.* [99] on the $\mathbf{j} - \mathbf{k} - \mathbf{k}' - \mathbf{j}'$ correlation in the elastic and inelastic scattering of Li₂ with Ar/Xe. Recent work by Perreault *et al.* [100, 101], has resolved the $\mathbf{j} - \mathbf{k} - \mathbf{k}' - \mathbf{j}'$ correlation in the rotationally inelastic scattering of HD($v = 1, j = 2$) with H₂/D₂.

1.3 Experimental Methods

The discussion in the preceding sections has focused on the desire to probe reactions in a fully state-to-state resolved manner and to measure the correlations between specific initial and final vectors in the system, with the ambition to fully resolve the dynamics of scattering events at the

molecular level. Experimentally, this requires reagent preparation such that reactants are in a single quantum state, and that the initial vectors of the system are defined. During the collision process it is essential that no competing processes occur, and consequently, experiments are generally conducted under moderately high vacuum conditions. Once the collision process has occurred, the scattered products must be state selectively detected in a way that allows determination of the final vectors in the system. Experiments conforming to such rigorous standards are not always trivial.

1.3.1 Reagent Preparation

Sufficient population of a single quantum state may be achieved experimentally *via* several methods:

- **Molecular beam techniques**, which supersonically expand gas into vacuum, lead to cooling of rotational degrees of freedom (as well as a relatively narrow velocity distribution). This can be further enhanced by expansion with a ‘seed gas’ [102, 103] which leads to further collisional cooling of internal states. However, on its own, this does not typically result in a reagent with sufficient quantum state purity.
- **Narrow band-width lasers** may be tuned to a specific ro-vibrational branch of an electronic transition, resulting in selection of a specific electronically [47, 51, 104] or vibrationally [29, 105, 106] excited state. In a recent study, Zare *et al.* have used Stark-induced adiabatic Raman passage (SARP) to affect 100% population transfer from a specific rovibrational level [107, 108], with the possibility of control down to a specific magnetic sub-state [109, 110].
- **Electric and magnetic fields** may be used to selectively guide molecules in a specific initial quantum state into a desired region based on their Stark or Zeeman interaction energies, respectively [111–113]. For molecules which possess a permanent dipole moment this can be achieved with a quadrupole or hexapole state selector [114]. Such a technique has been used for molecules such as OH(X) [115], NO(X) [116, 117],

OCS [118], and ND₃/NH₃(X) [118, 119]. More recently, Stark and Zeeman decelerators have been used to select specific states with purities exceeding 99.9% [111–113]; usefully, the velocity of the selected molecules is tunable and has a narrow distribution.

Several methods may be employed to specify the initial vectors of a system. A crossed molecular beam (CMB) apparatus allow definition of the the initial relative velocity, $\mathbf{k}$, of the system. Whilst the majority of CMB experiments cross beams at right angles [120], there are examples of counterpropagating beams [27, 80, 121–123], merged beams [124, 125], and even beams which allow the relative velocity vector (and consequently the collision energy) to be tuned by varying the angle between them [126–130].

Initial orientation of the bond axis, $\mathbf{r}$, or the rotational angular momentum, $\mathbf{j}$, may also be controlled [71, 111, 131]. Orientation of the bond axis of symmetric top molecules may be achieved by adiabatically guiding molecules from a hexapole (see above) into a homogeneous electric field [114, 132, 133]. This technique has been used extensively to orient the bond axes of molecules such as NO(X) [90, 96, 134] and OH(X) [91, 94] prior to the study of rotationally inelastic scattering. Polarisation of the molecular bond axis may also be achieved by optical methods, due to the interaction between polarised light and the molecule's transition dipole moment; Wang *et al.* [135, 136] have done a series of studies in which an infrared laser was used to pre-align CHD₃ molecules prior to reaction with Cl [137]. Whilst intense laser fields may also be used for the orientation and alignment of molecules, and have found wide applicability more generally [138–141], they have yet to be coupled with a CMB apparatus.

1.3.2 Product Detection

After the collision process it is necessary to state specifically detect the scattered products and any vector properties. Many methods exist to achieve this:

- **Electron Ionisation** (EI) coupled with time-of-flight (ToF) mass spectrometry (MS) may be used for product detection. Whilst EI in itself is not quantum state specific, products in different final states have different final translational energies, and consequently will

arrive at the detector at different times relative to the time at which the ions are formed. [142–145]. An advantage of this method is that all states are resolved in a single measurement, however, to capture products scattering through all angles (*i.e.* to determine k'), it is necessary to employ a rotatable detector.

- **Resonance enhanced multi-photon ionisation (REMPI)** employs a narrow bandwidth laser to state selectively excite products to an electronically excited state, using one or more photons, before ionisation using a further photon(s). The excitation and ionisation steps may be performed using either single or multiple colours; the benefit of two colour REMPI is that the power of the excitation laser may be kept low, avoiding saturation of the transition. A consequence of this is that polarised light may be used in the excitation step, to resolve information about the j' vector [13]. REMPI may be coupled to either TOF (above) or VMI (below) based detection. Many efficient REMPI schemes are available for a wide range of (typically neutral) molecules.
- **Velocity-map [146] Ion Imaging [147] (VMI)** techniques allow the direction of k' to be determined without the need to rotate the detector. Ions, typically produced using a REMPI scheme, are mapped onto a position sensitive detector using a static electric field. Ions with the same (LAB frame) velocity but different (spatial) positions after the collision event are mapped onto the same position on the detector, eliminating blurring caused by the finite volume within which the ions are initially formed [34, 148]. Whilst the entire angular scattering distribution is recorded simultaneously, each quantum state may have to be recorded independently depending on the method of ionisation, unlike for TOF detection. Since its advent, VMI has been used widely in several areas of reaction dynamics, including, but not limited to: inelastic [21, 25, 34, 148–151] and reactive [152–154] scattering, photodissociation [155–158], and Coulomb explosion [159–161].
- **Laser induced fluorescence (LIF)** may also be used to state selectively detect scattered products [162]. The product molecule is optically pumped to an electronic excited state by a laser tuned to a specific ro-vibrational transition, and the fluorescence emitted by

the molecule as it radiates back to the ground state is monitored. LIF may be used to measure integral cross sections (ICSs) [29, 163, 164] as the intensity of the fluorescence is related to the original population of the lower state; differential cross sections may also be determined [28, 165]. The alignment/orientation of j' may be measured in a similar manner to that described for REMPI [166–168].

A nice summary of many of these detection methods is given by Costen *et al.* [169]. Typical detectors for these measurements (aside from LIF) are composed of micro-channel plates (MCPs) coupled to a scintillator screen (such as a phosphor screen); when an ion hits the MCP plate it is amplified as a stream of electrons which impact on the scintillator screen, causing fluorescence. This fluorescence is then recorded (using a CCD camera or similar) and sent to a computer for further analysis.

1.4 Theoretical Methods

By virtue of their size, inelastic collisions in simple atom-diatom systems are well suited to study at the highest levels of theory. Nevertheless, a wide range of models are available: from full *ab initio* potential energy surfaces [170–172] upon which full classical and quantum mechanical calculations may be run, to simple models in which collisions are described in terms of ‘hard-spheres’ [173, 174]. The theoretical methods used in this thesis will be returned to in Chapter 2.

1.4.1 Potential Energy Surfaces

The concept of a potential energy surface (PES), which describes the potential energy landscape over which a system propagates, is central to the field of reaction dynamics. Such PESs are a key link between experiment and theory, describing the potential energy a system experiences as a function of all degrees of freedom. The number of degrees of freedom can sometimes be very large, particularly for polyatomic molecules. However, it is often possible to fix some degrees of freedom to a specific value (or even ignore them all together). For example, the PESs

used in this thesis to describe the scattering of NO(X) with the rare gases are calculated with the NO bond axis fixed at its equilibrium length [175]; this is sufficient in this case, as the NO molecule is in its ground vibrational state ($v = 0$) throughout the collision.[‡]

Ab initio calculation of such PESs rely on the Born-Oppenheimer approximation, in which the motion of electrons is instantaneous on the time scale of nuclear motion [34]. This means that for each nuclear geometry the electrons are considered to be in their lowest energy configuration instantaneously. If the approximation breaks down, then the electrons in the system are no longer in their lowest energy configuration, and motion occurs over many coupled adiabatic surfaces. Scattering of NO(X) and OH(X) with the rare gases has long been thought of as the ‘prototype’ for non-adiabatic effects [34, 111, 178], due to coupling with a low-lying spin-orbit state which results in coupled potential energy surfaces.

1.4.2 Dynamics

Once the PES(s) for a specific system is known, it is possible to perform theoretical calculations over the potential, which may be directly compared with experimental observables. Broadly, there are three distinct treatments of scattering, all of which are calculated by solving the relevant equations of motion: classical, semi-classical and quantum. Whilst classical and quantum mechanical (QM) methods often agree almost quantitatively [87, 88], there are systems and regions of a potential where quantum mechanics dominates [96, 179], for which it is necessary to use full quantum mechanical calculations to describe experimental observations.

Classical calculations provide information that is often mechanistically intuitive. Classically, all variables may be specified, and trajectories propagated over the relevant PES according to the classical equations of motion. Since the outcome of the trajectories depends on both the initial conditions and the region of the PES sampled during propagation, a very large number of trajectories is required to explore all possible mechanisms, from which vector correlations may be extracted. Quantisation of values, using the quasi classical trajectory method (QCT) [77, 180–182], allows comparison with QM and experimental observables.

[‡]The $v = 1$ state lies approximately 1816 cm^{-1} above the $v = 0$ state [176, 177].

Since there is no concept of phase in classical mechanics, no interference effects are observed, similarly tunnelling through barriers is not allowed.

Semi-classical methods [39, 96] are useful to gain further insight into inherently quantum mechanisms. Different classical paths are assigned a semi-classical phase shift, allowing study of interference effects, however, such methods are far from quantitative.

In quantum mechanical methods, particles are described according to their wave function. A scattering-matrix, which transforms the initial wave function into the final wave function, must be determined by solving the differential matrix equations known as the close coupled (CC) equations [183]. The scattering matrix contains all possible information about the system, allowing the calculation of observables. This is the most rigorous theoretical treatment. However, as the number of atoms in the system increases, calculations become computationally difficult. Some of the mechanistic insight gained through QCT calculations is lost in QM calculations. However, comparison between classical and quantum calculations is valuable for identifying features which are completely quantum mechanical in nature, compared to those which have a classical analogue.

1.5 Thesis Outline

The focus of this thesis is the vector correlations which describe the state-to-state resolved rotationally inelastic scattering of NO(X) with atomic (rare gas) and diatomic collision partners. In this chapter some of the motivations of both reaction dynamics and stereodynamics have been discussed, and a general review of experimental and theoretical methods has been given.

Chapter 2 will focus on the theoretical concepts necessary to study the quantum state resolved vector correlations throughout this thesis. Angular momentum coupling schemes for NO(X), N₂(X), and O₂(X) will be discussed, and the potential energy surfaces for the systems of interest presented. The scattering theory used throughout this thesis will be detailed, for both quantum mechanical and quasi classical trajectory methods, including methods for

calculating observables for comparison to experiment. Finally, a discussion of rotational angular momentum polarisation will be given.

In Chapter 3 the experimental apparatus required to measure quantum state resolved vector correlations will be described in detail; hexapole state selection, the crossed molecular beam apparatus, and detection methods will be discussed. The second part of the chapter will focus on the data analysis methods used to extract differential cross sections from the raw experimental data.

The inelastic scattering of NO(X) with O₂(X) will be investigated in Chapter 4. A modified onion peeling method is described which allows the extraction of the angular distribution (related to the $\mathbf{k} - \mathbf{k}'$ correlation) for each fragment pair, $(j'_{\text{NO}}, N'_{\text{O}_2})$, in such a way as to retain the relative population of each N'_{O_2} for a single j'_{NO} state. Analysis of NO(X) scattering with Ar is used as proof of concept. Experimental data are then presented, including both the state-to-state angular distributions and those averaged over the final rotational state of the O₂ molecule. Comparisons between scattering with Ar and O₂ are then given. A sliced imaging scheme is proposed as a method to allow measurement of the full pair-correlations in diatom-diatom scattering with higher resolution.

Chapter 5 will introduce the concept of the steric effect (the $\mathbf{r}/j - \mathbf{k} - \mathbf{k}'$ vector correlation); in the scattering of NO(X) in this thesis this corresponds to the initial orientation of the bond axis, $\mathbf{r}$. Preparation of the bond axis in the laboratory frame will be discussed both theoretically, and in terms of modifications to the experimental apparatus. This will be followed by presentation of the classical and (new) quantum mechanical theory used to calculate the bond orientation resolved polarisation dependent differential cross sections, r -PDDCSs. Finally, the data analysis methods required to extract the r -PDDCSs from the raw experimental data presented in Chapters 6 and 7 are discussed.

The effect of collisions with the ‘end’ of the NO molecule (the z -axis steric effect) is considered in Chapter 6. The first half of the chapter focuses on the integral steric effect in diatom-diatom scattering, where lessons learnt from the effect in diatom-atom scattering are used to infer information about the potentials for NO(X) + N₂(X) and O₂(X). In the second half

of the chapter the differential steric effect in the scattering of NO(X) with Ar on the spin-orbit manifold is presented. Features in the r -PDDCS are rationalised using quantum mechanics, and comparisons between scattering on the spin-orbit conserving and changing manifolds are given.

The effect of collisions with the ‘side’ of the NO molecule (the x -axis steric effect) is investigated for the first time in Chapter 7. The field strength dependence of the r -PDDCSs are presented, and its effect on the experimental data discussed; quantum mechanical and quasi-classical trajectory calculations are then used to rationalise the observed steric effect. Particular note is made of the importance of large impact parameter collisions for scattering in the ‘side-on’ orientation. A detailed comparison between scattering in the ‘end-on’ and ‘side-on’ geometries is given, including discussion of the bond axis orientation required to maximise the DCS. Exquisite control over forwards scattering is shown to be possible by specifying the direction of the orientation field.

The effect of bond axis orientation on the forwards scattered region of the DCS will be considered in more detail in Chapter 8. Here diffraction oscillations are superimposed over the structure in the angular scattering distribution; these features are shown to be extremely sensitive to the initial orientation of the NO bond axis prior to the collision. Quantum mechanical calculations are used to rationalise the strong effect of anisotropy in the potential, particularly for collisions at the ‘side’ of the molecule.

Chapter 9 contains a brief summary of the conclusions reached throughout this thesis.

Chapter 2

Theoretical Concepts

In this chapter the theoretical concepts central to the experiments in this thesis will be outlined, and the methods for theoretical calculations discussed. The structure and angular momenta couplings of the NO(X) (nitric oxide) molecule will be outlined in the first part of this chapter. This will be followed by a description of the potential energy surfaces (PESs) which describe the interaction of NO(X) with the atomic rare gases, as well as with diatomic collision partners; the closed shell N₂(X) molecule and the open shell O₂(X) molecule. The scattering theories used throughout this thesis will then be outlined for both classical and quantum mechanical treatments, including the methods with which observables are determined. Finally, a brief discussion of rotational angular momentum polarisation is given.

2.1 The NO(X) Molecule

In the ground electronic state, the nitric oxide (NO) molecule has a single unpaired electron in an anti-bonding π^* orbital, leading to an open shell molecule with non-zero spin and electronic orbital angular momentum. The ground state electronic configuration of the NO(X) molecule is

$$1\sigma^2 1\sigma^{*2} 2\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2 1\pi^{*1} . \quad (2.1)$$

Due to the presence of the unpaired electron, the NO molecule has electronic orbital angular momentum, $L = 1$, with a projection $\Lambda = \pm 1$ onto the internuclear axis, and spin angular momentum, $S = 1/2$, with a projection $\Sigma = \pm 1/2$ onto the internuclear axis. In its ground electronic state the coupling of the angular momenta in NO (for low and moderate rotational

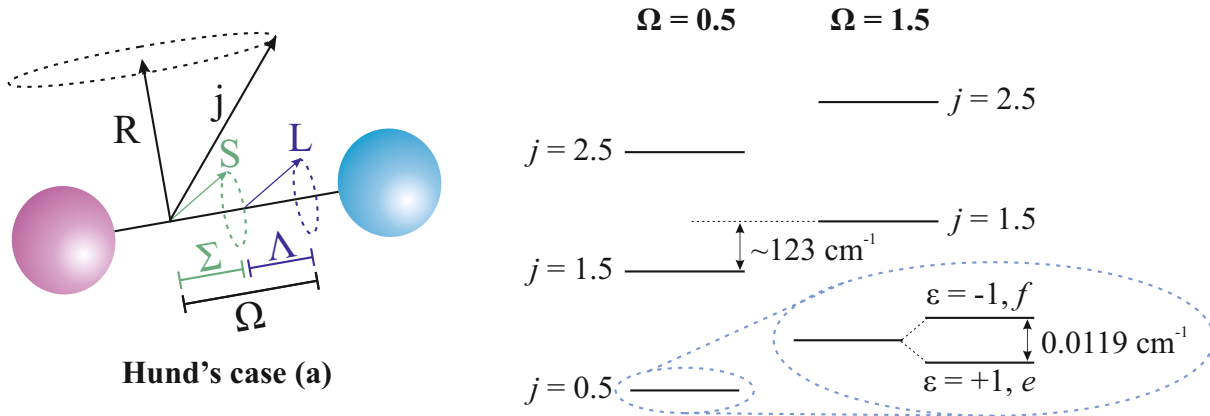


Figure 2.1: Left panel: Diagram of Hund's case (a) vector coupling of angular momenta in NO(X), adapted from Zare [186], as discussed in the text. Right panel: The resulting rotational energy levels of NO(X) for both spin-orbit manifolds ($\Omega = 0.5$ and $\Omega = 1.5$ on the left and right, respectively). The inset shows the Λ -doublet splitting of the energy levels into two states of definite parity, ε .

states) is best described by Hund's case (a) [184, 185], as shown in Figure 2.1. In this case, both the electronic orbital and electron spin angular momenta are strongly coupled to the internuclear axis [186, 187]. Consequently, the angular momentum of the nuclear framework, $\mathbf{R}$, couples to $\Omega = \Lambda + \Sigma$ (the sum of the projections of the electronic and spin angular momenta). This results in a vector, $\mathbf{j}$, the total rotational angular momentum, with a projection onto the internuclear axis, Ω , which can take the absolute values $\bar{\Omega} = 0.5$ ($F_1, {}^2\Pi_{0.5}$) and $\bar{\Omega} = 1.5$ ($F_2, {}^2\Pi_{1.5}$). This gives rise to two spin-orbit manifolds (shown in Figure 2.1), each of which forms a distinct ladder of rotational energy levels, j . $j = 0.5$ is associated only with the $\bar{\Omega} = 0.5$ spin-orbit manifold.

The molecular Hamiltonian (neglecting Λ -doubling) may be expressed as a function of the spin-orbit coupling ($\hat{H}_{\text{SO}}$) and nuclear rotation ($\hat{H}_{\text{rot}}$) [186]

$$\hat{H} = \hat{H}_{\text{SO}} + \hat{H}_{\text{rot}} \quad (2.2a)$$

$$= A_{\text{NO}} (\mathbf{L} \cdot \mathbf{S}) + B_{\text{NO}} (\mathbf{j} - \mathbf{S} - \mathbf{L})^2, \quad (2.2b)$$

where $A_{\text{NO}} = 123.13 \text{ cm}^{-1}$ and $B_{\text{NO}} = 1.6961 \text{ cm}^{-1}$ are the spin-orbit energy and the rotational constant of the NO molecule, respectively [188]. From the molecular Hamiltonian, it may be

shown that each rotational energy level, j , has an associated total rotational energy [186]

$$E(j) = B_{\text{NO}} \left[\left(j - \frac{1}{2} \right) \left(j + \frac{3}{2} \right) \pm \frac{1}{2} X \right], \quad (2.3)$$

where

$$X = \left[4 \left(j + \frac{1}{2} \right)^2 + Y(Y - 4) \right]^{1/2}, \quad (2.4)$$

and

$$Y = \frac{A_{\text{NO}}}{B_{\text{NO}}}. \quad (2.5)$$

The $\pm$ sign in Equation (2.3) distinguishes between the two spin-orbit manifolds, F_1 and F_2 , which are offset by an energy of A_{NO} , as shown in Figure 2.1.

The wave function for each spin-orbit state is proportional to the Wigner rotation matrices [186]

$$|j, m, \Omega\rangle = \sqrt{\frac{2j+1}{4\pi}} D_{m\Omega}^{j*}(\phi, \gamma, 0), \quad (2.6)$$

where m is the projection of j onto a space-fixed z -axis. These $|j, m, \pm\bar{\Omega}\rangle$ states are not eigenfunctions of the molecular Hamiltonian, as they do not possess well defined parity with respect to inversion [189]. Therefore, within a specific spin-orbit manifold the rotational wave function of NO(X) is given by the symmetric or antisymmetric combination of the two possible states according to [186]

$$|j, m, \bar{\Omega}, \varepsilon\rangle = \sqrt{\frac{1}{2}} (|j, m, +\bar{\Omega}\rangle + \varepsilon |j, m, -\bar{\Omega}\rangle), \quad (2.7)$$

which has a well defined parity with respect to inversion. This symmetric and antisymmetric pair of states make up the two components of a Λ -doublet, often referred to by their symmetry index, $\varepsilon = \pm 1$ (and their corresponding symmetry labels $\varepsilon = -1, f$ and $\varepsilon = +1, e$). The parity of a specific rotational state with respect to inversion is given by [190]

$$p = (-1)^{j-\varepsilon/2}. \quad (2.8)$$

The Λ -doublets may also be defined according to the symmetry of the electronic part of the wave function with respect to reflection in the plane of nuclear rotation. The state in which the unpaired electron (residing in the π^* orbital) lies perpendicular or parallel to the plane of rotation is denoted A' or A'' , respectively.

In NO(X), the splitting of the Λ -doublet levels is very small; $\sim 0.0119 \text{ cm}^{-1}$ for $j = 0.5$ in the ground spin-orbit state ($^2\Pi_{0,5}$) [191]. In the limit of Hund's case (a), the Λ -doublet splitting in the $\Omega = 0.5$ spin-orbit manifold increases linearly with j , whilst in the $\Omega = 1.5$ manifold the splitting varies as j^3 (although the absolute value is much smaller than for the $\Omega = 0.5$ state) [186]. For intermediate and high values of j' (> 10.5), Hund's case (a) no longer describes the angular momentum coupling in NO(X), since L and S are no longer strongly coupled to the internuclear axis, and mixing occurs between the two spin-orbit manifolds. As such, the wave function for each spin-orbit manifold may be written according to Hund's case (b) [186, 192]

$$|F_1, j, m, \epsilon\rangle = a|j, m, \bar{\Omega} = 0.5, \epsilon\rangle + b|j, m, \bar{\Omega} = 1.5, \epsilon\rangle \quad (2.9)$$

$$|F_2, j, m, \epsilon\rangle = a|j, m, \bar{\Omega} = 1.5, \epsilon\rangle - b|j, m, \bar{\Omega} = 0.5, \epsilon\rangle, \quad (2.10)$$

where a and b are mixing coefficients

$$a = \sqrt{\frac{X + (Y - 2)}{2X}} \quad (2.11)$$

$$b = \sqrt{\frac{X - (Y - 2)}{2X}}, \quad (2.12)$$

and X and Y are defined in Equations (2.4) and (2.5), respectively. In NO(X) this mixing effect is only small: for $j = 18.5$, $a = 0.970$ and $b = 0.244$ [193]. Since the highest rotational states considered here are typically no higher than $j = 18.5$, the Hund's case (a) coupling scheme will be used to describe NO(X).

2.2 The NO(X) + Rare Gas System

The isolated NO(X) molecule, described in Section 2.1, has a single unpaired electron in the π^* orbital which may lie either parallel or perpendicular to the plane of molecular rotation. Approach of a rare gas atom reduces the overall symmetry of the system from $C_{\infty v}$ to C_s , upon which the only possible symmetry operation is a reflection in the triatomic plane. The two possible electronic states of the system are labelled according to their symmetry; A' if the unpaired electron lies parallel to the triatomic plane and A'' if it lies perpendicular [194]. As such, two potential energy surfaces are required to describe the system. It is important to understand the distinction between the definitions of A' and A'' symmetry discussed here, compared to the case discussed in terms of the isolated NO molecule in Section 2.1.

The inelastic scattering of NO(X) with a rare gas atom occurs simultaneously on both the $V_{A'}$ and $V_{A''}$ surfaces [194]. For theoretical treatments of the scattering of NO(X) with an atom it is convenient to consider scattering on a linear combination of these surfaces, which are commonly referred to as the half-sum (V_{sum}) and half-difference (V_{diff}) potentials,

$$V_{\text{sum}}(R, \gamma) = \frac{1}{2} [V_{A''}(R, \gamma) + V_{A'}(R, \gamma)] = \sum_{\lambda} V_{\lambda 0}(R) d_{00}^{\lambda}(\gamma) , \quad (2.13a)$$

$$V_{\text{diff}}(R, \gamma) = \frac{1}{2} [V_{A''}(R, \gamma) - V_{A'}(R, \gamma)] = \sum_{\lambda} V_{\lambda 2}(R) d_{20}^{\lambda}(\gamma) , \quad (2.13b)$$

where $V_{\lambda m}(R, \gamma)$ are radially dependent expansion coefficients and $d_{mn}^{\lambda}(\gamma)$ are reduced Wigner rotation matrix elements [195]. When the NO(X) molecule is described according to Hund's case (a) spin-orbit conserving collisions can be considered to take place on the V_{sum} potential, whilst spin-orbit changing collisions occur on the V_{diff} potential [194, 196].

The V_{sum} and V_{diff} potential energy surfaces (PES) are shown for the NO(X) + Rg systems in Figure 2.2, where Rg = He [178], Ne [197], Ar [175, 195], Kr [198] and Xe [78]. In each case, the NO(X) bond axis is fixed at its equilibrium length of $1.15 \text{ \AA}$ [185] during the calculation of the potential, and consequently vibrational motion of the NO bond is ignored. The PES is described by two degrees of freedom: the distance between the atom and the centre of mass of

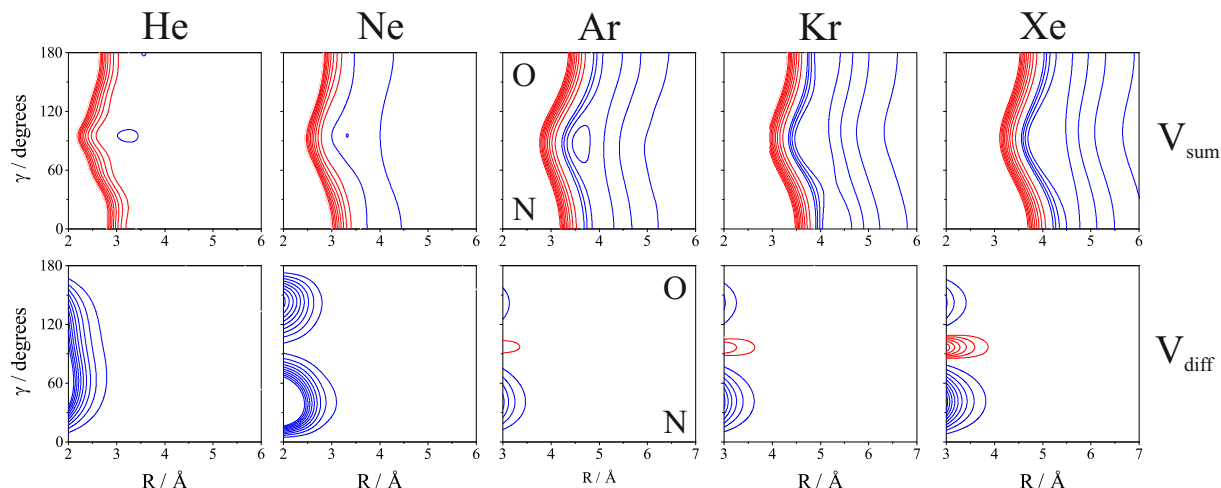


Figure 2.2: V_{sum} (top) and V_{diff} (bottom) potential energy surfaces, in Jacobi coordinates, for NO(X) + Rg, where Rg = He, Ne, Ar, Kr and Xe (from left to right). The attractive (blue) and repulsive (red) contours are separated by 25cm^{-1} and 100cm^{-1} , respectively, for V_{sum} , and 100cm^{-1} and 10cm^{-1} , respectively, for V_{diff} . $\gamma = 0^\circ$ and $\gamma = 180^\circ$ correspond to the Rg-NO and the Rg-ON geometries, respectively.

the diatom, $\mathbf{R}$, and the (Jacobi) angle, γ , between the bond axis, $\mathbf{r}$, and $\mathbf{R}$. The potentials are defined such that $\gamma = 0^\circ$ corresponds to collision of the rare gas atom with the ‘N’-atom of the NO molecule (Rg-NO), whilst $\gamma = 180^\circ$ corresponds to a collision with the ‘O’-atom of the NO molecule (Rg-ON).

The $V_{\text{sum}}(R, \gamma)$ potential for all of the NO(X) + Rg systems (with the exception of He) are weakly attractive for large diatom-atom separations, corresponding to contours shown in blue. Three attractive minima are observed; for the two possible linear arrangements ($\gamma = 0^\circ, 180^\circ$) and for a ‘T-shaped’ geometry ($\gamma \approx 90^\circ$), which is the global minimum. At small $\mathbf{R}$, all of the systems are repulsive (corresponding to contours shown in red). For both the V_{sum} and V_{diff} PESs the extent of the potential is larger in geometries corresponding to a collision with the ‘N-end’ of the NO molecule, *i.e.* both the attractive and repulsive contours extend further from the centre of mass when the system occupies this configuration than in the Rg-ON configuration. The form of the difference potential is markedly different to that of the sum potential. The $V_{\text{diff}}(R, \gamma)$ potential is strongly attractive for all of the systems, with two deep minima: the potential also varies much more as a function of γ than the sum potential. A weak repulsive feature is observed for Ar, Kr and Xe on the side of the NO molecule ($\gamma \approx 90^\circ$).

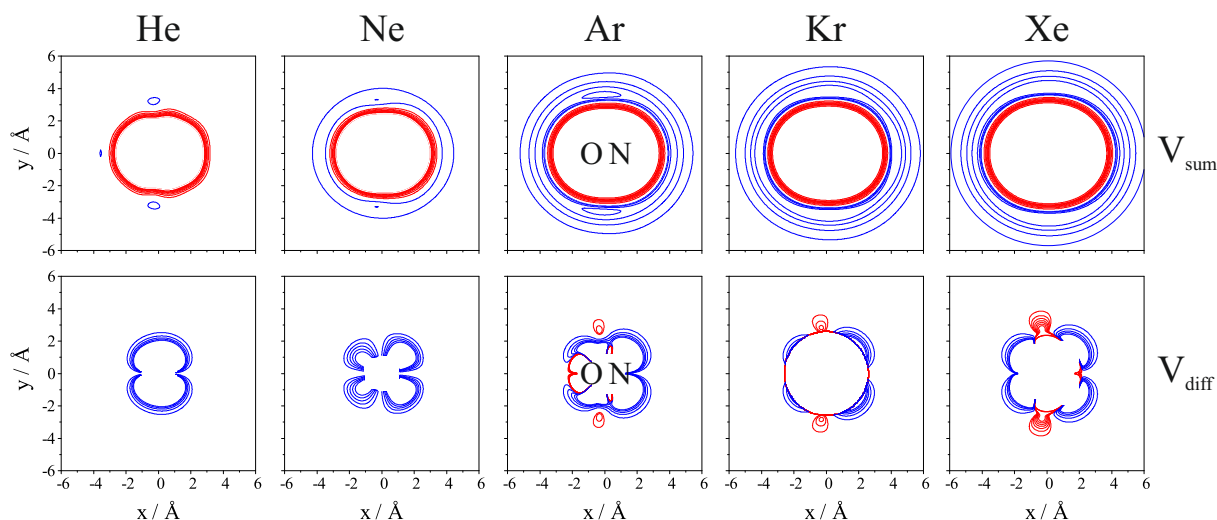


Figure 2.3: V_{sum} (top) and V_{diff} (bottom) potential energy surfaces, in Cartesian coordinates, for NO(X) + Rg, with Rg = He, Ne, Ar, Kr and Xe (from left to right). The attractive (blue) and repulsive (red) contours are separated by 25cm^{-1} and 100cm^{-1} , respectively, for V_{sum} , and 200cm^{-1} and 10cm^{-1} , respectively, for V_{diff} .

Figure 2.3 shows the potentials as a function of Cartesian coordinates, in which the shape of the potential about the NO molecule is more clear. The V_{sum} potential is elliptical in shape, with a repulsive wall surrounded by attractive features. The potentials are clearly asymmetric with respect to the $x = 0$ plane, which arises due to the heteronuclearity of the NO molecule. As the rare gas collision partners become larger and more polarisable [199], the repulsive wall occurs at a greater distance from the centre of mass, and the attractive minima become deeper. The V_{diff} potential is also asymmetric about the $x = 0$ plane, however, the asymmetry is much greater than on the sum potential, with deeper attractive wells.

2.3 The NO(X) + Diatom System

The interaction of NO(X) with a diatomic collision partner is more complicated than for the atomic rare gases discussed in Section 2.2. The angular momenta of both diatoms and their interaction with each other must be considered to build an accurate picture of the potential energy surfaces which govern such collisions. For simplicity the interactions discussed here are restricted to the case in which all four atoms lie in a single plane.

2.3.1 NO(X) + Nitrogen

Molecular nitrogen (N_2) is a closed shell diatom, with singlet multiplicity ($L = 0$ and $S = 0$).

The ground state electronic configuration of the N_2 molecule is

$$1\sigma^2 1\sigma^{*2} 2\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2, \quad (2.14)$$

which may be described by the $^1\Sigma_g^+$ term symbol. For nitrogen, the only contribution to the total angular momentum, J , is the rotational angular momentum, R , and as such the rotational Hamiltonian may be written as [186]

$$\hat{H}_{\text{rot}} = B_{N_2} R^2 = B_{N_2} N(N+1) = B_{N_2} j(j+1), \quad (2.15)$$

where $B_{N_2} = 1.998 \text{ cm}^{-1}$ is the rotational constant of the N_2 molecule [200].

Atomic nitrogen has non-zero nuclear spin, $I = 1$, for the naturally abundant ($^{14}N_2$) isotope, and as such molecular nitrogen exists as two nuclear spin isomers. The total wave function of a diatom takes the form

$$\psi_{\text{tot}} = \psi_e \psi_v \psi_r \psi_n, \quad (2.16)$$

where ψ_e , ψ_v , ψ_r and ψ_n are the electronic, vibrational, rotational and nuclear wave functions, respectively. For bosons, the total wave function must be symmetric with respect to nuclear exchange of identical bosons according to the Pauli principle [184, 185]. In the electronic and vibrational ground state of N_2 both ψ_e and ψ_v are symmetric with respect to the exchange of nuclei. The exchange of the nitrogen atoms is equivalent to a $\hat{c}_2$ rotation, a rotation by 180° about the centre of mass of the diatom, such that the rotational wave function may be described by

$$\hat{c}_2 \psi_r = (-1)^{\Delta j} \psi_r, \quad (2.17)$$

and ψ_r is symmetric for even Δj and antisymmetric for odd Δj . As such, for the total wave function to be symmetric, ψ_n must be symmetric and antisymmetric for even and odd Δj ,

Δj	ψ_r	ψ_n	g_n	isomer
even	symmetric	symmetric	2	ortho
odd	antisymmetric	antisymmetric	1	para

Table 2.1: Possible combinations of the rotational and nuclear wave functions (ψ_r and ψ_n , respectively) for $^{14}\text{N}_2$. The degeneracy, g_n , of each nuclear spin isomer is also shown.

respectively, as shown in Table 2.1. For homonuclear diatomics there are $I + 1$ symmetric ψ_n and I antisymmetric ψ_n . As such, the ratio between the ortho (even Δj) and para (odd Δj) isomers is 2:1.

Potential Energy Surface

The Jacobi coordinates (shown in Figure 2.4) required to describe the NO- N_2 system are extended from the diatom-atom case in Section 2.2: γ_{NO} and γ_{NN} describe the angular dependence of the NO and N_2 diatoms, respectively, whilst ϕ describes the dihedral angle between the diatoms. If $\phi = 0^\circ$ then all four atoms lie in the same plane. The distance $R_{\text{NO-NN}}$ defines the distance between the centres of mass of the two diatoms, and the diatom bond lengths are fixed at their equilibrium values of $r_{\text{NO}} = 1.15 \text{ \AA}$ [185] and $r_{\text{NN}} = 1.10 \text{ \AA}$ [201]. As such, vibrational motion of both diatoms is ignored in the calculation of the PES and any subsequent calculations.* The PES is calculated with the system constrained to planarity ($\phi = 0$): in this geometry the system belongs to the C_s group, which substantially reduces the complexity of the PES calculation [201].

The formalism described for the potential of an open shell diatom interacting with a closed shell atom, in Section 2.2, may be extended to the interaction of an open shell diatom with a closed shell diatom [203–205]. The approach of the N_2 molecule towards the NO molecule gives rise to two adiabatic states of A' and A'' symmetry, in an equivalent sense to that of the diatom-atom case. The symmetry depends only on whether the unpaired electron in the π^* orbital of the NO molecule is in the plane (A') or perpendicular to the plane (A'') of approach of

*It is assumed that under experimental conditions both diatoms are in the $v = 0$ state prior to the collision, and that no vibrational excitation occurs during the collision process as $\Delta E (v' = 1 \leftarrow v = 0) \approx 1816 \text{ cm}^{-1}$ for NO [176, 177] and $\Delta E (v' = 1 \leftarrow v = 0) \approx 2331 \text{ cm}^{-1}$ for N_2 [202].

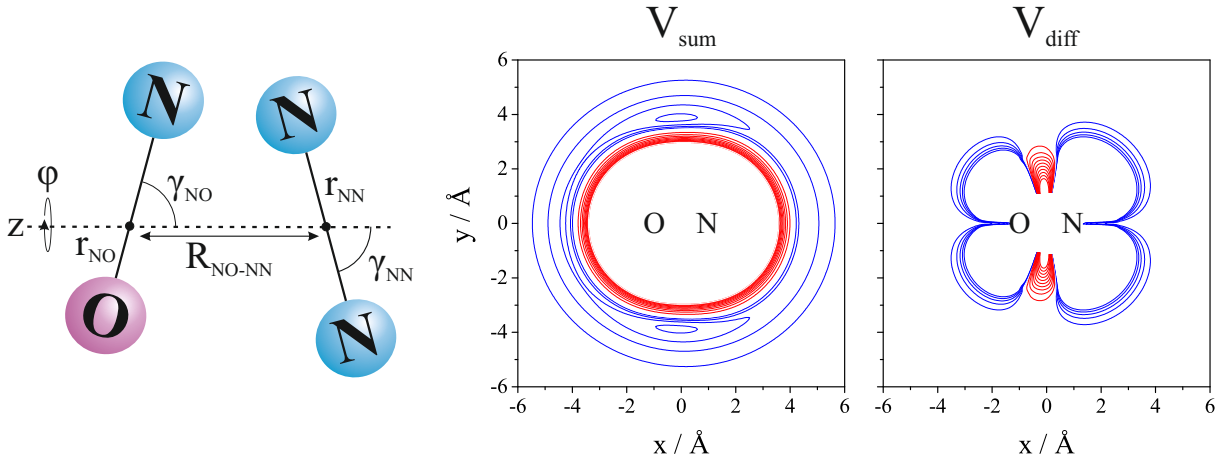


Figure 2.4: The NO-N₂ system. Left panel: Jacobi coordinates. Right panel: Potential energy surfaces (in Cartesian coordinates) corresponding to V_{sum} and V_{diff} for the NO(X) + N₂ system (averaged over all N₂ orientations). Attractive and repulsive contours are shown in blue and red respectively; repulsive contours are spaced by 100 cm⁻¹ whilst attractive contours are spaced by 20 cm⁻¹.

the N₂ molecule. This yields a half-sum and half-difference potential

$$V_{sum}(R, \gamma_{NO}, \gamma_{NN}) = \frac{1}{2} [V_{A''}(R, \gamma_{NO}, \gamma_{NN}) + V_{A'}(R, \gamma_{NO}, \gamma_{NN})] , \quad (2.18a)$$

$$V_{diff}(R, \gamma_{NO}, \gamma_{NN}) = \frac{1}{2} [V_{A''}(R, \gamma_{NO}, \gamma_{NN}) - V_{A'}(R, \gamma_{NO}, \gamma_{NN})] , \quad (2.18b)$$

where $R \equiv R_{NO-NN}$. An average over the rotation of the N₂ molecule provides a PES of reduced dimensionality, $V(R, \gamma_{NO})$, which is equivalent to interaction of the NO molecule with a spherically symmetric N₂ ‘target’ [201]. In this case the sum and difference potentials in Equation (2.18) are reduced to the diatom-atom case shown in Equation (2.13) (for which $\gamma \equiv \gamma_{NO}$).

The potential energy surface for the interaction of NO with N₂ [201] (averaged over all possible orientations of N₂) is shown in Figure 2.4. The features of the PES are similar to those of the NO + Rg PES (for the heavier rare gases), as discussed in Section 2.2. The V_{sum} potential is weakly attractive for large diatom-diatom distances, however the structure is more complex than observed for the NO + Rg systems. Although three minima are observed, corresponding to two linear geometries (NO-NN and ON-NN) and a global T-shaped minimum at $\gamma_{NO} \approx 90^\circ$, the global minimum extends around the ‘O’ end of the molecule. Both the V_{sum} and V_{diff} potentials are asymmetric with respect to $x = 0$ (*i.e.* reflection in the plane), due to the heteronuclearity of

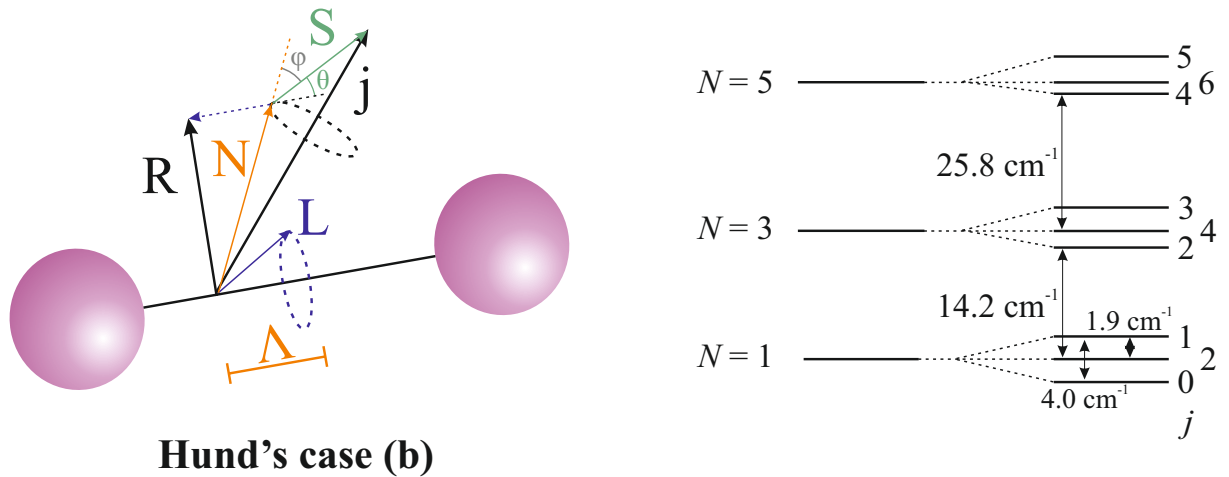


Figure 2.5: NO + O₂ System. Left panel: Diagram of Hund's case (b) vector coupling of angular momenta in O₂(X), adapted from Zare [186] and Brown [187], as discussed in the text. Right panel: the resulting rotational energy levels of O₂(X), showing both N and j , adapted from Reference [207].

the NO molecule. As in the case of the rare gas collision partners, the V_{sum} potential is longer range than the V_{diff} potential. The V_{diff} potential is strongly attractive, with repulsive lobes at the sides of the NO molecule, and is similar in nature to that of the NO + Xe system.

2.3.2 NO(X) + Oxygen

Molecular oxygen, O₂(X), has two unpaired electrons (with parallel spins) in two isoenergetic π^* orbitals, giving a ground electronic state of

$$1\sigma^2 1\sigma^{*2} 2\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 1\pi^{*2}. \quad (2.19)$$

Whilst in principle both the (singlet and triplet) Σ and (singlet) Δ states are possible, Hund's rules determine that the relative energies of the states are ${}^3\Sigma_g^- < {}^1\Delta_g < {}^1\Sigma_g^+$ [206], giving a triplet ground state with $S = 1$. The first and second excited electronic states are 7918 cm^{-1} [187, 206] and 21113 cm^{-1} [187] higher in energy than the ground state, and no electronic excitation is expected under the experimental conditions used in this thesis.

The coupling of the angular momenta in the ground electronic state of the O₂(X) molecule is best described by Hund's case (b), shown in Figure 2.5 [186, 187]. The spin-orbit coupling in this case is weak (or non-existent), consequently S is only weakly coupled to the internuclear

Δn	ψ_r	ψ_n	g_n
even	symmetric	antisymmetric	0
odd	antisymmetric	symmetric	1

Table 2.2: Possible combinations of the rotational and nuclear wave functions (ψ_r, ψ_n) for $^{16}\text{O}_2$. The degeneracy, g_n , of each nuclear spin isomer is also shown.

axis, and Ω is undefined. The projection of $\mathbf{L}$ onto the internuclear axis, Λ , is coupled to the rotational angular momentum of the molecular frame, $\mathbf{R}$, resulting in total angular momentum (excluding electronic spin), $\mathbf{N}$ (with a projection Λ onto the internuclear axis). For $\text{O}_2(\text{X})$ there is no orbital angular momentum, $\mathbf{L} = 0$, and therefore $\mathbf{N} = \mathbf{R}$. The electronic spin, $\mathbf{S} = 1$, is coupled to $\mathbf{N}$ to give the total angular momentum, $\mathbf{j}$. This spin-rotation coupling splits the rotational levels, N , into triads defined by $j = N - S$, $j = N$ and $j = N + S$ in the limit of Hund's case (b) [22, 24, 187, 207]. The magnitude of this splitting is small compared to the differences in energy between the different rotational energy levels, N , see Figure 2.5, and is not experimentally resolved here [207]. For excited rotational states the spin is not completely decoupled from the internuclear axis, and as such there is a weak spin-orbit coupling. Therefore, the angular momentum coupling is more accurately described as an intermediate coupling between Hund's case (a) and (b) [22, 24, 208–211].

Neglecting the spin-rotation coupling, the rotational Hamiltonian may be written [187]

$$\begin{aligned}\hat{H}_{\text{rot}} &= B_{\text{O}_2} \mathbf{R}^2 = B_{\text{O}_2} [\mathbf{N} - \mathbf{L}]^2 \\ &= B_{\text{O}_2} [N(N+1) + \mathbf{L}^2 - 2\mathbf{N} \cdot \mathbf{L}] ,\end{aligned}\tag{2.20}$$

where $B_{\text{O}_2} = 1.44 \text{ cm}^{-1}$ [208, 211] is the rotational constant of the O_2 molecule. The second and third terms in Equation (2.20) have no effect within Hund's case (b), however they do have non-zero matrix elements between different electronic states [187]. As such, the rotational levels have energies $B_{\text{O}_2} N(N+1)$, with the lowest level having $N = \Lambda = 0$. The selection rules for rotational transitions require that $\Delta j = \pm 1$ and $\Delta N = 0$ [187].

The spin-rotation coupling, considering only the end-over-end rotation of the molecule as a first approximation, has an interaction energy $E \propto 3 \cos^2 \theta - 1$, where θ is the angle between

S and the internuclear axis [211, 212], as shown in Figure 2.5. The three different possibilities for constructing the total angular momentum vector, j , result in a triad of states for each N . An additional interaction between the unpaired spins and the magnetic field set up by molecular rotation provides a further coupling between S and N with an interaction energy, $E \propto \cos \varphi$, where φ is the angle between S and N [211], shown in Figure 2.5. Upon superposition of these two effects, the three energy levels associated with N may be written according to [211, 212]

$$E_{N+1} = E_N + (2N+3)B_{O_2} - \lambda + \mu(N+1) - \left[\lambda^2 + (2N+3)^2 B_{O_2}^2 - 2\lambda B_{O_2} \right], \quad (2.21a)$$

$$E_{N-1} = E_N - (2N-1)B_{O_2} - \lambda - \mu N + \left[\lambda^2 + (2N-1)^2 B_{O_2}^2 - 2\lambda B_{O_2} \right], \quad (2.21b)$$

where $\lambda = 1.985 \text{ cm}^{-1}$ and $\mu = -0.008 \text{ cm}^{-1}$ are a measure of the coupling between S and the internuclear axis and S , and N , respectively [211]. The energy of the $j = N$ state is simply the rigid rotor energy [211, 212]

$$E_N = B_{O_2} N(N+1) = \frac{\hbar^2}{8\pi^2 I} N(N+1), \quad (2.22)$$

where $I = 4.92 \times 10^{-48} \text{ kg m}^2$ is the moment of inertia of the O_2 molecule. The spin-rotation interaction causes a magnetic dipole, and as such $\Delta N = \pm 2$ transitions become allowed [187].

The naturally abundant isotope of atomic oxygen, ^{16}O , has a nuclear spin of $I = 0$. The total wave function of molecular oxygen, Equation (2.16), must be symmetric with respect to exchange of identical bosons (as discussed in terms of N_2 in Section 2.3.1). Under experimental conditions the oxygen molecule is vibrationally cold, $v = 0$, and as such ψ_v is symmetric with respect to inversion. The rotational wave function behaves in an equivalent sense to that of N_2 , as described by Equation (2.17). Unlike the N_2 molecule, the O_2 molecule in its ground electronic state is antisymmetric upon exchange of atoms. There are only two possible combinations of the rotational and nuclear wave function that give rise to a symmetric total wave function; these are shown in Table 2.2. Since there are $I (= 0)$ antisymmetric and $I + 1 (= 1)$ symmetric ψ_{ns} , only odd rotational states are allowed by the Pauli principle. Consequently, the ground rotational state of the oxygen molecule is $N = 1$ (with $j = 0$ when considering

NO-O ₂ State	π_{NO}^*	Spin Coupling
$^2A''$	parallel	antiparallel
$^4A''$	parallel	parallel
$^2A'$	perpendicular	antiparallel
$^4A'$	perpendicular	parallel

Table 2.3: Definitions of the four electronic states of the NO-O₂ complex: each state is defined by whether the electron in the π_{NO}^* orbital is parallel or perpendicular to the plane of the complex (column 2), and whether the electron spins in the two molecules are parallel or antiparallel (column 3).

spin-rotation coupling). A diagram showing the rotational energy levels associated with O₂(X), under Hund's case (b), is shown in Figure 2.5.

Potential Energy Surface

When NO and O₂ molecules approach in their ground electronic states, four different electronic states are formed, each corresponding to a PES. As in the case of the interactions between NO and the rare gases, the PES may be distinguished by symmetry, but now also by spin multiplicity. The total electron spin angular momentum of the system is the sum of the spin multiplicity of the two diatoms ($s = s_{\text{NO}} + s_{\text{O}_2}$) leading to two possible spin states with $s = 0.5$ or $s = 1.5$, referred to as doublet and quartet spin states, respectively. According to Hund's first rule, the quartet state should be lower in energy due to electron-electron repulsion (supported by the work of Lee *et. al.* [213]), however, *Heitler-London* theory makes the opposite prediction, in that the minimum multiplicity should have the lowest energy [184, 214]. It should be noted that there is, as such, still uncertainty as to which spin state is the ground state.

As discussed in terms of the NO molecule, see Section 2.1), the occupied π orbitals of each diatom may be either parallel or perpendicular to the plane of the diatom-diatom complex (assuming that the complex is constrained to planarity). The π orbitals in the plane of the complex are symmetric with respect to reflection (in the plane), whilst the orbitals perpendicular to the plane are antisymmetric with respect to reflection, leading to A' and A'' symmetry, respectively. In the oxygen molecule an unpaired electron lies in each of these orbitals, leading

to an overall symmetry of

$$A' \otimes A'' \rightarrow A'' . \quad (2.23)$$

Since the NO molecule has either A' or A'' symmetry, the overall symmetry of the complex is

$$A'' \otimes A' \rightarrow A'' \quad \text{or} \quad A'' \otimes A'' \rightarrow A' . \quad (2.24)$$

Combining the symmetry and spin arguments, the four electronic states of the complex can be described by $^2A'$, $^2A''$, $^4A'$ and $^4A''$, where the superscripts denote the systems spin multiplicity. Information describing the overall spin-coupling of the states is given in Table 2.3, and more detailed descriptions may be found in the theses of Starkey [215] and Economides [216]. Due to the relatively low masses of NO and O₂, along with spin-orbit coupling being negligible in Hund's case (b), it is not expected that the doublet and quartet surfaces will show significant mixing [59, 213, 217].

Until very recently,[†] no complete *ab initio* PESs describing the interaction between NO(X) and O₂(X) was available, however a number of points on a planar PES have been calculated by Economides [216]. The Jacobi coordinate system for the NO + O₂ system is shown in Figure 2.6: where γ_{NO} and γ_{OO} describe the angle of NO and O₂ with the intermolecular axis, respectively, $r_{\text{NO}} = 1.15 \text{ \AA}$ [185] and $r_{\text{OO}} = 1.21 \text{ \AA}$ [218] are the equilibrium bond lengths of the diatoms, and $R_{\text{NO-OO}}$ describes the distance between the centre of mass of the two diatoms. As in the case of the NO-N₂ system, the angle ϕ describes the dihedral angle between the two molecules. To retain the symmetry distinction between the electronic states of the system during calculations of the PES it is necessary to restrict the system to planarity ($\phi = 0^\circ$) [213].

It is simpler to understand the PES in terms of fixed geometries than to consider each PES for all angles and separations of the collision partners. One may imagine two limiting cases: the O₂ bond axis either parallel (with $^4\Pi$ symmetry) or perpendicular (C_{2v}) to the NO bond axis. In each case, there are two isomers in which the NO molecule has either an NO or ON configuration when interacting with the O₂ molecule. Due to symmetry, rotation of the O₂

[†]The group of van de Meerakker [69] recently presented a full *ab initio* PES which was shown to give good agreement with experiments at collision energies of $E_{\text{coll}} = 160 \text{ cm}^{-1}$ [69] and 480 cm^{-1} [70].

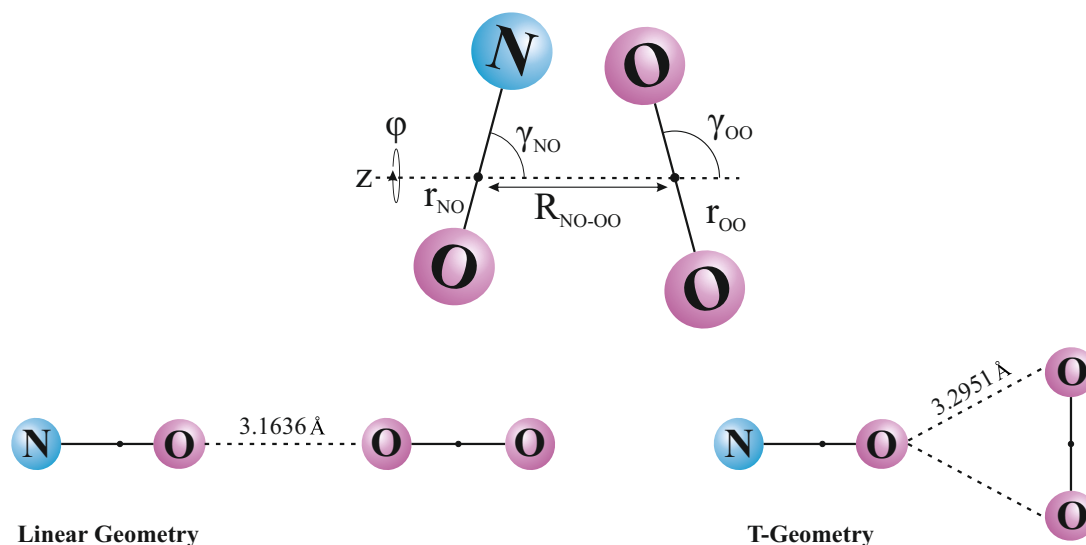


Figure 2.6: Jacobi coordinates for the NO-O₂ system (top) and predicted minimum energy geometries (bottom).

molecule by 180° leads to the same configuration. The bottom panel of Figure 2.6 shows the geometries predicted to be potential energy minima on the quartet surface according to Lee and Wright [213]. The energy difference between these two minima is approximately 6 cm⁻¹, and as such it is difficult to predict the global minimum on the quartet surface. However, one may distinguish between the two geometries in terms of the distance over which the interaction is felt. For large values of $R_{\text{NO-OO}}$ where the dipole/induced-dipole interaction is large, the linear orientation is expected to dominate. For smaller interaction distances, the ‘T-shaped’ geometry becomes more favourable since contributions from quadrupoles become important and electron repulsion occurs. However, these two geometries are only small minima on the quartet PES, and the surface is relatively flat; as such a wide range of different geometries are likely to be sampled [213].

2.4 Truncated Potential Energy Surfaces

Whilst the full PESs described in the previous sections are the most realistic description of the interactions between NO(X) and a collision partner, other simpler descriptions of the PES may be used to elucidate information about the origins of specific scattering effects. It can be instructive to consider the roles of attractive and repulsive forces on scattering; to this

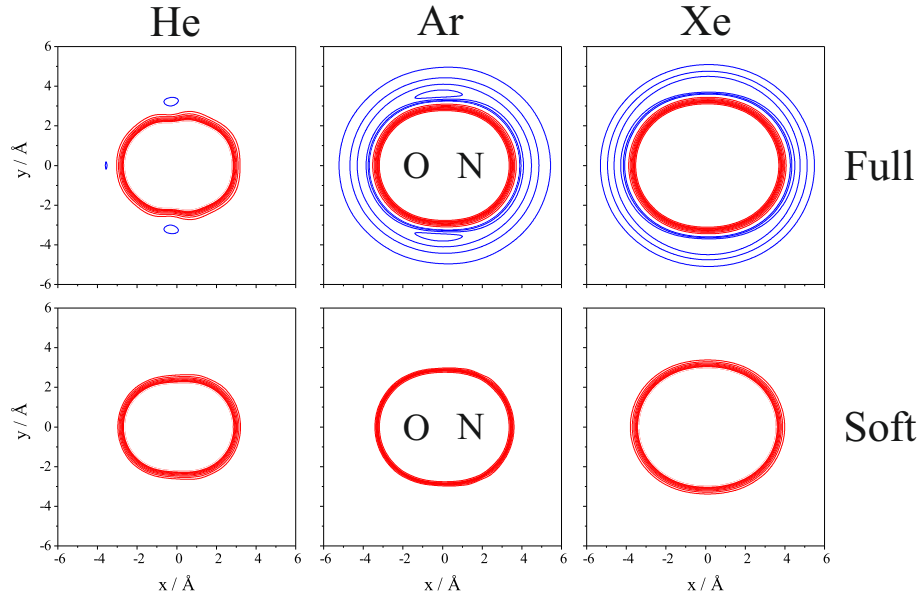


Figure 2.7: Full (top) and ‘soft’ (bottom) V_{sum} potential energy surfaces, in Cartesian coordinates, for $\text{NO}(\text{X}) + \text{Rg}$, with $\text{Rg} = \text{He}, \text{Ar}, \text{and Xe}$ (from left to right). The attractive (blue) and repulsive (red) contours are separated by 25cm^{-1} and 100cm^{-1} , respectively.

end the attractive part of the potential may be ‘damped-out’ by truncating the full potentials, described in Sections 2.2 and 2.3, such that only the repulsive part of the potential remains. There are several possible methods for truncating the potential [40, 219]; the method used in this thesis retains the difference potential during the truncation process and therefore allows any differences observed in the scattering dynamics to be attributed to the removal of the attractive interactions alone. The so-called ‘soft’ potential is calculated by scaling both the V_{sum} and V_{diff} PESs [40]

$$\tilde{V}_{\text{sum}} = f(R, R_0, R_{\text{shift}}, \eta) V_{\text{sum}} , \quad (2.25\text{a})$$

$$\tilde{V}_{\text{diff}} = f(R, R_0, R_{\text{shift}}, \eta) V_{\text{diff}} , \quad (2.25\text{b})$$

with a log-sigmoid function [40]

$$f(R, R_0, R_{\text{shift}}, \eta) = 1 - \frac{1}{1 + \exp\{-\eta(R - R_0 + R_{\text{shift}})\}} , \quad (2.26)$$

where η , R_0 , and R_{shift} are positive. η determines the steepness of the function; set such that at the collision energy the contour, $R(E_{\text{coll}})$, of the modified potential is identical to that of the

unmodified potential. R_{shift} decreases the value of R at which the point of inflection occurs, so that at a distance R_0 (equivalent to the contour of the V_{sum} PES at zero collision energy), the scaled potential falls below a predefined value, set as $\varepsilon E_{\text{coll}}$, with $\varepsilon = 0.1$. For the NO + Rg potentials described in Section 2.2 values of $\eta = 1.0 \text{ bohr}^{-1}$ and $R_{\text{shift}} = 10.0 \text{ bohr}$ were used during the truncation process.

Figure 2.7 shows the full and ‘soft’ (truncated) V_{sum} PESs for NO(X) + He, Ar, and Xe. No attractive features (blue contours) are observed in the ‘soft’ potential of all three systems, and only the repulsive ‘wall’ (red contours) of the potential is retained. Since the He system is predominantly repulsive, the truncation process does not strongly affect the potential, other than removing the attractive wells on the side of the NO molecule. The effects are much larger on the more attractive Ar and Xe PESs, as expected.

2.5 Scattering Theory

The theoretical description of diatom-atom scattering dynamics may broadly be split into two categories: methods involving classical mechanics and those involving quantum mechanics. Both methods employ dynamic calculations on potential energy surfaces such as those described in Sections 2.2 and 2.3. Whilst classical descriptions of the scattering event are only approximate (since they cannot reproduce the inherently quantum nature of the systems of interest), they often provide unique mechanistic insight into collision processes. Quantum mechanical descriptions provide a more accurate description of dynamics, however it is sometimes difficult to extract a meaningful mechanism from such calculations alone. Complementary use of these methods can also provide important information relating to which features are purely quantum mechanical in nature, and those which have classical analogues. Whilst the methods are discussed here in terms of atom-diatom scattering, such methods also exist for diatom-diatom scattering assuming that a high enough quality *ab initio* PES is available for the system of interest [14, 220, 221].

2.5.1 Quasi-Classical Trajectories

The quasi-classical trajectory (QCT) method used in this thesis was developed by Aoiz and co-workers [77, 180–182], and is based upon the trajectory method first developed by Karplus [222]. In this method, classical trajectories are propagated across a PES in discrete time steps, where at each step the spatial position and the related momenta of each particle in the system are calculated, before the trajectory is propagated to the next time step. The classical solution cannot be converged using a single trajectory, since the final position and momenta depend on the starting conditions of the trajectory. Several million trajectories, corresponding to many different initial conditions, are typically required to obtain accurate observables for the system.

For a diatom-atom system, the Hamiltonian, in Cartesian coordinates, is given by nine pairs of positions and momenta according to [222]

$$\hat{H} = \sum_{i=1}^3 \frac{p_{x_i}^2}{2m_A} + \sum_{i=4}^6 \frac{p_{x_i}^2}{2m_B} + \sum_{i=7}^9 \frac{p_{x_i}^2}{2m_C} + V(x_1, x_2, \dots, x_9) , \quad (2.27)$$

where the Cartesian coordinates for the atom, A, of mass m_A and the diatom BC (composed of masses m_B and m_C) are given by x_i , and p_{x_i} are the conjugate momenta of A ($i = 1 - 3$), B ($i = 4 - 6$), and C ($i = 7 - 9$). The kinetic energy of the system is described by the first three terms of Equation (2.27), whilst $V(x_1, x_2, \dots, x_9)$ gives the potential energy. Since the centre of mass of the system is implicitly contained in Equation (2.27), the Hamiltonian may be simplified by separating the motion of the centre of mass from the internal motion of the system. This is achieved by running the trajectories in a space fixed frame, shown in Figure 2.8, in which the centre of mass of the diatom is defined as the origin of the coordinate system. In this frame, only six pairs of positions and momenta are required to describe the system. The Jacobi coordinates q_1, q_2 and q_3 describe the position of C with respect to B (the bond axis vector, $\mathbf{r}$, of the diatom), whilst q_4, q_5 and q_6 describe the position of atom A with respect to the centre of mass of the diatom BC (the vector, $\mathbf{R}$). The conjugate momenta related to each coordinate are described by

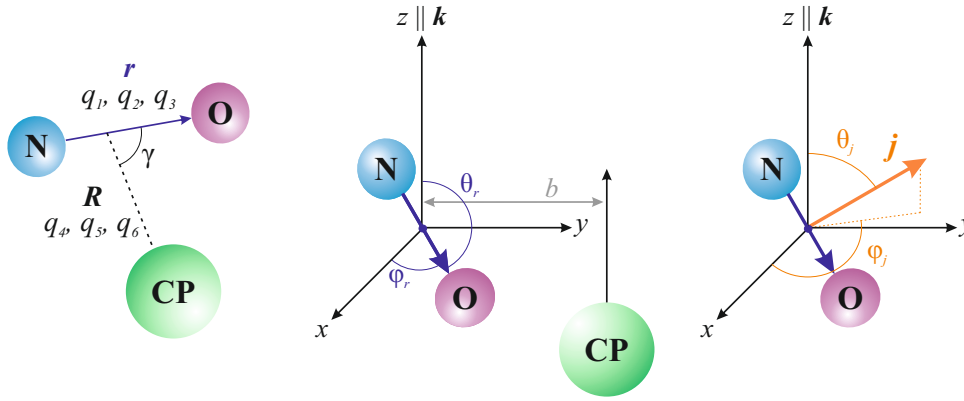


Figure 2.8: The space fixed frame (not to be confused with the scattering frame) used in quasi-classical trajectory calculations (middle and right): the collision partner approaches from the $+y -z$ quadrant and the z axis is defined by the relative velocity vector, $\mathbf{k}$. The initial orientation of the molecule (middle) is defined by the polar and azimuthal angles, θ_r and ϕ_r respectively, whilst $\mathbf{j}$ (right) is specified by θ_j and ϕ_j . The corresponding Jacobi coordinates are shown in the left hand panel.

p_{q_i} , $i = 1, 2, \dots, 6$, whilst the angle between $\mathbf{r}$ and $\mathbf{R}$ is defined by

$$\cos \gamma = \frac{R_x \cdot r_x + R_y \cdot r_y + R_z \cdot r_z}{|\mathbf{R}| |\mathbf{r}|} . \quad (2.28)$$

The simplified Hamiltonian (in Jacobi coordinates) may be written

$$\hat{H} = \sum_{i=1}^3 \frac{p_{q_i}^2}{2\mu_{BC}} + \sum_{i=4}^6 \frac{p_{q_i}^2}{2\mu_{A,BC}} + V(\mathbf{R}, \mathbf{r}, \gamma) , \quad (2.29)$$

where μ_{BC} and $\mu_{A,BC}$ are the reduced masses of the diatom and the $A + BC$ system, respectively. In Equation (2.29), the first and second terms describe the motion of the diatom and the motion of the atom relative to the diatom, respectively, whilst the third term describes the potential energy of the system.

In the space-fixed frame, shown in Figure 2.8, the principal axis, z , is parallel to the initial wavevector, $\mathbf{k}$, and the atom approaches in the yz ($y > 0$ and $z < 0$) plane. The third axis, x , is defined such that the frame is right handed. This should not be confused with the ‘scattering frame’ described in Section 2.6, in which the x -axis is described by the final wavevector, $\mathbf{k}'$. A large number of trajectories, typically of the order of 2×10^7 , are required to sample all initial conditions of the system and converge the resulting observables. The initial separation of the atom and diatom, $|\mathbf{R}|$, at time $t = 0$, is set such that the interaction between the two

is negligible [223]. The bond axis of the diatomic is kept at its equilibrium value by the use of Lagrangian multipliers [224], since the PES is calculated with a constant bond length. The positions and momenta of the nuclei are allowed to evolve across the PES according to [222]

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i} = \frac{\partial T}{\partial p_i}, \quad (2.30a)$$

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} = -\frac{\partial V}{\partial q_i} = -\left(\frac{\partial V}{\partial R} \frac{\partial R}{\partial q_i} + \frac{\partial V}{\partial r} \frac{\partial r}{\partial q_i} + \frac{\partial V}{\partial \cos \gamma} \frac{\partial \cos \gamma}{\partial q_i} \right), \quad (2.30b)$$

in 10 fs time steps. Here, q_i and p_i are the positions and momenta of the atom and diatom in the space-fixed frame, H is the Hamiltonian in Equation (2.29), T and V (which depends explicitly on r , R , and γ) are the kinetic and potential energy components of Equation (2.29), and t is the time. The fourth order Runge-Kutta algorithm followed by Hammond's predictor-corrector algorithm are used to numerically solve for the evolution of the system [224]. The trajectory is terminated when $|R|$ is beyond the defined 'interaction region'; the region beyond which the presence of the collision partner no longer influences the diatom.

The initial conditions of each trajectory must be specified in such a way that they correctly model the experiment. The experimental collision energy does not have a finite value, rather it is described by a Gaussian distribution about the mean collision energy, E_{coll} . This is achieved by running calculations over a grid of energies, which are then weighted according to the experimental distribution. The impact parameter, b , is defined as the distance between the initial position of the atom and the initial wavevector, k (the z -axis in the space fixed frame in Figure 2.8). The value of b is sampled from a quadratic distribution between 0 and b_{max} , such that $P(b) \propto 2\pi b$. The value of b_{max} is chosen such that above this value the probability of an inelastic scattering process occurring is zero. The impact parameter is a classical value that varies continuously, reflecting the fact that the classical orbital angular momentum, ℓ , is not quantised. The classical orbital angular momentum may be related to the quantum mechanical orbital angular momentum by $|\ell| = \mu v_{\text{rel}} b = \hbar \sqrt{\ell(\ell+1)}$.

The initial orientation of the NO bond axis, r , is defined by the polar and azimuthal angles θ_r and ϕ_r , respectively. When the 'N-end' of the NO molecule is directed towards the incoming

atom, $\theta_r = 0^\circ$, and $\mathbf{r}$ is parallel to the z -axis. The initial values of θ_r and ϕ_r are sampled between $(0, \pi)$ and $(0, 2\pi)$, respectively, such that the distribution of $\mathbf{r}$ (and consequently $\mathbf{j}$) is uniform.

Classically, the rotational angular momentum of the diatom may vary continuously. However, to allow comparison with quantum mechanical calculations and experimentally observed properties, it is necessary to quantise the initial and final rotational angular momenta *via* histogram binning, according to $|\mathbf{j}| = \hbar\sqrt{j(j+1)}$, before rounding to the nearest integer. Experimentally, the ground rotational state of the NO(X) molecule, $j = 0.5$, is selected. Classically, this corresponds to $j = 0$, and the NO molecule is not rotating before the scattering event occurs. During the propagation of the trajectory, $\mathbf{j}$ is allowed to vary continuously, as is classically allowed. Upon termination of the trajectory the final rotational angular momentum is histogram binned, according to $|\mathbf{j}'| = \hbar\sqrt{j'(j'+1)}$, and rounded to the nearest integer. The collision is considered to be elastic if $j' = j \pm 0.5$.

The direction of $\mathbf{j}$ is defined by the polar and azimuthal angles θ_j and ϕ_j , respectively, in the space fixed frame. If these angles are not uniformly distributed, the diatom will have a preferred sense and/or plane of rotation. The initial rotational angular momentum, $\mathbf{j}$, is perpendicular to the bond axis, $\mathbf{r}$, and therefore information on the distribution of $\mathbf{j}$ provides information on the distribution of $\mathbf{r}$ or *vice versa*. The direction of $\mathbf{j}'$, defined by $\theta_{j'}$ and $\phi_{j'}$, is noted at the end of the trajectory to allow calculation of the polarisation dependent differential cross sections, discussed in Section 2.6. As in the case of $\mathbf{j}$ and $\mathbf{r}$, the distribution of $\mathbf{j}'$ can be used to provide information on the distribution of the bond axis, $\mathbf{r}'$, after the collision.

Observable Properties

To allow comparison between theoretical calculations and experimental results, the relevant observables must be calculated. Some theoretical quantities have no measurable experimental counterpart, however they may provide further insight into the scattering process. The probability of a transition from an initial state, i , into a final state, f , with a specific impact

parameter, b , is given by the classical opacity function

$$P_{f \leftarrow i}(b) = \frac{N_{f \leftarrow i}(b)}{N_i(b)} , \quad (2.31)$$

where $N_i(b)$ is the number of trajectories with initial state i , and $N_{f \leftarrow i}(b)$ is the number of trajectories undergoing the process $f \leftarrow i$. The partial cross sections (PCS) are obtained from the opacity functions by

$$\sigma_{f \leftarrow i}(b) = 2\pi b P_{f \leftarrow i}(b) . \quad (2.32)$$

Integration of the partial cross section over all b gives the integral cross section (ICS) for the transition $f \leftarrow i$,

$$\sigma_{f \leftarrow i} = \int_0^{b_{\max}} 2\pi b P_{f \leftarrow i}(b) db = \pi b_{\max}^2 \frac{N_{f \leftarrow i}}{N_i} . \quad (2.33)$$

Whilst in principle the integral in Equation (2.33) extends to infinity, the value of $b_{\max}$ is chosen such that the opacity function drops to zero beyond this value, and $\int_0^{b_{\max}} P(b) db = 1$. The integral cross section may be thought of as the effective area that an atom must hit to scatter a molecule from an initial state, i , into a final state, f .

The differential cross section (DCS), describes the cross section as a function of the (scattering) angle, θ , between $\mathbf{k}$ and $\mathbf{k}'$. That is, the cross section for scattering into the conical solid angle, $d\omega = \sin \theta d\theta d\phi$,

$$\frac{d\sigma_{f \leftarrow i}}{d\omega}(\theta) = \frac{1}{4\pi} \frac{1}{\sin \theta} \frac{d^2\sigma_{f \leftarrow i}}{d\theta d\phi} . \quad (2.34)$$

Assuming no external forces act on the system, the scattering process is symmetric about $\mathbf{k}$, and the DCS shows no dependence on the azimuthal scattering angle, ϕ . The integral cross section may be recovered from the DCS by integrating across the surface of the scattering sphere

$$\sigma_{f \leftarrow i} = \int_0^{2\pi} \int_0^\pi \frac{d\sigma}{d\omega}(\theta) \sin \theta d\theta d\phi . \quad (2.35)$$

Classically, the DCS is obtained by histogram binning the trajectories into bins of width $\Delta\theta$ [13]

$$\frac{d\sigma_{f \leftarrow i}}{d\omega}(\theta) = \frac{1}{2\pi\Delta\cos\theta} \pi b_{\max}^2 \frac{N_{f \leftarrow i}(\theta + \Delta\theta)}{N_i(\theta + \Delta\theta)}, \quad (2.36)$$

where $N_{f \leftarrow i}(\theta + \Delta\theta)$ are the number of trajectories undergoing the process $f \leftarrow i$ which are scattered through an angle between θ and $\theta + \Delta\theta$. To obtain a smooth DCS with good angular resolution this method requires a large number of trajectories, therefore it is preferable to expand the DCS as a series of Legendre polynomials [225]

$$\frac{d\sigma_{f \leftarrow i}}{d\omega}(\theta) = \frac{\sigma_{f \leftarrow i}}{4\pi} \sum_k (2k+1) a_{f \leftarrow i}^k P_k(\cos\theta), \quad (2.37)$$

where $P_k(\cos\theta)$ is the k^{th} Legendre polynomial and the expansion coefficients, $a_{f \leftarrow i}^k$, are the expectation values of the state resolved Legendre polynomials,

$$a_{f \leftarrow i}^k = \langle P_k(\cos\theta) | f \leftarrow i \rangle = \frac{1}{N_{f \leftarrow i}} \sum_{n=1}^{N_{f \leftarrow i}} P_k(\cos\theta_n), \quad (2.38)$$

and θ_n is the scattering angle associated with the n^{th} trajectory for the process $f \leftarrow i$.

2.5.2 Close-Coupled Quantum Mechanics

All of the close-coupled quantum mechanical (CC QM) calculations presented in this thesis were performed using the HIBRIDON [226] suite of codes. In these calculations the rotational wave function is propagated by solving the CC QM equations of Victor and Dalangro [183, 227]: using the Log-Derivative method [228] at short ranges, and the Airy propagator [196, 229] at longer range. In these calculations, all information about the scattering process is contained in the scattering matrix ($\hat{S}$ -matrix), which relates the incoming and outgoing wave functions according to

$$\hat{S} |\Psi_{\text{in}}^J\rangle = |\Psi_{\text{out}}^J\rangle, \quad (2.39)$$

where Ψ_{in}^J and Ψ_{out}^J are the incoming and outgoing wave functions, respectively, and J describes the total angular momentum of the system. For pure coherent states, the incoming and outgoing partial waves, representing the motion of the incoming/outgoing atom as a function of total angular momentum, can be written as a combination of the rovibrational eigenfunctions of the system [184]

$$|\Psi_{\text{in}}^J\rangle = \sum_i c_i |\psi_i^J\rangle \quad (2.40a)$$

$$|\Psi_{\text{out}}^J\rangle = \sum_f c_f |\psi_f^J\rangle. \quad (2.40b)$$

The coefficients, c_i and c_f , are constrained to $\sum_{i/f} |c_{i/f}|^2 = 1$ to ensure proper normalisation of the wave function. All observable properties related to the collisions of a system may be calculated from the $\hat{S}$ -matrix. However, it is more convenient to define the transition matrix ($\hat{T}$ -matrix),

$$\hat{T} = 1 - \hat{S}. \quad (2.41)$$

The $\hat{T}$ -matrix may be applied to the initial wave function in a similar way to the $\hat{S}$ -matrix,

$$\hat{T} |\Psi_{\text{in}}^J\rangle = (1 - \hat{S}) |\Psi_{\text{in}}^J\rangle \quad (2.42a)$$

$$= |\Psi_{\text{in}}^J\rangle - |\Psi_{\text{out}}^J\rangle. \quad (2.42b)$$

The square modulus of the transition matrix element, $|T_{f \leftarrow i}^J|^2$, is equal to the probability of scattering from $|\psi_f\rangle \leftarrow |\psi_i\rangle$ [223].

Observable Properties

The observable properties measured experimentally may be obtained from the CC QM calculations in a similar fashion to the classical properties in Section 2.5.1. The quantum mechanical opacity function is the probability of a process occurring with a specific total angular momentum, J ,

$$P_{f \leftarrow i}(J) = |T_{f \leftarrow i}^J|^2. \quad (2.43)$$

In the limit $J = j + \ell \gg j$, the classical and quantum mechanical opacity functions in Equations (2.31) and (2.43), respectively, have the same meaning and $b \propto \ell = \hbar J / \mu v_{\text{rel}}$. The state-to-state partial cross sections are calculated according to

$$\sigma_{f \leftarrow i}^J = \frac{\pi}{k^2} \frac{2J+1}{2j+1} [2 \min(J, j) + 1] P_{f \leftarrow i}(J), \quad (2.44)$$

where $k = p/\hbar = \mu v_{\text{rel}}/\hbar$ is the initial wavevector. The state-to-state integral cross sections are calculated from the partial cross sections by summation over all partial waves up to J_{max} (beyond which the opacity function is zero)

$$\begin{aligned} \sigma_{f \leftarrow i} &= \frac{\pi}{k^2} \sum_{J=0}^{2J+1} \frac{2J+1}{2j+1} [2 \min(J, j) + 1] P_{f \leftarrow i}(J) \\ &= \sum_J \frac{2J+1}{2j+1} [2 \min(J, j) + 1] \left| T_{f \leftarrow i}^J \right|^2. \end{aligned} \quad (2.45)$$

The summation over all partial waves is equivalent to the integral over all impact parameters in the QCT ICS in Section 2.5.1. The summation in the QM ICS reflects the quantised nature of the total angular momentum, as opposed to the continuous nature of the impact parameter classically.

The quantum mechanical DCS is calculated according to Equation (2.34). It is helpful to first define the scattering amplitude, $f_{f \leftarrow i}(\theta)$, for a specific $f \leftarrow i$ transition [223]

$$f_{f \leftarrow i}(\theta) = \frac{1}{2ik} \sum_J \frac{2J+1}{2j+1} [2 \min(J, j) + 1] P_J(\cos \theta) T_{f \leftarrow i}^J. \quad (2.46)$$

The DCS may then be written as the square modulus of the scattering amplitude [230]

$$\frac{d\sigma_{f \leftarrow i}}{d\omega}(\theta) = |f_{f \leftarrow i}(\theta)|^2 \quad (2.47a)$$

$$\begin{aligned} &= \frac{1}{4k^2} \sum_J \sum_{J'} \frac{2J+1}{2j+1} \frac{2J'+1}{2j+1} [2 \min(J, j) + 1] \\ &\quad \times [2 \min(J', j) + 1] P_J(\cos \theta) P_{J'}(\cos \theta) T_{f \leftarrow i}^J T_{f \leftarrow i}^{J'}{}^*. \end{aligned} \quad (2.47b)$$

The double summation over J leads to the possibility for interference between different partial waves, which are defined independently of each other by their individual $\hat{T}$ -matrix elements.

2.6 Rotational Angular Momentum Polarisation

Rotational angular momentum polarisation refers to the situation in which the distribution of $\mathbf{j}'$ (or $\mathbf{j}$ before the collision) with respect to a reference axis or plane is anisotropic. Experimentally, the reference plane is defined by the plane of overlap of the two molecular beams. When discussing the rotational polarisation of $\mathbf{j}'$, the orientation and alignment of the vectors have distinct definitions both classically and in quantum mechanics. The descriptions used for angular momentum polarisation may also be used to describe the polarisation of the NO bond axis, $\mathbf{r}$, (and correspondingly $\mathbf{j}$) which is discussed in detail in Chapter 5.

Classically, a distribution is oriented if the direction of $\mathbf{j}'$ is parallel or antiparallel to a specified reference axis; this is equivalent to the molecule rotating either clockwise or anticlockwise relative to the reference axis. A distribution is aligned if $\mathbf{j}'$ lies preferentially along a specific reference axis, however, there is an equal chance of the vector pointing in the positive or negative direction with respect to the axis.

Quantum mechanically, the projection of $\mathbf{j}'$ onto a specific axis is quantised, as defined by specific $m_{j'}$ states, such that $m_{j'} = \pm 1/2, \dots, \pm (j' - 1), \pm j'$, with a total of $2j + 1$ projections onto the reference axis. Rotational angular momentum polarisation arises from unequal populations of $m_{j'}$ states. For an oriented distribution $m_{j'}$ preferentially takes positive or negative values, whilst for an aligned distribution small or large values of $|m_{j'}|$ are preferentially populated, but the $\pm m_{j'}$ states are equally populated. Unlike the classical case, $\mathbf{j}$ and $\mathbf{j}'$, and therefore m_j and $m_{j'}$, are quantised.

The Scattering Frame For the theoretical description of rotational angular momentum polarisation one must define a principal frame (the ‘scattering frame’) relating the initial and final relative velocity vectors ($\mathbf{k}$ and $\mathbf{k}'$, respectively) and the final rotational angular momentum of the NO(X) molecule, shown in Figure 2.9. In the scattering frame, the principal axis (z), is

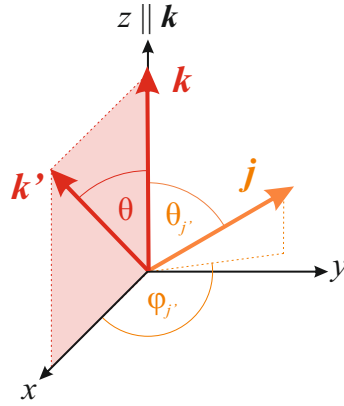


Figure 2.9: Schematic of the scattering frame. The z -axis is defined by the initial relative velocity, $\mathbf{k}$, the x -axis is such that the atom is scattered with final relative velocity, $\mathbf{k}'$, into the $+xz$ plane. The y -axis is defined such that the frame is right handed. The scattering angle, θ , describes the polar angle between the initial and final relative velocity vectors. The angles $\theta_{j'}$ and $\phi_{j'}$, describe the direction of the rotational angular momentum, $\mathbf{j}'$.

parallel to the initial relative velocity vector, $\mathbf{k}$. After the collision, the particle is scattered into the $+xz$ half of the plane, leading to scattering about the axis being symmetric. The y -axis is chosen such that the frame is right handed. The polar angle, θ , between $\mathbf{k}$ and $\mathbf{k}'$ is known as the scattering angle. The final rotational angular momentum in the scattering frame is defined by the polar and azimuthal angles, $\theta_{j'}$ and $\phi_{j'}$, respectively.

Classical $\mathbf{j}'$ -PDDCSs

Classically, the probability of a particle being scattered through an angle θ , with a final rotational angular momentum pointing in the direction $(\theta_{j'}, \phi_{j'})$ is described by a probability density function (PDF) [231, 232],

$$P(\theta, \theta_{j'}, \phi_{j'}) = \frac{1}{4\pi} \sum_{k=0}^{\infty} (2k+1) \sum_{q=-k}^k n_q^{(k)}(\theta) C_{kq}^*(\theta_{j'}, \phi_{j'}) , \quad (2.48)$$

where $C_{kq}^*(\theta_{j'}, \phi_{j'})$ are the complex conjugates of the modified spherical harmonics, $C_{kq}(\theta_{j'}, \phi_{j'})$. The expansion coefficients, $n_q^{(k)}(\theta)$, of the modified spherical harmonics are the normalised rotational polarisation dependent differential cross sections ($\mathbf{j}'$ -PDDCSs) [231, 233]

$$n_q^{(k)}(\theta) = \frac{2\pi}{\sigma} \frac{d\sigma_q^{(k)}}{d\omega}(\theta) = \frac{1}{2} \sum_{\kappa \geq |q|} (2\kappa+1) \langle C_{\kappa-q}(\theta, 0) C_{kq}(\theta_{j'}, \phi_{j'}) \rangle C_{\kappa-q}(\theta, 0) , \quad (2.49)$$

where σ is the integral cross section defined in Equation (2.45) and $\langle \dots \rangle$ is the expectation value of the modified spherical harmonics. The classical PDF for finding $\mathbf{j}'$ pointing along the direction specified by $(\theta_{j'}, \phi_{j'})$ is obtained by integration of Equation (2.48) over all scattering angles [180],

$$P(\theta_{j'}, \phi_{j'}) = \frac{1}{4\pi} \sum_{k=0}^{\infty} (2k+1) \sum_{q=-k}^k a_q^{(k)} C_{kq}^*(\theta_{j'}, \phi_{j'}) , \quad (2.50)$$

where the θ -independent polarisation parameters, $a_q^{(k)}$, are given by [180, 231]

$$a_q^{(k)} = \int_{-1}^{+1} n_q^{(k)}(\theta) d\cos\theta = \frac{2\pi}{\sigma} \int_{-1}^{+1} \frac{d\sigma_q^{(k)}}{d\omega}(\theta) d\cos\theta = \langle C_q^k(\theta_{j'}, \phi_{j'}) \rangle . \quad (2.51)$$

The normalised j' -PDDCSs in Equation (2.49) describe the spatial polarisation of the final rotational angular momentum as a function of scattering angle [87]. The monopole ($k=0$, $q=0$) moment of the normalised j' -PDDCS is equivalent to the $\mathbf{k} - \mathbf{k}'$ angular distribution function. Consequently, the renormalised j' -PDDCS

$$\rho_q^{(k)}(\theta) = \frac{n_q^{(k)}(\theta)}{n_0^{(0)}(\theta)} , \quad (2.52)$$

describes the j' -PDDCS independently of the scattering intensity at the angle, θ . Hertel-Stoll normalisation [234] is required to obtain real j' -PDDCSs, $\rho_q^{\{k\}}(\theta)$, which have direct physical meaning, from the generally complex renormalised j' -PDDCS in Equation (2.52) according to

$$\rho_0^{\{k\}} = \rho_0^{(k)} , \quad (2.53a)$$

$$\rho_{q+}^{\{k\}} = \frac{1}{\sqrt{2}} \left[(-1)^q \rho_{+q}^{(k)}(\theta) + \rho_{-q}^{(k)}(\theta) \right] , \quad 1 \leq q \leq k , \quad (2.53b)$$

$$\rho_{q-}^{\{k\}} = \frac{1}{\sqrt{2}i} \left[(-1)^q \rho_{+q}^{(k)}(\theta) - \rho_{-q}^{(k)}(\theta) \right] , \quad 1 \leq q \leq k . \quad (2.53c)$$

These real renormalised j' -PDDCSs provide information about the direction of the final rotational angular momentum, $\mathbf{j}'$, with respect to the scattering plane. The orientation of $\mathbf{j}'$ is described by the $k=1$ rank moments, and the alignment by the $k=2$ rank moments. The j' -PDDCSs should be differentiated from the bond axis polarisation dependent differential cross

sections, r -PDDCSs, discussed in Chapter 5. The real renormalised polarisation parameters, $a_q^{\{k\}}$, may be calculated in an analogous manner from Equation (2.51).

Quantum Mechanical j' -PDDCSs

Unlike in classical mechanics, in quantum mechanics it is not possible to precisely describe the direction of j' , due to the uncertainty principle. Instead j' is described as a mixture of different quantum states in $m_{j'}$, the magnetic sublevels of j' ; the populations and coherences between such states are contained in the density operator, $\hat{\rho}$. For a wave function that can be written as a linear combination of $|jm\rangle$ states [73],

$$|\psi\rangle = \sum_{m=-j}^j c_m |jm\rangle, \quad (2.54)$$

the density operator fully describing the system may be written [73, 235]

$$\hat{\rho} = |\psi\rangle\langle\psi| = \sum_{m_1, m_2} c_{m_1} c_{m_2}^* |jm_1\rangle\langle jm_2|, \quad (2.55)$$

where the sum over m_1 runs from $m_1 = -j$ to $m_1 = +j$, and similarly for m_2 . The individual density matrix elements are given by [13, 73, 236]

$$\langle jm|\hat{\rho}|jm'\rangle = \sum_{m_1, m_2} c_{m_1} c_{m_2}^* \langle jm|jm_1\rangle\langle jm_2|jm'\rangle = c_m c_{m'}^*, \quad (2.56)$$

where c_{m_1} and c_{m_2} are complex numbers. Note that, here, the m and m' states do not represent the initial and final values of the projection quantum number, but rather are used to denote different values of m . The basis sets, $|jm\rangle$, are the rotational eigenstates of the $\hat{j}^2$ and $\hat{j}_z^2$ operators. The population of each $|jm\rangle$ state is described by the diagonal elements of the density matrix, where $m = m'$. The off-diagonal elements describe the coherence between different $|jm\rangle$ and $|jm'\rangle$ states. Equations (2.54) to (2.56) may be used to describe both the initial and final rotational angular momenta; that is, both the j - and j' -PDDCSs.

For a pure, well defined rotational state, the elements of the density matrix may be written in terms of Clebsch-Gordan coefficients [231, 236]

$$\langle j'm'_1 | \hat{\rho}(\cos \theta) | j'm'_2 \rangle = \frac{1}{2j'+1} \sum_{k=0}^{2j'} (2k+1) \sum_{q=-k}^k n_q^{(k)}(\theta) \langle j'm'_1, kq | j'm'_2 \rangle, \quad (2.57)$$

where $\hat{\rho}(\cos \theta)$ is the scattering angle resolved density operator, and $n_q^{(k)}(\theta)$ are the normalised j' -PDDCSs, which may be written in terms of the QM scattering amplitudes in Equation (2.46) [83],

$$n_q^{(k)}(\theta) = \frac{2\pi}{\sigma} \frac{1}{4k^2} \frac{1}{2j'+1} \sum_{m, m'_1, m'_2} f_{j'm'_1 \Omega' \epsilon' \leftarrow jm \Omega \epsilon}(\theta) f_{j'm'_2 \Omega' \epsilon' \leftarrow jm \Omega \epsilon}^*(\theta) \times \langle j'm'_1, kq | j'm'_2 \rangle. \quad (2.58)$$

The trace of the density matrix in Equation (2.57) is equal to the probability of finding the system in a specific rotational state, j' , with a particular scattering angle, θ , irrespective of the polarisation of j' . The QM renormalised j' -PDDCS may be calculated *via* the same method as the classical renormalised j' -PDDCS, according to Equation (2.52). The real renormalised j' -PDDCSs are calculated from the complex renormalised j' -PDDCS using the Hertell-Stoll normalisation described in Equation (2.53).

Minimum Uncertainty States Since the exact direction of j' (or similary j) cannot be precisely defined, it is not possible to construct a PDF. However, a minimum uncertainty state, $|\theta_{j'}, \phi_{j'}\rangle$, may be described, where j' is localised as strongly as possible about the direction described by $(\theta_{j'}, \phi_{j'})$ [235, 236]. This localised state may be determined by rotating the $|j'j'\rangle$ eigenstate to the $(\theta_{j'}, \phi_{j'})$ direction according to [235, 236]

$$\begin{aligned} |\theta_{j'}, \phi_{j'}\rangle &= \hat{R}(\theta_{j'}, \phi_{j'}) |j'j'\rangle \\ &= \sum_{m=-j'}^{j'} D_{m,j'}^{j'}(\phi_{j'}, \theta_{j'}, 0) |j'm\rangle. \end{aligned} \quad (2.59)$$

The population of the minimum uncertainty state, may then be written [235, 236]

$$Q(\theta_{j'}, \phi_{j'}) = \frac{\langle \theta_{j'}, \phi_{j'} | \hat{\rho} | \theta_{j'}, \phi_{j'} \rangle}{\text{Tr} \rho}, \quad (2.60)$$

which, after some standard angular momentum algebra, may be expressed as a series expansion in which the expansion coefficients are proportional to the polarisation moments,

$$Q(\theta_{j'}, \phi_{j'}) = \frac{1}{4\pi} \sum_{k=0}^{2j'} (2k+1) \sum_{q=-k}^k \langle j' j', k 0 | j' j' \rangle a_q^{(k)} C_{kq}^*(\theta_{j'}, \phi_{j'}) . \quad (2.61)$$

This population distribution function is almost identical to its classical counterpart in Equation (2.50), apart from the Clebsch-Gordan coefficients which account for the quantum mechanical uncertainty. In the limit of the correspondence principle, $j' \rightarrow \infty$, the Clebsch-Gordan coefficients approach unity, resulting in an equivalence between the classical and quantum mechanical descriptions [235, 236].

2.7 Summary

In this chapter the theoretical framework required for the work in this thesis has been discussed. Descriptions of the angular momentum couplings in the NO(X) molecule have been given, as well as those for the N₂(X) and O₂(X) molecules. The potential energy surfaces describing the interaction of the NO(X) molecule with the (atomic) rare gas and the more complex N₂ and O₂ (diatomic) collision partners have been presented. The classical and quantum mechanical theoretical scattering methods used throughout this thesis have been discussed, including the calculation of experimental observables. Finally, the theory of the polarisation of the rotational angular momentum of the NO(X) molecule after the collision event has been presented for both classical and quantum mechanical methods.

Chapter 3

Experimental Methods

To experimentally probe the vector correlations which describe the scattering of an NO(X) molecule with atomic and diatomic collision partners, it is necessary to control specific vectors before the collision and detect others after the scattering event. Control of the initial relative velocity of the collision partners, $\mathbf{k}$, is achieved by the use of a crossed molecular beam (CMB) apparatus. Prior to the scattering event it is possible to orient the NO(X) bond axis, $\mathbf{r}$, using a static electric field. The process used to detect the scattered NO molecules may be modified to allow the measurement of the rotational angular momentum vector, $\mathbf{j}'$. It is important to characterise the experimental parameters relevant to the geometry of the apparatus, as well as system specific parameters related to the molecular beams themselves; this enables computational modelling of the experiment leading to an efficient method for data analysis.

In this chapter the methods for experimental measurement of the inelastic scattering of fully quantum state selected NO(X) with the rare gases (and homonuclear diatomics) are presented. The general experimental apparatus is described, including; a detailed characterisation of the molecular beams, a description of the method for initial state selection of the NO molecule, and the processes by which the scattered molecules are detected. Finally, the data analysis methods used to extract the scattering distributions from the raw experimental data are discussed.

3.1 Experimental Apparatus

The experiment, shown schematically in Figure 3.1, employs a crossed molecular beam (CMB) apparatus with initial hexapole quantum state selection [38, 120, 237, 238] and final state

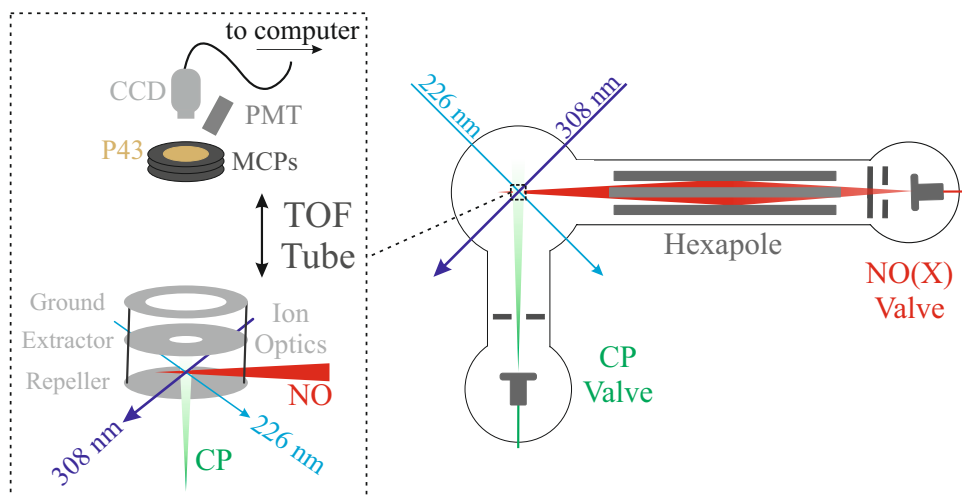


Figure 3.1: Schematic of the crossed molecular beam experimental apparatus. The ion-optics and time of flight tube (inset) are perpendicular to the plane defined by the molecular beams and lasers.

detection *via* $(1+1')$ resonantly enhanced multi-photon ionisation (REMPI) [239] coupled with velocity-map [146] ion imaging [147] (VMI). The initial wavevector, $\mathbf{k}$, is defined by the experimental geometry of the molecular beams. The experimental apparatus has been described in extensive detail previously [39, 75, 189]. The details specific to the experiments undertaken will be outlined within the relevant chapters, and the modifications required for orientation of the NO(X) bond axis, $\mathbf{r}$, prior to the collision event will be discussed in Chapter 5.

The NO(X) molecular beam, typically referred to as the primary beam, is formed using a pulsed General Valve with 10% NO seeded in Ar at a backing pressure of 3 bar, and a repetition rate of 10 Hz. The gas is supersonically expanded into the vacuum chamber (which has beam-off pressures on the order of 1×10^{-7} mbar) resulting in adiabatic cooling of the gas. The use of a seed gas aids in this cooling, as well as suppressing clustering during the expansion process. As such the molecules in the molecular beam reside almost exclusively in their ground rovibrational state, $|j = 0.5, \Omega = 0.5, v = 0\rangle$. However, the Λ -doublet states are equally populated due to their energetic near degeneracy. The beam is skimmed ($d = 3$ or 5 mm), at a distance of approximately 3 cm from the face plate of the pulsed valve, such that the most rotationally cold and collinear part of the beam is selected.* To ensure quantum state selection of the initial state, the beam is then passed through an electrostatic hexapole of length 165 cm, which focuses

*The skimmer prevents the spatial edges of the molecular beam expansion which are sub-supersonic, where rotational and translational cooling is less efficient, from entering the hexapole.

the low field seeking $|j = 0.5, \Omega = 0.5, \varepsilon = -1, f\rangle$ state into the interaction region; collimation occurs at the entrance to the scattering chamber.

Upon reaching the centre of the scattering chamber, the primary molecular beam is crossed at right angles by the secondary molecular beam. The secondary beam is composed of the pure collision partner (either a rare gas or homonuclear diatomic), and is formed by a pulsed Jordan valve, operating at 5 Hz. The beam is operated at half the rate of the primary beam in order to allow on-the-fly background subtraction of the unscattered NO signal, minimising the errors associated with experimental drift. The backing pressure for the beam is determined for the specific collision partner such that no clustering is observed, and is typically on the order of 2 bar. The secondary beam is skimmed ($d = 3$ mm), before entry to the scattering chamber, at a distance of approximately 8 cm from the interaction region. After the scattering process the product NO is detected using quantum state-selective REMPI [239], described in more detail in Section 3.4. The excitation and ionisation lasers cross at right angles, in the plane defined by the molecular beams. The NO ions are then extracted along the time of flight (TOF) tube (0.7/1.0 m) using a series of ion optics to ensure velocity-mapping conditions [146, 147], before impacting on to a detector (composed of two micro-channel plates and a phosphor screen) where the experimental data is recorded with a CCD camera and sent to a computer for further analysis.

3.2 Molecular Beams

Careful measurements of the molecular beams used in the experiment are required to ensure that the collision energy of the system and the beam profiles are accurately modelled during analysis. There are two methods by which the collision energy of a system may be calculated; firstly, by directly measuring the velocity of the two molecular beams [240] and then calculating the mean collision energy, or by simultaneously fitting the collision energy and pixel-to-velocity ratio to the radii of a series of experimental images [189]. Two types of beam valves are used to produce pulsed molecular beams in this thesis: the General Valve (Series 9) and the Jordan electromechanical valve [241]. The General valve is very robust, and importantly, it is not easily

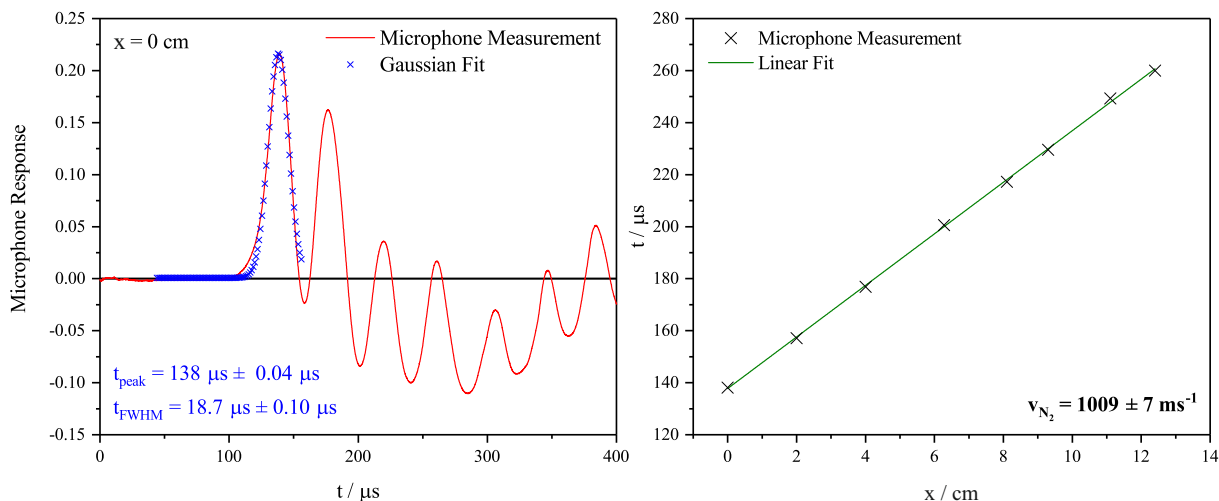


Figure 3.2: The procedure for using a microphone to calculate the velocity of a molecular beam of pure N_2 expanded through a Jordan valve. The left panel shows a single time trace, at distance $x = 0 \text{ cm}$, recorded by the microphone (red line), along with a Gaussian fit (blue crosses) to the initial microphone response. The right hand panel shows a plot of the measured (black crosses) distance, x , between the microphone and the face plate of the valve against the time taken for the gas pulse to arrive at the microphone, $t(x)$. The linear fit (green line) to the data has a gradient equal to $1/v$.

corroded by the NO in the primary molecular beam. The Jordan valve, whilst not as reliable and easily corroded, offers better performance with respect to the velocity spread of the molecular beam [240]. The Jordan and General valves are operated with conical and free jet type nozzles, respectively.

3.2.1 Molecular Beam Velocity

The velocity of a molecular beam composed of a specific gas (or mixture of gases) may be determined by placing a microphone within the vacuum chamber directly in the path of the beam. The molecular beam is fired, at time t_0 (which is known precisely), and the microphone responds to the pulse at position x at time t . Since the (mean) velocity of the molecular beam is fixed, the change in the response time of the system as a function of distance, $t(x)$, may be measured by recording the response time at several distances between the microphone and the beam valve. The distance is measured using a set of electronic Vernier callipers, with an accuracy of $5 \mu\text{m}$. The (mean) velocity of the molecular beam may then be calculated by a linear fit to a plot of distance against time, according to $v = dx/dt$.

Figure 3.2 shows a trace of the microphone response to a molecular beam of pure N_2 from a Jordan valve at a position $x = 0\text{cm}$. The Gaussian fit to the first peak in the time trace (*i.e.* the initial response of the microphone) is also shown, giving a time of arrival of $t(0) = 138\mu\text{s} \pm 0.04\mu\text{s}$. The microphone responds to the change in pressure (and not the flux density) upon arrival of the gas pulse, which is passed to an oscilloscope for analysis. The microphone response continues to ring for several milliseconds after the arrival of the gas pulse, due to the lack of resistance in vacuum. A plot of distance against time is also shown, along with the linear fit to the data; the gradient is equivalent to one over the velocity of the molecular beam, v_{N_2} . It is clear that there is very little scatter in the data ($R^2 = 0.99972$), showing the high precision of this method.

Upon supersonic expansion from a pulsed molecular beam valve into vacuum the internal energy of a gas is converted into kinetic energy, with a corresponding speed, which may be calculated by considering the thermodynamics of an expanding ideal gas [242, 243]

$$|v| = \sqrt{\frac{2k_B}{m} \left(\frac{\gamma}{\gamma - 1} \right) T}, \quad (3.1)$$

where $\gamma = C_p/C_v$ (*i.e.* the ratio of the heat capacities at constant pressure and volume), m is the mass of the gas, T describes the stagnation temperature, and k_B is the Boltzmann constant. For a mixture of 10% NO seeded in Ar, Equation 3.1 predicts a beam velocity of approximately 620ms^{-1} .[†] This accurately reproduces the experimentally measured velocity of the NO beam expanded *via* a General Valve (shown in Table 3.1), however, it should be noted that the thermodynamic equation poorly predicts the velocity of beams formed using a Jordan valve due to the mechanism of operation [240].

Table 3.1 shows the velocities of the molecular beams used in this thesis, measured using the microphone apparatus described above. The experimental beam velocity for the O_2 molecule, presented in Chapter 4, was measured before the microphone apparatus was installed; as such,

[†]Assuming that the General valve heats up during operation, due to the friction of the valve plunger and the resistance on the current applied to the valve, resulting in a stagnation temperature of $T \approx 334\text{K}$ [189]. Assuming a stagnation temperature equivalent to room temperature ($T = 298\text{K}$), the resultant velocity is 580ms^{-1} .

Collision Partner	v / ms^{-1}	$E_{\text{coll}} / \text{cm}^{-1}$	$E_{\text{coll}}^{\text{theory}} / \text{cm}^{-1}$
He	—	514 [92]	570*
Ne	965 ± 18	662 ± 12	662
Ar	726 ± 5	651 ± 5	651
Kr	531 ± 1	618 ± 2	618
Xe	337*	—	503*
N ₂	1009 ± 7	845 ± 7	845
NO (10% in Ar)	617 ± 2	—	—

Table 3.1: Measured (mean) velocity, v , of molecular beams composed of Ne, Ar, Kr, Xe and N₂ from a Jordan valve, and 10% NO in Ar from a General Valve. In each case the resulting (mean) collision energy, E_{coll} , is shown for scattering between the collision partner and NO (in Ar), along with the collision energy used in theoretical calculations. Where experimental values are not available [*] the thermodynamic values, according to Equation (3.1), for the velocity were used. All data in this thesis are shown for these collision energies unless otherwise stated. The experimental data for He refers to that of Stolte and coworkers [92].

the velocity is calculated from the collision energy, using the method described in Section 3.2.2. The trend is as expected; the heavier rare gases (Ar and Kr) have molecular beams with a lower mean velocity than those of the lighter rare gases (Ne). The velocity of the N₂ molecule may be expected to lie between Ne and Ar, if one considers only mass effects, however the recorded velocity is significantly higher. This can be understood by considering the ratio of the heat capacities, γ : $\gamma = 5/3$ and $\gamma = 7/5$ for an atom and diatom (excluding vibrations), respectively.[‡] The smaller ratio of the specific heat capacities for diatoms leads to a larger value for the $(\gamma/\gamma - 1)$ term in Equation (3.1), and therefore a higher (mean) velocity.

The microphone apparatus may also be used to calculate the opening time of the beam valve, by placing the microphone very close to the beam valve to ensure that velocity spreads play a minimal role in the profile of the beam. Previous work by Gordon [240] found opening times of $165 \mu\text{s}$ and $22 \mu\text{s}$ for the General and Jordan valves, respectively. The velocity spreads in the molecular beam are calculated by operating the molecular beam under experimental conditions (to ionise trace NO). The laser delay is then scanned and the ion yield at each time recorded,

[‡]For an atom the specific heat capacity at constant pressure and constant volume are $5/2$ and $3/2$, respectively. For a diatom (excluding degrees of freedom arising from vibrations, which are not accessed at these temperatures) the values are $7/2$ and $5/2$, respectively [244]. These values are calculated from thermodynamics for the case of an ideal gas, and some deviations are expected.

to create a temporal profile of the molecular beam, which may then be fitted to a Gaussian (with contributions from both the opening time and the beam velocity spread). Simulations by Gordon [240] suggest that the speed spread of a 10% beam of NO in Ar (formed *via* a General valve) is approximately 8% of the mean speed, which is congruent with work by Eliooff [245], corresponding to a FWHM speed spread of 49ms^{-1} . For the Jordan valve the beam speed spread is calculated to be approximately 5% of the mean beam speed. These values are used throughout this thesis in calculations and simulations of the molecular beams.

3.2.2 Experimental Collision Energy

If the speed of both molecular beams is known, then the (mean) experimental collision energy may be calculated (assuming that the beams cross at right-angles) according to

$$E_{\text{coll}} = \frac{1}{2}\mu v_{\text{rel}}^2, \quad (3.2)$$

where μ is the reduced mass of the system and, v_{rel} is the relative velocity

$$|v_{\text{rel}}|^2 = |v_{\text{NO}}|^2 + |v_{\text{CP}}|^2, \quad (3.3)$$

and v_{NO} and v_{CP} are the velocities of the molecules in the NO and collision partner beams respectively. The collision energies for the systems discussed in this thesis are shown in Table 3.1. The errors are calculated by propagating the error in the velocities of each collision partner measured using the microphone method. The experimental measurements for NO(X) + He, made by Stolte and co-workers [92], are shown for comparison, although calculations in this thesis are done at the thermodynamic value calculated according to Equation (3.1).

The pixel-to-velocity ratio, which describes the conversion between the velocity in the centre of mass frame and distances on the detector (in units of pixels), may be described by

$$p = \frac{|v_{\text{NO}}|}{n}, \quad (3.4)$$

where v_{NO} is the initial velocity of the NO molecule. n , the number of pixels, may be obtained by overlaying the Newton triangle and an ion image containing both molecular beams: trace NO is seeded in the secondary molecular beam such that the ‘velocity’ of the ground state of the NO molecules in both beams may be imaged. The number of pixels corresponding to the NO (primary) side of the Newton triangle may then be calculated and p determined. It is important to note that the pixel-to-velocity ratio depends on several experimental factors, including but not limited to the extraction voltages used for velocity-mapping, the length of the time of flight tube (0.7/1.0m) and the presence of an orientation field in the interaction region.

If the speed of both molecular beams is not known, then the (mean) experimental collision energy may be calculated from the radii of the experimental ion images. The radius of the Newton sphere for a specific rotational state with outgoing energy, E'_T , is proportional to the outgoing velocity of the NO molecule, after the collision

$$r = \frac{1}{p} \frac{m_{\text{CP}}}{m_{\text{NO}} + m_{\text{CP}}} \sqrt{\frac{2E'_T}{\mu}}, \quad (3.5)$$

where m_{CP} and m_{NO} are the masses of the collision partner and NO molecule, respectively, and μ is the reduced mass of the system. The outgoing energy of the (atom-diatom) system is defined by

$$\begin{aligned} E'_T &= E_{\text{coll}} - \Delta E_{\text{rot}} \\ &= E_{\text{coll}} - B_{\text{NO}} [j'(j' + 1) - j(j + 1)], \end{aligned} \quad (3.6)$$

where ΔE_{rot} is the change in rotational energy of the NO molecule during the collision process and $B_{\text{NO}} = 1.6961 \text{ cm}^{-1}$ [188] is the rotational constant for the NO molecule. The radius of the experimental ion image is calculated by extracting the radial distribution (integrated over all angles). The radial distribution is then fitted to a Gaussian function and the peak of the Gaussian taken as the radius of the ion image. This process is shown in the left hand panel of Figure 3.3, for the collisions of NO + Ar scattering into $\Delta j = 7$. Due to the non-Gaussian shape of the experimental data at low values of r , it is necessary to fit only the outer edge of the distribution,

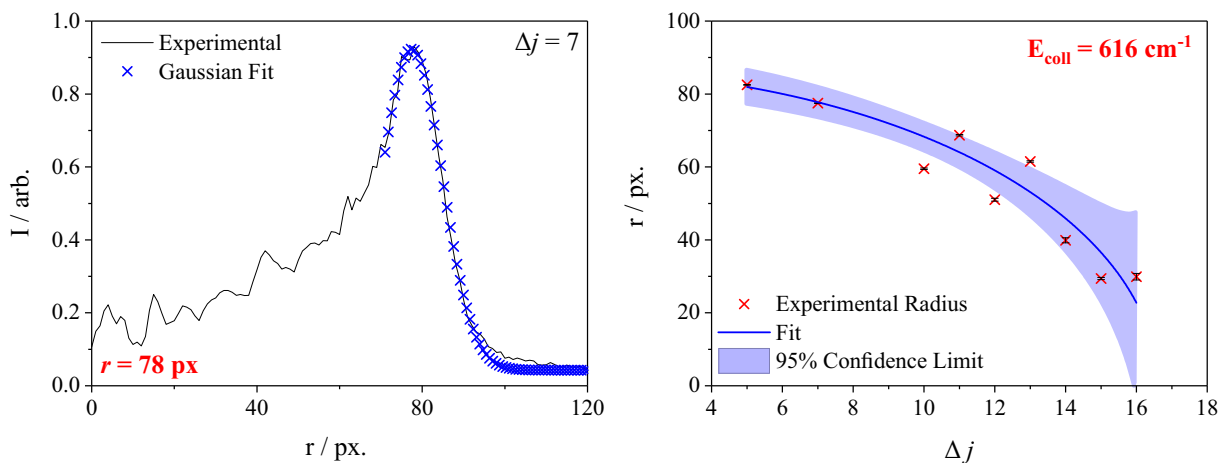


Figure 3.3: Fitting method to calculate the collision energy of NO + Ar scattering. The radial distribution (black line), fitted to a Gaussian (blue crosses), is shown in the left hand panel, for $\Delta j = 7$. The calibration curve of Δj against r , for spin-orbit conserving transitions, is shown in the right hand panel: the experimental radius is shown by red crosses, the fit to Equation (3.5) is shown by a blue line, and the blue shaded area shows the 95% confidence limit of the fit. Error bars for each radius are calculated by considering the error in the Gaussian fit to the radial distribution shown in the left hand panel.

since it is this that defines the radius of the image. The centre of the Gaussian is taken to be equivalent to the outer radius of the Newton sphere, $r = 78.5 \pm 0.1$ px., for this specific state.

Figure 3.3 shows a plot of r against Δj for the spin-orbit conserving collisions of NO with Ar, and the resulting fit to Equation (3.5). The radius of the Newton sphere decreases with Δj as expected, with increased rotational energy transfer giving rise to the decreased outgoing velocity of the NO molecule after the collision. The fit to the experimental radii gives a value of $E_{\text{coll}} = 616 \pm 36 \text{ cm}^{-1}$ and $p = 5.5 \pm 0.3 \text{ ms}^{-1} \text{ px}^{-1}$. It should be noted that the data was recorded with initial orientation of the NO bond axis, and a TOF tube of length 1.0m, giving rise to a smaller value of p than used in Chapter 4 for the unoriented collisions of NO + Ar/O₂. The uncertainty in the collision energy was calculated from the 95% confidence limit of the fit to the data in Figure 3.3. The agreement between the collision energy calculated from the two methods is within the errors of each method, giving confidence in the calculated collision energies in Table 3.1; with the radius calibration method giving a lower value of E_{coll} than the microphone measurement ($E_{\text{coll}} = 651 \pm 5 \text{ cm}^{-1}$), as well as a larger uncertainty in the (mean) collision energy. This is not unexpected since the microphone allows direct measurement of

the velocity of each molecular beam (and therefore the collision energy), whilst the radius calibration method is somewhat more indirect.

3.2.3 Rotational Temperature of the Molecular Beam

In statistical mechanics the population of rotational states in a system may be described in terms of the rotational temperature of the system [244]. The higher the rotational temperature, the larger the population of rotational states above the ground rotational state of interest. It is preferential for the rotational temperature of a molecular beam to approach as closely to $T_{\text{rot}} = 0\text{K}$ as possible, to ensure that the entire population of the beam is in the ground spin-orbit and rotational state. Experimentally, a skimmer is employed to select the central, rotationally coldest part of the molecular beam before entrance to the hexapole [242].

The rotational temperature of the molecular beam may be investigated by recording a REMPI spectrum of the $\text{NO}(A \leftarrow X)$ transition, without hexapole state selection, in which the ion count as a function of wavelength is recorded. The experimentally recorded REMPI (see Section 3.4.2) spectrum for the primary beam composed of 10% NO in Ar is shown in Figure 3.4, recorded with 40 laser shots at each wavelength, with a spacing of 0.005 nm in the region $\lambda = 2261 - 2263 \text{ \AA}$. Care was taken to avoid saturating the transitions, by using the lowest laser power possible to record the signal. The series of peaks in the experimental spectrum corresponds to the different rotational states of NO which are populated in the molecular beam; the intensity of each peak is defined not only by the population of that specific state but also the transition probability for the electronic ($A \leftarrow X$) transition. To calculate the population of each state present in the molecular beam, the experimentally recorded intensity must be divided by the branch dependent transition probability for that state (obtained from LIFBASE [246]).

It is necessary to record the position and intensity of each peak in the spectrum and, after assigning each peak to a specific rotational state, j , to plot a Boltzmann plot. The population of a molecule in a specific rotational state, j , may be calculated according to [244]

$$P(j) = g(j) \exp\left(\frac{-E_{\text{rot}}(j)}{k_{\text{B}}T_{\text{rot}}}\right), \quad (3.7)$$

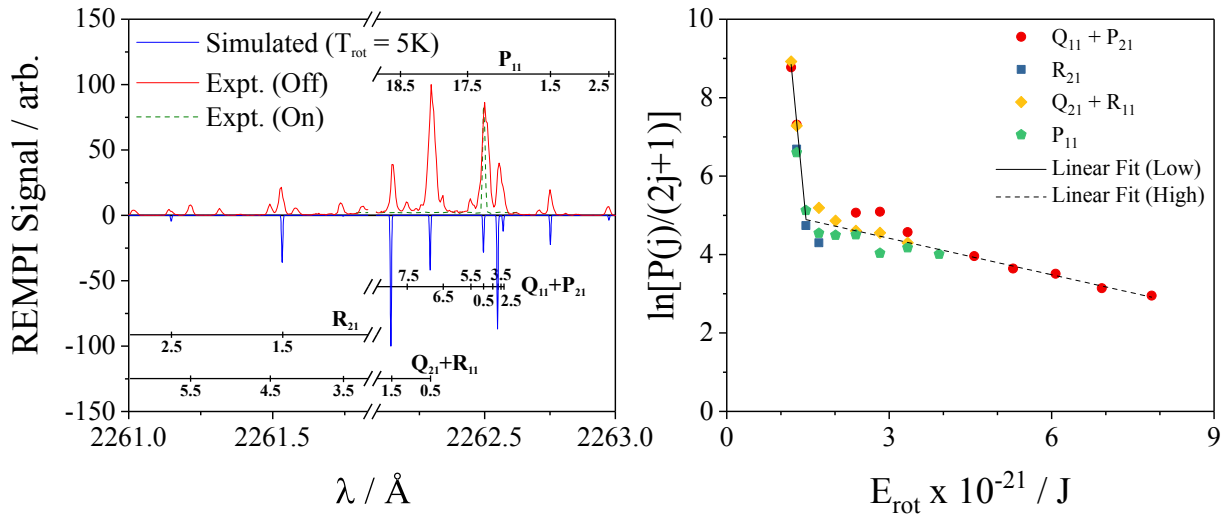


Figure 3.4: Analysis of the rotational temperature, T_{rot} , of the primary molecular beam (10% NO seeded in Ar). Left: experimental (red line) and LIFBASE [246] simulation at $T_{\text{rot}} = 5\text{ K}$ (blue line) of the REMPI spectrum of NO, with no hexapole electric field applied to the beam. The experimental (scaled) REMPI spectrum of NO, with an applied hexapole electric field, is shown by grey (dashed) lines. The R_{21} , P_{11} , $Q_{21} + R_{11}$, and $P_{21} + Q_{11}$ branches are shown for the rotational states observed. The break in the x -axis (between 2261.8 and 2262.1 Å) arises due to the intense peak in signal observed on the R_{21} line at these wavelengths, corresponding to the $|j = 0.5, \epsilon = -1, f\rangle$ state. Right: Boltzmann plot of the data from the experimental REMPI scan, where the pure branches, P_{11} and R_{21} , are shown by green pentagons and blue squares, respectively, and the mixed $Q_{11} + P_{21}$ and $Q_{21} + R_{11}$ branches are shown by red circles and yellow diamonds, respectively. Linear fits are shown for the low and high rotational energy regimes, by full and dashed black lines, respectively.

where $g(j) = 2j + 1$ is the degeneracy of the rotational state j , $E_{\text{rot}}(j)$ is the rotational energy, k_B is the Boltzmann constant and T_{rot} is the rotational temperature of the molecular beam. Plotting $\ln[P(j)/2j + 1]$ against $E_{\text{rot}}(j)$, gives a gradient of $-1/k_B T_{\text{rot}}$, allowing extraction of the rotational temperature. The data extracted from the experimental REMPI spectrum is plotted in the right hand panel of Figure 3.4. More than one population is shown for each rotational state due to the two Λ -doublet states and the possibility for recording each state on multiple branches. Whilst some scatter is observed in the data, two regimes are clearly observed; these will be referred to as the low ($j = 0.5 - 2.5$) and high ($j = 3.5 - 13.5$) rotational energy regimes. Linear fits to the data in each regime give two clear rotational temperatures: $T_{\text{rot}} = 5.03 \pm 0.18\text{ K}$ and $T_{\text{rot}} = 233.80 \pm 9.20\text{ K}$ in the low and high regimes, respectively. It should be noted that the contributions from the higher energy part of the molecular beam, which arise from effusive or subsonic components of the molecular beam [102], are not of concern, since their relative populations are low. Furthermore, the use of hexapole state selection (the principles of which are

described in Section 3.3), focuses only the $|j = 0.5, \Omega = 0.5, \varepsilon = -1, f\rangle$ state into the scattering chamber.

The green dashed line in Figure 3.4 shows the REMPI spectrum recorded with the hexapole electric field applied; the intensity has been scaled such that the peaks of interest match the intensity of the peaks in the scan in which no hexapole field is applied (since the spectra are recorded with different MCP voltages due to the large difference in signal intensity with and without the field). The hexapole-on REMPI spectrum shows that the vast majority of molecules are in the desired $|j = 0.5, \Omega = 0.5, \varepsilon = -1, f\rangle$ rotational state when they reach the interaction region, corresponding to only a single peak in the spectrum (the other peak occurs in the region not shown).

The experimental rotational temperature may be used to simulate the REMPI spectrum expected at the specific T_R obtained from the Boltzmann plot, using the LIFBASE software [246], as shown in the left hand panel in Figure 3.4. The match between the major peaks in the experimental and simulated spectra (at $T_{\text{rot}} = 5$ K) is good; it is important to note that the peaks which dominate in the experimental spectrum correspond to the low rotational energy regime of the molecular beam. For the rare gas collision partners the ‘rotational temperature’ of the molecular beam is undefined, since these collision partners are atomic, and as such there are no concerns about state selection beyond the atoms being in their ground electronic state. In Chapter 4, the effects of the expansion of a diatomic gas into a vacuum without further state selection will be discussed in terms of the $\text{O}_2(\text{X})$ molecule.

3.3 Hexapole State Selection

The rotational levels of the $\text{NO}(\text{X})$ molecule are split into two nearly degenerate Λ -doublets, with only a very small difference in energy (about 0.0119cm^{-1} for $j = 0.5$ in the ground spin-orbit state [191]). As such, the population of the two Λ -doublets is almost identical after supersonic expansion of the molecular beam, and if a single state is not selected then all experimental measurements will average over the initial e and f states, as is the case in

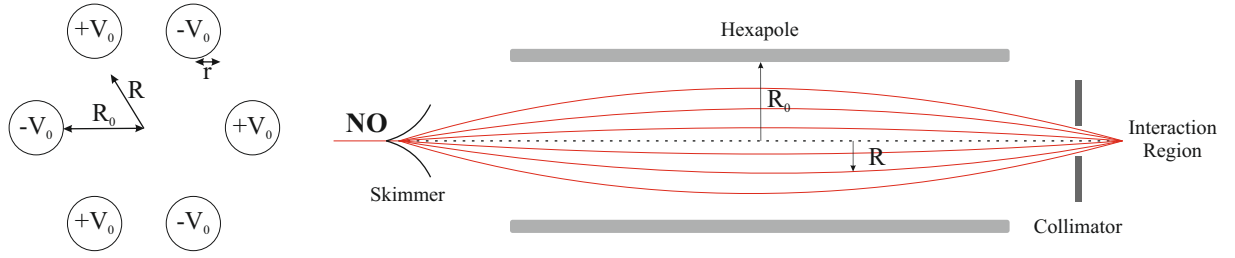


Figure 3.5: Hexapole State Selection. Left: Cross-section of the hexapole state selector; positive and negative voltages, $\pm V_0$, are applied to alternate hexapole rods (diameter $d = 2.5$ mm) with typical voltages of ± 10 kV required to focus the $|j = 0.5, \Omega = 0.5, \epsilon = -1, f\rangle$ state of the NO(X) molecule. R_0 and R are the inner radius of the hexapole and the radial displacement of the molecule from the centre line, respectively. Right: Schematic of focusing of low field seeking states along the length of a hexapole.

many previous studies of NO(X) [25, 148, 149, 163]. Experimentally, selection of the initial Λ -doublet state of interest is achieved by passing the NO(X) beam (after supersonic expansion and passage through a skimmer) through a hexapole electric field, generated by six cylindrical rods (diameter $d = 2.5$ mm) to which alternating positive and negative voltages are applied. A cross section through the hexapole state selector is shown in the left hand panel of Figure 3.5. This technique utilises the *Stark* effect (the shifting of a molecule's energy levels in an electric field) to guide low field seeking states down the length of the field, whilst expelling high field seeking states.

In a static electric field, $\mathbf{E}$, the first order Stark interaction energy between the molecule and the field is [114]

$$V_{\text{stark}} = -\boldsymbol{\mu} \cdot \mathbf{E} = -\mu E \cos \theta_{\mu E}, \quad (3.8)$$

where $\mu = 0.16$ D is the permanent dipole moment of the NO molecule [247, 248] and $\theta_{\mu E}$ is the polar angle between the dipole and the electric field of strength, E . In an ideal hexapole field (which is three-fold axially symmetric),[§] the radial potential from the centre of the rods is [114, 249]

$$V(R) = V_0 \left(\frac{R}{R_0} \right)^3 \cos 3\phi, \quad (3.9)$$

[§]To create an ideal hexapole field it is necessary to use electrodes with hyperbolic shapes [117, 249]. The use of cylindrical electrode, see Figure 3.5, provides a good approximation of the ideal field; such electrodes have been widely used [42, 93, 94, 114, 117, 247].

where R and ϕ are cylindrical coordinates, V_0 is the applied potential and R_0 is the inner radius of the hexapole.

The magnitude of the ideal hexapole field may be calculated at a radial distance, R , from the centre of the hexapole according to

$$E = -\frac{dV}{dR} = -3V_0 \frac{R^2}{R_0^3}. \quad (3.10)$$

By combining Equations (3.8) and (3.10) it can be shown that molecules in the hexapole field experience a radial force

$$F(R) = -\frac{dE}{dR} = \mu \langle \cos \theta_{\mu E} \rangle \frac{dE}{dR} = \frac{6V_0 \mu R}{R_0^3} \langle \cos \theta_{\mu E} \rangle, \quad (3.11)$$

where

$$\langle \cos \theta_{\mu E} \rangle \approx \frac{\varepsilon |m\Omega|}{j(j+1)}, \quad (3.12)$$

as they travel along the length of the hexapole.

From Equation (3.11), it is clear that molecules with $\varepsilon = -1$, f will experience a restoring force toward the centre of the hexapole, whilst molecules with $\varepsilon = +1$, e will be high field seeking and diverge from the path of the hexapole [120]. The field down the length of the hexapole causes low field seeking states to undergo harmonic motion about the centreline, with a frequency depending on the m , j , and Ω quantum numbers. The potential applied to the rods may be tuned such that the $|j = 0.5, \Omega = 0.5, \varepsilon = -1, f\rangle$ state undergoes half a wavelength of harmonic motion, leading to molecules being focused into the interaction region.

The oscillation frequency of a molecule in the hexapole field is proportional to the magnitude of the electric dipole moment, $|\mu|$. Since $|\mu_{\text{NO}}| = 0.16\text{D}$ [247, 248] is very small, the frequency of the oscillation of molecules in the field is very low (*i.e.* the wavelength is very long). As such, the hexapole required to focus a specific state of NO(X) is very long (1.65 m in this experiment) at moderate applied voltages (in the region of $\pm 10\text{kV}$): this limits the density of the focused beam that can be achieved. Shorter (30 cm) hexapoles have been used to state

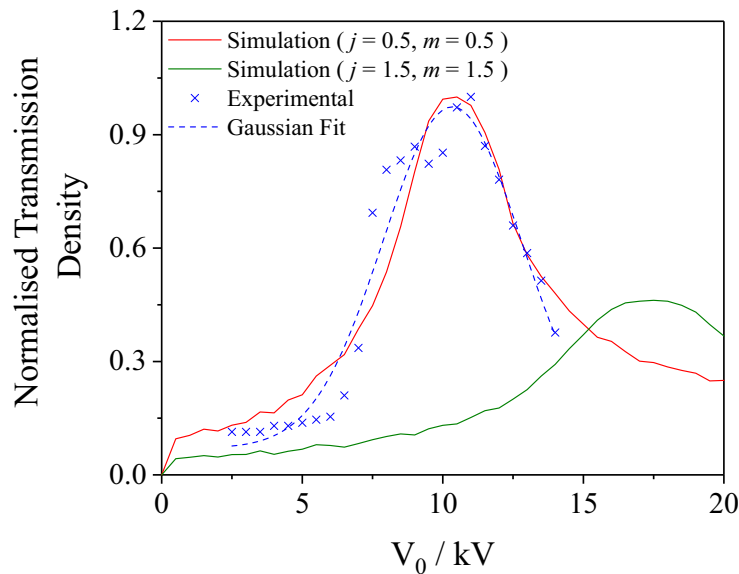


Figure 3.6: Normalised transmission density of NO(X) $|j, m = |j|, \Omega = 0.5, \varepsilon = -1, f\rangle$ into the interaction region as a function of applied voltage (on the hexapole rods). The red and green lines show the simulated transmission density for $j = 0.5$ and $j = 1.5$ respectively, whilst the blue crosses show the experimental signal obtained from the hexapole focused NO(X) in the $j = 0.5$ state, with a Gaussian fit to the data shown by blue dashed lines. The transmission density of the $j = 0.5$ state is normalised such that the peak value is unity, whilst the $j = 1.5$ state is normalised to the relative population of the state prior to entrance to the hexapole.

select NO(X), however these require application of much higher voltages [117]. For molecules with a larger permanent electric dipole, such as OH(X) with $|\mu_{\text{OH}}| = 1.66 \text{ D}$ [250], much shorter hexapoles may be used for state selection [41, 42, 93, 94].

It is important to note that measurement of the high field seeking ($\varepsilon = +1, e$) state is not possible using hexapole state selection, as the state is defocused by the field and expelled from the hexapole. In principle, the measurement could be made by taking the difference between the Λ -doublet unresolved signal (*i.e.* the signal with the hexapole field off) and the Λ -doublet resolved $\varepsilon = -1, f$ state signal. This could be achieved on a shot-by-shot basis by switching the hexapole on and off on alternate laser shots. It is also possible to focus low field-seeking states of higher rotational levels of NO(X), by tuning the voltage applied to the hexapole; for example, to focus the $|j = 2.5, \Omega = 0.5, |m| = 2.5, \varepsilon = -1, f\rangle$ state, simulations predict focusing occurs for voltages of approximately $\pm 25 \text{ kV}$. However, the population of such states in the beam is very small after supersonic expansion and the signal from such states would be low.

Figure 3.6 shows the experimental signal from hexapole-focused NO(X) and the calculated transmission of the $|j, m = |j|, \Omega = 0.5, \epsilon = -1\rangle$ state, for $j = 0.5$ and 1.5 . The transmission density has been normalised such that the $j = 0.5$ state is unity at its peak, whilst the $j = 1.5$ state is scaled according to the relative population, at $T_{\text{rot}} = 5\text{ K}$, prior to entrance to the hexapole ($P_{0.5}:P_{1.5} = 2.2:1$). The maximum transmission density in both the experimental and simulated cases is observed to occur at approximately 10.3 kV, and this voltage was applied to the hexapole rods throughout the work in this thesis. The calculated transmission density fits the experimentally observed transmission well in the region of peak transmission, both in terms of the peak position and the width of the tuning peak, however the fit at low voltages is less good. This arises from the smaller force that molecules feel when a low voltage is applied to the rods, leading to molecules approaching closer to the rods. In this limit, the ideal hexapole approximation is not valid as the molecules feel an asymmetric field from the six rods of the hexapole. The experimental state selectivity in the interaction region is calculated by considering the relative transmission of the two states at the voltage for which maximum transmission of the $j = 0.5$ state is observed; $\approx 90\%$ of molecules in the interaction region are in the $j = 0.5$ state, and $\approx 10\%$ reside in the $j = 1.5$ state.

3.4 Detection

For a completely state-to-state resolved experiment, the NO(X) molecules that are rotationally excited during the scattering event must be state selectively detected. This is achieved by resonantly enhanced multi-photon ionisation (REMPI) [239] coupled with velocity map [146] ion imaging [147] (VMI).

3.4.1 Laser Systems

A XeCl excimer laser (Lambda-Physik EMG 202 MSC), lasing at 308 nm, was used to generate approximately 120 mJ/pulse of light. The beam was passed through a beam splitter, and approximately 90% of the excimer output was used to pump a tunable dye laser (Lambda-Physik

FL3002), with the lasing medium Coumarin 450/Coumarin 2 in methanol, to produce 452 nm light. The light was then frequency doubled with a BBO crystal to approximately 226 nm and the wavelength tuned to a specific rovibrational NO ($A \leftarrow X$) transition. The output of the dye laser was passed through a Rochon polariser and (optionally) a photoelastic modulator (PEM), to allow the polarisation of light to be controlled on a shot-by-shot basis. Before entering the scattering chamber the light was collimated using an iris (on the order of 1 mm), before it intersected the molecular beams at 45° in a coplanar fashion. The remaining 10% of the 308 nm output was also directed into the scattering chamber, in the plane of the molecular beams and perpendicular to the dye laser output, for the near-threshold ionisation of NO(A) molecules to NO^+ ions. The excimer beam is slightly divergent and so the beam was loosely focused into the scattering centre using a $f = 300$ mm focal length lens. The overlap of the two lasers results in a detection volume of approximately $1.0 \text{ mm} \times 1.5 \text{ mm} \times 3 \text{ mm}$ [189, 251, 252].

3.4.2 Detection Scheme

Upon exiting the hexapole state selector, the NO(X) molecules in the f Λ -doublet of the ground rotational state are focused into the centre of the scattering chamber, where they collide at right angles with a skimmed beam of the collision partner of interest. During the collision process rotational energy transfer (RET) occurs from the initial linear momenta of the collision partners into the rotational energy of the NO(X) molecule. Consequently, many final rotational states of the NO molecule are populated over the surface of a Newton sphere, with the radius of the sphere corresponding to the specific final rotational state of the NO molecule and the initial collision energy of the system. The distribution of these ions around the Newton sphere contains all the information about the angular distribution of the scattered products, as well as polarisation information.

The scattered NO(X) molecules were state selectively ionised using a $(1 + 1')$ REMPI scheme [239]. The wavelength of the dye laser described in Section 3.4.1, in the region of 226 nm, is tuned to a specific final NO($X, \Omega', j', \epsilon'$) state to cause the transition from the NO($X^2\Pi$) ground state to the excited NO($A^2\Sigma^+$) electronic state. A 308 nm photon

from the excimer laser is then used to selectively ionise molecules in the NO(A) state. This specific ionisation scheme allows the dye laser power to remain low, avoiding saturation of the NO(A) $\leftarrow$ NO(X) transition, which would prevent accurate determination of polarisation effects [239].

The Newton sphere of the NO⁺ ions, corresponding to a particular final rotational quantum state, is then velocity-mapped [146] onto a position sensitive detector with diameter ≈ 40 mm. This is achieved using an inhomogeneous electric field to focus ions with the same LAB frame velocity (but different initial positions) onto the same point on the detector, minimising blurring due to the finite detection volume [146, 253]. The field is generated using a set of three ion optics: a positively charged extractor and repeller and a ground electrode. In the experiments here typical voltages were 1500 V on the repeller and 600 – 850 V on the extractor plate. Tuning the ratio of the extractor and repeller voltages allows focusing of the velocity-mapped ions onto the detector at the end of the time of flight tube. One may also change the ratio such that the ions are mapped spatially onto the detector, allowing the interaction volume to be imaged and information about the width of the laser beams to be obtained.

The position sensitive detector is composed of a set of two microchannel plates (MCPs) coupled to a P43 phosphor screen: typical operating voltages correspond to application of approximately ± 900 V to the MCPs (*i.e.* a potential difference of 1800 V across the pair) and 3.4 kV to the phosphor screen. Each MCP is composed of 1×10^7 channels, each of diameter $10 \mu\text{m}$. The front MCP in the TOF tube is pulsed from ground to a set voltage (-900 V) to create a gate across the detector over the NO time of flight region, reducing the effect of background ions formed by the lasers on the recorded data. When an ion impacts on the front face of the detector and enters a channel, a cascade of electrons is accelerated towards the (back) MCP (held at $+900$ V), amplifying the observed signal. The ejected electrons from the MCPs hit the phosphor screen creating fluorescence, which is recorded by a charge coupled device (CCD) camera (Allied Vision Manta G-031). The intensity recorded by the camera is sent to a computer for on-the-fly processing and storage before further data analysis.

A single laser shot may produce between 1 and 10 ions, depending on the detection efficiency of the detector, the laser power and the absolute cross section of the process being studied. To converge an image, tens of thousands of laser shots are required, with the exact number depending on the signal-to-noise ratio and the number of ions per shot. When collecting bond-axis resolved data (discussed in Chapters 5 through 7) the number of data acquisition channels is doubled, and as such the number of laser shots required typically also doubles.

Post Processing

All of the ion images presented in this thesis have been corrected for the non-uniformity of ion hits due to detector inhomogeneity, which can be a problem when reading the experimental data directly from the video stream of a CCD camera [240]. Each ion hit on the detector is several pixels wide (depending on the MCP gain), and their non-uniformity can lead to blurring in the velocity space of the image. To correct for this, a centroiding algorithm with event counting implemented by Gordon [240] is used (modified to allow reconstruction of the raw image as required). Images are analysed directly from the output stream of the detector. First, camera noise is filtered below a user defined threshold, to remove background but retain ion hits. The centroiding algorithm then finds the centre of mass of each individual ion signal, and fits circles to each raw ion hit. To achieve convergence, which cannot be done by centroiding alone, a Gaussian blur is applied (with a typical FWHM of 2-3 pixels) when the ion images is rebuilt from the centroided data [240].

3.5 Data Analysis Method

The experimental image recorded on the detector is the two-dimensional projection of a three-dimensional Newton sphere; in which the intensity is maximal at the outer edges of the sphere, but contributions from ions with out-of-plane components produce intensity within the imaged radius on the detector. The distribution of directions of the final velocity of the NO^+

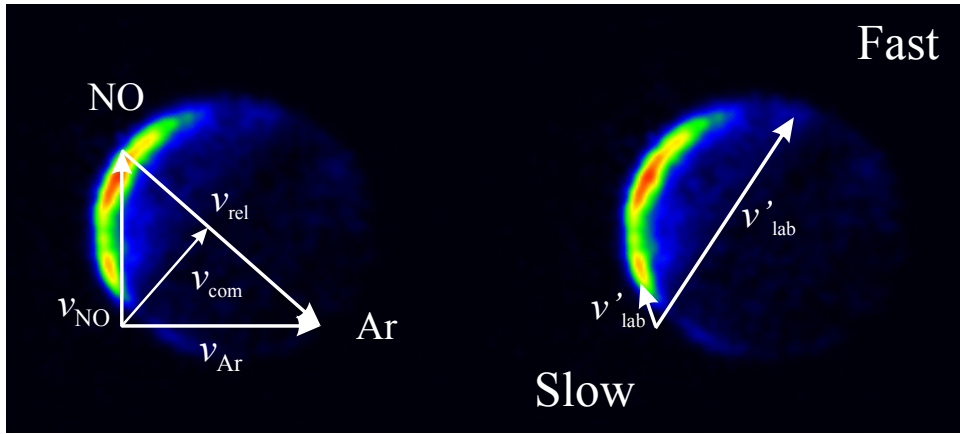


Figure 3.7: Experimental ion image for the scattering of NO(X) with Ar into the final $|j' = 7.5, \Omega' = 0.5, \epsilon' = +1, e\rangle$ state. The left hand panel depicts the ‘crushed’ Newton sphere overlaid with the Newton triangle showing the initial velocity of NO (v_{NO}) and Ar (v_{Ar}), the initial relative velocity of the system (v_{rel}), and the initial centre of mass velocity, v_{com} . The right hand panel shows the same ‘crushed’ Newton sphere with the LAB frame velocity of the NO molecule after the collision event, v'_{lab} , for scattering into the near (slow) and far (fast) sides of the Newton sphere.

ions with respect to the initial relative velocity, v_{rel} , is related to the DCS for the scattering process. Assuming that no external fields are present, scattering is symmetric about v_{rel} and scattering through the polar angle, θ , should be equally probable for all azimuthal angles. This symmetry is not observed in the experimental image for the NO(X) + Ar scattering process $|j' = 7.5, \Omega = 0.5, \epsilon' = +1, e\rangle \leftarrow |j = 0.5, \Omega = 0.5, \epsilon = -1, f\rangle$, shown in Figure 3.7, in which the image is rather asymmetric about v_{rel} .

The asymmetry arises due to different LAB frame velocities at different positions on the Newton sphere: where a LAB frame velocity of zero, $v_{\text{LAB}} = 0 \text{ ms}^{-1}$, occurs at the right angle of the Newton triangle. Molecules scattered into the side of the Newton sphere closest to the LAB zero (bottom left corner) have smaller LAB frame velocities than those scattered through the same polar angle but into the ‘far’ side of the Newton sphere (top right corner). Molecules with large LAB frame velocities will therefore spend less time in the detection volume than those with small LAB frame velocities, giving rise to a lower detection probability. In the experimental image this effect is observed as a bright ‘slow’ and dim ‘fast’ side of the Newton sphere. This geometry dependent effect must be accounted for during analysis of the experimental image.

For a single scattering event, n , the intensity of the detected signal at a pixel with coordinates (x_n, y_n) can be written as a product of three factors [39, 40, 86]: the polarisation information (which is assumed not to depend on the experimental parameters described above); the angular scattering probability, $P_{\text{scatt}}(\theta_n)$, which is related to the DCS of the state of interest; and the instrument function, which describes the variation in the detection probability of NO ions due to experimental parameters.

$$i(x_n, y_n, j_n, j'_n, j_n^*, \Gamma_n) = z(x_n, y_n, j_n, j'_n) P_{\text{scatt}}(\theta_n) A(x_n, y_n, j'_n, j_n^*, \Gamma_n), \quad (3.13)$$

where $z(x_n, y_n, j_n, j'_n)$ is the instrument function and $A(x_n, y_n, j'_n, j_n^*, \Gamma_n)$ describes all the polarisation information for the process of interest. j_n and j'_n are the initial and final rotational angular momenta of the NO molecule, j_n^* is the rotational level the NO molecule is excited to in the A state and $\Gamma_n = (\Theta_n, \Phi_n, \chi_n)$ represents the Euler angles which describe the relative orientation of the detector frame (defined by the laser propagation vectors) and scattering frame (defined by the plane which contains the initial and final relative velocity vectors, $\mathbf{k} - \mathbf{k}'$).

The total intensity at a pixel (x, y) is the integral over the instrument function, the scattering probability and any polarisation correction factors [39, 40, 252, 254]:

$$\begin{aligned} I(x, y, j, j', j^*, \Gamma) &= \int \int \int \int \int \int \int n_{\text{NO}}(\mathbf{r}_{\text{NO}}, \mathbf{v}_{\text{NO}}, t'_{\text{NO}}) n_{\text{CP}}(\mathbf{r}_{\text{Rg}}, \mathbf{v}_{\text{CP}}, t'_{\text{CP}}) \\ &\quad \times f_{t_{\text{NO}}} f_{t_{\text{CP}}} \frac{v_{\text{rel}}}{v'_{\text{NO}}} \sigma(v_{\text{rel}}) P(\mathbf{r}_{\text{det}}) P_{\text{scatt}}(\theta) A(x, y, j', j^*, \Gamma) \\ &\quad \times \delta(t_{\text{NO}} - t'_{\text{NO}}) \delta(t_{\text{CP}} - t'_{\text{CP}}) dt'_{\text{NO}} dt'_{\text{CP}} dv_{\text{NO}} dv_{\text{CP}} dt_{\text{coll}} d\mathbf{r}_{\text{coll}} d\mathbf{r}_{\text{det}} \end{aligned} \quad (3.14a)$$

$$\approx \sum_n z(x_n, y_n, j_n, j'_n) P_{\text{scatt}}(\theta_n) A(x_n, y_n, j'_n, j_n^*, \Gamma_n), \quad (3.14b)$$

where n_{NO} and n_{CP} are the number densities of the NO and collision partner beams, depending on the the initial position, $\mathbf{r}$, initial velocity, $\mathbf{v}$, and time, t . $f_{t_{\text{NO}}}$ and $f_{t_{\text{CP}}}$ define the velocity distributions of the NO and collision partner molecular beams respectively. σ is the cross section for the collision process, and $P(\mathbf{r}_{\text{det}})$ is the probability that the molecule is detected at position $\mathbf{r}_{\text{det}}$, which depends on the laser position and the time at which the laser is fired. The

Dirac delta functions ensure that both the NO molecule and the collision partner are at position $\mathbf{r}_{\text{coll}}$ at the time of the collision, t_{coll} . The ratio $v_{\text{rel}}/v'_{\text{NO}}$ is necessary to obtain the correct flux of the NO molecules. The integrals are performed over all initial positions and starting times, and over the collision and detection volumes defined by the molecular beam and laser overlap, respectively.

Once all of the experimental parameters have been determined for the geometry and collision partner of interest, see below, a Monte Carlo integration of Equation (3.13) may be performed computationally [189, 252, 254]. The initial conditions are sampled from the experimental distributions, and the final positions on the detector recorded and weighted by the correction probability for each individual collision. To produce a converged simulation of the instrument function typically requires on the order of 1×10^8 ‘trajectories’. Experimentally, an ion hit can be spread over multiple pixels on the detector; to account for this, Gaussian blurring was applied to the simulated ion image at the end of the calculation.

3.5.1 Flux Density Correction

The process of calculating the instrument function, z , also known as the flux density correction, for the experimental apparatus used in this thesis has been discussed in detail elsewhere [75, 189] and is only summarised below. Calculation of the function requires detailed knowledge of experimental parameters related to both the molecular beams and detection lasers used, and their geometry in relationship to one another. Both molecular beams must be characterised in terms of the mean velocity of the gas pulse, $|v|$, the full-width-at-half-maximum (FWHM) of the Gaussian profile of the velocity distribution of the beam, σ_v , the FWHM of the Gaussian temporal distribution of the beam, σ_t , and the FWHM of the Gaussian profile of the spatial width of the molecular beam at the scattering centre, σ_w . Both the excitation and ionisation lasers must also be characterised in terms of the FWHM of the Gaussian intensity profile across the width of the laser beam at the scattering centre. Finally, the position of the interaction/detection region with respect to both laser beams and both molecular beams must be characterised.

Collision Partner	He	Ne	Ar	Kr	Xe	N ₂	NO (10% in Ar)
$ v / \text{ms}^{-1}$	1867	965	726	531	337	1009	617
$\sigma_v / \text{ms}^{-1}$	93	48	36	27	17	50	49

Table 3.2: Mean velocities, $|v|$, and velocity spreads, σ_v , used to describe the molecular beams.

The (mean) velocity (and the FWHM of the velocity distribution) of each molecular beam is characterised using the microphone measurements [240] detailed in Section 3.2.1; these are shown in Table 3.2. The FWHM Gaussian profile of the temporal distribution of the molecular beams depends only on the pulsed valve used and not on the collision partner: these were shown by Gordon [240] to be $\sigma_t = 165 \mu\text{s}$ and $\sigma_t = 22 \mu\text{s}$ for the General and Jordan valve, respectively. The width of the secondary molecular beam is largely determined by the diameter of the skimmer with which it is collimated ($d = 3 \text{ mm}$): however since the beam is slightly divergent, using simple geometry and knowledge of the spread in beam velocity one may calculate the width of the beam at the interaction region to be $\sim 4 \text{ mm}$. Since the primary beam is focused by the hexapole, the width is relatively small and has previously been shown to be $\sim 2 \text{ mm}$ [189, 252].

The detection volume is defined by the overlap of the excitation and ionisation lasers, and may be determined by taking a spatial image of the detection volume; by applying voltages to the extractor and repeller such that a uniform field gradient is achieved. Previous work [189, 252] has given widths of $\sim 1.5 \text{ mm}$ and $\sim 3 \text{ mm}$ for the dye and excimer laser, respectively. The larger width of the excimer laser reflects the fact that it is only loosely focused at the detection region. The proportion of $(1+1')$ REMPI, compared to $(1+1)$ REMPI, has been shown to be greater than 90% [189, 252].

3.5.2 Polarisation Correction

The polarisation dependence of the intensity in Equation (3.13) can be modelled using the quantum mechanical renormalised polarisation dependent differential cross section (j' -PDDCS), $\rho_q^{\{k\}}$, described in Section 2.6. For a specific transition ($j' \leftarrow j$) and rotational

branch, the polarisation dependence may be written [86, 254]

$$A(x_n, y_n, j'_n, j_n^*, \Gamma_n) = CS \left[1 + \sum_{kq} F_q^{\{k\}}(\Gamma_n) \rho_q^{\{k\}}(\theta_n) \right]. \quad (3.15)$$

where C is a constant and S is a line strength. For detection with linearly polarised light only the $k = 2, q = 0, 1, 2$ moments contribute to the polarisation dependence, whilst for circularly polarised light only the $k = 1, q = -1$ moment contributes.

The $F_q^{\{k\}}(\Gamma_n)$ function contains all the geometric information necessary to calculate the contribution of a certain $\rho_q^{\{k\}}(\theta_n)$ moment for a single scattering event [86, 254]:

$$F_{1-}^{\{1\}}(\Gamma_n) = \frac{3}{2} h^{(1)}(j', j^*) c_1(j') \sin \Theta_n \sin \Phi_n \sin 2\beta, \quad (3.16a)$$

$$F_0^{\{2\}}(\Gamma_n) = \frac{1}{4} h^{(2)}(j', j^*) c_2(j') [3 \sin^2 \Theta_n \cos 2\chi_n \cos 2\beta - (3 \cos^2 \Theta_n - 1)], \quad (3.16b)$$

$$F_{1+}^{\{2\}}(\Gamma_n) = \frac{\sqrt{3}}{4} h^{(2)}(j', j^*) c_2(j') [2 \sin \Theta_n \cos \Phi_n \sin 2\chi_n + 2 (\sin \Theta_n \cos \Theta_n \sin \Phi_n \cos 2\chi_n - \sin 2\Theta_n \cos \Phi_n) \cos 2\beta], \quad (3.16c)$$

$$F_{2+}^{\{2\}}(\Gamma_n) = \frac{\sqrt{3}}{4} h^{(2)}(j', j^*) c_2(j') [\{ (1 + \cos^2 \Theta_n) \cos 2\Phi_n \cos 2\chi_n - 2 \cos \Theta_n \sin 2\Phi_n \sin 2\chi_n \} \cos 2\beta - \sin^2 \Theta_n \cos 2\Phi_n], \quad (3.16d)$$

where $c_k(j')$ are normalisation factors (proportionality constants related to the polarisation parameters and renormalised j' -PDDCSs) which take the values [86, 231, 254]

$$c_1(j') = [j'(j' + 1)]^{-1/2}, \quad (3.17a)$$

$$c_2(j') = \left[\frac{(2j' + 3)(2j' - 1)}{j'(j' + 1)} \right]^{1/2}. \quad (3.17b)$$

$h^{(k)}(j', j^*)$ is a line strength factor for the polarisation moment of order k [255] and β is the polarisation angle of the excitation laser (relative to the direction of propagation); for linearly and circularly polarised light $\beta = 0^\circ$ and $\beta = 45^\circ$, respectively. It should be noted that only circularly polarised light may be used to probe rotational orientation. The pixel dependent

intensity, for a single collision event, in Equation (3.13) may be rewritten

$$i(x_n, y_n, j_n, j'_n, j_n^*, \Gamma_n) = z(x_n, y_n, j_n, j'_n) P_{\text{scatt}}(\theta_n) \left[1 + \sum_{kq} F_q^{\{k\}}(\Gamma_n) \rho_q^{\{k\}}(\theta_n) \right]. \quad (3.18)$$

The Classical Kinematic Apse Model

When the quantum mechanical polarisation moments are not known, the classical kinematic apse model [86–88] may be used for polarisation corrections. It has been shown that this model is a relatively good approximation for the collisions of NO(X) with the rare gases [86–88, 179], however it is less good for the equivalent collisions of NO(A) [51, 52, 67, 256] due to the more attractive nature of the PESs. The kinematic apse lies in the scattering plane and is defined by

$$\hat{a} = \frac{\mathbf{k}' - \mathbf{k}}{|\mathbf{k}' - \mathbf{k}|}, \quad (3.19)$$

where $\mathbf{k}$ and $\mathbf{k}'$ are the initial and final relative velocity vectors, respectively. For an impulsive collision between a hard sphere and a rigid ellipse under the kinematic apse model, it is assumed that the projection quantum number, m_a , of the total rotational angular momentum, $\mathbf{j}$, onto $\hat{a}$, is conserved during the collision [257, 258]. Since NO(X) is hexapole state selected in its ground rotational state, $j = 0.5$, the projection of $\mathbf{j}$ onto $\hat{a}$ will be conserved throughout the collision and $m_j^a = m_{j'}^a = \pm 0.5$, with the kinematic apse as the quantisation axis. For inelastic collisions in which $j' > 0.5$, $\mathbf{j}'$ is confined perpendicular to the kinematic apse, $\hat{a}$.

For linearly polarised light, the probability of a molecule absorbing a photon is proportional to $\langle \cos \theta_{\mu\epsilon} \rangle$, where $\theta_{\mu\epsilon}$ is the angle between the transition dipole moment of NO (μ) and the electric vector of the laser (ϵ) [186]. For P and R branch transitions μ is perpendicular to $\mathbf{j}'$, whilst for Q branch transitions μ is parallel to $\mathbf{j}'$ (where $\mathbf{j}'$ is cylindrically symmetric about the apse). Figure 3.8 shows the distributions of the transition dipole moment for the R/P and Q branches, alongside the kinematic apse and the resulting $\mathbf{j}'$ for both forwards and backwards scattering processes. It is clear that the detection probability for a given branch varies at different positions on the Newton sphere; this must be accounted for in any experimental analysis.

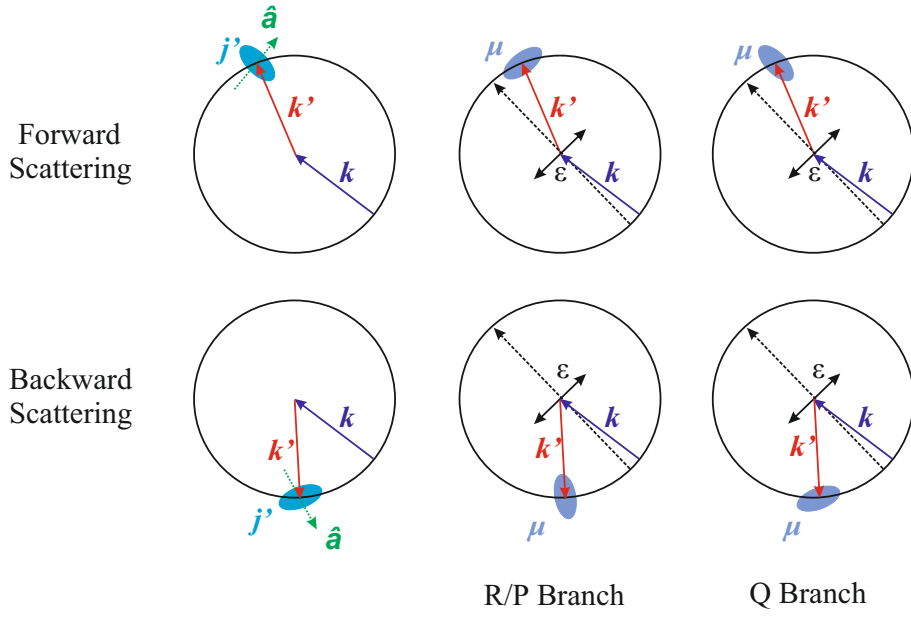


Figure 3.8: Diagram showing j' and $\hat{a}$ for forwards (top) and backwards (bottom) scattering, alongside the corresponding distributions of μ for R/P (middle) and Q (right) branch transitions.

The probability that a molecule in a final rotational state, j' , will absorb a photon is [38, 189, 251, 252]

$$A(x, y, j', j^*, \chi_p) \propto \sum_{m_{j^*}} \left| \langle \psi^*(j^*, m_{j^*}) | \mu \cdot \epsilon | \psi'_a(j', m_{j'}^a) \rangle \right|^2, \quad (3.20)$$

where $\psi^*(j^*, m_{j^*})$ and $\psi'_a(j', m_{j'}^a)$ are the wave functions following $\text{NO}(A \leftarrow X)$ excitation and after scattering respectively. m_{j^*} and $m_{j'}^a$ are the projections of j^* and j' along ϵ and along the kinematic apse, $\hat{a}$, respectively. The scattered wave function in the apse frame is obtained by rotating the scattered wave function in the laser frame through $\theta_{\hat{a}\epsilon}$ (the angle between $\hat{a}$ and ϵ) [38]

$$\psi'_a(j', m_{j'}^a) = \sum_{m_{j'}} d_{m_{j'}, m_{j'}^a}^{j'}(\theta_{\hat{a}\epsilon}) \psi'(j', m_{j'}) , \quad (3.21)$$

where $d_{m_{j'}, m_{j'}^a}^{j'}(\theta_{\hat{a}\epsilon})$ is a reduced Wigner rotation matrix [186]. Upon substitution into Equation (3.20) it can be shown that

$$A(x, y, j', j^*, \chi_p) \propto \sum_{m_{j'}^* m_{j'}} \left| d_{m_{j'}, m_{j'}^a}^{j'}(\theta_{\hat{a}\epsilon}) \langle \psi^*(j^*, m_{j^*}) | \mu \cdot \epsilon | \psi'(j', m_{j'}) \rangle \right|^2. \quad (3.22)$$

The m -dependent detection probability for the absorption of linearly polarised light by a molecule is given by [259]

$$|\langle \psi^*(j^*, m_{j^*}) | \boldsymbol{\mu} \cdot \boldsymbol{\epsilon} | \psi'(j', m_{j'}) \rangle|^2 = S_{jj^*} \begin{pmatrix} j^* & 1 & j' \\ m_{j^*} & 0 & -m_{j'} \end{pmatrix}^2 \delta_{m_{j'}, m_{j^*}} , \quad (3.23)$$

where S_{jj^*} is the Hönl-London factor for the ${}^2\Sigma \leftarrow {}^1\Pi$ transition [260] and (...) is a 3- j symbol. Therefore, the transition dependent probability due to the collision induced alignment (CIA) may be written [38, 189, 257, 258] using Equation (3.23)

$$A(x, y, j', j^*, \chi_p) = S_{jj^*} \sum_{m_{j^*}} \left| d_{m_{j'}, m_{j^*}}^a(\theta_{a\epsilon}^{j'}) \begin{pmatrix} j^* & 1 & j' \\ m_{j^*} & 0 & -m_{j'} \end{pmatrix} \right|^2 . \quad (3.24)$$

Since both $\mathbf{k}$ and $\mathbf{k}'$ are well defined on the Newton sphere, the kinematic apse may be calculated at each point and therefore, it is possible to calculate the polarisation dependent transition probability arising from CIA at each point on the Newton sphere.

3.5.3 Fourier Fitting of the Experimental Image

The angular distribution in Equation (3.13) may be expanded in terms of Legendre polynomials

$$P_{\text{scatt}}(\theta) = \sum_l \frac{2l+1}{2} a_l P_l(\cos \theta) , \quad (3.25)$$

where a_l are expansion coefficients and $P_l(\cos \theta)$ is the l^{th} Legendre polynomial. As such the experimental intensity in Equation (3.13) can be approximated as a linear combination of the basis functions

$$I(x, y) \approx \sum_n i(x_n, y_n, j_n, j'_n, \Gamma_n) = \sum_l \frac{2l+1}{2} a_l B_l(x_n, y_n, j_n, j'_n, \Gamma_n) , \quad (3.26)$$

where the basis function is

$$B_l(x, y, j, j', \Gamma) \approx \sum_n b_l(x_n, y_n, j_n, j'_n, \Gamma_n) \\ \approx \sum_n P_l(\cos \theta_n) z(x_n, y_n, j_n, j'_n) \left[1 + \sum_{kq} F_q^{\{k\}}(\Gamma_n) \rho_q^{\{k\}}(\theta_n) \right], \quad (3.27)$$

for the quantum mechanical polarisation correction or

$$B_l(x, y, j, j', \Gamma) \approx \sum_n b_l(x_n, y_n, j_n, j'_n, \Gamma_n) \\ \approx \sum_n P_l(\cos \theta_n) Z(x_n, y_n, j_n, j'_n) A(x_n, y_n, j'_n, j_n^*, \Gamma_n), \quad (3.28)$$

for the apse model polarisation correction. Similarly, the instrument function may also be calculated by summing over all trajectories,

$$Z(x, y) \approx \sum_n z(x_n, y_n). \quad (3.29)$$

The experimental image is not fitted as a 2D image, but as a series of its 1D Fourier moments to increase computational speed. The experimental image and the calculated basis functions are converted from Cartesian, $I(x, y)$, to polar, $I(r, \theta_r)$, coordinates and written as a sum of their Fourier moments [39, 189, 261, 262]

$$I(r, \theta_r) = f_0(r) + 2 \left(\sum_{-m}^0 f_m(r) \sin m\theta_r + \sum_0^m f_m(r) \cos m\theta_r \right), \quad (3.30)$$

where the Fourier moments are [39, 189]

$$f_m(r) = (2 - \delta_{0m}) \int_0^{2\pi} I(r, \theta_r) \cos m\theta_r d\theta_r, \quad (3.31a)$$

$$f_{-m}(r) = (2 - \delta_{0m}) \int_0^{2\pi} I(r, \theta_r) \sin m\theta_r d\theta_r. \quad (3.31b)$$

These moments describe the anisotropy of the image as a function of the distance from the image centre. For example the $f_{+1}(r)$ and $f_{+2}(r)$ moments describe the orientation and alignment,

respectively, of the image parallel to the relative velocity vector, whilst the $f_{-1}(r)$ and $f_{-2}(r)$ describe the orientation and alignment of the image perpendicular to $\mathbf{k}$. The Fourier moments are fitted using a genetic algorithm in which the expansion coefficients of the DCS, a_n , are allowed to vary iteratively to minimise the value of [39, 189]

$$\chi^2 = \frac{1}{2m_{\max} + 1} \sum_{-m_{\max}}^{m_{\max}} \int \frac{[f_m^{\exp}(r) - \sum \frac{2n+1}{2} a_n f_m^n(r)]^2}{f_{m=0}^{\exp}(r)} dr \quad (3.32)$$

where $f_m^{\exp}(r)$ and $f_m^n(r)$ are the m^{th} Fourier moment of the experimental image and the m^{th} moment of the n^{th} basis image respectively. The values of a_n from the fit to the experimental image are then used to reconstruct the DCS according to Equation (3.25).

3.5.4 Error Analysis

The main source of error in the determination of the DCS from the experimental image is the calculation of the flux density correction. Whilst the experimental parameters are carefully determined (Section 3.5.1), small discrepancies in the laser positions or other parameters can lead to relatively large errors in the instrument function leading to errors in the fitted DCS. The errors effectively reflect the accuracy of the flux density calculation. The error at each angle is calculated by fitting the fast and slow side of the experimental image along with the full image and calculating the standard deviation, σ , according to

$$\sigma(\theta) = \sqrt{\frac{1}{3} \sum_{i=1}^3 [x_i(\theta) - \mu(\theta)]^2} \quad \text{where} \quad \mu(\theta) = \frac{1}{3} \sum_{i=1}^3 x_i, \quad (3.33)$$

where $x_i = 1, 2, 3$ are the values of the angular distributions for the slow side, fast side and full image, respectively.

3.6 Summary

This chapter has explored the experimental methods used to record the experimental data in this thesis. The necessary data analysis methods used were also discussed, including the importance

of correctly reproducing the flux density correction, and the measurements necessary to allow this. Throughout the chapters in this thesis the analysis methods discussed here will be drawn upon, with the details of each measurement (and the relevant data analysis) discussed further within each specific chapter.

Chapter 4

Inelastic Scattering of NO(X) with Oxygen

The scattering of an open shell diatom in its ground electronic state, with a structureless atom has been widely studied, particularly for NO(X) [35, 39, 40, 78, 88, 123, 181, 263] and OH(X) [42, 43, 45, 91, 264]. The extension of these systems to include diatomic (or even polyatomic) collision partners has largely been limited to those molecules with closed shell ground state electronic structures [22, 24, 57, 130, 201, 217, 265–269], such as OH + H₂/D₂ [46, 60, 270], NO + D₂ [33, 52, 271–273] and OH + HX [64, 93, 94], where X = F, Cl, Br and I. The complexity of these systems is restricted, since there are no spin-coupling effects between the two molecules, and the number of PESs required to describe the system are limited [268]. Only a few studies have been extended to include open-shell collision partners [57, 59, 61, 68, 217, 274]; such systems require consideration of spin-spin coupling, and are difficult to study theoretically as scattering may occur on a large number of coupled PESs which are not trivial to calculate.

Previous experimental measurements of scattering with both closed-shell and open-shell collision partners have largely been limited to integral cross sections and steric asymmetries (see Chapter 5). However, more recent studies in the group of van de Meerakker [272, 273] have been able to resolve DCSs for the inelastic scattering of NO(X) with H₂/D₂. However, no strong evidence for rotational excitation of the collision partner was observed, which can be rationalised by the mismatch in the rotational energy levels of the two systems [271]. Moreover, H₂ and D₂ have been shown to behave as ‘pseudo-atomic’ collision partners, with scattering dynamics very similar to those for scattering with He [52, 67, 271, 275]. Recently, Luxford *et al.* [67] have been able to probe the pair-correlated stereodynamics in the NO(A) + N₂ system,

resolved in both the NO and N₂ final rotational state, albeit with no initial state selection of the N₂ partner.

Experimentally, achieving complete quantum state resolution in both the initial and final states of both diatoms is a challenge. Initial quantum state resolution in both reagents has been achieved in collisions with H₂ and D₂ [60, 272], where it is possible to use cryogenic cooling to select only ortho or para molecules prior to expansion of the molecular beam. Kirste *et al.* [68] were able to achieve initial quantum state purity in the collision of NO(X) with OH(X) using hexapole focusing and stark deceleration, respectively. The recorded absolute cross sections were resolved in only the final state of the scattered OH molecule (detected using LIF), and no information about the co-product state was recorded. For a truly quantum state resolved experiment, a detection scheme which resolves the final state of both diatoms is necessary. In this chapter it will be shown how the advent of VMI techniques has begun to allow experimental measurements of the pair-correlated differential cross sections [52, 67, 276].

Previous work on the inelastic scattering of NO(X) with O₂(X) by Bieler [217] and Bacon [59] was not resolved in the initial Λ -doublet of the NO(X) molecule, and focused on final Λ -doublet and spin-orbit branching ratios, as well as fixed scattering angle differential cross sections. At high collision energies ($E_{\text{coll}} \approx 2000\text{cm}^{-1}$) [217], only weak spin-orbit excitation was observed, attributed to the ‘washing out’ of long-range attractive effects at such high collision energies. A much stronger effect was observed by Bacon *et al.* [59], and theoretically predicted by Lee *et al.* [213], at a collision energy of 442cm^{-1} . This suggests that there is a relatively strong attractive interaction between the two diatoms, due to spin-coupling [59], which is expected to manifest as ℓ -type rainbows in the DCSs for low rotational excitation [77–80, 113, 263]. Very recently, the group of van de Meerakker were able to experimentally determine the pair-correlated scattering of NO with O₂ at collision energies of $E_{\text{coll}} = 160\text{cm}^{-1}$ [69] and 480cm^{-1} [70].

In principle, collisions between NO and O₂ can lead to the formation of the NO₃ radical species [59, 277–279]; however, the energy barrier to reach this region is very high ($\approx 16000\text{cm}^{-1}$) [278, 279] and inaccessible at the experimental collision energy. It should be

noted that whilst oxygen is somewhat more complicated as a collision partner than the rare gases, the diatom shares some similarities with Ar due to its symmetry and lack of dipole moment (although unlike the rare gases, it does possess a quadrupole moment). This allows for useful comparisons with QM calculations and experimental data for the inelastic scattering of NO(X) by Ar.

In this chapter the inelastic scattering of NO(X) with O₂(X) is studied, with full quantum state resolution in the NO(X) molecule, and partial resolution of the O₂(X) co-product state. A new method for the analysis of the experimental ion images from diatom-diatom scattering based on a modified ‘onion-peeling’ algorithm is discussed. A detailed comparison of the scattering of NO(X) with Ar and O₂(X) is also presented.

4.1 Experimental Parameters

The experimental apparatus used to study the collision of NO(X) with O₂(X) was discussed in detail in Chapter 3, and only specifics are discussed here. The secondary beam was composed of pure O₂, with a backing pressure of 1.5 bar.* Experimental data was recorded while employing a photoelastic modulator (PEM) to select the vertical (V) polarization of the 226 nm radiation axis, *i.e.* polarization parallel to the time-of-flight axis. Data were recorded on the $Q_{21} + R_{11}$ mixed branch for scattering into the final e state, and the P_{21} pure and $Q_{11} + P_{21}$ (mixed) branches for scattering into the final f state with $j' < 9.5$ and $j' \geq 9.5$, respectively. The data presented in this chapter were recorded with the help of Dr. Bethan Nichols, Dr. Sean Gordon, and Eleanor Squires.

Radial and Angular Distributions

The radial distribution of an ion image is used in the following analysis to define parameters related to the Newton sphere formed in the experiment. The radial distribution describes the intensity of an ion image across all angles at a specific radius. The radial intensity may be

*No evidence for clustering in the molecular beam was observed between backing pressures of 0.5 and 2.5 bar.

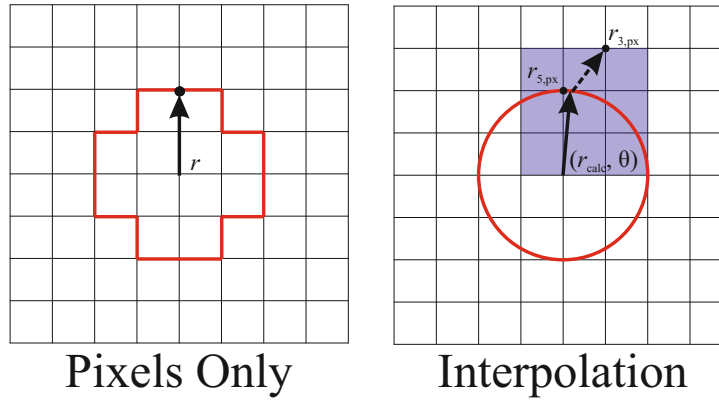


Figure 4.1: Schematic of an example detector composed of 8 by 8 pixels. The position of each pixel is defined by the top left corner, shown by a black dot. The left panel shows the ‘circle’ that is read if the radius is considered to be an integer value. The right panel shows the circle that is read upon interpolation of the intensity of several pixels, for the position shown as a black dot this corresponds to weighted intensity contributions from all the pixels highlighted in purple, as described in the text.

calculated according to

$$I(r) = \int_0^{2\pi} i(r, \phi) d\phi, \quad (4.1)$$

where $i(r, \phi)$ is the intensity of a pixel at a given radius, r , and angle, ϕ , in the experimental ion image. The angular distribution, $I(\phi)$, describes the intensity of an ion image as a function of angle, either at a specific radius or as an average across all radii, according to

$$I(\phi) = \int_0^{|r_{\max}|} i(r, \phi) dr. \quad (4.2)$$

Due to the nature of the CCD camera used to record experimental data, pixels may only take integer values, with the position of each pixel being defined as the top-left corner of each pixel, shown by the black circle in Figure 4.1, on an example ‘detector’ composed of 8 by 8 pixels. When a circle of radius 2 pixels is drawn onto the ‘detector’, due to the computational need for the pixels numbers to be integer, the traced radius appears pixelated and in this extreme example is clearly not a good representation of a circle. To account for this an interpolation routine is used, in which the intensity at position (r_{calc}, ϕ) is calculated by summing the intensity of the pixel, r_{px} (which is the nearest integer value of r_{calc}), and its eight closest neighbours weighted by an inverse-distance function. The inverse-distance function ($\propto 1/r$) ensures that pixels which lie closest to the radius of the circle contribute more to the intensity of the pixel than pixels

which lie further from the circle as drawn. The resulting interpolated intensity is written

$$i(r, \phi) = \sum_{n=1}^9 \frac{i_n(r, \phi)}{r} = \sum_{n=1}^9 \frac{i_n(r_{\text{calc}}, \phi)}{|r_{n,\text{px}} - r_{\text{calc}}|}, \quad (4.3)$$

where i_n is the intensity of the pixel being considered, n is the number of the pixel included in the interpolation, $r_{n,\text{px}}$ is the radius of the pixel being considered (which must take an integer value) and r_{calc} is the ‘true’ radius of the circle (which takes a real value). The value of $n = 9$ is chosen, as any pixels beyond this distance contribute a negligible amount to the intensity once weighted by the inverse-distance function. Any angular distribution, $I(\phi)$, read from the ion image at a radius, r , may be interpolated using the same method.

4.1.1 Oxygen Molecular Beam

Whilst the use of a hexapole in the experimental set-up leads to selection of the $|j = 0.5, \Omega = 0.5, \varepsilon = -1, f\rangle$ state in the (primary) NO molecular beam, the rotational states populated in the secondary molecular beam are simply determined by the supersonic expansion of the collision partner (O_2) into vacuum. According to statistical mechanics, the population of a rotational state i in a system is [244]

$$p_i = \frac{m_i}{M} = g_i \frac{\exp\left(-\frac{\Delta E_{\text{rot}}(i)}{k_{\text{B}} T_{\text{rot}}}\right)}{q^R}, \quad (4.4)$$

where M is the total number of molecules in the system, m_i is the number of particles in rotational state, i , q^R is the rotational partition function, where g_i accounts for the degeneracy of the rotational state, i , k_{B} is the Boltzmann constant, and $\Delta E_{\text{rot}}(i) = E_{\text{rot}}(i) - E_{\text{rot}}^*$, where E_{rot}^* is the energy of the ground rotational state. T_{rot} is the rotational temperature of the system. The O_2 molecule is assumed to be a linear rotor and as such the rotational partition function may be written

$$q^R = \sum_{i=1}^{\infty} g_i \exp\left(-\frac{\Delta E_{\text{rot}}(i)}{k_{\text{B}} T_{\text{rot}}}\right). \quad (4.5)$$

The summation is calculated between the rotational ground state, which for O_2 is $i = N = 1$, and infinity. At experimental energies a finite number of states are populated, and it is sufficient to set the maximum of the sum sufficiently high such that $\exp(-\Delta E_{\text{rot}}(i)/k_{\text{B}}T_{\text{rot}}) \rightarrow 0$. Due to the spin-rotation splitting of $\text{O}_2(\text{X})$, one must also account for the triad of rotational states $i = j = N - 1, N, N + 1$, with rotational energies calculated according to Equations (2.21) and (2.22). Since experimentally these spin-rotation states are not resolved, the populations must be summed over all possible j , for any rotational state N , according to

$$p_N = \frac{m_N}{M} = \frac{\sum_{j=N-1}^{j=N+1} \exp\left(-\frac{\Delta E_{\text{rot}}(j)}{k_{\text{B}}T_{\text{rot}}}\right)}{q^{\text{rot}}}, \quad (4.6)$$

where the rotational partition function may be written

$$q^R = \sum_{N=1}^{\infty} \sum_{j=N-1}^{j=N+1} g_j \exp\left(-\frac{\Delta E_{\text{rot}}(j)}{k_{\text{B}}T_{\text{rot}}}\right). \quad (4.7)$$

The ground rotational state of the O_2 molecule when considering the spin-rotation coupling is $N = 1, j = 0$ and $E_{\text{rot}}^* = E_{\text{rot}}(N = 1, j = 0)$.

In molecular oxygen rotation around the bond axis does not affect the rotational energy ($K = 0$), however angular rotation both in and out of the plane of the molecule is quantised, with permitted values of $m_j\hbar$, $m_j = 0, \pm 1, \dots, \pm j$, corresponding to $g_j = 2j + 1$ values. Therefore the population of the rotational state N is given by

$$p_N = \frac{m_N}{M} = \frac{\sum_{j=N-1}^{j=N+1} (2j + 1) \exp\left(-\frac{\Delta E_{\text{rot}}(j)}{k_{\text{B}}T_{\text{rot}}}\right)}{\sum_{N=1}^{\infty} \sum_{j=N-1}^{j=N+1} (2j + 1) \exp\left(-\frac{\Delta E_{\text{rot}}(j)}{k_{\text{B}}T_{\text{rot}}}\right)}. \quad (4.8)$$

The population of O_2 rotational states, N_{O_2} , at several rotational temperatures is shown in the right hand panel of Figure 4.2. It is clear that as the rotational temperature of the beam increases the population of higher initial rotational states becomes non-negligible, for example for $T_{\text{rot}} = 10\text{K}$ and $T_{\text{rot}} = 20\text{K}$ states up to and including $N_{\text{O}_2} = 5$ and $N_{\text{O}_2} = 7$ are populated, respectively.

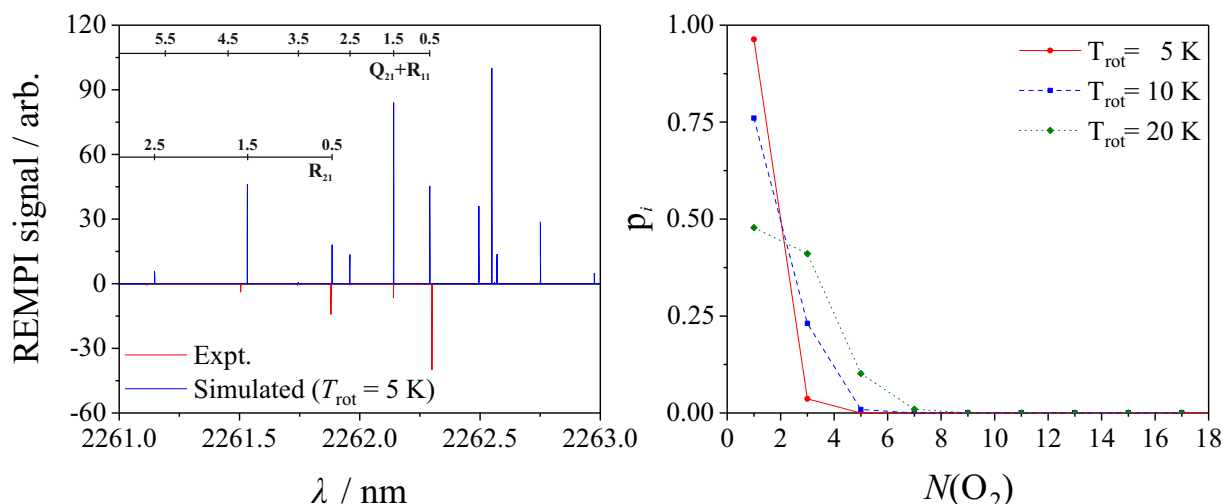


Figure 4.2: Population of $\text{O}_2(\text{X})$ states in the secondary molecular beam. Left: experimental REMPI scan of the secondary molecular beam (red line), composed of trace NO in O_2 , compared to the simulated REMPI scan (from LIFBASE [246], with $T_{\text{rot}} = 5$ K). Right: Effect of rotational temperature on the population of the rotational states of molecular oxygen before the scattering event. Rotational temperatures of $T_{\text{rot}} = 5$ K, 10 K and 20 K are shown by red lines with circles, blue (dashed) lines with squares, and green (dotted) lines with diamonds, respectively.

A REMPI scan of the secondary molecular beam (shown in Figure 4.2), carried out by seeding trace NO into the O_2 beam, gives a rotational temperature of approximately $T_{\text{rot}} = 5$ K (using the methods described in Section 3.2.3); as such the majority ($\approx 96.3\%$) of the oxygen molecules in the beam will be in their ground rotational state, with a small contribution from $N(\text{O}_2) = 3$ ($\approx 3.7\%$). It should be noted that not all rotational states were probed experimentally; T_{rot} was assigned based on the relative intensities of the $j = 0.5$ transition on the R_{21} and $Q_{21} + R_{11}$ branches.[†]

Since very little is known about the form of the DCS for $\text{NO}(\text{X}) + \text{O}_2(\text{X})$, the effect of initially rotationally hot O_2 in the molecular beam is difficult to evaluate. Previous work on the $\text{NO}(\text{X}) + \text{Ar}$ system [290, 291], in which the $\text{NO}(\text{X})$ initial state was not selected for, has shown that the effects of population of excited rotational states in the molecular beam leads to only a small effect on the calculated j' -PDDCS and therefore the observed experimental scattering distribution. Figure 4.3 shows the CC QM DCSs for the collision of $\text{NO}(\text{X})$ with Ar, into several final rotational states, originating in the ground and first excited rotational state of NO, alongside

[†]Initial selection of a single O_2 rotational state is possible *via* a variety of methods, including, but not limited to: use of a seed gas coexpanded with O_2 [102, 280–282], laser cooling [283, 284], use of specialised beam valve nozzles [285–287], and Zeeman deceleration [288, 289].

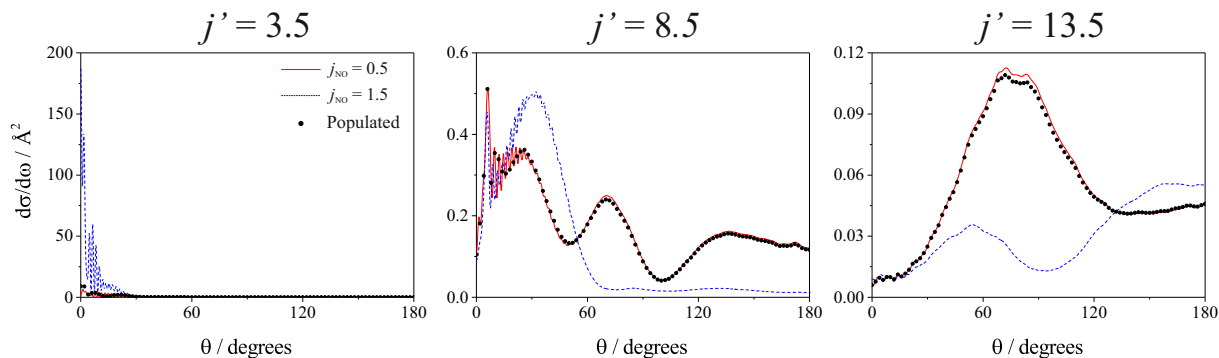


Figure 4.3: QM DCS for the collision of NO(X) with Ar for the transitions $|j', \Omega' = 0.5, \varepsilon = -1, f\rangle \leftarrow |j, \Omega = 0.5, \varepsilon = -1, f\rangle$ where $j'_{\text{NO}} = 3.5, 8.5, \text{ and } 13.5$, from left to right. $j = 0.5$ (red lines) and 1.5 (blue dashed lines) are shown alongside the DCS from the mixed initial state of $j = 0.5$ and 1.5 , weighted according to the experimental populations of O_2 in the molecular beam.

the ‘experimental’ DCS which is the weighted sum of the $j_{\text{NO}} = 0.5$ and 1.5 DCSs. Whilst the form of the $j_{\text{NO}} = 0.5$ and $j_{\text{NO}} = 1.5$ DCSs is very different, due to the population of the beam being largely in the ground state, the mixed DCS is very similar to the ground state DCS. As such, it is a good approximation to consider only scattering from the $j_{\text{NO}} = 0.5$ state. From this the effect of rotationally hot O_2 in the secondary molecules beam may be inferred. Since only odd rotational states of O_2 may be populated, one may expect the DCSs originating from $N_{\text{O}_2} = 1$ and 3 to be markedly different. However, the small proportion of the $N_{\text{O}_2} = 3$ state in the beam is likely to not significantly contribute to the observed angular scattering distribution.

Using a ‘dummy’ DCS the effect of the excited rotational states on the collision energy and thus the radius of the experimental ion image may be modelled. Figure 4.4 shows the effect of increasing N_{O_2} on the (simulated) ion image and radial distribution for scattering into NO ($j' = 11.5, \varepsilon = -1, f$) using a ‘dummy’ DCS for a fixed collision energy, $E_{\text{coll}} = 550 \text{ cm}^{-1}$ (as calculated in Section 4.1.2). Increasing N_{O_2} leads to a larger Newton sphere as more energy is available for translation after the collision occurs. The rotational distribution of N_{O_2} in the molecular beam for the experimental rotational temperature, $T_{\text{rot}} = 5 \text{ K}$, leads to a radius very similar to that observed for scattering from the 100% populated ground state ($N_{\text{O}_2} = 1$), and as such one need not consider the effect of higher rotational states on the final radius of the Newton sphere.

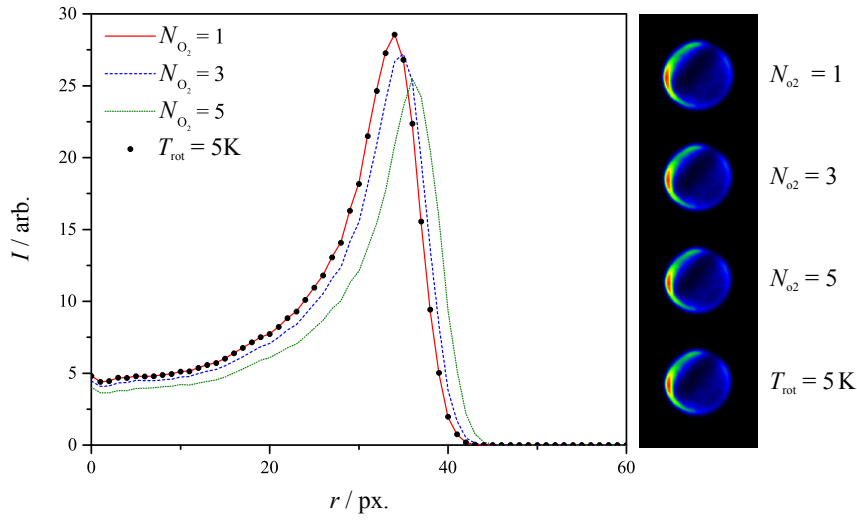


Figure 4.4: Simulations (right) and radial distributions (left) using a ‘dummy’ PDDCS showing the effect of the initial rotational state of O_2 on the final Newton sphere radius (for the $|j'_{NO} = 11.5, \Omega' = 0.5, \epsilon' = -1, f\rangle$ state, averaged across all final N'_{O_2}) in the collision of NO with O_2 . The radial distribution is shown for $N_{O_2} = 1, 3$, and 5 using red, blue (dashed) and green (dotted) lines respectively. The radial distribution observed at the ‘experimental’ rotational temperature is shown by black circles.

4.1.2 Average Experimental Collision Energy

As discussed in detail in Section 3.2.2, the radius of the experimental Newton sphere is determined by the outgoing velocity of the NO molecule after the collision event, with a pixel-to-velocity ratio that allows conversion between the velocities in the LAB frame and the pixels on the camera used to record the ion image according to Equation (3.4). For NO molecules with a velocity $u'_{NO} = 617 \text{ ms}^{-1}$ the pixel-to-velocity ratio for this series of experiments is calculated to be $p = 8 \text{ ms}^{-1} \text{ px}^{-1}$. The radius of the Newton sphere may then be calculated from Equation (3.5).

The average experimental collision energy may be calculated by fitting the radii of the Newton spheres for each j'_{NO} , using the function

$$r = \frac{1}{p} \frac{m_{O_2}}{m_{O_2} + m_{NO}} \sqrt{\frac{2 \{E_{\text{coll}} - B_{NO} [j' (j' + 1) - j (j + 1)]\}}{\mu}}, \quad (4.9)$$

where m_{NO} and m_{O_2} are the atomic masses of NO and O_2 , respectively, μ is the reduced mass of the system, E_{coll} is the experimental collision energy, B_{NO} is the rotational constant

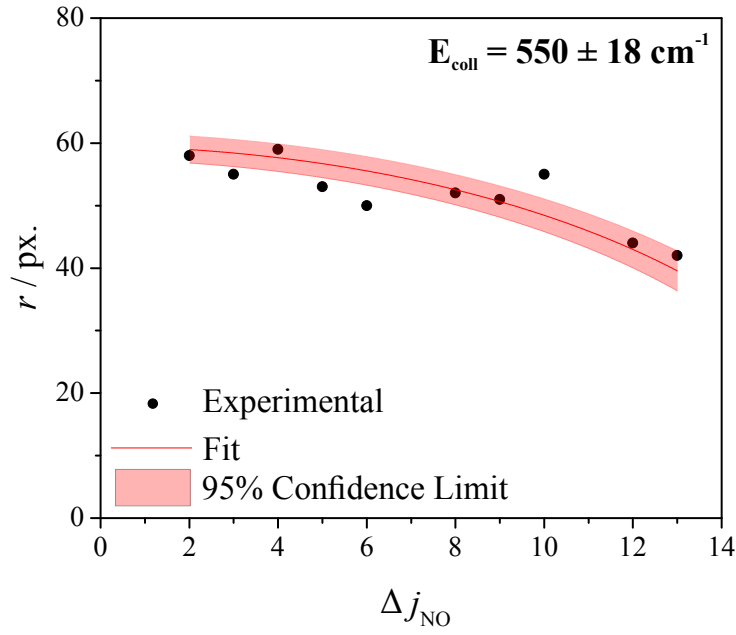


Figure 4.5: Plot of experimental radii against final rotational state, Δj_{NO} for the (spin-orbit conserving) inelastic scattering of NO(X) with O₂(X). The experimental radii are defined by black dots, the red line shows the best fit to the experimental data, and the red shaded area shows the 95% confidence limit of the fit.

of NO(X), $j = 0.5$ and j' are the initial and final rotational states of NO, respectively, and p is the pixel-to-velocity ratio. It should be noted that no information about the O₂ rotational state is required for this fit, since the outer radius of each image corresponds to elastic collisions of the O₂ molecule, $\Delta E_{\text{rot}}^{\text{O}_2} = 0$. The fit shown in Figure 4.5 gives a (mean) collision energy for the system of $E_{\text{coll}} = 550 \pm 18 \text{ cm}^{-1}$. Since the velocity of the NO molecule ($v_{\text{NO}} = 617 \text{ m s}^{-1}$) is known, the velocity of the O₂ molecular beam may be calculated according to Equations (3.2) and (3.3)

$$v_{\text{O}_2} = \sqrt{\frac{2E_{\text{coll}}}{\mu} - v_{\text{NO}}^2}, \quad (4.10)$$

giving an initial O₂ velocity of $v_{\text{O}_2} = 685 \text{ m s}^{-1}$.

4.1.3 Instrument Resolution

The experimental apparatus has a finite resolution arising from several factors, including the volume of the laser interaction region, and the velocity spreads in the molecular beams, as discussed in Section 3.5. This resolution must be accounted for in the data analysis process. To

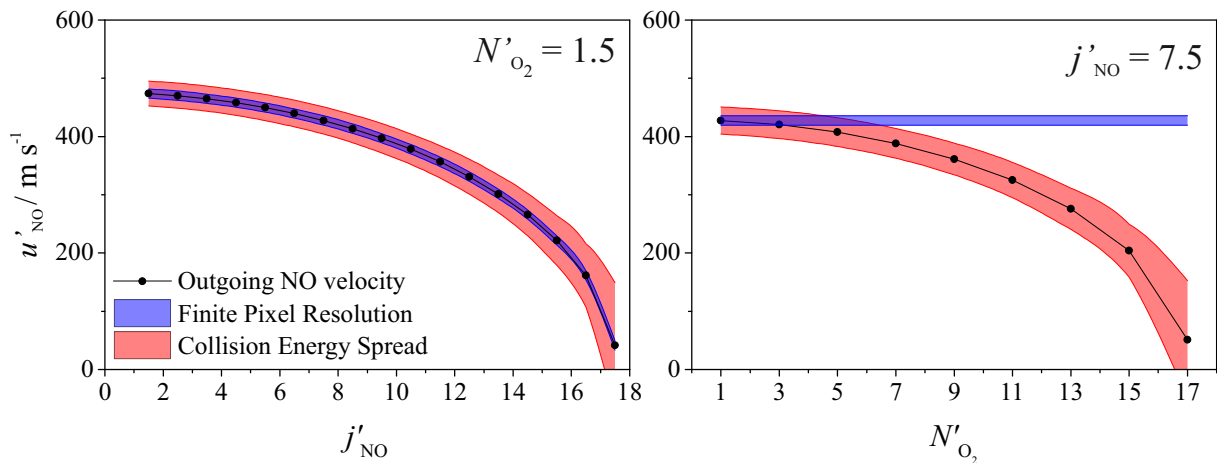


Figure 4.6: Plots showing the effect of the collision energy spread (red shading) and finite pixel resolution (blue shading) on the outgoing velocity of the rotationally excited NO molecule (black line with circles). Left panel: variation of instrument resolution with final NO rotational state, for elastic collisions of O₂, ($j'_{\text{NO}}, N'_{\text{O}_2} = 1$). Right panel: variation of instrument resolution with final O₂ rotational state, ($j'_{\text{NO}} = 7.5, N'_{\text{O}_2}$), for which the pixel resolution is plotted for $u'_{\text{NO}} (N'_{\text{O}_2} = 1)$ to show the overlap of the three lowest rotational states of O₂ in outgoing NO velocity.

minimise such factors, the pulse widths of the molecular beams were kept as short as possible, and the probe laser interaction volume was kept as tight as possible. A further factor in the instrument resolution arises from the finite resolution of the CCD camera used to record the experimental data; since each pixel can be considered to represent a velocity of 8 m s^{-1} (the pixel-to-velocity ratio, p), any features with a corresponding energy difference narrower than this will not be resolved. The angular resolution of the Newton sphere (and therefore the extracted angular distributions) is currently estimated to be between 10 and 20 degrees.

Figure 4.6 shows the effect of the collision energy spread (defined by the spreads in the velocity of the two molecular beams) and the finite pixel resolution of the camera on the outgoing velocity of the NO molecule, as a function of ($j'_{\text{NO}}, N'_{\text{O}_2} = 1$) (left) and ($j'_{\text{NO}} = 7.5, N'_{\text{O}_2}$) (right). The mean outgoing velocity is plotted as points, whilst the coloured boxes show the effect of the collision energy spread, as well as the finite pixel resolution for each state. The product velocity resolution is largely limited by the initial velocity spread in the molecular beams, since the collision energy spread is typically much larger than the pixel resolution. For a specific j'_{NO} , the pixel resolution becomes important when considering the three lowest rotational states of the O₂ molecule after the collision: the pixel-to-velocity ratio

is such that, for these states, the NO molecule has an outgoing translational energy within the pixel resolution. That is, the Newton spheres for $N'_{O_2} = 1, 3$ and 5 will all contribute intensity into the same pixel, leading to difficulties in resolving these states. This is particularly relevant as ions often impact on several neighbouring pixels.

4.2 Theoretical Methods

Until very recently,[‡] there was no *ab initio* PES for the inelastic scattering of NO(X) with O₂(X). Consequently, the O₂ molecule was treated as a structureless Ar atom with the mass of O₂ for the purpose of QM calculations. Calculations were performed on the NO(X) + Ar V_{sum} and V_{diff} PESs of Alexander [230], using the HIBRIDON suite of codes [226]. To allow comparison with the experimental data, the results were averaged over the experimental collision energy distribution; modelled as a Gaussian distribution with a mean collision energy of 550cm^{-1} , and a full-width-at-half-maximum of 50cm^{-1} . Calculations were performed at six sample points across the energy distribution. Rotational levels up to $j'_{\text{NO}} = 20.5$, both Λ -doublet levels ($\epsilon = \pm 1$) and spin-orbit manifolds ($\Omega = 0.5, 1.5$) were included in the scattering wave function. The maximum partial wave was set to $J = 160.5$, corresponding to a classical impact parameter of $6.8\text{\AA}$, in order to achieve convergence of the calculations. In cases where NO(X) + Ar data are shown they were calculated using similar methods, at a mean collision energy of $E_{\text{coll}} = 532\text{cm}^{-1}$, with a full-width-at-half-maximum of 50cm^{-1} , on the same PES but using the true mass of Ar.

4.3 Data Analysis Method

Inelastic collisions of NO(X) with O₂(X) may result in rotational excitation of both collision partners: for any given NO(X) rotational state, j'_{NO} , a series of O₂(X) rotational states, N'_{O_2} , may be populated. Each of these $(j'_{\text{NO}}, N'_{O_2})$ states will give rise to a specific outgoing translational

[‡]van de Meerakker and coworkers [69] recently produced a full *ab initio* potential for NO + O₂; for which experimental measurements were shown to be in relatively good agreement at collision energies of $E_{\text{coll}} = 160\text{cm}^{-1}$ [69] and $E_{\text{coll}} = 480\text{cm}^{-1}$ [70].

energy for the system according to

$$E'_T(j'_{\text{NO}}, N'_{\text{O}_2}) = E_{\text{coll}} - \Delta E_{\text{rot}}^{\text{NO}} - \Delta E_{\text{rot}}^{\text{O}_2}, \quad (4.11)$$

where E_{coll} is the collision energy and ΔE_{rot}^n are the changes in rotational energy for $n = \text{NO}, \text{O}_2$. The pairwise correlation between the two diatoms, $(j'_{\text{NO}}, N'_{\text{O}_2})$, adds considerable complexity to the analysis of the experimental ion images when compared with atom-diatom scattering. For a final rotational state of NO, which is state-selectively probed using the REMPI scheme, the experimental ion image is a sum over all the rotational states of the oxygen co-product that are populated during the collision. In an experimental image of sufficient resolution this appears as a series of concentric rings, corresponding to the many ‘pancaked’ Newton spheres for different N'_{O_2} , but the same j'_{NO} co-product.

The radial size of the NO ion image, with specific $(j'_{\text{NO}}, N'_{\text{O}_2})$, varies as a function of both O_2 and NO rotational excitation (see Equation (4.11)). Since the initial NO quantum state is selected experimentally, using a hexapole state selector, and the scattered NO molecules are state selectively detected using the REMPI scheme, the rotational energy term for NO, $\Delta E_{\text{rot}}^{\text{NO}}$, is well defined. The initial rotational state of O_2 is dominated by the $N_{\text{O}_2} = 1$ state, as shown by the populations calculated in Section 4.1.1. In principle, therefore, the nested NO ion images corresponding to the different O_2 co-product final rotational states may be analysed to yield DCSs for each fragment pair, $(j'_{\text{NO}}, N'_{\text{O}_2})$.

The ion images corresponding to the final state $|j'_{\text{NO}} = 7.5, \Omega' = 0.5, \epsilon' = +1, e\rangle$, for inelastic scattering with Ar and O_2 are shown in Figure 4.7. Due to the finite resolution of the instrument, discussed in Section 4.1.3, the nested Newton spheres are not observed as separate rings in the ‘crushed’ ion image. However, the presence of the excited states of the O_2 collision partner can be seen in the broad distribution of intensity in the experimental image compared to that observed for $\text{NO(X)} + \text{Ar}$ scattering. The outer radius of the Newton sphere is equivalent to an elastic collision with respect to O_2 ($N'_{\text{O}_2} = 1 \leftarrow N_{\text{O}_2} = 1$), with increasing rotational excitation leading to rings of smaller radii, as the outgoing translational energy in the

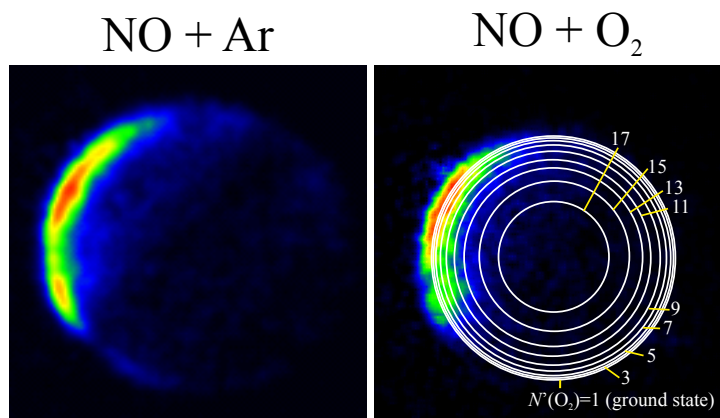


Figure 4.7: Experimental ion image for NO + Ar (left) and O₂ (right) scattering into the $|j'_{\text{NO}} = 7.5, \Omega' = 0.5, \epsilon' = +1, e\rangle$ state. In the case of O₂ the radius of the Newton sphere for each final oxygen state, N'_{O_2} , is superimposed on top of the image. Due to nuclear spin statistics only odd states may be populated, with the ground state $N'_{\text{O}_2} = 1$ defining the outer radius of the image. $N'_{\text{O}_2} = 17$ is the highest energetically accessible quantum state.

system is reduced. As discussed in Section 2.3.2, due to the nuclear spin statistics of O₂ only odd rotational states are populated. In practice, the difference in scattered NO velocity between the lowest rotational levels of oxygen $N'_{\text{O}_2} = 1 - 5$ is very small ($\approx 40 \text{ cm}^{-1}$, neglecting spin-rotation coupling), equivalent to a few pixels on the detector ($\approx 5 \text{ px}$). This blurring of the Newton spheres for different N'_{O_2} , particularly the overlap of the lowest rotational states within a few pixels, increases the complexity of image analysis, since contributions from several different Newton spheres must be accounted for at each radius.

The angular distribution for each N'_{O_2} rotational state must be recovered sequentially to account for contributions from higher rotational states, which makes using the fitting methods described in Section 3.5 difficult. There are currently many methods available for the analysis of ion images containing multiple nested Newton spheres that have been ‘pancaked’ onto a 2D detector, including Abel-inversion [292–296], ‘onion-peeling’ [297, 298] and numerical methods [299–301] such as entropic analysis and forwards convolution. These methods have typically been used to analyse photofragment images, in which multiple product velocities must be measured in the same experiment. Whilst these requirements are similar to those of the diatom-diatom scattering described here, each of these methods have their own strengths and weaknesses. For both Abel-inversion and available onion-peeling algorithms, ion images are typically required to be cylindrically symmetric, whilst numerical methods are typically

not constrained by symmetry. Abel-inversion is also prone to noise dependent artefacts, with noise typically forced towards the center (line or point) of the ion image [294–296]. This is particularly problematic in the case of NO + O₂ scattering since the highest N'_{O_2} states will produce Newton spheres with very small radii, close to the center of the ion image.

An onion-peeling method, outlined in Section 4.3.1, was chosen for modification as, aside from the symmetry constraints (which can be corrected for in the method outlined here), no noise is induced in the image during the analysis process. Onion peeling methods were first introduced by Bordas *et al.* [292] to analyse the results of photoelectron images, before being extended to photofragment images by Manzhos and Looock [298]. A wide range of different photofragment ion images have been analysed using this method [292, 298, 299, 302], however in all cases the method relies on the ion image possessing cylindrical symmetry. The analysis method described here follows a similar procedure, adapted to allow for the fact that ion images in these scattering experiments do not possess cylindrical symmetry [39, 75].

4.3.1 Outline of the Onion-peeling Method

In the following section, the modified onion-peeling method used to analyse the experimental ion images will be outlined; more detailed discussion of specific parts of the analysis process are given in Appendix A, and will be referred to at the relevant point in the text. Figure 4.8 shows a schematic of the modified onion-peeling method used to extract angular distributions and populations of the final O₂ rotational states, using scattering into the $|j'_{\text{NO}} = 7.5, \Omega' = 0.5, \varepsilon' = +1, e\rangle$ state as an example. The recorded experimental image is initially instrument function corrected (to account for flux density effects) by dividing the experimental image through by the simulated instrument function (discussed further in Section A.1). The overlap between the instrument function and the experimental image was confirmed by reading the radial intensity, $I(r)$, of both images, as shown in the top left hand panel of Figure 4.9. The radial intensity in both cases was fitted to a Gaussian; the center of which is taken to be the radius of the Newton sphere for the N'_{O_2} state of interest, in the first instance $N'_{\text{O}_2} = 1$.

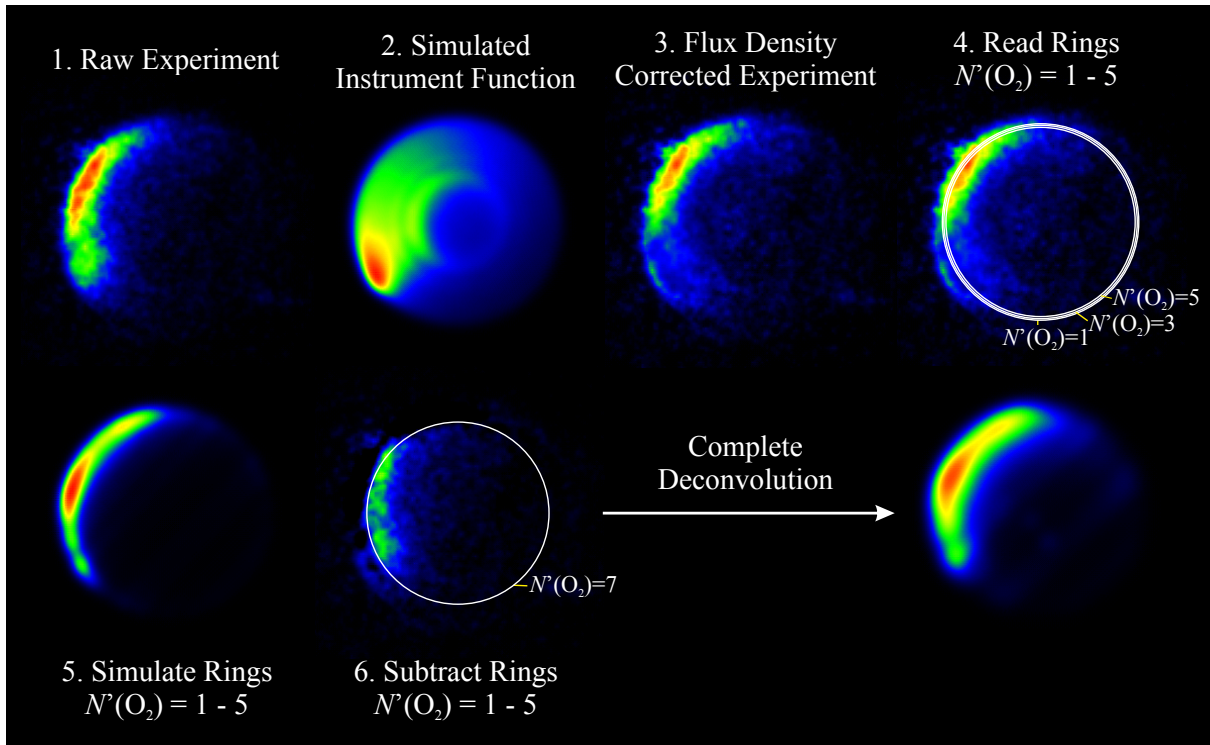


Figure 4.8: Schematic showing the onion-peeling methodology used to analyse ion images recorded for the inelastic scattering of $\text{NO} + \text{O}_2$, shown here for scattering into the $|j'_{\text{NO}} = 7.5, \Omega' = 0.5, \varepsilon' = +1, e\rangle$ state. The raw experimental image (1) is flux density corrected (3) using the simulated instrument function (2) for the specific experimental configuration. The lowest energy rotational states are then extracted from the corrected image (4) by reading the radius equivalent to the Newton sphere for the specific $(j'_{\text{NO}}, N'_{\text{O}_2})$ fragment pair. The intensity from the outer rings of the image may then be simulated using the extracted DCS (5), before they are deconvoluted from the experimental image by image subtraction (6). The process is repeated until the entire image has been ‘unpeeled’. The experimental ion image may then be back-simulated from the extracted experimental DCSs and O_2 rotational populations (7). Further details are given in the text.

The DCS is then read as the (angular) intensity profile, I , around the ring at a radius corresponding to the Newton sphere of the relevant state, calculated according to Equation (4.9).[§] Further discussion about this process is given in Section A.2. The ion image for the extracted O_2 state is then simulated with this angular distribution and the calculated apse correction, according to the method described in A.3, and accounting for the rotational excitation of the O_2 molecule. The contribution of the specific O_2 state is then removed from the experimental ion image by subtracting the appropriately weighted simulated image from the

[§]Note that the radius at which the state is read (calculated from the radial intensity plot in Figure 4.9), is not equivalent to the very edge of the experimental image. This arises due to the spread in the velocities of the molecular beams, resulting in a distribution of collision energies; this distribution results in a ‘blurring’ of the ion image which must be accounted for to find the ‘edge’ of the image.

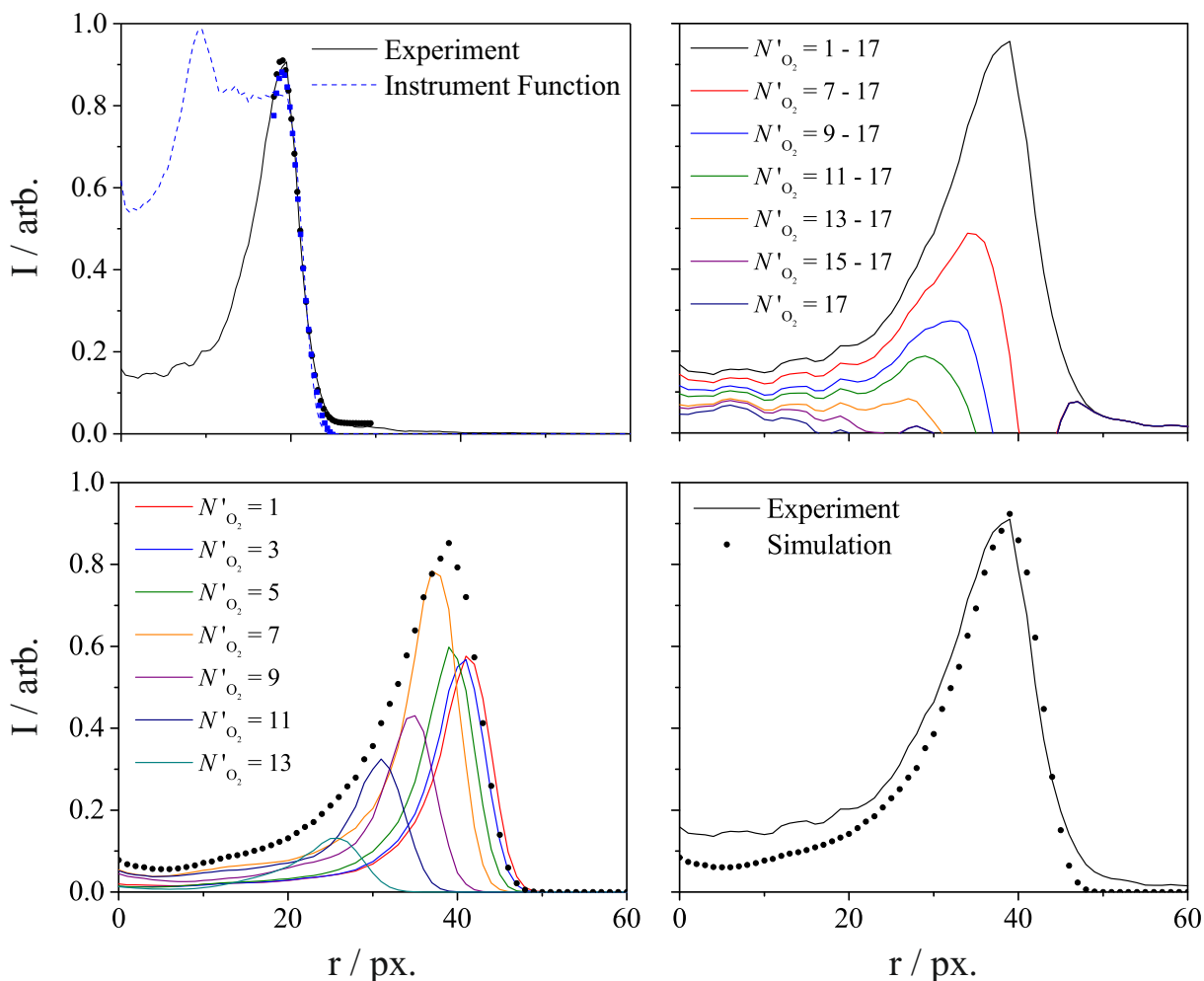


Figure 4.9: Radial intensity, I , plots for different stages of the analysis process. The top left panel shows the experimental (black line) and instrument function (blue dashed line) radial intensity as well as Gaussian fits (points in black and blue, respectively). The centre of the Gaussian is taken to be the Newton sphere radius for the ground state, $N'_{O_2} = 1$. The top right panel shows the experimental radial distributions after each deconvolution step; the full experimental image is shown by the black line. The bottom left panel shows the simulated radial distributions used to deconvolute the image, whilst the bottom right panel shows the experimental distribution (black line) and the rebuilt simulation (black dots).

raw experimental image. The ‘new’ experimental image, corresponding to higher O_2 co-product rotational states, has now had any contributions from the lower N'_{O_2} states removed.

The process is then repeated, by first reading the DCS around the calculated radius of the next O_2 rotational state of the ‘new’ instrument function corrected experimental ion image, then simulating the ion image for that state, weighting the simulation based upon the experimental image, and subtracting the simulation from the experimental image. The process was continued until the signal-to-noise ratio became too low to allow the extraction of further states, or until

the energetic maximum state, was reached. Due to the very low scattering intensity into high N'_{O_2} states, the angular distributions for such states were not analysed for all j'_{NO} . The radial intensities from the experimental image after each subsequent subtraction are shown in the top right hand panel of Figure 4.9; as each state is ‘unpeeled’ there is a decrease in intensity in the experimental image, with the radius of the resulting subtracted image becoming smaller as the O_2 rotational state becomes higher. Some intensity is observed on the outer edge of the subtracted experimental image, $r > 45$ px., arising from noise at the edge of the ion image, as well as any imperfections in velocity mapping.

The difference in rotational energy between the lowest oxygen rotational states, $N'_{O_2} = 1, 3$ and 5, is very small (as shown in Figure 4.6), leading to Newton spheres of very similar radii for the $(j'_{NO}, N'_{O_2} = 1 - 5)$ pairs when crushed onto the detector. The DCS is read across a 1 pixel wide bin; as such it was found to be necessary to read the DCS for each of these states in the same step. Therefore, it was not possible to obtain DCSs resolved for $N'_{O_2} = 1 - 5$, and only the average DCS for these states is returned with confidence. For states with $N'_{O_2} > 5$, the energy difference (and corresponding radial difference on the detector) between adjacent O_2 states was large enough to allow the contributions to each state to be considered independently.

Due to the sequential extraction of the N'_{O_2} resolved DCSs from the experimental image, by removal of the intensity contributions from each oxygen state, populations of N'_{O_2} within each j'_{NO} state may be calculated by considering the integral of each state resolved DCS. The complete back-simulation may then be rebuilt from the simulations calculated for each N'_{O_2} state during the process and the associated O_2 co-product rotational state populations. The bottom left hand panel of Figure 4.9 shows the radial distributions for each simulation after they have been weighted according to the relative population of states in the system. The experimental radial intensity, bottom right hand panel of Figure 4.9, is reproduced well by the summation of these weighted simulations.

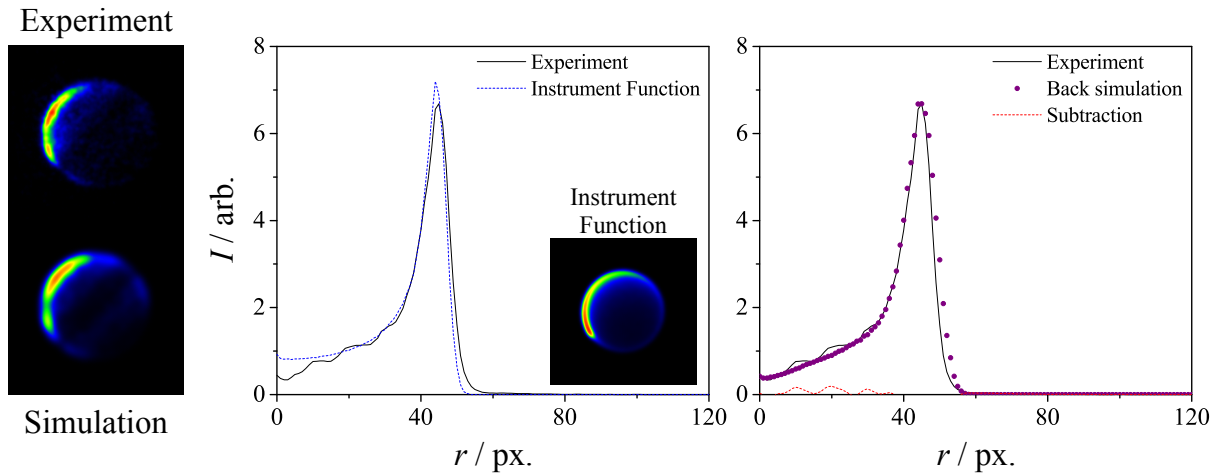


Figure 4.10: Radial intensity, I , for the different stages of the analysis process for the single Newton sphere formed by the scattering of NO + Ar into $|j' = 7.5e, \Omega' = 0.5\rangle$. The left panel shows the experimental (black line) and instrument function (blue dashed line) radial intensity. The right hand panel shows the effect of using the onion-peeling method for an atomic collision partner: the simulation (purple circles), from the DCS extracted from the experimental ion images, may be subtracted from the experimental radial intensity (black line), to effectively remove all intensity from the initial image. The experimental (top) and simulated (bottom) ion images are shown in the right hand panel; the simulated instrument function is shown as an inset in the middle panel.

4.4 Proof of Concept: Analysis of NO + Ar Scattering

The methodology described in Section 4.3 was tested on images recorded for the scattering of NO with Ar. Since only the NO molecule may be rotationally excited during the collision, only a single Newton sphere is detected for each final NO rotational state. Figure 4.10 shows the analysis process for the scattering of NO + Ar into the $j'_{\text{NO}} = 7.5e, \Omega' = 0.5$ state. The process is largely the same as in the case for which multiple Newton spheres are present: firstly, the theoretical radius of the experimental image was calculated, and then the DCS extracted from the flux density corrected experimental image. The extracted DCS was then used to back-simulate an ion image with the appropriate apse correction, which is observed to be in good agreement with the raw experimental image. Since no further Newton spheres are present in the experimental image after subtraction of the back-simulated image, the resulting ion image should be effectively zero if all of the information from the experimental image has been accurately extracted. From the radial distributions plotted in Figure 4.10, it is clear that

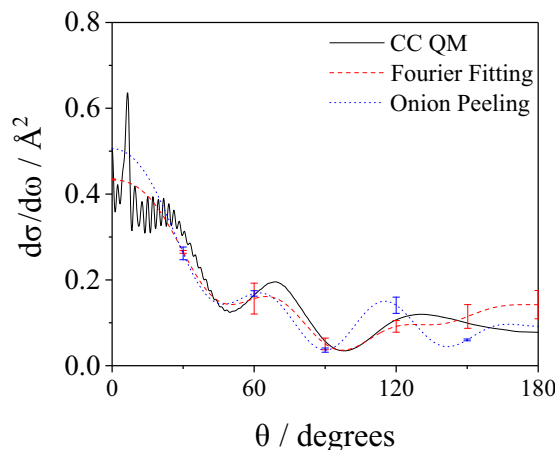


Figure 4.11: DCS for scattering of NO + Ar into $|j' = 7.5e, \Omega' = 0.5\rangle$. The CC QM DCS, shown by a black line; the experimentally derived DCS obtained by fitting the images in Fourier space (denoted Fourier fitting) [39], shown by a red dashed line; and the DCS from the onion-peeling method, shown as a blue dotted line. The QM data have been averaged over the experimental collision energy distribution. Error bars for the Fourier fitting were calculated by fitting the slow and fast sides of the image separately [39], whilst error bars for the onion-peeling method are calculated using the slow and fast side of the image as well as fitting with a radius of ± 1 pixel.

this is largely true. However, some signal is observed to remain due to noise from background signal.

Figure 4.11 shows the QM DCS for NO + Ar scattering into the $|j'_{\text{NO}} = 7.5e, \Omega' = 0.5\rangle$ state, and those extracted from the raw experimental image *via* the onion-peeling methodology, and the Fourier fitting process described in Section 3.5 [39]. Since the experimental apparatus provides no information on the absolute ICS of the state of interest, both extracted DCSs have been normalised to the integral of the CC QM data, to facilitate comparison. The onion-peeling method is in good agreement with both the CC QM and fitted DCS, suggesting that the methodology is able to accurately extract the angular distributions from raw experimental images. Small differences are observed between the two extraction methods and the CC QM DCS in the backward scattered region, this is due to the low signal intensity in this region.

4.5 Experimental Results

The raw experimental ion images for the inelastic scattering of NO with molecular oxygen, into a specific j'_{NO} , are shown in Figures 4.12 and 4.13 for spin-orbit conserving transitions into

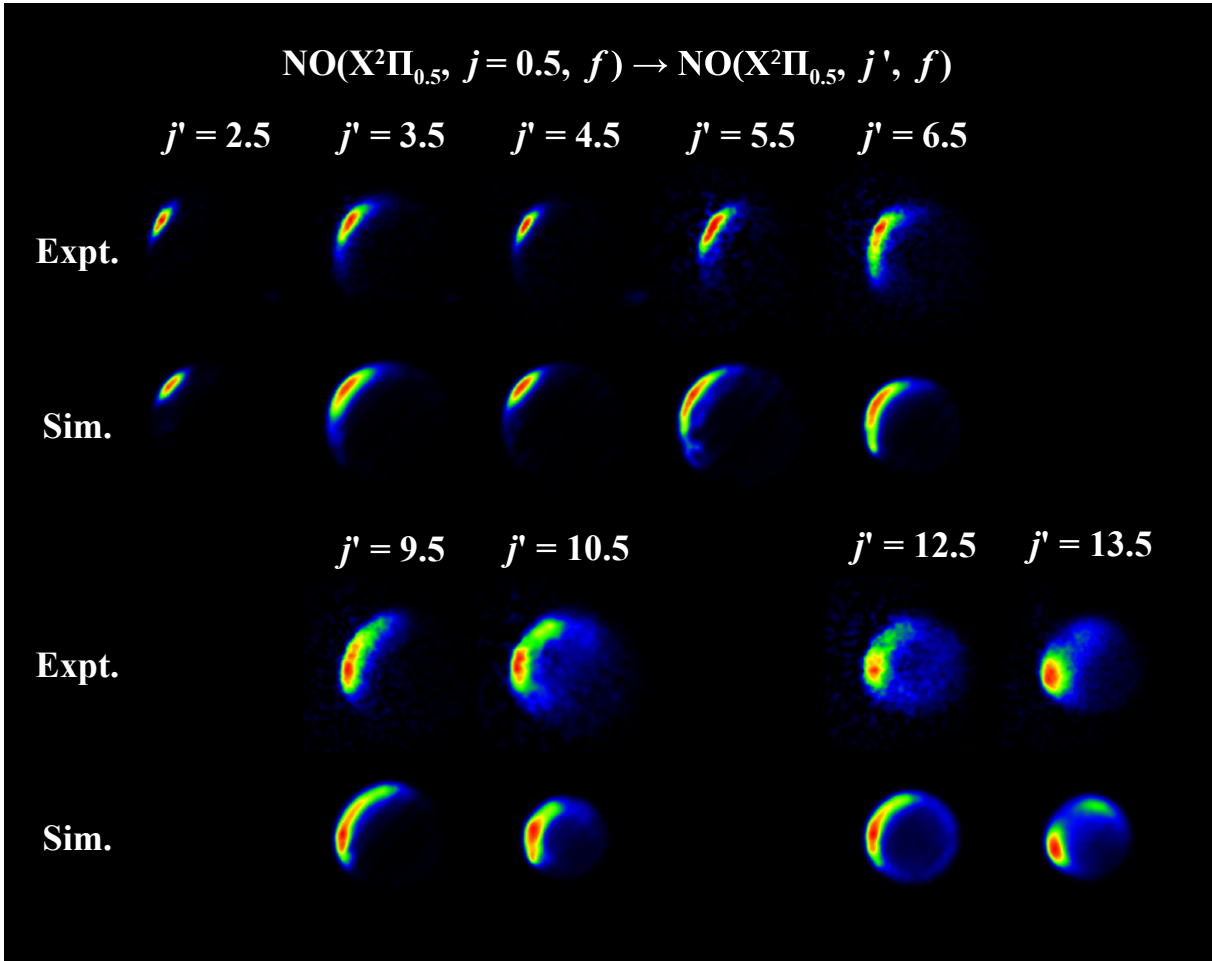


Figure 4.12: Ion images for the inelastic scattering of NO + O₂ resulting in the $|j', \Omega' = 0.5, \epsilon' = -1, f\rangle$ states of NO. The experimental and back-simulated images are shown in the top and bottom rows, respectively. Back-simulations were calculated using extracted DCSs and relative O₂ populations.

the final f and e Λ -doublet states of NO, respectively. The experimental image (top row) and the complete back-simulated image (bottom row) are shown in each case. The back-simulated image is the result of the simulation of each individual O₂ rotational state with the extracted DCSs, weighted by their relative populations and summed across all N'_{O_2} . The agreement between the experimental images and the back-simulations is reasonably good, aside from the inherent noise in the experimental image. This suggests that the extracted DCSs not only reproduce the angular distribution of the scattering, but also the relative populations of the N'_{O_2} states for each NO quantum state. Some of the more detailed structure in the experimental images is not observed in the final back-simulation, showing the limitation of the onion-peeling method in extracting fine details, and the limited resolution of the experimental data (in the

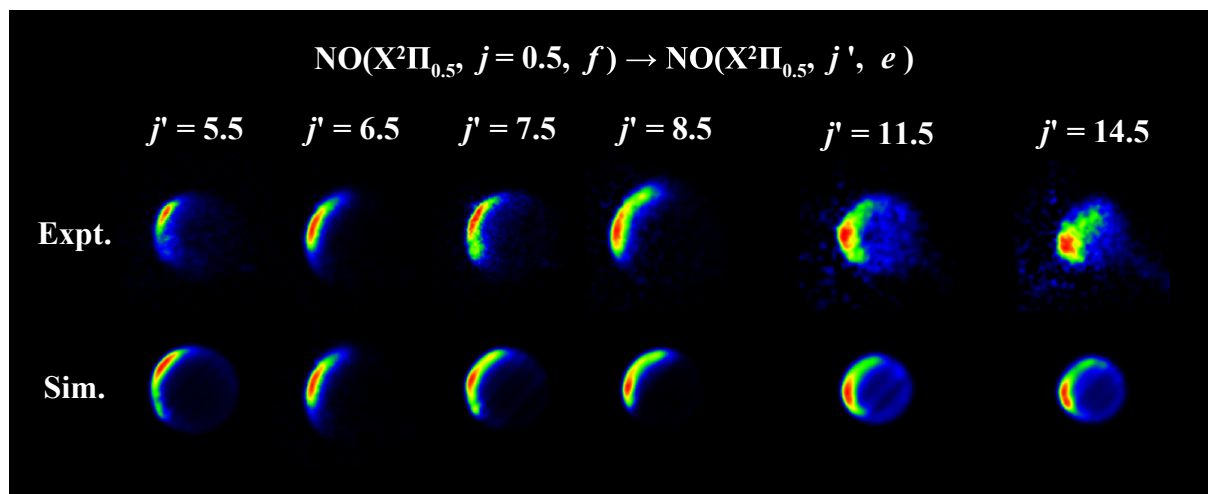


Figure 4.13: Ion images for the inelastic scattering of NO + O₂ resulting in the $|j', \Omega' = 0.5, \varepsilon' = +1, e\rangle$ states of NO. The experimental and back-simulated images are shown in the top and bottom rows, respectively. Back-simulations were calculated using extracted DCSs and relative O₂ populations.

current experimental configuration estimated to between 10 and 20 degrees). In general, lower j'_{NO} states are reproduced better by this method than higher rotational states, due to the lower level of noise in the former experimental ion images.

The ion images become smaller with increasing j'_{NO} , for both final Λ -doublets, due to the larger rotational energy transfer required to access higher rotational states. For higher rotational states, larger amounts of the initial translational energy, E_{coll} , are transferred into the rotational excitation of the NO molecule, and less energy is available for the outgoing translation of the collision partners. The corresponding outgoing velocity of the NO molecule is therefore smaller than for the low final rotational states, leading to a smaller Newton sphere of ions being created.

The products become increasingly backward scattered as the rotational state of the NO molecule increases, similar to the trend observed in the collision of NO with the rare gases [39, 75]. This can be understood by considering the type of collisions which lead to scattering into specific rotational states: ‘head-on’ collisions, leading to scattering through large angles, are required to populate higher values of j'_{NO} , whilst more ‘glancing’ collisions, which populate lower rotational states, lead to scattering through much smaller angles. In each case the experimental ion image (and as such the returned angular distribution) is dominated by the presence of a single peak. There is little evidence for a secondary maximum, which is typically

associated with the collisions of NO with the rare gases [39, 79], however this may be due to the overlap of contributions from multiple oxygen quantum states within the image.

4.5.1 State-to-State Angular Distributions

The state-to-state angular distributions for transitions into several final NO rotational states, resolved in the final oxygen rotational state, N'_{O_2} , are shown in Figure 4.14. Remember that for the lowest oxygen rotational states, $N'_{O_2} = 1 - 5$, only the average angular distribution is returned with confidence using the onion-peeling processes, due to the energy resolution of the experiment. Within each j'_{NO} state the intensities of the angular distributions give information about the relative population of each oxygen rotational state. No information about the j'_{NO} populations is available using the current experimental apparatus, and the scales for each j'_{NO} are arbitrary upon extraction, depending on the absolute intensity in the experimental ion image. To facilitate comparison, the sum of all N'_{O_2} states, for a specific j'_{NO} , are normalised to one.

Differences can be discerned between low, moderate and high j'_{NO} regimes. As noted in terms of the experimental ion images, the angular distributions become more backwards scattered with increasing rotational excitation of the NO molecule; this was also previously noted by Bacon *et al.* [59]. From the state-to-state resolved DCSs it is also clear that for a specific j'_{NO} the DCSs become more backwards scattered for larger N'_{O_2} . This may be understood in much the same way; to achieve large RET, collisions must be more ‘head-on’, consequently the O_2 molecule must undergo larger angle scattering for high N'_{O_2} than low N'_{O_2} .

The pair-correlated scattering dynamics of the NO and O_2 collision partners may be qualitatively understood by considering the differences between ‘head-on’ and glancing collisions for different rotational energy transfer regimes. ‘Glancing’ collisions, which occur preferentially for large impact parameter collisions, and correspond to low angle scattering, do not result in very much rotational excitation. As such, for $j'_{NO} = 4.5f$, whilst enough energy is available to access high rotational states of O_2 , the ‘glancing’ nature of collision does not provide sufficient torque for the population of $N'_{O_2} > 9$. For more ‘head-on’ collisions with low impact parameters, scattering occurs into larger angles, as seen for $j'_{NO} = 14.5e$, allowing

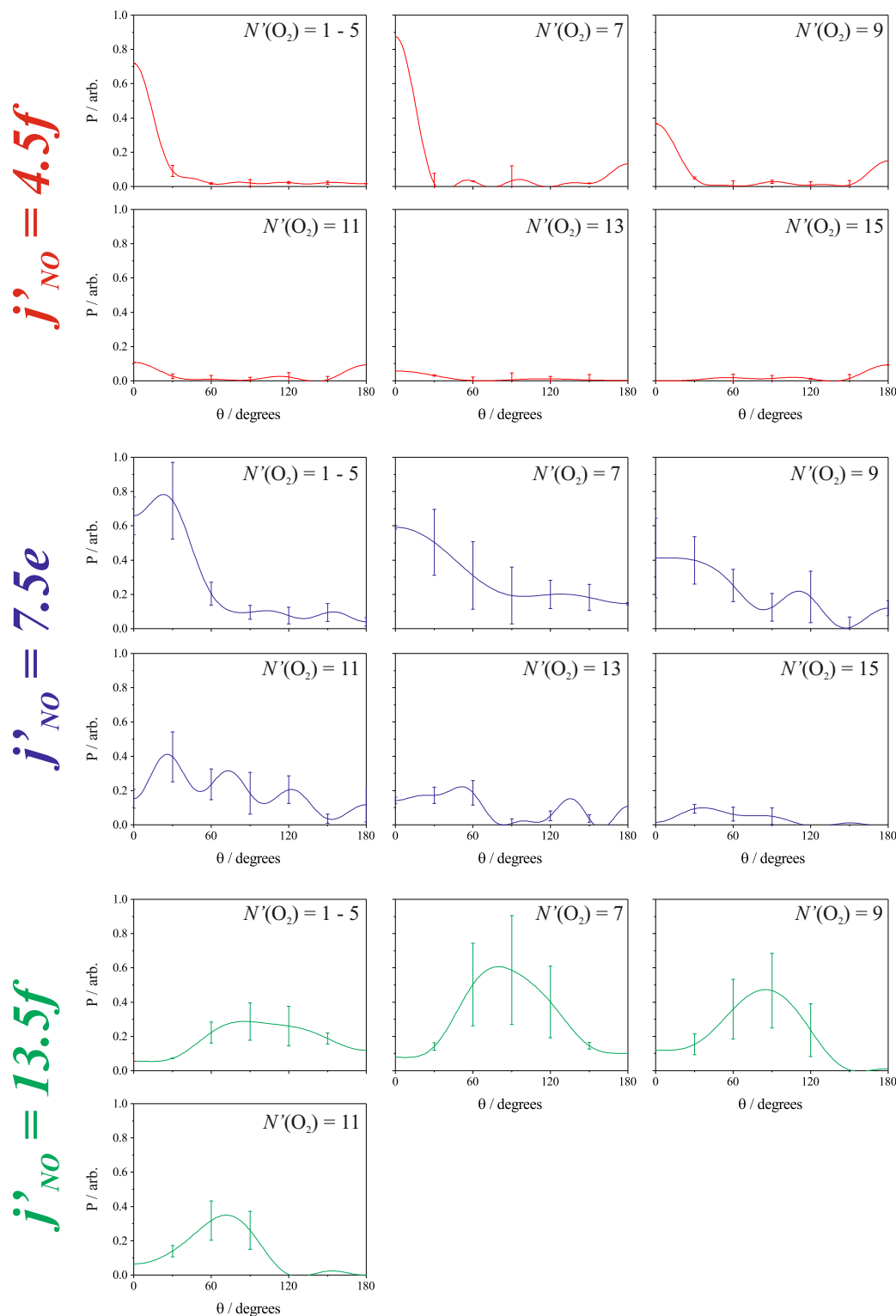


Figure 4.14: Experimentally determined angular distributions for the collision of NO with O₂, (partially) resolved in the final rotational state of O₂, scattering into the $|j'_{\text{NO}}, \Omega' = 0.5, \varepsilon'\rangle$ state of NO, where $j'_{\text{NO}} = 4.5f, 7.5e$, and $13.5f$ (from top to bottom), are plotted in red, blue and green, respectively. Note that the experiments cannot resolve the separate angular distributions for $N'_{\text{O}_2} = 1 - 5$, and so these are attributed the same angular distribution and intensity and plotted in a single panel. Angular distributions are fitted using a Legendre polynomial expansion up to and including the 8th order polynomial. Error bars are calculated by considering the standard error for the fast and slow side of the ion image combined with the error in changing the Newton sphere radius by ± 1 pixel.

significant rotational excitation of the O₂ collision partner and population of high N'_{O_2} states, although these are limited by the total ingoing collision energy. In intermediate cases, such as $j'_{NO} = 7.5e$, enough energy is available to allow access to many oxygen states. In this case more ‘head-on’ collisions give rise to the sideways and backwards scattering observed at middle and high N'_{O_2} , whilst more ‘glancing’ collisions give forward scattering at low N'_{O_2} .

4.5.2 Population of Oxygen Rotational States

For a specific NO rotational state, all the oxygen rotational states are extracted from a single ion image *via* the onion-peeling method, described in Section 4.3; consequently, information about the relative population, $P(N'_{O_2})$, with which these states are formed is also obtained. The population of each state is contained inherently within the angular distribution extracted from the experimental image, therefore the integral of the distribution over all angles provides a relative measure of the cross section for that O₂ co-partner quantum state. As such, the relative cross section of each N'_{O_2} for a specific j'_{NO} may be determined. It should be noted that at the experimental collision energy the maximum populated O₂ rotational state is constrained by energy conservation to $N'_{O_2} = 19$ and 1, for $j'_{NO} = 1$ and 17, respectively.

The relative populations for all the states analysed here are shown in Figure 4.15, for both the *f* and *e* final states of NO. The form of the population curve is similar for the low, moderate, and high j'_{NO} regimes, with a peak in the population at mid- N'_{O_2} . Since the lowest three oxygen rotational states ($N'_{O_2} = 1, 3$ and 5) are extracted simultaneously from the experimental ion image, as they are too close in energy to distinguish at the resolution of the experiment, they have been assigned the same populations (represented in the figure by a single point associated with $N'_{O_2} = 3$). As j'_{NO} increases, the population of O₂ in higher rotational states increases, with a corresponding decrease in the population of the lowest energy rotational states. For those states in which both the final *e* and *f* states of NO were recorded, the population distributions are observed to be similar (within error) for both types of transition.

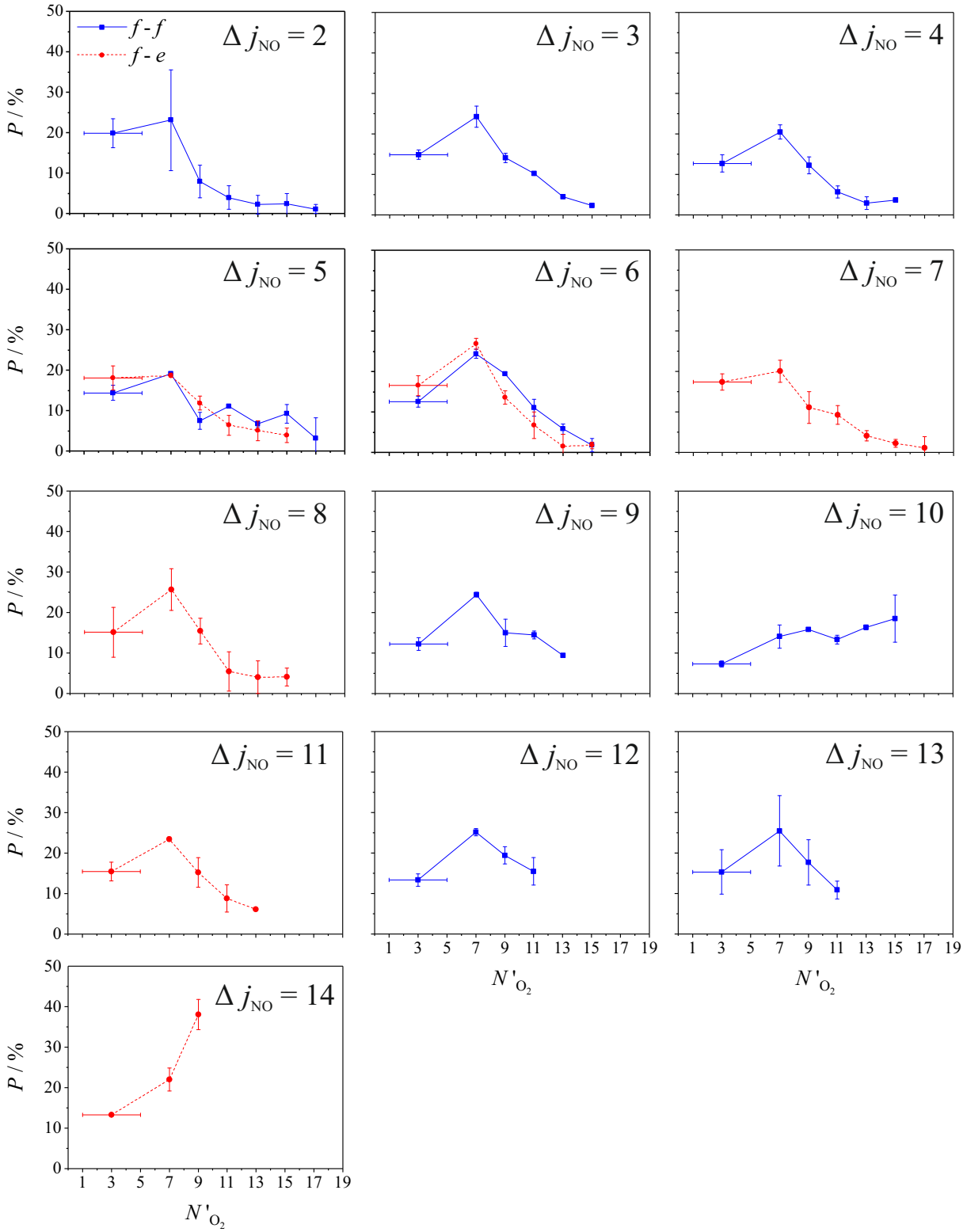


Figure 4.15: Relative percentage population of N'_{O_2} for NO + O₂ scattering in to states defined by $|j'_{NO}, \Omega' = 0.5, \epsilon'\rangle$, where $\epsilon' = -1, f$ (blue lines with squares) and $\epsilon' = +1, e$ (red dashed lines with circles). Error bars are calculated by considering the population of states for the fast and slow sides of the image and ring radii of ± 1 pixel. Since only the average population for $N'_{O_2} = 1 - 5$ may be extracted, all three states are shown by a single point at $N'_{O_2} = 3$, with an error bar extending across all three states.

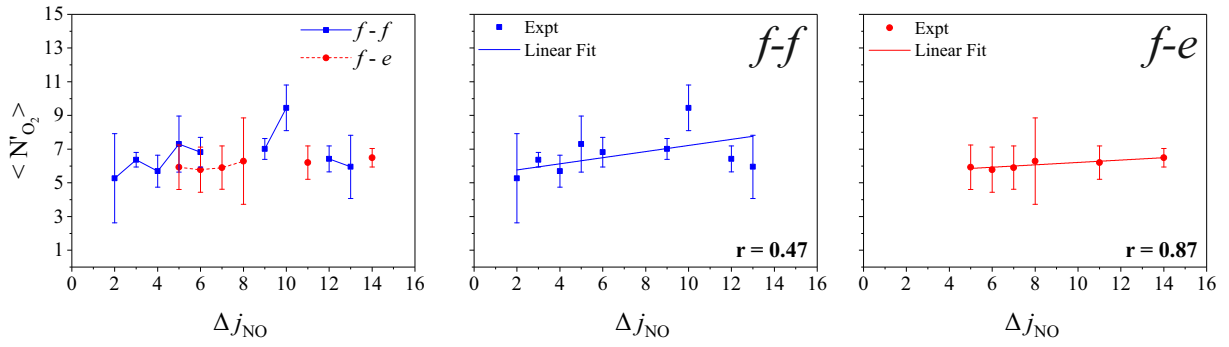


Figure 4.16: Average oxygen rotational state, $\langle N'_{O_2} \rangle$, for the final f (blue squares) and e (red circles) states of NO. $\langle N'_{O_2} \rangle$ is calculated according to Eq. (4.12), with error bars calculated by considering the errors in the calculation of the population of each N'_{O_2} state. The middle ($f-f$) and right ($f-e$) panels show a linear fit through the data, and the Pearson correlation coefficient, r , in each case.

The observed trends in the population of the N'_{O_2} states may be rationalised by considering the average final rotational state of O_2 , for a specific final rotational state of NO. The average final state of the O_2 molecule may be calculated as the sum of all energetically accessible N'_{O_2} weighted according to their population

$$\langle N'_{O_2} \rangle = \sum_{N'_{O_2}} P(N'_{O_2}) N'_{O_2}, \quad (4.12)$$

where $P(N'_{O_2})$ is the population of the oxygen rotational state, N'_{O_2} . The left hand panel of Figure 4.16, shows the average final rotational state as a function of j'_{NO} for the final f and e Λ -doublets. Also shown are linear fits to the experimental data, and the Pearson correlation coefficient for the data, r .

For both final Λ -doublets a subtle increase in the average oxygen rotational state is observed with increasing j'_{NO} (a value of $r > 0$); the correlation coefficients confirm that the strength of the association is reasonably good for $f-f$ ($r = 0.47$) transitions and good for $f-e$ ($r = 0.87$) transitions. This shows that higher oxygen rotational states may (on average) be populated when the NO molecule is excited into higher rotational states, as was observed in the N'_{O_2} resolved angular distributions in Figure 4.14. This trend can be understood by considering the dynamics of collisions in terms of different N'_{O_2} , but the same j'_{NO} , as discussed in terms of the angular distributions in Section 4.5.1. As N'_{O_2} increases, the angular distribution becomes more

back-scattered, as more ‘head-on’ collisions are required to achieve larger rotational energy transfer. As mentioned previously, ‘head-on’ type collisions are likely to induce large amounts of rotational excitation in both the NO and O₂ collision partner. As such higher values of j'_{NO} correlate with somewhat higher values of N'_{O_2} , as these states become preferentially populated by low impact parameter collisions, increasing the average value of the oxygen rotational state.

4.5.3 State Averaged Angular Distributions

To gain further insight into the collisions of NO with O₂, the average angular distribution for a specific j'_{NO} may be calculated by taking the weighted sum of the state-to-state resolved angular distributions, shown in Figure 4.14, over all populated oxygen rotational states, according to

$$P(\theta, j'_{\text{NO}}) = \sum_{N'_{\text{O}_2}} P(\theta, j'_{\text{NO}}, N'_{\text{O}_2}) P(j'_{\text{NO}}, N'_{\text{O}_2}) , \quad (4.13)$$

where $P(\theta, j'_{\text{NO}}, N'_{\text{O}_2})$ is the angular distribution for a specific j'_{NO} and N'_{O_2} and $P(j'_{\text{NO}}, N'_{\text{O}_2})$ is the relative population of each $(j'_{\text{NO}}, N'_{\text{O}_2})$ pair. The resulting angular distribution shows the preferential scattering angles as a function of j'_{NO} only; these are shown in Figures 4.17 and 4.18 for spin-orbit conserving scattering into the final f and e states of NO, respectively. Since the angular distribution for each j'_{NO} has an arbitrary intensity when recovered from the experimental ion image, the normalised angular distributions, $P(\theta, j'_{\text{NO}})$, are plotted here. The conclusions drawn from these averaged angular distributions confirm the conclusions drawn from the experimental ion images. Forward scattering is dominant in the lowest j'_{NO} states, with increasingly sideways and then backwards scattering observed as j'_{NO} increases. Furthermore, no secondary maxima are observed in the O₂ state averaged angular distributions, which are typically dominated by a single peak (unlike in the case of NO scattering with Ar [39, 75, 303]).

Figures 4.17 and 4.18 also compare the experimental angular distributions against CC QM calculations which treat the O₂ collision partner as if it were a closed-shell atom. Calculations were performed on the NO + Ar PES described in Section 2.2, using the mass of O₂ for the collision partner, as described in Section 4.2. The QM DCSs were normalised in the same way

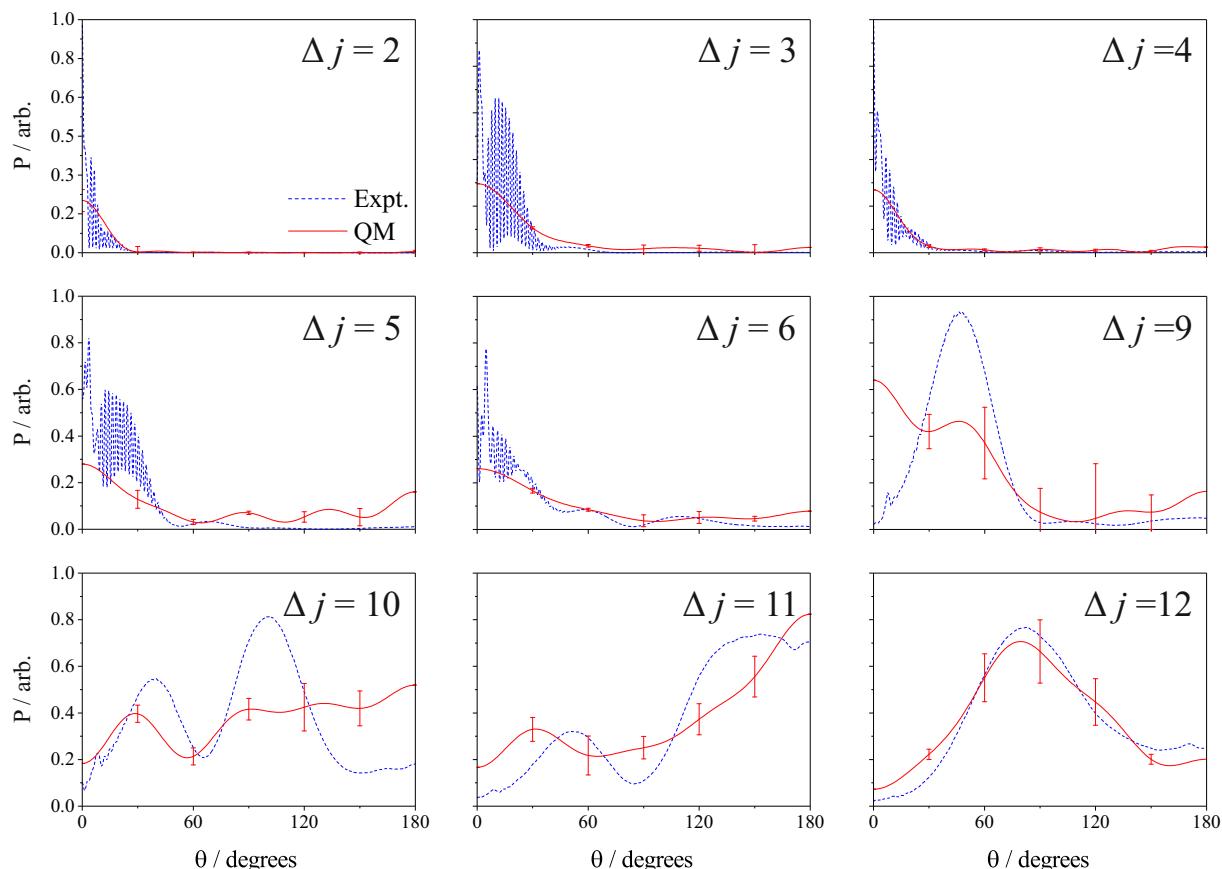


Figure 4.17: State averaged normalised angular distributions for NO + O₂ scattering into final states defined by $|j', \Omega' = 0.5, \varepsilon = -1, f\rangle$. Angular distributions are population weighted averages across all N'_{O_2} states. Error bars are calculated by propagating the errors in the state-to-state resolved angular distributions in Figure 4.14. QM calculations (blue line) show the angular distribution for a ‘spherical’ (atom-like) O₂ molecule colliding with NO on the NO + Ar PES (using the mass of O₂) as detailed in Section 4.2, calculated with a Gaussian spread of collision energy.

as the experimental angular distributions to facilitate comparison. The agreement between the experimental data and the QM calculations is not expected to be good, given the approximate nature of the theory. However, the data sets show qualitatively similar behaviour, and the QM calculations largely reproduce the general experimental structure. This suggests that the PESs governing the scattering of NO with Ar and O₂ are similar, and that spin-coupling only has a (relatively) small effect on the N'_{O_2} averaged angular distributions. Of course, to gain information about the fully resolved (j'_{NO}, N'_{O_2}) correlated angular distribution, the diatomic nature of O₂ would have to be considered, along with spin-coupling effects arising from the biradical nature of molecular oxygen.[‡] The differences between scattering with Ar and O₂ collision partners is explored further in Section 4.5.5.

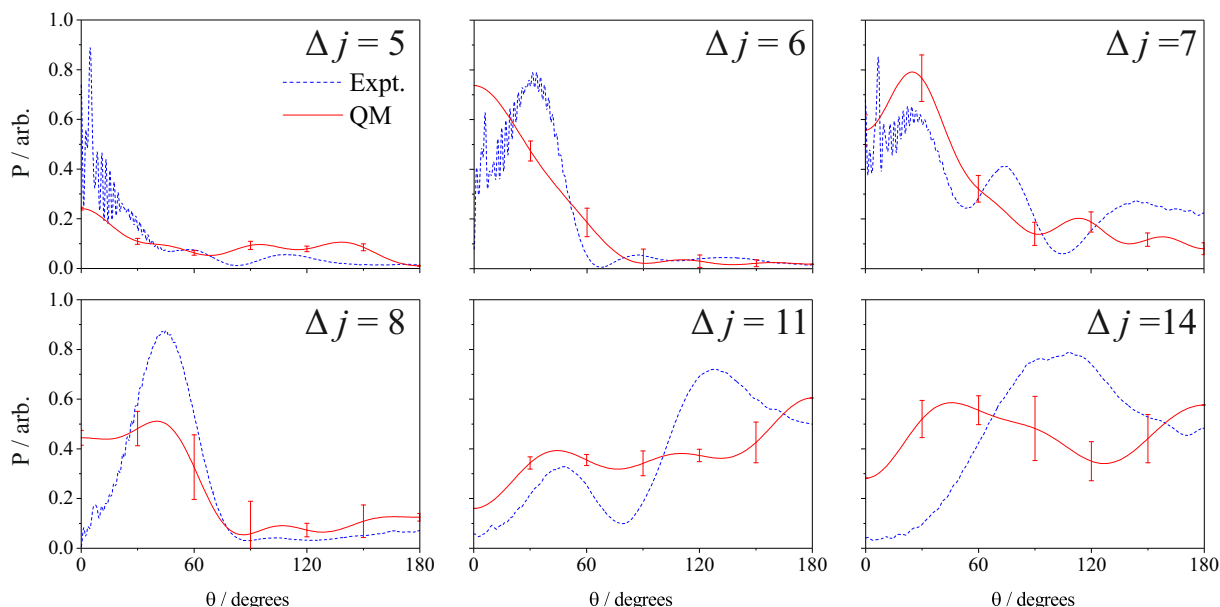


Figure 4.18: State averaged normalised angular distributions for NO + O₂ for scattering into final states defined by $|j', \Omega' = 0.5, \varepsilon = -1, e\rangle$. Experimental angular distributions (red lines) are population weighted averages across all N'_{O_2} states. Error bars are calculated by propagating the errors in the state-to-state resolved angular distributions in Figure 4.14. QM calculations (blue dashed lines) show the angular distribution for a ‘spherical’ (atom-like) O₂ molecule colliding with NO on the NO + Ar PES (using the mass of O₂) as detailed in Section 4.2, calculated with a Gaussian spread of collision energies (FWHM = 50 cm⁻¹).

4.5.4 Parity Pairs

In the unoriented scattering of NO(X) with the rare gases so called ‘parity pairs’ have been observed [39, 75, 179, 304, 305], in which the DCSs of pairs of states with a common value of

$$n = j'_{\text{NO}} - \frac{\varepsilon \varepsilon'}{2}, \quad (4.14)$$

have very similar DCSs; for the experiments described here $\varepsilon = -1, f$. This behaviour arises as the parity pair transitions are coupled by the same term in the interaction potential [179, 305]. A comparison of the normalised angular distributions, averaged over N'_{O_2} , is shown in Figure 4.19 for $n = 6, 9$ and 12 for which $j'_{\text{NO}} = 6.5, 9.5$ and 12.5 for transitions into the final f state and $j'_{\text{NO}} = 5.5, 8.5$ and 11.5 for transitions into the final e state. Broadly speaking there appears to be a similar parity pair effect at play, within the resolution of the experimental data, this is particularly pronounced for $n = 12$ ($12.5f$ and $11.5e$) where the errors in the averaged DCS

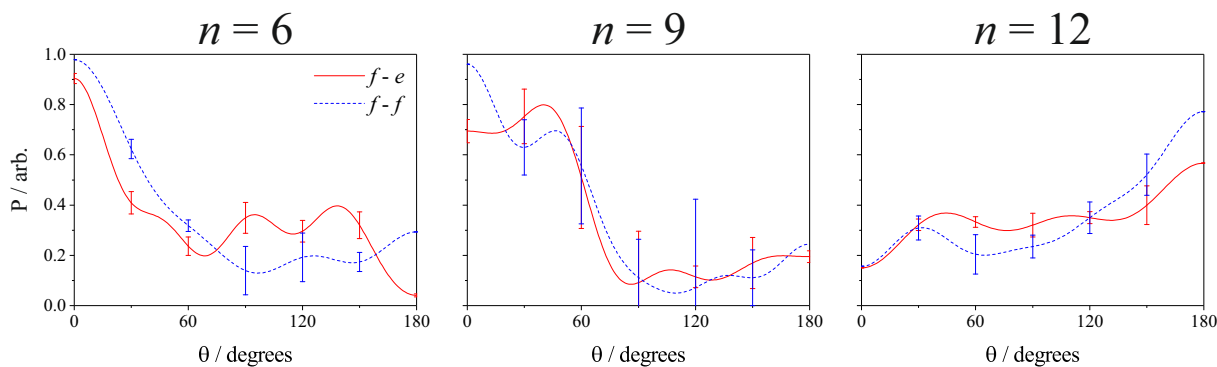


Figure 4.19: Normalised angular distributions for ‘parity-pairs’ of NO + O₂ scattering where $n = 6, 9$, and 12 from left to right. The final e and f states are shown by red and blue (dashed) lines respectively. Error bars are calculated by propagating the errors from the state-to-state resolved angular distributions in Figure 4.14.

are the smallest. It would also be of interest to see whether these effects are also observed in the N'_{O_2} resolved data presented in Section 4.5.1; however, this will require measurements with higher resolution than currently possible using this experimental apparatus.

4.5.5 Comparison with NO + Ar Scattering

The ion images for the scattering of NO with Ar and O₂ into $|j', \Omega' = 0.5, \epsilon' = +1, e\rangle$ are presented in Figure 4.20. The most obvious difference between the collision partners is the increased width of the intensity present in the NO + O₂ case when compared to Ar. This is due to the convolution of multiple oxygen states for each specific j'_{NO} ; each N'_{O_2} state contributes intensity at a Newton sphere radius proportional to the outgoing velocity of the NO molecule. The O₂ rotational states do not appear as separate Newton spheres due to the experimental resolution discussed in Section 4.1.3, rather the states are blurred together due to the collision energy distribution, as well as the ‘crushed’ nature of the Newton sphere recorded experimentally. Methods to improve the resolution of these images is discussed in Section 4.6. For collisions with atomic argon only a single outgoing NO velocity is achieved for each j'_{NO} , since there can be no rotational excitation of an atom, and as such only a single Newton sphere is formed and the band of intensity is much narrower. As discussed in terms of the NO + O₂ ion images in Figures 4.12 and 4.13, the ion images (for both collision partners) become smaller with increasing j'_{NO} , as more energy goes into rotational energy transfer and less is available

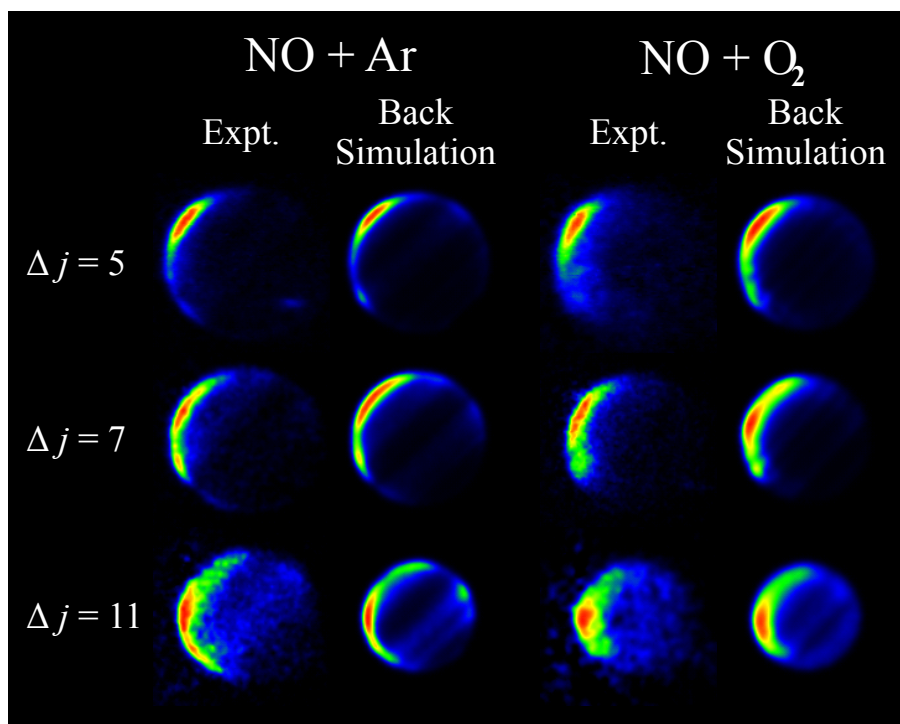


Figure 4.20: Ion images for the scattering of NO with Ar (left) and O₂ (right) into the $|j'_{\text{NO}}, \Omega' = 0.5, \epsilon = +1, e\rangle$ states, with $j'_{\text{NO}} = 5.5, 7.5$ and 11.5 (from top to bottom). In each case the experimental image is shown in the left hand panel and the back-simulated image in the right hand panel.

for the outgoing translation of the NO molecule. The images become more sideways (and then backwards) scattered with increasing j'_{NO} due to the need for increasingly ‘head-on’ collisions (resulting in large scattering angles) to induce large amounts of RET.

The scattering distribution observed for the two collision partners is similar, with an intense forward scattered peak in both cases. A more subtle feature is the presence of a secondary peak in the sideways scattered region of the NO + Ar images, which is not observed for scattering with O₂, at moderate and high Δj . This is observed more clearly by plotting the average normalised angular distribution for the oxygen and argon collision partners, as extracted from experimental ion images using the same method, shown in Figure 4.21. At low Δj the angular distributions for O₂ and Ar are similar, however the distributions vary more for middle and high Δj . The secondary maximum observed in the NO + Ar angular distributions is not observed for the NO + O₂ system; there is a small secondary peak in the case of $j'_{\text{NO}} = 7.5e$, however this is on the scale of the error bar and it is unclear whether this is significant. Since very little

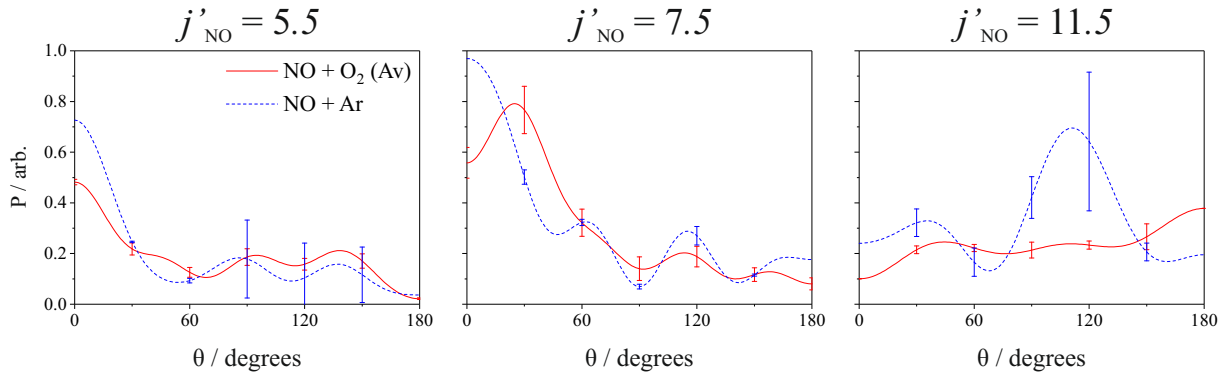


Figure 4.21: Normalised angular distributions for the scattering of NO with O₂ (red lines) and Ar (blue dashed lines) into the final states defined by $|j'_{\text{NO}}, \Omega' = 0.5, \epsilon' = +1, e\rangle$. Angular distributions for O₂ are population weighted averages across all N'_{O_2} states. Error bars are calculated by propagating the errors in the state-to-state resolved angular distributions in Figure 4.18.

is known about the PES for NO + O₂,[‡] it is difficult to ascertain why no secondary structure is observed. Secondary structure in the collision with the rare gases arises due to rotational rainbows [33, 39, 79, 271, 306], which arise due to the anisotropy of the repulsive part of the potential (see further discussion in Section 7.5.1). Typically the lack of secondary structure observed in collisions of NO(X) with He [80, 178], is attributed to the largely repulsive nature of the V_{sum} potential. As such the lack of secondary structure observed here may arise due to a largely repulsive PES. However, it is also possible that any secondary structure is ‘washed out’ by averaging over the N'_{O_2} states.

4.6 Future Work: Sliced Imaging

Whilst it has been shown that the $(j'_{\text{NO}}, N'_{\text{O}_2})$ pair-wise correlation may be extracted from the ‘crushed’ ion image currently measured experimentally, the 2D projection of the 3D Newton sphere onto the detector has been shown to cause many difficulties (particularly related to resolution) when extracting information from the experimental image. Improvements in the resolution of the experiment may be achieved using a slice imaging apparatus, coupled with a time stamping camera [307–309]. Such a technique allows the reconstruction of the ‘central slice’ of the Newton sphere, resulting in isolation of the nested Newton spheres, and direct

analysis of a single $(j'_{\text{NO}}, N'_{\text{O}_2})$ pair of rotational states without interference from any other N'_{O_2} .

Whilst a range of initial O_2 states were populated in this work, the group of van de Meeraker have recently used an Evan Lavie [287] valve to produce O_2 predominantly in its ground state, $N'_{\text{O}_2} = 1$, with populations of 23%, 18%, and 59%, for $j_{\text{O}_2} = 0, 1$, and 2, respectively. A narrower distribution of experimental collision energies may also be achieved using Stark and/or Zeeman deceleration on the NO and/or O_2 molecular beam, respectively [111–113, 289]. It is likely that both better quantum state selection and higher resolution (achieved through slice imaging) are required to fully disentangle the pair-correlations between NO and O_2 , and other such systems.

A Time Stamping Camera: The PImMS Sensor The Pixel Imaging (multi-)Mass Spectrometry camera (PImMS) [307–309] records both the spatial (x and y) positions, along with the time, t , of each ion hit on the detector. The time stamped data may then be used to rebuild the experimental image in three dimensions (x , y and t), and the ‘central slice’ of the Newton sphere may be extracted. Two versions of the PImMS camera are currently available, with either the PImMS1 sensor (72×72 pixels) or the PImMS2 sensor (324×324 pixels): with each pixel composed of 4 registers, corresponding to the ability to record four ions per pixel per acquisition cycle. Both sensors operate with a time precision of 12.5 ns [308]. Using a conventional CCD camera, which records the (x, y) positions of ion hits, it is possible to place a time gate over the detector [310] such that the it is ‘on’ for less than 10 ns. However, this would require repetition of the experiment at various time delays to capture the full product distribution (and not just the ‘central slice’). This would require long acquisition times to converge experimental images due to the inherently low ion counts, and hence low signal intensity, in inelastic scattering experiments. Importantly, the PImMS camera may directly replace the CCD camera (301×301 pixels) currently used on the experiment.

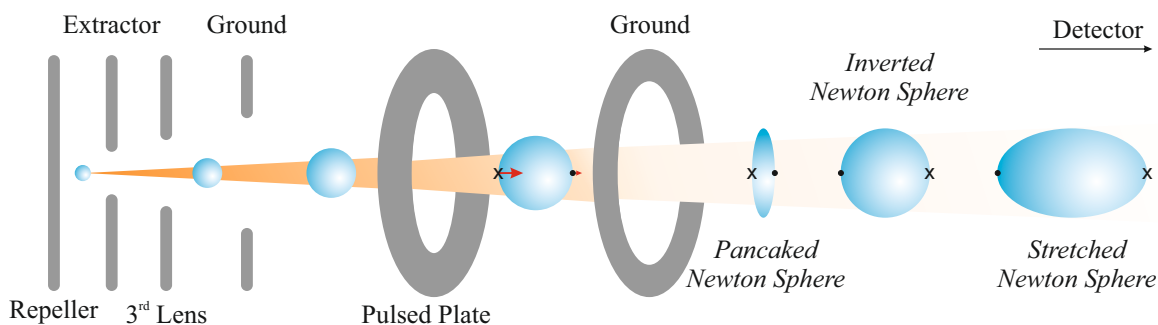


Figure 4.22: Schematic of Post-Extraction Inversion Slice Imaging (PEISI), as described in the text. Adapted from Reference [315].

4.6.1 Post-extraction Inversion Slice Imaging

Whilst there are several methods capable of achieving slice imaging (optical slicing [311–313], pulse-field extraction slicing [313, 314] and direct current (DC) slicing [312]), work by Squires [315] suggests that a modified version of DC slicing based on post-extraction differential acceleration (PEDA) [316], is most suitable for the temporal resolutions required with this specific experimental apparatus. PEDA is typically used to gain higher TOF resolution in mass spectrometry by time focusing ions onto a detector. Post-extraction inversion slice imaging (PEISI) is based on similar concepts, but allows time defocusing of ions, causing a spread in arrival times at the detector, whilst maintaining velocity mapping [315].

A schematic illustrating PEISI is shown in Figure 4.22 [315]. The slicing apparatus is made up of two sets of electrodes; firstly the extraction lens (repeller, extractor and ground, as described in Section 3.4) coupled with an additional slicing electrode similar to that used in standard 4 plate DC slice imaging [312]. The second set of electrodes, further along the TOF tube, is composed of two additional electrodes, one pulsed at a high voltage and the other grounded. PEISI increases the temporal stretch of the Newton sphere according to the following scheme [315]:

1. Ions are extracted by the first set of ion optics, used in standard DC slice imaging, and the Newton sphere begins to expand.
2. The ions enter a field free region, moving down the TOF tube towards the detector. The temporal width of the sphere continues to expand in this region.

3. Upon entering the region between the second set of plates a high voltage (approximately 2kV) is applied to the pulsed plate, causing a field gradient between the plates which induces differential acceleration [316]. Ions closest to the pulsed plate (near the back of the Newton sphere) experience a stronger field than those closer to the detector (near the front of the Newton sphere).
4. Due to the difference in acceleration experienced by ions at different positions on the Newton sphere, ions at the back of the sphere advance on ions at the front, and the absolute temporal width of the Newton sphere is decreased.
5. As the ions continue along the flight tube this process continues until the Newton sphere is 'pancaked'. At this position the temporal width of the ions is minimised.
6. Ions that were initially at the back of the Newton sphere now 'overtake' those ions which were initially at the front, and the entire Newton sphere is inverted.
7. Once the ions have left the pulsed region, the expansion of the Newton sphere continues as the ions move along the TOF tube, stretching along the TOF direction until impacting with the detector.

Significant temporal stretches of the Newton sphere may be achieved using this method, with the width of the ion packet depending on the position of the pulsed plate relative to the grounded plate, and the position of the first and second sets of electrodes with respect to each other [315]. Variation of the position of the second set of electrodes leads to magnification of the Newton sphere to a radius larger than that of the (40 mm) detector; this may be compensated for by modifying the aperture size in both the pulsed and ground electrodes in Figure 4.22 [315]. Simulations of the experimental apparatus (modified for 3D slicing with PEISI) using SIMION 8.0 [317] with a flight tube of length 1 m (extended from 0.7 m used in the NO + O₂ experiments), and the optimum positions of the two sets of electrodes and aperture sizes, results in an optimum stretch of ~ 260 ns. This corresponds to approximately 20 time slices using a PImMS camera (with time bins of 12.5 ns).

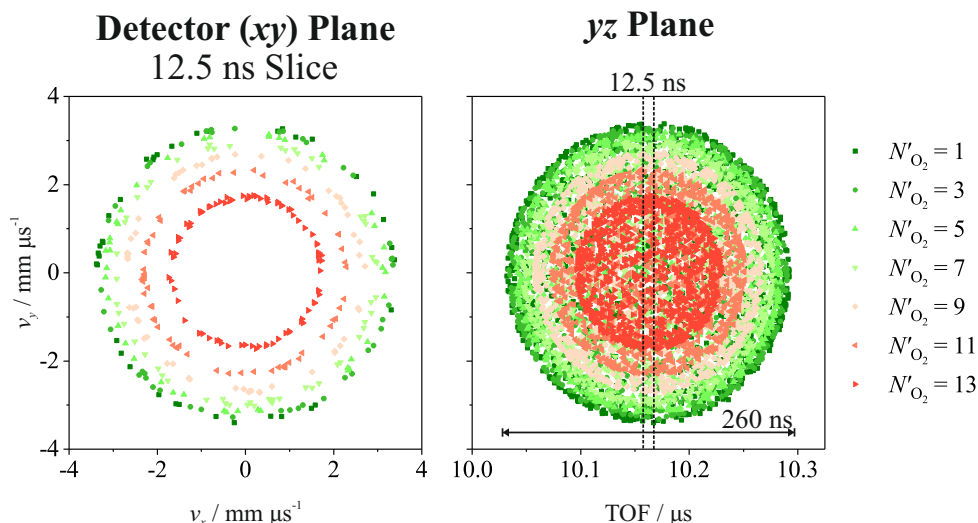


Figure 4.23: Simulated 2D views of the Newton spheres formed by scattering of NO and O₂ into $j'_{\text{NO}} = 10.5$ for all energetically accessible N'_{O_2} . The ions are shown on approach to the detector, *i.e.* as they move along the TOF axis (right), as well as those which lie within the central 12.5 ns bin (left). The total width of the Newton sphere is 260 ns, allowing for the possibility of approximately 20 slices (of 12.5 ns) through the sphere using the PImMS camera.

Since the objective of implementing PEISI is to allow for higher resolution images of diatom-diatom collisions, it is important to consider the multiple Newton spheres formed for a single final rotational state of NO. Figure 4.23 shows simulations of the Newton sphere of ions after the collision of NO with O₂, for all N'_{O_2} energetically accessible for scattering into the $j'_{\text{NO}} = 10.5$ state. All simulations were done using SIMION 8.0 [317]. As discussed previously, as the rotational energy of the O₂ molecules increases, less translational energy is available to the NO molecule, resulting in Newton spheres of smaller radii. It is important that the ‘central slice’ samples the central portion of each sphere, although it should be noted that for smaller spheres a larger proportion of the sphere will be sampled in each slice. This requires that the Newton spheres for each O₂ rotational state are all perfectly concentric upon hitting the detector. From analysis of the simulations in Figure 4.23, it is clear that good velocity mapping may be achieved using PEISI, since no large distortions of the ions are observed and the images clearly show neat concentric rings. The central slice (a 12.5 ns bin) of the Newton sphere is also shown, sampling the central slice of each Newton sphere, here the small radial widths of each ring clearly show the success of the velocity mapping. The Newton spheres corresponding to the lowest N'_{O_2} still have very similar radii; however, due to the removal of any out-of-plane

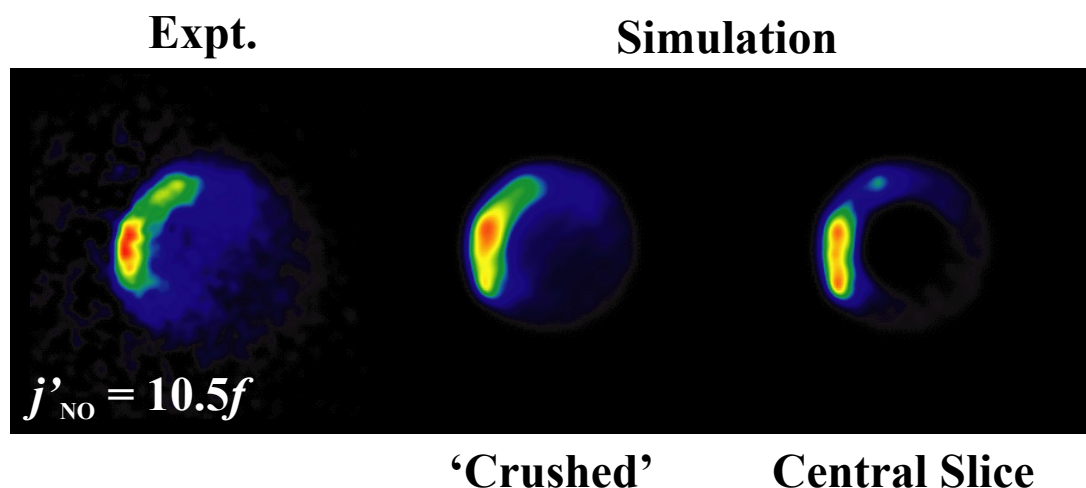


Figure 4.24: Experimental (left) and simulated (right) ion images for the scattering of NO with O₂ into the ($j'_{\text{NO}} = 10.5f, N'_{\text{O}_2}$) state, using the experimentally extracted DCSs weighted according to the experimental N'_{O_2} populations. The ‘crushed’ image, recorded with the current experimental apparatus is shown on the left, and the central slice through the image as recorded using PEISI and a PImMS camera (with a time slice of 12.5 ns) is shown on the right.

scattering by taking a central time slice, the rings are much clearer. It is unlikely, even using this method, that the lowest N'_{O_2} states will be fully resolved, due to the resolution of the final detector onto which the image will be mapped.

The resolution of the ion images achieved using the current experimental set-up and proposed 3D imaging apparatus can be compared by simulating the ion images for each apparatus using the experimentally extracted angular distribution and a kinematic apse collision induced alignment correction. All parameters, except those related to the slicing process, are equivalent in the two simulations. Figure 4.24 shows the experimentally obtained image alongside simulations of both the ‘crushed’ and ‘sliced’ ion images for the scattering of NO and O₂ into ($j'_{\text{NO}} = 10.5f, N'_{\text{O}_2}$). To simulate the central slice of the ion image, each ion trajectory is binned according to its position in the Newton sphere, into the number of time slices possible for each rotational state, before extracting the central slice for each Newton sphere. The simulated central slice of the ion image clearly shows a different distribution to that of the ‘crushed’ ion image. Referring back to the extracted (average) DCS, shown in Figure 4.17, the ion image is a much clearer representation of the observed angular distribution, since all out-of-plane scattering components have been removed from the ion image.

4.7 Summary

In this chapter the inelastic scattering of NO(X) with O₂(X), resulting in rotational excitation of both collision partners, was investigated using experimental ion images of the scattered NO(X) molecule. In the first part of the chapter the complexities of diatom-diatom scattering were discussed. Due to the presence of multiple Newton spheres (arising from the multiple N'_{O_2} for each j'_{NO}) within each recorded ion image, a new analysis method to extract the $(j'_{\text{NO}}, N'_{\text{O}_2})$ resolved angular distributions was described. The method is based upon an ‘onion-peeling’ algorithm modified to account for the lack of symmetry in the experimental ion image; recovering the angular distributions from low to high O₂(X) rotational states sequentially. The method was shown to resolve angular distributions in j'_{NO} and partially in N'_{O_2} . The lowest rotational states of the O₂ molecule were extracted as an average over $N'_{\text{O}_2} = 1 - 5$, due to the overlap of the Newton spheres for each state at the current experimental resolution.

It was shown that the state-to-state resolved angular distributions could be rationalised in a similar way to the scattering of NO with an atom, but including the rotational motion of the diatomic partner. Increasingly higher rotational states of NO require more ‘head-on’ collisions resulting in sideways and backwards scattered products, whilst low rotational states, arising due to ‘glancing’ collisions, result in forwards scattering. Similarly, within a specific j'_{NO} , as the rotational state of the O₂ co-product increases, scattering becomes more sideways and then backwards scattered, due to the same mechanism. This model may also be used to account for the average rotational state of the O₂ molecule after the collision, with a trade-off between those states which are energetically accessible and the type of collision (‘head-on’ *versus* ‘glancing’) necessary to access a specific N'_{O_2} . It was observed that the population of each N'_{O_2} for a specific j'_{NO} , peaks for intermediate N'_{O_2} . Parity pairs, between states with the same $n (= j'_{\text{NO}} + \epsilon'/2)$ but different ϵ' , were observed in the N'_{O_2} averaged angular distributions, similar to those observed for the collisions of NO with the rare gases. Comparisons of the (atomic) Ar and (diatomic) O₂ collision partners, showed that despite the more complex nature

of the O₂ molecule, the averaged angular distributions are very similar to those observed for the simpler atomic Ar collision partner.

Finally a method to allow better experimental resolution of NO + O₂ collisions was proposed, in which the use of slice imaging coupled with a time stamping camera would allow extraction of the central slice of the nested Newton spheres.

Chapter 5

Methods for Bond Axis Orientation

The concept of a ‘steric effect’ is prevalent throughout many branches of chemistry. In an atom-diatom collision, the simplest case in which such effects are relevant, the diatom bond axis may be polarised prior to the collision and the effect monitored by recording the angular scattering distributions in each polarisation. In this simple system, polarisation corresponds to the polarisation of either the bond axis, $\mathbf{r}$, or the initial rotational angular momentum, $\mathbf{j}$. These two vectors are not independently distributed [13], and therefore, knowledge of the distribution of $\mathbf{j}$ allows inference of the distribution of $\mathbf{r}$, or *vice versa*.

Polarisation may refer to either orientation or alignment, which have distinct definitions [73, 186]; information about both is required to fully describe the steric effects of a particular system. Consider a diatom: the bond axis, $\mathbf{r}$, is oriented if it is directed either parallel or antiparallel to a specified axis, whilst the bond axis is aligned if it is directed either parallel or perpendicular to the axis. The same type of description may be used in reference to $\mathbf{j}$. It is important to note that not all molecules of interest may be both oriented and aligned in their ground state.

The effect of initial polarisation of the diatom is quantified by the measurement of the relevant two or three vector correlations. The two vector correlation, $\mathbf{r}/\mathbf{j} - \mathbf{k}$, describes the preference for scattering into a final rotational state, $\mathbf{j}'$, with respect to the polarisation of the bond axis. This effect is often reported as the integral steric asymmetry of the system [71, 219, 230],

$$S = \frac{\sigma_A - \sigma_B}{\sigma_A + \sigma_B}, \quad (5.1)$$

where $\sigma_{A/B}$ describe the ICS when the collision takes place in polarisation A or B. The nature of these polarisations depends on the experiment undertaken: for orientation of the bond axis of a diatom either parallel or antiparallel to the initial relative velocity ($\mathbf{k}$) of the system, A and B correspond to the ICS for collisions with either ‘end’ of the molecule. Meanwhile, if the bond axis is originally aligned, polarisations A and B correspond to collisions with the side and end of the molecule. The three vector correlation, $\mathbf{r}/j - \mathbf{k} - \mathbf{k}'$, includes information about how the initial polarisation of the diatom affects scattering into a specific angle.

Steric effects have been studied across a wide range of different systems over the last 50 years [318], including: inelastic scattering [35, 64, 91, 94, 96, 97, 219, 230], electron transfer [319, 320], energy transfer [65], and reactive scattering [93, 132, 179, 275, 321–332]. Early work by Bernstein [120, 132, 323, 325] focused on the reaction asymmetry of $\text{CH}_3\text{I} + \text{Rb}$, in which methyl iodide was oriented before collision with Rb atoms. The experiment showed a strong reactive asymmetry, attributed to a ‘steric cone of non-reaction’ [325], in which attack of the Rb atom is blocked by the methyl group [132, 321–325]. Loesch *et al.* [327–329, 333] reported a steric asymmetry for the reaction $\text{Sr} + \text{HF} (v = 1, j = 1) \rightarrow \text{SrF}(v', j') + \text{H}$, in which the HF molecule was aligned such that either the ‘side’ or ‘end’ of the molecule was directed towards the incoming Sr atom. It was shown that the preference for ‘end-on’ *versus* ‘side-on’ collisions depended strongly on collision energy [333]: with ‘side-on’ collisions favoured at lower collision energies, and ‘end-on’ ones at higher energies.

More recent experiments by Liu and co-workers [135, 136, 334–336] have revolved around understanding the stereodynamics of the $\text{Cl} + \text{CD}_3\text{H}$ reaction, in which the C-H bond axis is initially aligned. Studying the reaction in 8 different geometries allowed the extraction of the *r*-PDDCS, which describes the steric preference of the reaction as a function of the alignment of the C-H bond. A large number of studies have been undertaken to describe the ‘end-on’ steric asymmetry in the inelastic collisions of oriented $\text{NO}(\text{X})$ [90, 92, 95–97, 134, 219, 230, 275] and $\text{OH}(\text{X})$ [64, 91, 93, 94] with a range of different atomic and diatomic collision partners. Steric effects have also been observed for scattering with surfaces [337, 338]. Further pertinent examples will be returned to in Chapters 6 and 7.

In this chapter, the experimental and theoretical methods required to describe the polarisation of the NO bond axis prior to a scattering event will be described. The extrinsic polarisation of the internuclear axis, including the experimental apparatus required to adiabatically orient the NO bond axis, will be discussed. This is followed by an overview of the classical theory and a new quantum mechanical theory which describe the scattering dynamics of a diatom oriented in an arbitrarily directed field. The chapter is concluded with a description of the methods used to analyse the experimentally measured steric effects presented in Chapters 6 and 7.

5.1 Intrinsic *versus* Extrinsic Polarisation

It is important to distinguish between the intrinsic and extrinsic polarisation of reactants [13, 231, 339, 340]. Extrinsic polarisation depends on the experimental set-up used to orient or align the reactant molecule(s) prior to the scattering event. The polarisation is a consequence only of external, laboratory, circumstances. Intrinsic polarisation, however, describes the collision process itself, and contains all the information required to describe the dependence of the cross section for the scattering process on the anisotropy of $\mathbf{j}/r$ of the reactants [340]. Such polarisation is ‘inherent’ to the collision process, and independent of the external (laboratory) circumstances prior to the collision taking place. With enough different reagent preparations or geometries it is possible to extract all relevant differential polarisation moments [71].

The extrinsic polarisation moments are described in the laboratory (LAB) frame, shown in Figure 5.1, in which the Z-axis is parallel to the static electric field, $\mathbf{E}$ (or radiation polarisation vector, $\boldsymbol{\varepsilon}$, used in the orientation/alignment process). The dipole moment, $\boldsymbol{\mu}$, is described by the polar and azimuthal angles, $\Theta_{\mu E}$ and $\Phi_{\mu E}$, respectively, and its distribution is described by the extrinsic polarisation moment which will be described in Section 5.2. The scattering frame, in which the intrinsic polarisation is described, depends on the initial and final relative velocity vectors of the collision; the z -axis is defined parallel to $\mathbf{k}$, the xz plane contains $\mathbf{k}'$, and

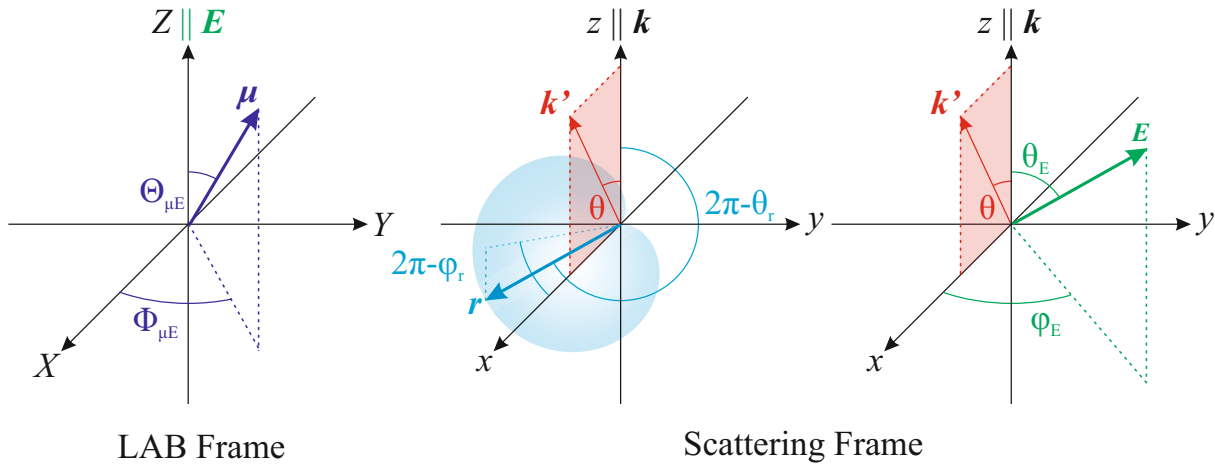


Figure 5.1: Definition of the laboratory (LAB) frame (left) and the scattering frame (right). In the LAB frame the Z-axis is coincident with E , and the direction of dipole moment, μ , is defined by the polar and azimuthal angles, $\Theta_{\mu E}$ and $\Phi_{\mu E}$, respectively. In the scattering frame the z-axis is coincident with k , k' lies in the xz plane, and y is chosen such that the frame is right handed. The direction of the static electric field, E , in the scattering frame is defined by the polar and azimuthal angles, θ_E and ϕ_E . The distribution of r is shown by blue shading; the most probable value is shown by an arrow, defined by the polar and azimuthal angles, θ_r and ϕ_r , respectively.

the y-axis is defined such that the frame is right-handed. In this frame, the electric field vector, E , is described by the polar and azimuthal angles, θ_E and ϕ_E , respectively. The bond axis, r , in the scattering frame is distributed symmetrically about E , with the most probable direction antiparallel to the electric field vector.

5.2 Extrinsic Polarisation: Preparation of the Bond Axis Distribution

The general expression for the extrinsic probability density function (PDF) [13] of the internuclear axis in the LAB frame may be written as a multipolar expansion [73, 339]

$$P(\Theta_r, \Phi_r) = \sum_{k=0} \sum_{q=-k}^k \left(\frac{2k+1}{4\pi} \right) A_q^{(k)} C_{kq}^* (\Theta_r, \Phi_r) , \quad (5.2)$$

where Θ_r and Φ_r are the polar and azimuthal angles describing the direction of the internuclear axis with respect to a specific laboratory axis. This axis is typically defined to coincide with the external electric field or radiation polarisation vector used in the orientation/alignment process

(and is typically the LAB frame Z-axis). $C_{kq}(\Theta_r, \Phi_r)$ are modified spherical harmonics, and $A_q^{(k)}$ are polarisation moments with values given by [339]

$$A_q^{(k)} = \langle C_{kq}(\Theta_r, \Phi_r) \rangle , \quad (5.3)$$

in which $\langle \dots \rangle$ indicates averaging over the distribution in Equation (5.2).

The rank, k , of the polarisation moments may be even or odd, with even moments describing orientation and odd moments alignment. The monopole polarisation moment ($k = 0$) describes the normalisation of the distribution. Moments with rank $k > 0$ are successively the dipole, quadrupole, octopole, *etc.*, with a maximum rank $k_{\max} = 2j$, for a molecule in a well defined rotational state [186]. Consequently, for NO(X) in its ground rotational state, $j = 0.5$, the bond axis may only be oriented and not aligned. The inherent symmetry of a diatomic molecule means that the distribution of $\mathbf{r}$ about the LAB frame Z-axis is azimuthally symmetric. Therefore, moments with $q \neq 0$ are zero, and Equation (5.2) may be rewritten in terms of Legendre polynomials

$$P(\Theta_r) = \sum_{k=0}^{k_{\max}} \left(\frac{2k+1}{2} \right) A_0^{(k)} P_k(\cos \Theta_r) , \quad (5.4)$$

where $P_k(\cos \Theta_r)$ are Legendre polynomials of the k^{th} degree.

The specific expression for the extrinsic polarisation moments depends on the technique used in the preparation of the internuclear axis distribution. Several methods exist for the orientation and/or alignment of molecules prior to a collision. Of these, the most common may be split into three categories: optical methods (orientation/alignment of j) [20, 135, 136, 327, 328, 334, 335, 339, 341–343], brute force methods (orientation of $\mathbf{r}$) [327, 330, 331, 344–346], and adiabatic orientation (of $\mathbf{r}$) *via* the Stark effect [120, 131, 347]. Such methods have been the subject of several reviews [71, 131, 347], and are not described here for brevity. Adiabatic orientation is used in this thesis to achieve the highest possible degree of orientation (which is limited in the brute force method [131]).

5.2.1 Adiabatic Orientation

When a static electric field is applied to Λ -doublet selected molecules (in a specific rotational state), the wave function of NO(X) may be written as a combination of the field free e and f states according to [90, 134, 219, 230]

$$|jm\bar{\Omega}E\rangle = \frac{1}{\sqrt{2}} [\alpha(E)|jm\bar{\Omega}e\rangle + \beta(E)|jm\bar{\Omega}f\rangle], \quad (5.5)$$

where $\bar{\Omega}$ is the absolute value of the projection of j onto the internuclear axis, and E is the electric field strength. $\alpha(E)$ and $\beta(E)$ are field dependent mixing parameters, the magnitudes of which are calculated according to [90]

$$|\alpha(E)| = \sqrt{1 - \frac{1}{\sqrt{1 + E_{\text{red}}^2}}} \quad \text{and} \quad |\beta(E)| = \sqrt{1 + \frac{1}{\sqrt{1 + E_{\text{red}}^2}}}, \quad (5.6)$$

where the strength of the reduced electric field is

$$E_{\text{red}} = \frac{2W_{\text{stark}}}{W_{\Lambda}}, \quad (5.7)$$

and

$$W_{\text{stark}} = -\langle \mu_D \cdot E \rangle = -\mu_D E \langle \cos \Theta_{\mu E} \rangle_{\text{max}} = -\mu_D \epsilon E \frac{|m\Omega|}{j(j+1)}, \quad (5.8)$$

represents the linear Stark effect [347], which was also discussed in terms of hexapole state selection in Section 3.3. W_{Λ} is the Λ -doublet splitting between the e and f states, μ_D is the static electric dipole moment of the NO(X) molecule, E is the applied static electric field (which coincides with the LAB frame Z -axis), and $\Theta_{\mu E}$ is the angle between the electric field and the dipole moment.

In the limit of an infinite reduced field, $E_{\text{red}} \rightarrow \infty$, $|\alpha(E_{\infty})| = |\beta(E_{\infty})| = 1$. Assuming initial selection of the f Λ -doublet, when no field is applied the unoriented f Λ -doublet is recovered from Equation (5.5), since $|\alpha(0)| = 0$ and $|\beta(0)| = \sqrt{2}$ [96, 179]. The magnitudes of the mixing parameters, for the initial $|j = 0.5, |m| = 0.5, \bar{\Omega} = 0.5, \epsilon = -1, f\rangle$ state as a function

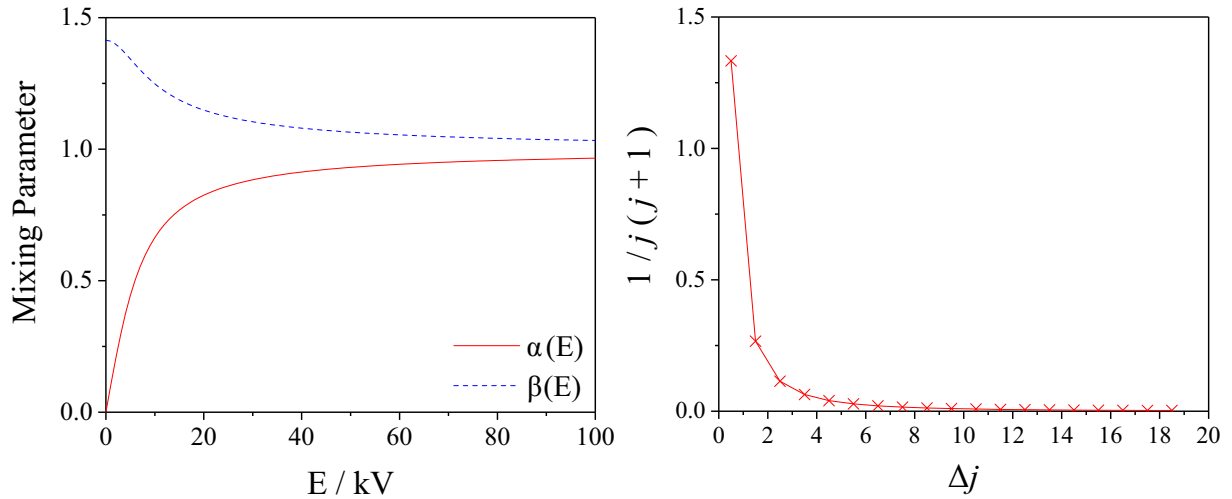


Figure 5.2: Adiabatic orientation. Left panel: dependence of the mixing parameters α and β , see Equation (5.6), on the magnitude of an applied electric field. Right panel: the reduced electric field, E_{red} , in Equation (5.7) may be approximated as $1/j(j+1)$. Shown for all values of j accessible after a rotationally inelastic collision of NO with Ar.

of electric field strength are shown in the left panel of Figure 5.2. Defining m_E as the projection of j onto the electric field, if $m_E > 0$ then $|\alpha\beta|$ is taken to be negative, whilst for $m_E < 0$ $|\alpha\beta|$ is positive.

The molecule will continue to experience a static electric field even after the collision event, and as such the potential for orientation of the final rotational states must be considered. Assuming a spin-orbit conserving transition ($\Delta\Omega = 0$) and taking the value of $m = |m_{\text{max}}|$ such that $|m\Omega| \approx |j\Omega|$, Equation (5.8) may be expressed as

$$W_{\text{stark}} \propto 1/j(j+1) . \quad (5.9)$$

Since, on the spin-orbit conserving manifold, W_{Λ} varies linearly with j [186, 191],

$$E_{\text{red}} \propto W_{\text{stark}}/W_{\Lambda} \propto 1/j(j+1) , \quad (5.10)$$

and E_{red} tends to zero as j increases. Applying this to Equation (5.6) it can be shown that, in the limit of $E_{\text{red}} \rightarrow 0$, $\alpha(E) \rightarrow 0$ and $\beta(E) \rightarrow \sqrt{2}$, equivalent to the case in which no electric field is applied (and there is no mixing of the Λ -doublet states). Figure 5.2 shows the relationship

between j and $1/j(j+1)$; for $j > 2.5$, $E_{\text{red}} \approx 0$, and as such (at the moderate electric fields used experimentally) mixing of the Λ -doublets for final states with $j > 0.5$ may be neglected.

Using the symmetrised wave function for the unoriented Λ -doublets, in Equation (2.7), the oriented state in Equation (5.5) may be written as

$$|jm\Omega E\rangle = \frac{1}{2} [(\alpha + \beta) |jm\Omega\rangle + (\alpha - \beta) |jm - \Omega\rangle] . \quad (5.11)$$

The probability distribution for the orientation of the bond axis (which is parallel to the dipole moment), is then

$$P(\Theta_{\mu E}) = \frac{2j+1}{16\pi} \int_0^{2\pi} \left| (\alpha + \beta) D_{m\Omega}^j(\Phi_{\mu E}, \Theta_{\mu E}, 0) + (\alpha - \beta) D_{m-\Omega}^j(\Phi_{\mu E}, \Theta_{\mu E}, 0) \right|^2 d\Phi_{\mu E} , \quad (5.12)$$

by making the substitution

$$|jm\Omega\rangle = \sqrt{\frac{2j+1}{4\pi}} D_{m\Omega}^j{}^*(\Phi_{\mu E}, \Theta_{\mu E}, 0) . \quad (5.13)$$

Upon integration over $d\Phi_{\mu E}$ (and taking into account the azimuthal symmetry of $\mathbf{r}$ about $\mathbf{E}$), Equation (5.12) may be written (assuming the initial f Λ doublet in which $\Omega m_E < 0$) [192, 230]

$$\begin{aligned} P(\Theta_{\mu E}) &= \frac{1}{4} \left\{ \left[(\alpha + \beta) d_{m\Omega}^j(\Theta_{\mu E}) \right]^2 + \left[(\alpha - \beta) d_{m-\Omega}^j(\Theta_{\mu E}) \right]^2 \right\} \\ &= \frac{1}{4} (\alpha^2 + \beta^2 - 2|\alpha\beta| \cos \Theta_{\mu E}) \\ &= \frac{1}{2} (1 - |\alpha\beta| \cos \Theta_{\mu E}) , \end{aligned} \quad (5.14)$$

where $d_{m\pm\Omega}^j(\Theta_{\mu E})$ are reduced Wigner rotation matrix elements. The minus sign in equation (5.14) implies that the ‘N-end’ of the NO molecule points towards the negative pole of the electric field. This may be rewritten in terms of a 1st degree Legendre polynomial [97, 252],

as in Equation (5.4),

$$P(\Theta_{\mu E}) = \sum_k \frac{2k+1}{2} A_0^{(k)} P_k(\cos \Theta_{\mu E}) = \frac{1}{2} \left[A_0^{(0)} + A_0^{(1)} P_1(\cos \Theta_{\mu E}) \right], \quad (5.15)$$

where the $A_0^{(0)}$ moment is unity as the distribution is normalised. The extrinsic polarisation moment $A_0^{(1)}$ is equivalent to the expectation value $\langle P_1(\cos \Theta_{\mu E}) \rangle$, according to [164]

$$\langle P_1(\cos \Theta_{\mu E}) \rangle = \int_{-1}^1 P_1(\cos \Theta_{\mu E}) P(\Theta_{\mu E}) d(\cos \Theta_{\mu E}) = -\frac{1}{3} \frac{2|\alpha\beta|}{\alpha^2 + \beta^2} = -\frac{1}{3} |\alpha\beta|. \quad (5.16)$$

For the $\Omega = 0.5$, $j = 0.5$ state, in the high field limit ($\alpha = \beta = 1$), the orientation moment is equal to $A_0^{(1)} = -1/3$.

5.2.2 Experimental Apparatus

To experimentally achieve adiabatic orientation of the NO(X) bond axis prior to the collision process, it is necessary to modify the experimental apparatus described in Chapter 3. A set of four orientation rods was added to the interaction region, as shown in Figure 5.3, which are used to create a static electric field. The rods are placed directly between the extractor and repeller plates of the ion optics, and are spaced 10mm apart both horizontally and vertically, such that the interaction volume lies in the center of the four electrode array. The geometry of the rods depends on whether orientation with respect to the x -, y - or z -axis (in the scattering frame) is under consideration. The geometries required for orientation parallel (z -axis) or perpendicular (x -axis) to $\mathbf{k}$, in the plane of the molecular beams, are shown in Figure 5.3.

The voltage applied to the electrode rods is ± 8 kV, corresponding to an electric field strength of 9.2 kV cm^{-1} [96, 97, 252]. At this field, the mixing coefficients $|\alpha|$ and $|\beta|$, in Equation (5.6), take values of 0.64 and 1.26, respectively. The bond axis distribution of the NO molecule, given by Equation (5.14), is shown in Figure 5.4 for the experimental field, an infinite field, and no applied field. In the absence of an electric field the bond axis is isotropically distributed, however, upon application of a field the bond axis becomes polarised parallel to the electric field.

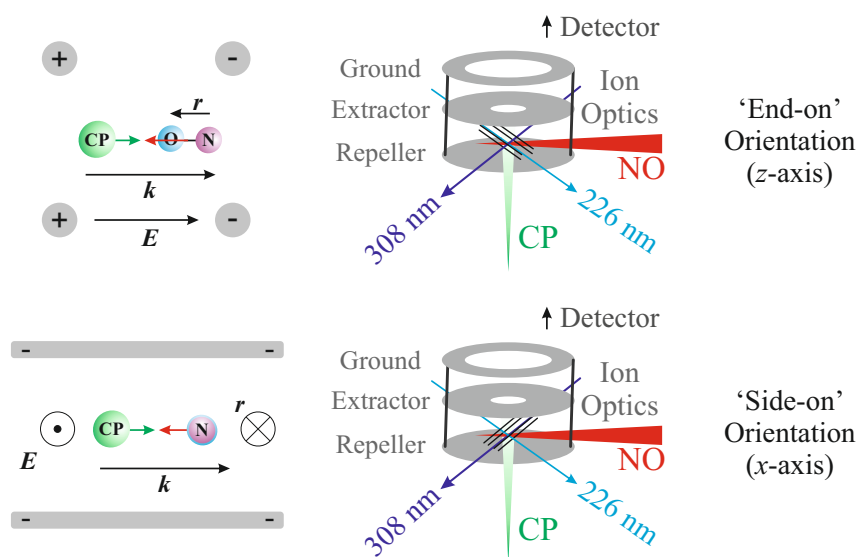


Figure 5.3: Experimental bond orientation ion optics. Left: Cross section through the orientation rods, along the direction of the 308 nm laser. Right: Schematic of the experimental ion optics for bond axis orientation. Orientation with respect to the z - and x -axes are shown in the top and bottom panel, respectively.

The ‘N’ atom of the molecule is directed towards the negative electrode, whilst the ‘O’ atom is directed towards the positive electrode, corresponding to μ (and consequently r) pointing antiparallel to the electric field vector. The experimental field results in a relatively high degree of orientation when compared to the infinite field (maximum) probability.

The presence of the orientation electrodes between the velocity-mapping ion optics leads to distortions in the velocity mapping field [96, 97, 252]. As such, it is necessary to rapidly switch to velocity-mapping voltages (from the orientation voltages) approximately 500 ns before the NO molecules are ionised. The velocity-mapping voltages lie between the voltages applied to the extractor and repeller, resulting in a more consistent velocity-mapping field. The extraction field is not strong enough to cause further orientation of the NO molecule during velocity-mapping (see Section 5.2.1). After 200 laser shots the polarity of the orienting field is reversed allowing both orientations to be recorded, as well as minimising experimental drift.

The time between the switch to VMI voltages and the ionisation of the NO molecules is of some importance; if the switch occurs too late velocity-mapping becomes very difficult, whilst if the switch occurs too early the distribution of the bond axis will become isotropic again (*i.e.* the molecules will no longer be oriented). To test the effect of the switching time on the x -axis steric

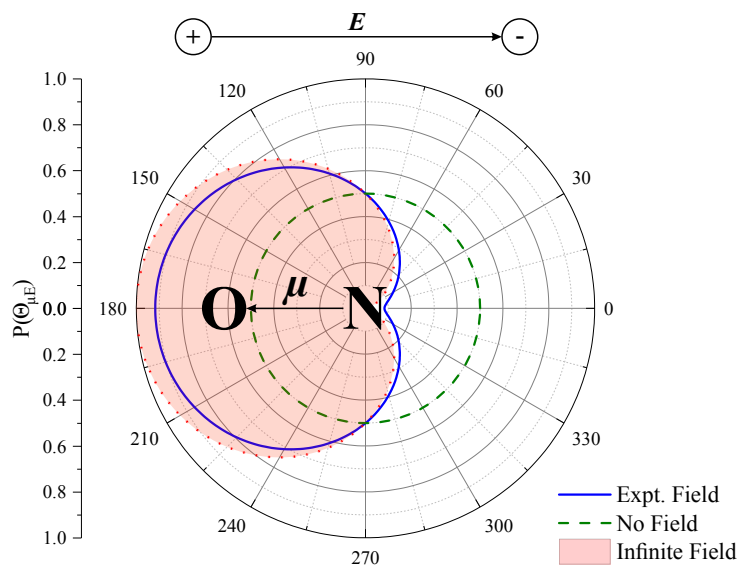


Figure 5.4: Polar plot of the probability distribution, see Equation (5.14), for the angle between the NO(X) dipole moment and the electric field, $P(\Theta_{\mu E})$. The distribution is shown at infinite field (red shaded), experimental (9.2 kV cm^{-1}) field (blue line) and no field (green dashed line).

effect, the value of the integral steric asymmetry (see Equation (5.1)), S_x , at several switching times, t_{switch} , were recorded for transitions into the $j' = 8.5e$ state using vertically polarised light on the $Q_{21} + R_{11}$ (mixed) branch. Data at each time step were acquired until approximately 17,000 ion hits were recorded (across both field orientations), the intensity in a 200×200 square on the slow side of each image (500×500) was then used to calculate the approximate steric asymmetry (according to Equation (5.1), in which σ is replaced by the intensity of the image), the results of which are shown in the left hand panel of Figure 5.5. The standard deviation across each batch of 20,000 laser shots ($\sim 5,000$ ion hits) was used to calculate the error bars. Time zero corresponds to the switch between orientation and velocity-mapping voltages occurring at the same time that the excitation laser reaches the interaction region.

The raw ion images show that as t_{switch} becomes larger, the $\pm x$ -orientations become qualitatively more similar, corresponding to a smaller proportion of the NO molecules being polarised at the time of the scattering event. By $t_{\text{switch}} = 21.5 \mu\text{s}$ all sense of orientation is gone and the two ion images appear identical. The value of S_x for time delays up until approximately $2.5 \mu\text{s}$ produces experimental values which are equivalent to the QM value within the errors of the measurement. After this switch time a linear decline in the value of S_x is observed,

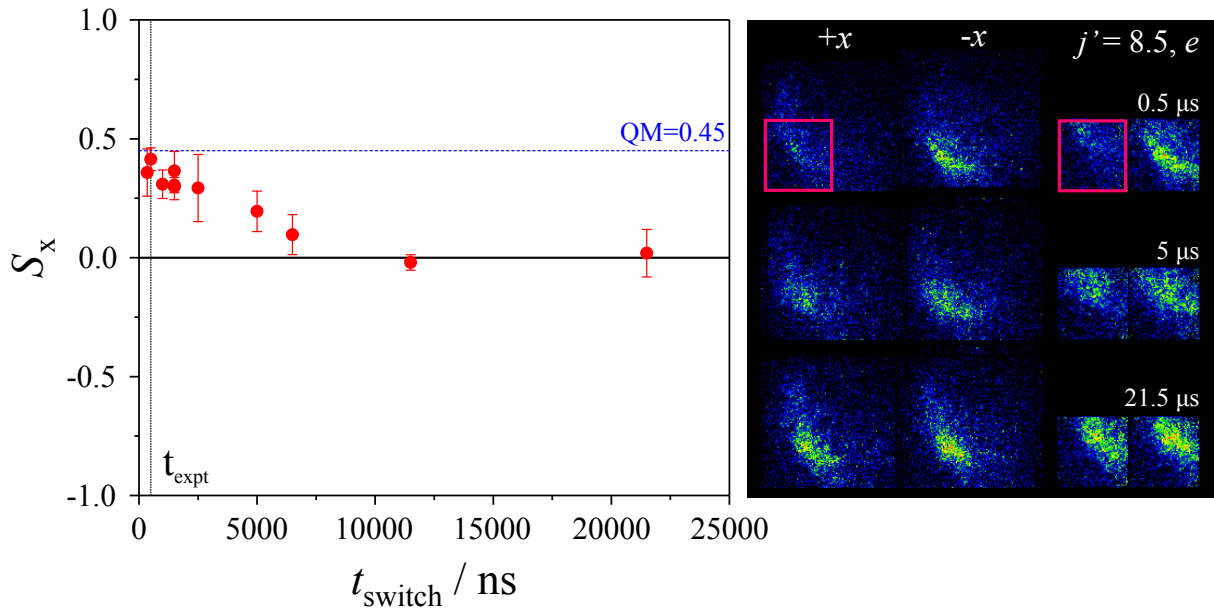


Figure 5.5: Effect of switch time on x -axis integral steric asymmetry for transitions resulting in $j' = 8.5e$. Left panel: experimental integral steric asymmetry as function of t_{switch} (the time between the switch to the velocity-mapping field and the laser reaching the interaction region). The CC QM value is shown by a blue dashed line, and the switch time used experimentally is shown by a black dotted line. Right panel: ion images for $t_{\text{switch}} = 0.5, 5.0$ and $21.5 \mu\text{s}$, and the 200×200 square used to approximate the steric effect.

until at very long switching times $S_x \approx 0$. This is congruent with the work of Nichols [252], which has shown that a delay between switching from orientation to velocity-mapping fields of approximately $1 \mu\text{s}$ does not strongly affect the magnitude of the steric effects observed. The value of $t_{\text{switch}} \approx 500 \text{ ns}$ at which the experimental data in Chapters 6 and 7 were recorded is shown by a black line and falls within the regime where the value of the QM integral effect is well reproduced experimentally.

5.3 Intrinsic Polarisation: Orientation Resolved Differential Scattering

The intrinsic effect of bond axis polarisation on the scattering process may be expressed in terms of the r -polarisation dependent differential cross sections (r -PDDCSs). These are not to be confused with the j' -PDDCSs (often referred to as the PDDCSs) described in Chapter 2, which describe the polarisation of the final rotational angular momentum. The intrinsic polarisation

moments describe the steric preferences of the collision, and are not (unlike the extrinsic moments) dependent on the method of preparation of the system, but rather are determined only by the dynamics of the collision [340]. The r -PDDCSs may be described theoretically using quasi-classical trajectories or quantum mechanics; both methods are described below.

5.3.1 Classical Orientation

The quasi-classical treatment of the $\mathbf{k} - \mathbf{r} - \mathbf{k}'$ vector correlation has been described in detail elsewhere [252, 339], and only the most important equations are reproduced here. The treatment is comparable to the treatment of the $\mathbf{k} - \mathbf{j} - \mathbf{k}'$ correlation [231, 233], since $\mathbf{r}$ and $\mathbf{j}$ are not independently distributed [13].

The intrinsic polarisation may be written in terms of a PDF, in much the same way as the extrinsic polarisation in Equation (5.7). In the intrinsic case the probability of scattering into a specific angle, θ , is a function of the direction of the internuclear axis, $\mathbf{r}$; described by the scattering frame polar and azimuthal angles, θ_r and ϕ_r , respectively. The PDF is written as an expansion of modified spherical harmonics [97, 252]

$$P(\theta, \theta_r, \phi_r) = \frac{1}{4\pi} \sum_k \sum_{q=-k}^{+k} (2k+1) R_q^{(k)}(\theta) C_{kq}^*(\theta_r, \phi_r) , \quad (5.17)$$

where $R_q^{(k)}(\theta)$ are the r -PDDCSs, which describe the scattering angle dependence of the collision as a function of the initial polarisation of the bond axis. The r -PDDCSs themselves are the multipole moments of the expansion [97, 252]

$$R_q^{(k)}(\theta) = \int P(\theta, \theta_r, \phi_r) C_{kq}(\theta_r, \phi_r) d\omega_r = \langle C_{kq}(\theta_r, \phi_r) \rangle , \quad (5.18)$$

where $d\omega_r = d(\cos \theta_r) d\phi_r$. The monopole moment, $R_0^{(0)}(\theta)$, describes the angular distribution in the absence of orientation of the bond axis, *i.e.*

$$R_0^{(0)}(\theta) = \frac{2\pi}{\sigma_{\text{iso}}} \frac{d\sigma_{\text{iso}}}{d\omega} . \quad (5.19)$$

where σ_{iso} and $d\sigma_{\text{iso}}/d\omega(\theta)$ are the ICS and DCS in the absence of bond orientation, respectively. Since the distribution about the internuclear axis is invariant with respect to reflection in the scattering $(\mathbf{k}\mathbf{k}')$ plane, $P(\theta, \theta_r, \phi_r) = P(\theta, \theta_r, 2\pi - \phi_r)$. It is therefore possible to show that the r -PDDCSs are real [97, 252]

$$R_q^{(k)}(\theta) = (-1)^q R_{-q}^{(k)}(\theta) = \left[R_q^{(k)}(\theta) \right]^* . \quad (5.20)$$

By convoluting the intrinsic and extrinsic distributions the oriented DCS may be expressed [97, 231, 339, 340]:

$$\left[\frac{d\sigma}{d\omega}(\theta) \right] = \frac{\sigma_{\text{iso}}}{2\pi} \sum_k \sum_{q=-k}^k (2k+1) R_q^{(k)}(\theta) a_q^{(k)} , \quad (5.21)$$

where $a_q^{(k)}$ are the extrinsic bond axis polarisation moments with respect to the scattering frame. Since the bond axis distribution is prepared in the LAB frame it is necessary to describe the value of the moments in the scattering frame [340, 348]

$$a_q^{(k)} = \sum_{q'=-k}^k D_{qq'}^{k*}(\phi_E, \theta_E, \chi_E) A_{q'}^{(k)} , \quad (5.22)$$

where $A_{q'}^{(k)}$ are the polarisation moments of the reactants in the LAB frame, $D_{qq'}^{k*}(\phi_E, \theta_E, \chi_E)$ is a Wigner rotation matrix and $(\phi_E, \theta_E, \chi_E)$ are the Euler angles relating the LAB and scattering frames. Equation (5.22) may be simplified by considering the axial symmetry of the bond axis about $\mathbf{E}$, which results in only the $q = 0$ moments in the LAB frame being non-zero. Since $\chi_E = 0$ the Wigner rotation matrix corresponds to a modified spherical harmonic, and the scattering frame polarisation moments may be rewritten [340, 348]

$$a_q^{(k)} = C_{kq}(\theta_E, \phi_E) A_0^{(k)} . \quad (5.23)$$

Using the symmetry relations in Equation (5.20), it is possible to express the bond axis oriented DCS in Equation (5.21) as a function of the angles (θ_E, ϕ_E) , which describe the orientation of

the electric field in the scattering frame [339]

$$\left[\frac{d\sigma}{d\omega}(\theta) \right]_{\theta_E}^{\phi_E} = \frac{\sigma_{\text{iso}}}{2\pi} \sum_k (2k+1) A_0^{(k)} \sum_{q=0}^k \frac{2}{1+\delta_{q0}} R_q^{(k)}(\theta) C_{kq}(\theta_E, 0) \cos q\phi_E. \quad (5.24)$$

The extrinsic moments $A_0^{(k)}$, from Equation (5.16), may then be used to write the oriented DCS in Equation (5.21) in terms of the LAB frame moments [339],

$$\begin{aligned} \left[\frac{d\sigma}{d\omega}(\theta) \right]_{\theta_E}^{\phi_E} &= \frac{\sigma_{\text{iso}}}{2\pi} \left[R_0^{(0)}(\theta) + 3A_0^{(1)} \left\{ R_0^{(1)}(\theta) P_1(\cos \theta_E) + 2R_1^{(1)}(\theta) C_{11}(\theta_E, 0) \cos \phi_E \right\} \right] \\ &= \frac{\sigma_{\text{iso}}}{2\pi} \left[R_0^{(0)}(\theta) - |\alpha\beta| \left\{ R_0^{(1)}(\theta) \cos \theta_E - \sqrt{2} R_1^{(1)}(\theta) \sin \theta_E \cos \phi_E \right\} \right]. \quad (5.25) \end{aligned}$$

5.3.2 Quantum Mechanical Orientation

Previous work on the quantum mechanical equations for the orientation of the NO bond axis (or any symmetric top) [90–92, 95–97, 134, 179, 219, 230] has been restricted to orientation of the bond axis parallel or antiparallel to $\mathbf{k}$ (that is, orientation along the $\pm z$ -axis in the scattering frame). In collaboration with Prof. Javier Aoiz* and Prof. Pablo Jambrina† a new theory, presented below, has been developed to describe scattering dynamics in the presence of an arbitrarily directed orientation field.

In the LAB frame the initial state of the NO(X) molecule in the presence of a static electric field may be written [219, 230]

$$|jm_E \bar{\Omega} E\rangle = \frac{1}{\sqrt{2}} [\alpha |jm_E \bar{\Omega} e\rangle + \beta |jm_E \bar{\Omega} f\rangle], \quad (5.26)$$

where m_E is the projection of $\mathbf{j}$ along the field direction, $\mathbf{E}$, α/β are field dependent mixing parameters (described in Section 5.2), $\bar{\Omega}$ is the absolute value of Ω , and e/f denote the initial parities of the (unmixed) Λ -doublet levels. Since the initial wave function in Equation (5.26) is referenced to the direction of the static electric field, a rotation is required to express the LAB

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frame Λ -doublet wave function in terms of the initial scattering frame wave functions

$$|jm_E \bar{\Omega} \varepsilon\rangle = \sum_m D_{m,m_E}^j(\phi_E, \theta_E, 0) |jm \bar{\Omega} \varepsilon\rangle, \quad (5.27)$$

where ε defines the parity of the initial state, m refers to the projection of j along k , and $D_{m,m_E}^j(\phi_E, \theta_E, 0)$ is a Wigner rotation matrix. $|jm \bar{\Omega} \varepsilon\rangle$ is the initial wave function with respect to the scattering frame. Upon substitution into Equation (5.26), the initial wave function in a static electric field of arbitrary direction is obtained

$$|jm_E \bar{\Omega} E\rangle = \frac{1}{\sqrt{2}} \sum_m D_{m,m_E}^j(\phi_E, \theta_E, 0) [\alpha |jm \bar{\Omega} e\rangle + \beta |jm \bar{\Omega} f\rangle]. \quad (5.28)$$

In the case in which the electric field is oriented along the initial relative velocity, k , the angles of rotation are $(\phi_E, \theta_E, 0) = (0^\circ, 0^\circ, 0^\circ)$, and therefore the previously described result for orientation along the z -axis [96, 97, 134, 192, 230]

$$|jm_E \bar{\Omega} E\rangle = \frac{1}{\sqrt{2}} \sum_m \alpha |jm \bar{\Omega} e\rangle + \beta |jm \bar{\Omega} f\rangle, \quad (5.29)$$

is recovered.

Assuming that the field is insufficiently strong to mix the Λ -doublets of the final state (see Section 5.2.1), Equation (5.28) may be written in terms of the relevant scattering amplitudes

$$f_{j'm'\Omega'\varepsilon' \leftarrow jm_E \Omega E}(\theta) = \frac{1}{\sqrt{2}} \sum_m D_{m,m_E}^j(\phi_E, \theta_E, 0) [\alpha f_{j'm'\Omega'\varepsilon' \leftarrow jm \Omega e}(\theta) + \beta f_{j'm'\Omega'\varepsilon' \leftarrow jm \Omega f}(\theta)]. \quad (5.30)$$

The oriented differential cross sections are defined as the square modulus of the oriented scattering amplitude

$$\left[\frac{d\sigma}{d\omega}(\theta) \right]_{\theta_E}^{\phi_E} = \frac{1}{k^2} \sum_{m'} |f_{j'm'\Omega'\varepsilon' \leftarrow jm_E \Omega E}(\theta)|^2, \quad (5.31)$$

and substitution of Equation (5.30) results in

$$d\sigma_E(\theta) = \frac{1}{2k^2} \sum_{m', m_E} \left| \sum_m D_{m, m_E} [\alpha F_{m' \epsilon' m_e} + \beta F_{m' \epsilon' m_f}] \right|^2, \quad (5.32)$$

where $d\sigma_E(\theta) \equiv [d\sigma/d\omega(\theta)]_{\theta_E}^{\phi_E}$ is the DCS in the presence of a static electric field of arbitrary direction. For simplicity, the notation $f_{j'm'\Omega'\epsilon'\leftarrow jm\Omega E}(\theta) \equiv F_{m' \epsilon' m_E}$ and $D_{m, m_E}^j(\phi_E, \theta_E, 0) \equiv D_{m, m_E}$ is used henceforth. Considering only a single value of $|m_E|$, Equation (5.32), may be expanded

$$\begin{aligned} d\sigma_E(|m_E|) = \frac{1}{2k^2} & \left[\sum_{m_1, m_2} \sum_{m'} \alpha^2 D_{m_1 m_E} D_{m_2 m_E}^* F_{m' \epsilon' m_1 e} F_{m' \epsilon' m_2 e}^* \right. \\ & + \sum_{m_1, m_2} \sum_{m'} \alpha \beta D_{m_1 m_E} D_{m_2 m_E}^* \left(F_{m' \epsilon' m_1 f} F_{m' \epsilon' m_2 e}^* + F_{m' \epsilon' m_2 e} F_{m' \epsilon' m_1 f}^* \right) \\ & \left. + \sum_{m_1, m_2} \sum_{m'} \beta^2 D_{m_1 m_E} D_{m_2 m_E}^* F_{m' \epsilon' m_1 f} F_{m' \epsilon' m_2 f}^* \right]. \end{aligned} \quad (5.33)$$

Note that m_E may take either a positive or negative value: when $m_E > 0$ $\alpha\beta = -|\alpha\beta|$, and when $m_E < 0$, $\alpha\beta = |\alpha\beta|$.

The summation over m_E in Equation (5.32) necessitates that

$$d\sigma_E(\theta) = \frac{1}{2} [d\sigma_E(m_E = 1/2) + d\sigma_E(m_E = -1/2)]. \quad (5.34)$$

At this point it is possible to use Equations (5.33) and (5.34) to calculate the oriented DCS directly from the scattering amplitudes. However, it is also possible to derive simplified expressions which depend explicitly on the angles which describe the orientation of the electric field in the scattering frame. After some cumbersome algebra, the expression for the oriented DCS may be written,

$$[d\sigma(\theta)]_{\theta_E}^{\phi_E} = \frac{1}{k^2} [\alpha^2 Q_1 - |\alpha\beta| \cos \theta_E Q_2 - |\alpha\beta| \sin \theta_E \cos \phi_E Q_3 + \beta^2 Q_4], \quad (5.35)$$

where

$$Q_1 = \sum_{m'} |F_{m'\epsilon'1/2e}|^2 \quad (5.36a)$$

$$Q_2 = \sum_{m'} \left(F_{m'\epsilon'1/2f} F_{m'\epsilon'1/2e}^* + F_{m'\epsilon'1/2f}^* F_{m'\epsilon'1/2e} \right) \quad (5.36b)$$

$$Q_3 = \sum_{m'} \left(F_{m'\epsilon'-1/2f} F_{m'\epsilon'1/2e}^* + F_{m'\epsilon'-1/2f}^* F_{m'\epsilon'1/2e} \right) \quad (5.36c)$$

$$Q_4 = \sum_{m'} |F_{m'\epsilon'1/2f}|^2. \quad (5.36d)$$

This may be rewritten in terms of the r -PDDCS

$$[d\sigma(\theta)]_{\theta_E}^{\phi_E} = \frac{\sigma_{\text{iso}}}{2\pi} \left\{ R_0^{(0)}(\theta) + 3A_0^{(1)} \left[R_0^{(1)}(\theta) P_1(\cos \theta_E) + 2R_1^{(1)}(\theta) C_{11}(\theta_E, 0) \cos \phi_E \right] \right\}, \quad (5.37)$$

where

$$\frac{\sigma_{\text{iso}}}{2\pi} R_0^{(0)}(\theta) = \frac{1}{k^2} (\alpha^2 Q_1 + \beta^2 Q_4) \quad (5.38a)$$

$$\frac{\sigma_{\text{iso}}}{2\pi} R_0^{(1)}(\theta) = \frac{1}{k^2} Q_2 \quad (5.38b)$$

$$\frac{\sigma_{\text{iso}}}{2\pi} R_1^{(1)}(\theta) = -\frac{1}{\sqrt{2}k^2} Q_3, \quad (5.38c)$$

$C_{11}(\theta_E, 0) = -(1/\sqrt{2}) \sin \theta_E$, and $A_0^{(1)} = \langle P_1(\cos \theta_{\mu E}) \rangle$ is calculated according to Equation (5.17). Upon comparison, it is clear that Equation (5.37) is equivalent to the classical case in Equation (5.25).

Whilst bond orientation along the z - and x -axes will be discussed in detail in Chapters 6 and 7, respectively, it is useful to consider the effect of orientation of the NO bond axis along the y -axis, ($\theta_E = 90^\circ, \phi_E = 90^\circ$). The y -axis oriented DCS may be written

$$\begin{aligned} [d\sigma(\theta)]_{90}^{90} &= \frac{1}{k^2} [\alpha^2 Q_1 + \beta^2 Q_4] = \frac{\sigma_{\text{iso}}}{2\pi} R_0^{(0)}(\theta) \\ &= \alpha^2 \frac{d\sigma_{\epsilon' \leftarrow e}}{d\omega}(\theta) + \beta^2 \frac{d\sigma_{\epsilon' \leftarrow f}}{d\omega}(\theta). \end{aligned} \quad (5.39)$$

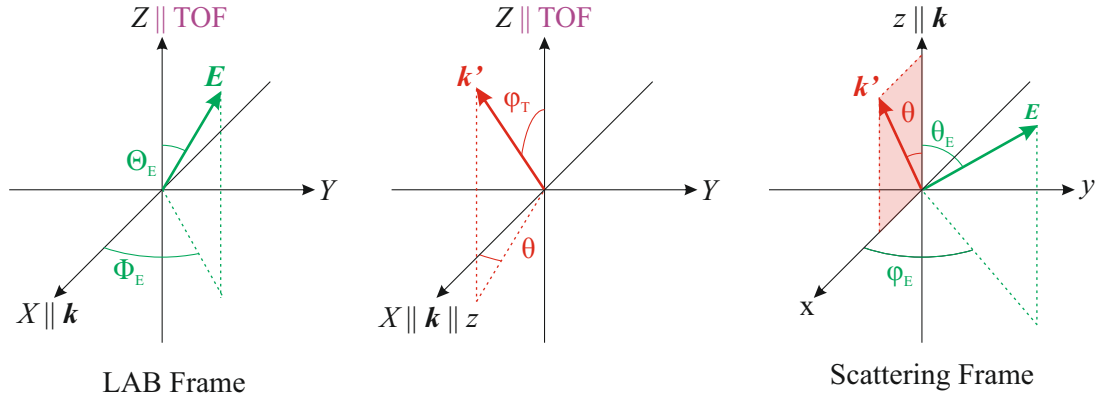


Figure 5.6: LAB frame (left) and scattering frame (right) for the Monte Carlo simulation of experimental ion images. The central panel describes the polar and azimuthal scattering angles, θ and ϕ_T , respectively.

Consequently, the DCSs for polarisation along the y -axis are equivalent to the (incoherent) sum of the contributions from the e and f states (weighted by the relevant mixing parameters) resulting from the superposition of states in the electric field. It is important to distinguish the ‘isotropic’ (field dependent) DCS in Equation (5.39) from the DCS in the absence of a field. In the field free case (assuming initial selection of the f Λ -doublet *via* hexapole state selection) $\alpha^2 = 0$ and $\beta^2 = 2$ and therefore

$$d\sigma(\theta) = 2 \frac{1}{k^2} Q_4 = \frac{1}{k^2} \sum_{m'} |F_{m'e'1/2f}|^2 = \frac{d\sigma_{e' \leftarrow f}}{d\omega}(\theta). \quad (5.40)$$

5.4 Data Analysis

The data analysis process described in Section 3.5, for unoriented ion-images, must be extended to include the effects of bond axis polarisation on the experimental ion image. In order to simulate the experimental apparatus it is necessary to define the direction of the electric field with respect to the experimental geometry. The LAB frame, shown in Figure 5.6, (which should not be confused with the LAB frame described in section 5.2), is set-up such that the Z -axis coincides with the time-of-flight (TOF) direction. The X -axis is parallel to the initial relative velocity, $\mathbf{k}$, which lies in the plane of the molecular beams, and the Y -axis is chosen such that the frame is right handed. The direction of the electric field is described by the polar and azimuthal angles, Θ_E and Φ_E , respectively.

The bond axis resolved DCS in Equation (5.24) is written in terms of the extrinsic and intrinsic distributions of the NO bond axis, in which the direction of the electric field is expressed in the scattering frame. Experimentally, however, the electric field is defined in the LAB frame, by the angles (Θ_E, Φ_E) . The relationship between the two frames of reference is described by a rotation through a series of angles. Consider the spherical harmonics in equation (5.24),

$$C_{10}(\theta_E, 0) = C_{10}(\theta_E, \phi_E) \quad (5.41a)$$

$$C_{11}(\theta_E, 0) \cos \phi_E = -\frac{1}{\sqrt{2}} [C_{11}(\theta_E, \phi_E) - C_{1-1}(\theta_E, \phi_E)] . \quad (5.41b)$$

These may be written in terms of the LAB frame spherical harmonics according to

$$C_{kq}(\theta_E, \phi_E) = \sum_{q'} D_{q'q}^k(\alpha, \beta, \gamma) C_{kq'}(\Theta_E, \Phi_E) , \quad (5.42)$$

where $D_{q'q}^k(\alpha, \beta, \gamma)$ is the Wigner rotation matrix describing the rotation between the LAB and scattering frames, with the Euler angles $(\alpha, \beta, \gamma) \equiv (\pi, -\pi/2, -\phi_T)$. ϕ_T describes the out-of-plane angle between the plane containing the molecular beams and the TOF axis, such that when $\phi_T = 0$, the final relative velocity, $\mathbf{k}'$, is coincident with Z .

Applying the Wigner rotation matrices [186], for the case in which $k = 1$, $q = 0$, Equation (5.42) may be written

$$\begin{aligned} C_{10}(\theta_E, \phi_E) &= \frac{1}{\sqrt{2}} [C_{1-1}(\Theta_E, \Phi_E) - C_{11}(\Theta_E, \Phi_E)] \\ &= \sin \Theta_E \cos \Phi_E . \end{aligned} \quad (5.43)$$

The $k = 1$, $q = 1$ case in Equation (5.41b) is more complex. The scattering frame spherical harmonics may be written in terms of the LAB frame spherical harmonics

$$C_{1\pm 1}(\theta_E, \phi_E) = \frac{e^{\pm i\phi_T}}{2} [i \sin \Theta_E \sin \Phi_E \mp \cos \Theta_E] , \quad (5.44)$$

and therefore, Equation (5.41b) may be written

$$\begin{aligned} C_{11}(\theta_E, 0) \cos \phi_E &= -\frac{1}{\sqrt{2}} [C_{11}(\theta_E, \phi_E) - C_{1-1}(\theta_E, \phi_E)] \\ &= \sin \phi_T \sin \Theta_E \sin \Phi_E + \cos \phi_T \cos \Theta_E . \end{aligned} \quad (5.45)$$

The bond axis resolved DCS in Equations (5.24) (classical) and (5.37) (QM) can therefore be expressed in terms of the LAB frame angles,

$$\begin{aligned} [d\sigma(\theta)]_{\theta_E}^{\phi_E} &= \frac{\sigma_{\text{iso}}}{2\pi} \left\{ R_0^{(0)}(\theta) + 3A_0^{(1)} \left[R_0^{(1)}(\theta) \sin \Theta_E \cos \Phi_E \right. \right. \\ &\quad \left. \left. - \sqrt{2} R_1^{(1)}(\theta) (\sin \phi_T \sin \Theta_E \sin \Phi_E + \cos \phi_T \cos \Theta_E) \right] \right\} . \end{aligned} \quad (5.46)$$

5.4.1 z -Axis Orientation

Orientation along the scattering frame z -axis corresponds to collisions in which one end of the NO molecule is directed towards the incoming collision partner. For an ‘O-end’ collision, the bond axis is parallel to the z -axis ($\theta_E = 0^\circ$), which is denoted $+z(\text{O})$, whilst $-z(\text{N})$ is used to denote a ‘N-end’ collision in which the bond axis is antiparallel to the z -axis ($\theta_E = 180^\circ$). In the LAB frame this corresponds to application of the static electric field, perpendicular to the TOF axis and either parallel or antiparallel to $\mathbf{k}$, $(\Theta_E, \Phi_E) = (90^\circ, 0^\circ)$ and $(90^\circ, 180^\circ)$, respectively. Therefore, Equation (5.46) may be simplified

$$[d\sigma(\theta)]_{\theta_E}^{\phi_E} = \frac{\sigma_{\text{iso}}}{2\pi} \left\{ R_0^{(0)}(\theta) + 3A_0^{(1)} R_0^{(1)}(\theta) \cos \Phi_E \right\} . \quad (5.47)$$

As the electric field lies either parallel or antiparallel to $\mathbf{k}$, the NO bond axis is distributed evenly about $\mathbf{k}$, and scattering is azimuthally symmetric (hence the lack of dependence on the ϕ_T term in Equation (5.46)). Consequently, the two ion images corresponding to the electric field lying parallel ($\Phi_E = 0^\circ$) or antiparallel ($\Phi_E = 180^\circ$) to $\mathbf{k}$ in the LAB frame are equivalent to the $+z(\text{O})$ and $-z(\text{N})$ polarisations, respectively, in the scattering frame. As such, the two ion images will be referred to by their scattering frame polarisations.

The Integral Steric Effect

The integral steric effect, describing the $\mathbf{r} - \mathbf{k}$ two vector correlation, is calculated according to Equation (5.1), which for orientation along the $\pm z$ -axis may be written

$$S_z = \frac{\sigma_{-z(\text{N})} - \sigma_{+z(\text{O})}}{\sigma_{-z(\text{N})} + \sigma_{+z(\text{O})}}, \quad (5.48)$$

where $\sigma_{\pm z}$ corresponds to the ICS for collisions in which the electric field is oriented parallel or antiparallel to $\mathbf{k}(\parallel z)$. The absolute value of $\sigma_{\pm z}$ cannot be determined from the current experimental apparatus, due to several unknown factors, including the flux density of the molecular beams, the shot-to-shot laser power, and the number of scattered molecules in the interaction region. However, the cross section is proportional to the relative intensity of each image, which can be calculated by summing the intensity, $I_{\pm z}$, across all of the pixels in the image according to

$$\sigma_{\pm z} \propto \sum_{xy} I_{\pm z}(x, y), \quad (5.49)$$

where x and y describe the row and column number of the pixel.

The interaction region in the $\pm x$ geometries is equivalent, and consequently any flux density effects in Equation (5.48) cancel. Combining Equations (5.48) and (5.49) the integral steric asymmetry may be calculated by counting the centroided ion hits on the detector [240] according to

$$S_z = \frac{\sum_{xy} I_{-z(\text{N})}(x, y) - \sum_{xy} I_{+z(\text{O})}(x, y)}{\sum_{xy} I_{-z(\text{N})}(x, y) + \sum_{xy} I_{+z(\text{O})}(x, y)}. \quad (5.50)$$

The z -axis integral steric asymmetry can be shown to be directly proportional to the renormalised $r_0^{(1)}$ bond orientation moment

$$\frac{r_0^{(1)}}{r_0^{(0)}} = \frac{S_z}{|\alpha\beta|}, \quad (5.51)$$

by combining Equations (5.37) and (5.48), where the integral polarisation moments are [340]

$$r_q^{(k)} = \int_{-1}^1 R_q^{(k)}(\theta) d(\cos \theta) . \quad (5.52)$$

The error in the measurement of S_z , for each final rotational state, is calculated as the standard deviation of S_z across each batch of 20,000 laser shots (from a total of approximately 200,000).

The Differential Steric Effect

The bond orientation dependent DCSs may be obtained using a similar methodology to that described for unoriented ion images in Section 3.5.3. Analysis of the $\pm z$ ion images corresponds directly to extraction of the bond resolved angular distribution. Consequently, for a single scattering event, the intensity of the detected signal at a pixel with position (x, y) on the detector, may be written in terms of the oriented angular distributions:

$$i_{\pm z}(x_n, y_n, j_n, j'_n, j_n^*, \Gamma_n) = z(x_n, y_n, j_n, j'_n) P_{\pm z}(\theta_n) A(x_n, y_n, j'_n, j_n^*, \Gamma_n) , \quad (5.53)$$

where $P_{\pm z}(\theta_n)$ describes the oriented DCS as a function of scattering angle according to Equation (5.47), $z(x_n, y_n, j_n, j'_n)$ describes the instrument dependent detection probability and $A(x_n, y_n, j'_n, j_n^*, \Gamma_n)$ describes the polarisation dependence, as described in Section 3.5. This is equivalent to Equation (3.13), which describes the intensity as a function of the unoriented DCS.

The oriented DCS may then be expanded in terms of Legendre polynomials, as in Equation (3.25), and the intensity of the $\pm z$ images fitted as a linear combination of the corresponding basis functions. Whilst the relative difference in intensity between the two DCSs are known (from the steric asymmetry in Equation (5.48)), the absolute value of the ICSs are unknown, and it is necessary to normalise both DCSs (using the same factor) to the QM DCSs to facilitate comparison. The errors are calculated *via* the same methodology as for the unoriented angular distributions in Section 3.5.4: the error is equivalent to the standard deviation of the fits to the slow and fast sides of the experimental image, alongside the whole image for each orientation.

The renormalised $R_0^{(1)}(\theta)$ moments, which describe the polarisation along the $\pm z$ -axis, may be calculated by considering the relationship between the normalised difference of the oriented DCSs,

$$d\sigma_{\text{diff}}(\theta) = \frac{d\sigma_{-z(\text{N})}(\theta) - d\sigma_{+z(\text{O})}(\theta)}{d\sigma_{-z(\text{N})}(\theta) + d\sigma_{+z(\text{O})}(\theta)}, \quad (5.54)$$

and the $R_q^{(k)}(\theta)$ moments, resulting in

$$\frac{R_0^{(1)}(\theta)}{R_0^{(0)}(\theta)} = \frac{d\sigma_{\text{diff}}(\theta)}{|\alpha\beta|}. \quad (5.55)$$

5.4.2 x -Axis Orientation

Orientation of the NO bond axis along the scattering frame x -axis ($\theta_E = 90^\circ$, $\phi_E = 0^\circ$ or 180°), corresponding to collisions with the ‘side’ of the NO molecule, is more complicated than for orientation along the z -axis. In this geometry the LAB frame angles describing the direction of the electric field are $(\Theta_E, \Phi_E) = (90^\circ, 90^\circ)$ or $(90^\circ, 270^\circ)$, and $\mathbf{E}$ is perpendicular to (but still in-the-plane of) $\mathbf{k}$. Equation (5.46) is therefore reduced to

$$[d\sigma(\theta)]_{\theta_E}^{\phi_E} = \frac{\sigma_{\text{iso}}}{2\pi} \left\{ R_0^{(0)}(\theta) - 3\sqrt{2}A_0^{(1)}R_1^{(1)}(\theta) \sin\phi_T \sin\Phi_E \right\}, \quad (5.56)$$

which depends on the out-of-plane scattering angle, ϕ_T , described in Figure 5.6. As such, the oriented DCS depends on the elevation of the scattering products out of the plane of the molecular beams, and is not symmetric about $\mathbf{k}$. This is simple to rationalise, since the NO bond axis is no longer symmetrically distributed about $\mathbf{k}$. It is important to note that when scattering occurs directly along the TOF axis ($\phi_T = 0^\circ$), Equation (5.56) will be reduced further

$$[d\sigma(\theta)]_{\theta_E}^{\phi_E} = \frac{\sigma_{\text{iso}}}{2\pi} R_0^{(0)}(\theta), \quad (5.57)$$

which is equivalent to scattering along the y -axis (corresponding to the center-line of the image).

Figure 5.7 shows the experimental ion image for the x -axis oriented scattering of NO with Ar into the $|j' = 7.5e, \Omega' = 0.5\rangle$ state. Whilst the lack of symmetry is not obvious from the

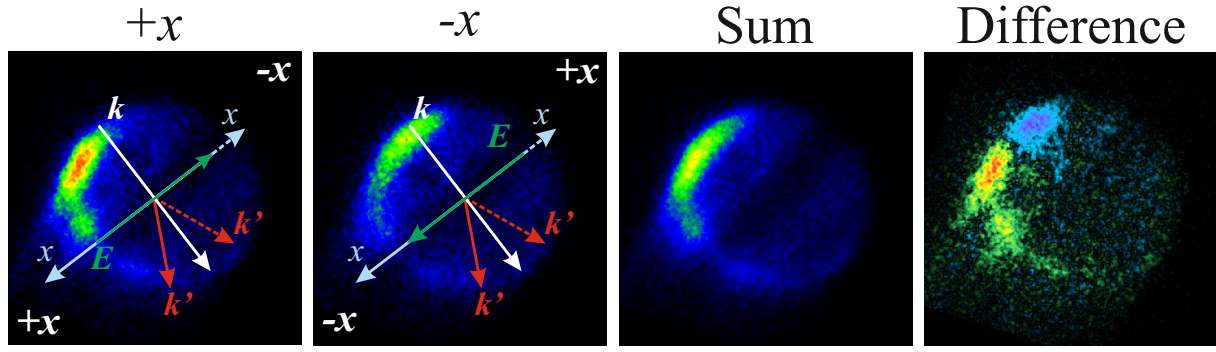


Figure 5.7: Experimental x -axis oriented ion images for scattering into the $|j' = 7.5e, \Omega' = 0.5\rangle$ state. The two LAB frame orientations, $+x$ and $-x$, are shown in the far-left and middle-left panels, respectively. The initial relative velocity vector, $\mathbf{k}$ is shown by a white arrow, and the applied static electric field is shown by a green arrow. Scattering (of NO) into the ‘slow’ and ‘fast’ sides of the Newton sphere are shown by dashed and solid arrows, respectively. $\mathbf{k}'$ and the x -axis defined by it are shown in red and pale blue, respectively. The scattering frame orientations ($\pm x$) are noted in the ‘slow’ and ‘fast’ corners of each image. The corresponding sum and difference images are shown on the right.

raw ion-images themselves, as the detection probability on the ‘slow’ side (bottom-left) of the image is much greater than that on the ‘fast’ side (top-right), it is useful to consider where the x -axis of the scattering frame lies. Consider the far-left panel, labelled $+x$, in which the electric field is defined from the bottom-left to the top-right of the image: for scattering of NO into the left-hand (‘slow’) side of the image the x -axis (in the scattering frame) is also described from the bottom-left to the top-right of the image, since the x -axis is defined by the $\mathbf{k} - \mathbf{k}'$ plane. Therefore, the x -axis is parallel to $\mathbf{E}$ and the polarisation is $+x$. Now, consider scattering into the top-right of the image: the electric field still points from bottom-left to top-right, but now the x -axis points from top-right to bottom-left and is therefore antiparallel to $\mathbf{E}$, corresponding to $-x$ scattering. When the electric field points from the bottom-left to the top-right, then the analysis is reversed. Of course, for any out-of-plane scattering, the situation is more nuanced, *i.e.* $\phi_T \neq 90^\circ$, however the same sort of analysis holds. For simplicity the images will be referred to according to the polarisation on the ‘slow’ side of the image as noted above the ion images in Figure 5.7.

The $R_0^{(0)}(\theta)$ and $R_1^{(1)}(\theta)$ moments in Equation (5.56) may be written in terms of the sum

$$d\sigma_{\text{sum}}(\theta) = [d\sigma(\theta)]_{90^\circ}^{180^\circ} + [d\sigma(\theta)]_{90^\circ}^{0^\circ} = 2 \frac{\sigma_{\text{iso}}}{2\pi} R_0^{(0)}(\theta) , \quad (5.58)$$

and difference

$$d\sigma_{\text{diff}}(\theta) = [d\sigma(\theta)]_{90^\circ}^{180^\circ} - [d\sigma(\theta)]_{90^\circ}^{0^\circ} = -2\sqrt{2}|\alpha\beta|\frac{\sigma_{\text{iso}}}{2\pi}R_1^{(1)}(\theta)\sin\phi_T, \quad (5.59)$$

of the two experimental images (where $\phi_E = 0^\circ$ and $\phi_E = 180^\circ$ correspond to the $+x$ and $-x$ orientations, respectively). This conveniently separates the contributions from the two moments, and allows independent fits (in Fourier space) to the experimental sum and difference images, using a similar method to that described in Section 3.5. The intensities of the sum and difference images at a pixel coordinate (x, y) , for a single scattering event are proportional to Equations (5.58) and (5.59), and may be written as

$$i_{\text{sum}}(x_n, y_n, j_n, j'_n, j_n^*, \Gamma_n) = 2z(x_n, y_n, j_n, j'_n)R_0^{(0)}(\theta_n)A(x_n, y_n, j'_n, j_n^*, \Gamma_n), \quad (5.60)$$

for the summed image and

$$\begin{aligned} i_{\text{dif}}(x_n, y_n, j_n, j'_n, j_n^*, \Gamma_n) = & -2\sqrt{2}|\alpha\beta|R_1^{(1)}(\theta_n)z(x_n, y_n, j_n, j'_n) \\ & \times A(x_n, y_n, j'_n, j_n^*, \Gamma_n)\sin\phi_{T,n}, \end{aligned} \quad (5.61)$$

for the difference image.

The $R_q^{(k)}(\theta)$ moments in Equations (5.60) and (5.61) may both be expanded in terms of spherical harmonics

$$R_0^{(0)}(\theta) = \sum_l \frac{2l+1}{2} a_l C_{0l}(\theta, 0) \quad (5.62a)$$

$$R_1^{(1)}(\theta) = \sum_l \frac{2l+1}{2} a_l C_{1l}(\theta, 0). \quad (5.62b)$$

The intensity can therefore be written as a linear combination of the basis functions according to

$$i(x_n, y_n, j_n, j'_n, j_n^*, \Gamma_n) = \sum_l \frac{2l+1}{2} a_l b_l(x_n, y_n, j_n, j'_n, \Gamma_n), \quad (5.63)$$

with the basis functions

$$b_l(x_n, y_n, j_n, j'_n, \Gamma_n) = 2C_{0l}(\theta, 0) z(x_n, y_n, j_n, j'_n) A(x_n, y_n, j'_n, j_n^*, \Gamma_n) \quad (5.64a)$$

$$b_l(x_n, y_n, j_n, j'_n, \Gamma_n) = -2\sqrt{2}|\alpha\beta|C_{1l}(\theta, 0) z(x_n, y_n, j_n, j'_n) \\ \times A(x_n, y_n, j'_n, j_n^*, \Gamma_n) \sin \phi_{T,n}, \quad (5.64b)$$

for the sum and difference images, respectively. The basis sets are calculated *via* Monte Carlo simulation and the experimental summed and difference images are fitted in Fourier space as described in Section 3.5.3.

The $\pm x$ DCSs may be retrieved by substituting the extracted experimental $R_q^{(k)}(\theta)$ moments into Equation (5.56) with the relevant values of $\Phi_E = 90^\circ$ or 270° , and $\phi_T = 90^\circ$. As in the z -axis polarised case, the relative intensity of the two moments is conserved during the analysis process, however, to compare the results to the QM r -PDDCSs and DCSs it is necessary to scale the experimental data using a single factor. The integral steric asymmetry for polarisation along the $\pm x$ -axis can be calculated from the extracted renormalised $r_q^{(k)}$ moments in Equation (5.52), according to

$$\frac{r_1^{(1)}}{r_0^{(0)}} = -\frac{S_x}{\sqrt{2}|\alpha\beta|}. \quad (5.65)$$

5.5 Summary

In this chapter the experimental and theoretical methods required for bond axis resolved scattering of the NO molecule have been described; these are the basic underpinnings of the work presented in Chapters 6, 7 and 8. The theory behind adiabatic orientation was discussed, alongside the experimental apparatus used to achieve such orientation in the laboratory. The theoretical treatment of scattering after the orientation of the NO bond axis in an arbitrarily directed field has been described using both classical and quantum mechanics. Finally, methods for data analysis and extraction of both integral and differential steric effects from experimental data were discussed.

Chapter 6

z -Axis Bond Orientation in the Inelastic Scattering of NO(X)

Orientation of the NO bond axis along the $\pm z$ -axis (where $+z$ is parallel to $\mathbf{k}$) corresponds to approach of the collision partner toward either the ‘N-end’ or ‘O-end’ of the NO molecule, as shown in the cartoons in Figure 6.1. Investigations into the effects of bond axis orientation on rotationally inelastic scattering have largely focused on the scattering of NO(X) [90, 92, 95, 134, 179, 219, 230] and OH(X) [64, 91, 93, 94, 192]. Both experiments and theory have generally focused on integral steric effects, and only recently have the first measurements of differential steric effects (for the spin-orbit conserving collisions of NO(X) + Ar) been reported [96, 97], although more progress has been made in reactive systems [327, 330, 334, 335, 345, 346, 349]. For collisions of OH(X) with the rare gases, largely classical (‘ball-and-stick’) behaviour was observed [91], in which a preference for ‘H-end’ collisions was observed for all but the lowest rotational states. In comparison, scattering of NO(X) with the rare gases results in large steric

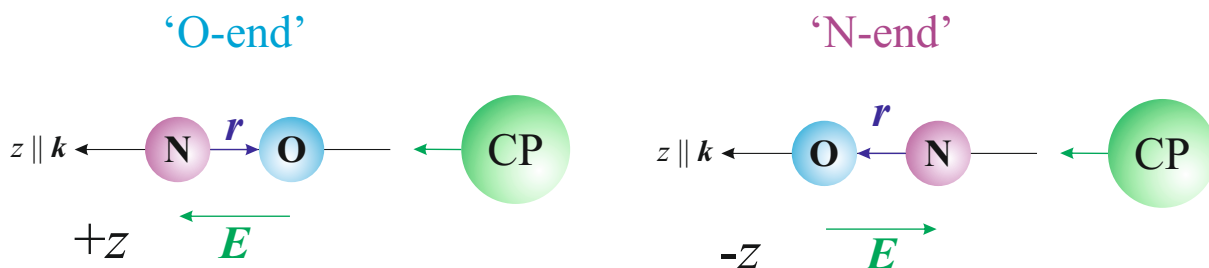


Figure 6.1: Cartoon depicting $+z$ (left) and $-z$ (right) bond axis orientation (in the scattering frame), corresponding to ‘O-end’ and ‘N-end’ scattering, respectively. ‘CP’ describes an atomic or diatomic collision partner.

effects and an oscillation between positive and negative values for odd and even values of Δj [90–92, 95, 134]; this effect has been attributed to quantum mechanical interference [179].

As discussed in Chapter 5, the integral steric effect is often quantified by the integral steric asymmetry, which for z -axis orientation is

$$S_z = \frac{\sigma_{-z(\text{N})} - \sigma_{+z(\text{O})}}{\sigma_{-z(\text{N})} + \sigma_{+z(\text{O})}}, \quad (6.1)$$

where $\sigma_{+z(\text{O})}$ and $\sigma_{-z(\text{N})}$ are the ICSs for collisions in the $\pm z$ -orientations. From Equation (6.1) it can be seen that positive values of S_z correspond to a preference for scattering from the ‘N-end’ of the molecule; similarly, a negative value shows a preference for scattering from the ‘O-end’ of the molecule. Note that S_z is directly proportional to the renormalised $r_0^{(1)}$ moment of the r -PDDCS, according to

$$\frac{r_0^{(1)}}{r_0^{(0)}} = \frac{S_z}{|\alpha\beta|}, \quad (6.2)$$

where the integral polarisation moments are calculated according to Equation (5.52). Further insight into the effect of bond orientation on scattering may be obtained through measurement of the differential steric asymmetry, which quantifies the steric preference as a function of scattering angle [97]. The differential steric effect may (in a similar way to the integral effect) be described by the normalised difference of the bond orientation resolved DCSs,

$$d\sigma_{\text{diff}}(\theta) = \frac{d\sigma_{-z(\text{N})}(\theta) - d\sigma_{+z(\text{O})}(\theta)}{d\sigma_{-z(\text{N})}(\theta) + d\sigma_{+z(\text{O})}(\theta)}, \quad (6.3)$$

which is proportional to the scattering angle dependent renormalised $R_0^{(1)}(\theta)$ moment,

$$\frac{R_0^{(1)}(\theta)}{R_0^{(0)}(\theta)} = \frac{d\sigma_{\text{diff}}(\theta)}{|\alpha\beta|}. \quad (6.4)$$

This chapter will be divided into two parts. In the first section, the experimental and theoretical integral steric asymmetry for the scattering of NO(X) with N₂(X) and O₂(X) will be presented for both the spin-orbit conserving and changing collisions. In the second section the

differential steric effect for the spin-orbit changing collisions of NO with Ar will be discussed, and comparisons between scattering on the two spin-orbit manifolds made. Finally, future work to allow extraction of pair-correlated steric effects between NO and a diatomic collision partner will be discussed.

6.1 Experimental and Theoretical Methods

The experimental apparatus used to study the bond axis oriented collisions of NO(X) with both diatoms and atoms was described in detail in Chapters 3 and 5. All experimental data were recorded and analysed using the methodologies discussed in Section 5.4.1, at the collision energies in Table 3.1. Only the e final Λ -doublet states were recorded as, at the experimental field strength, transitions into both final Λ -doublets are approximately equivalent [96, 97]. All data were recorded using unpolarised light on the mixed branch $Q_{21} + R_{11}$ and $Q_{22} + R_{12}$, for spin-orbit conserving and changing collisions, respectively. The only exception was the $|j' = 4.5, \Omega' = 1.5, \varepsilon' = +1, e\rangle$ state, which was recorded on the P_{12} branch, as the mixed branch overlaps the R_{22} branch for the $|j' = 1.5, \Omega' = 1.5, \varepsilon = -1, f\rangle$ transition. The electric (orientation) field, described in Section 5.2.2, was switched every 200 laser shots to record both orientations and ensure no experimental drift.*

The integral steric asymmetry data presented in Section 6.2 were recorded for the $|j', \Omega', \varepsilon' = +1, e\rangle \leftarrow |j = 0.5, \Omega = 0.5, E\rangle$ transitions resulting from collisions between NO(X) and Ar, N₂(X), and O₂(X), on both the spin-orbit conserving and changing manifolds. The integral steric asymmetry was calculated according to Equation 5.50. The experimental ion images presented in Section 6.3 were recorded for the $|j', \Omega' = 1.5, \varepsilon' = +1, e\rangle \leftarrow |j = 0.5, \Omega = 0.5, E\rangle$ transitions of NO(X) scattering with Ar. The effect of the unpolarised laser light on the recorded ion images was accounted for during the fitting procedure by applying the relevant CC QM polarisation correction (see Section 3.5.2). The experimental DCSs and r -PDDCSs were extracted using the methods described in Section 5.4.1.

*It should be noted that this data was recorded in collaboration with Dr. Sean Gordon.

Collision Partner	$E_{\text{coll}} / \text{cm}^{-1}$	$J_{\text{max}} (\propto \ell_{\text{max}})$	$b_{\text{max}} / \text{\AA}$
He	570	66.5	6.0
Ar ($\Delta\Omega = 0$)	532	160.5	6.5
Ar ($\Delta\Omega = 1$)	651	180.5	7.0
Xe	503	216.5	8.0
N ₂	845	250.5	10.0

Table 6.1: Parameters for CC QM and QCT calculations describing the collision of NO with He, Ar, Xe, and N₂. The two values shown for Ar arise from the use of a General valve (spin-orbit conserving transitions) [95, 96] or a Jordan valve (spin-orbit changing transitions) to form the secondary molecular beam. The collision energy is equivalent to the mean experimental collision energy.

CC QM and QCT calculations were performed according to the methods described in Chapter 2, and extended for bond axis orientation in Chapter 5. All calculations were run at fixed collision energies, corresponding to the mean experimental energies shown in Table 6.1. The two different collision energies for Ar arise from the use of two different molecular beam valves to form the secondary molecular beam; the differential steric asymmetry data for the collision of NO with Ar presented in Section 6.3, were recorded using a Jordan valve ($E_{\text{coll}} = 651 \text{ cm}^{-1}$), whilst the complementary data presented in Appendix B were recorded using a General valve ($E_{\text{coll}} = 532 \text{ cm}^{-1}$). No theoretical calculations were run for collisions with O₂, as there is currently no suitable *ab initio* PES available.[†]

QM calculations were done on the relevant V_{sum} and V_{diff} PESs, described in Chapter 2, using the HIBRIDON suite of codes [226]; rotational levels up to $j' = 20.5$, both Λ -doublets levels ($\epsilon \pm 1$) and spin-orbit manifolds ($\Omega = 0.5, 1.5$) were included in the wave function, the maximal partial wave (to ensure convergence) for each system is shown in Table 6.1. QCT calculations were run using approximately 1×10^6 trajectories on the relevant V_{sum} potential. Note that no QCT calculations are presented for scattering in which the spin-orbit manifold changes, since classically there is no concept of such transitions. Both QM and QCT observables were then calculated according to the methods presented in Chapter 2 and expanded for bond orientation in Chapter 5. For the differential steric effects presented in Section 6.3, QM calculations were

[†]Recently van de Meerakker and coworkers [69] have produced an NO + O₂ PES, which has been shown to be in good agreement for scattering at collision energies of $E_{\text{coll}} = 160 \text{ cm}^{-1}$ [69] and 480 cm^{-1} [70].

performed over a range of collision energies between $E_{\text{coll}} = 530\text{cm}^{-1}$ and $E_{\text{coll}} = 740\text{cm}^{-1}$ with a spacing of 30cm^{-1} , which were weighted by a Gaussian energy distribution with a FWHM of 35cm^{-1} and a mean value of $E_{\text{coll}} = 651\text{cm}^{-1}$.

6.2 Integral Steric Effects in Diatom-Diatom Scattering

The z -axis integral steric effect has been studied extensively for the collisions of NO(X) with the rare gases [90, 92, 95, 134, 179, 219, 230, 240, 350]. Similar measurements have been undertaken for OH(X) [91, 192, 351]. The next step-up in complexity from an atomic collision partner is a diatomic partner; such steric effects have been studied less, have focused on closed shell partners, and are often only fully quantum state resolved in a single collision partner (typically the open shell molecule). ter Meulen *et al.* [64, 93, 94] have recorded the integral steric effect for the collisions of $\text{OH}(X^2\Pi_{3/2}, v=0, j=3/2, f) + \text{HX}$ ($X = \text{Cl}, \text{Br}, \text{I}$), as well as collisions with CO [63], N_2 [63], and (normal/para)- H_2 [192]. The spin-orbit conserving scattering of NO(X) with D_2 has also been studied, and the steric effect shown to be very similar to that of scattering with He [275].

The integral steric asymmetry of the scattering of NO with N_2 and O_2 will be presented here for the first time. Due to their lack of dipole moments, N_2 and O_2 are not oriented in the electric field prior to collision. However, it is worth noting that the O_2 molecule may be aligned in the molecular beam [274, 281, 352]. No initial state selection was performed on the collision partner molecular beam, and several initial rotational states of the diatomics are expected to be populated; this was discussed in detail in reference to O_2 in Chapter 4. Whilst in principle possible [59, 277–279], no reactivity is expected for O_2 at the collision energies achieved experimentally. There are no reports of a direct reaction between N_2 and NO in their respective ground states.

The added complexity of a diatomic, as opposed to an atomic, collision partner was described in some depth in Chapter 4 and, for brevity, will not be reproduced here. In the diatom-diatom system, both molecules may undergo RET during the collision, leading to a

pair of final rotational states, $(j'_{\text{NO}}, j'_{\text{N}_2})$ and $(j'_{\text{NO}}, N'_{\text{O}_2})$, for collisions with N_2 and O_2 , respectively. The final state of the NO molecule is probed state-selectively using REMPI (as described in Chapter 3), however no information about the final rotational state of the collision partner is retrieved. As such, the experimental value of S_z may be considered to be an average across all ‘unobserved’ rotational states of the collision partner.

The experimental, CC QM, and QCT values of S_z , as a function of Δj , for the spin-orbit conserving and changing transitions of NO with Ar, N_2 , and O_2 resulting in the $|j'\Omega', \epsilon' = +1, e\rangle$ state, are shown in Figure 6.2. Note that no QCT calculations are shown for the spin-orbit changing collisions, as the model is intrinsically closed shell in nature and cannot describe such effects. The agreement between the QCT calculations and the experimental data is generally poor for collisions with both Ar and N_2 . In fact $S_z \sim 0$ for intermediate Δj , that is, there is no classical steric effect for these values of Δj . The agreement is much better at very low and high Δj , suggesting classical mechanisms are important for scattering into these rotational states.

The agreement between experimental and QM calculations is very good for the scattering of NO with Ar, although it is somewhat better on the spin-orbit conserving manifold than the spin-orbit changing one. This may, at least in part, be attributed to the difference potential, on which spin-orbit changing transitions are assumed to occur under Hund’s case (a); any small inaccuracies in the individual A' and A'' potentials are exacerbated when the difference is taken. The energy dependence of S_z on each spin-orbit manifold, discussed in Section 6.2.1, must also be considered when accounting for the better agreement on the spin-orbit conserving manifold.

The experimental values of S_z for scattering with N_2 on both spin-orbit manifolds agree less well with the QM theory than is observed for scattering with Ar. This cannot be simply accounted for by an energy dependence (discussed in Section 6.2.1), suggesting that the underlying PES, the scattering methods, or some combination of both does not accurately describe collisions in the system. This is not entirely surprising, since the NO- N_2 complex was constrained to planarity during the calculation of the PES, and averaged over all geometries of the N_2 molecule, reducing the system to the interaction of NO with a ‘spherical N_2 atom’

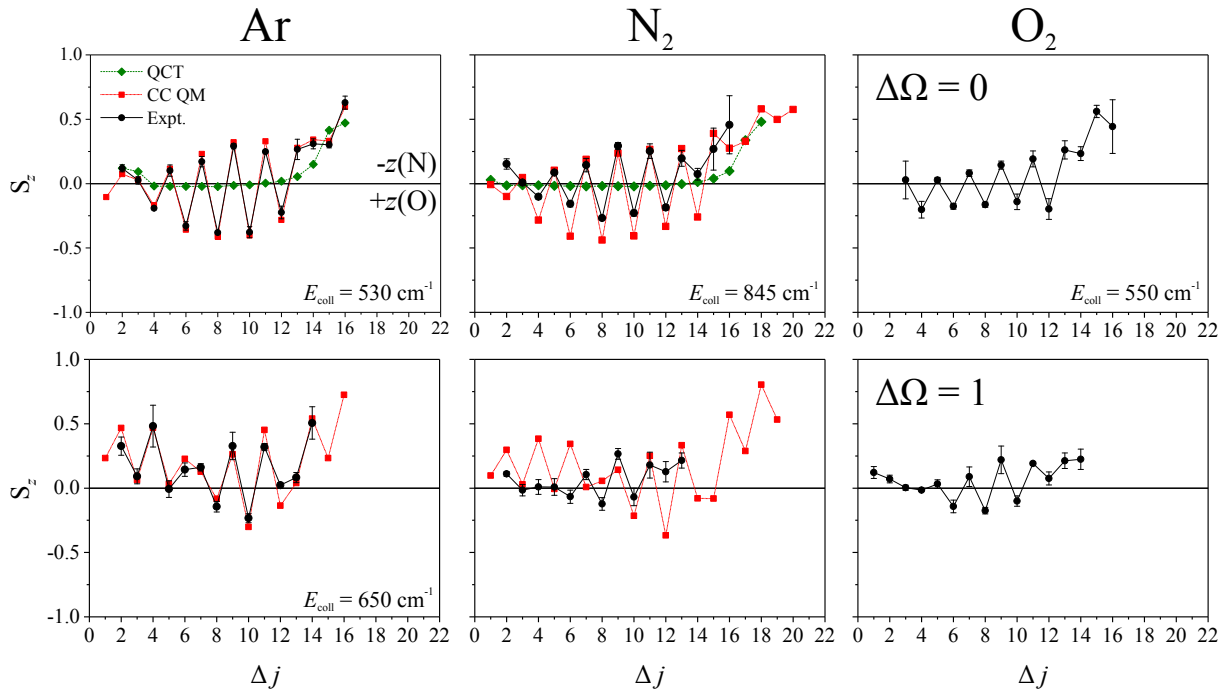


Figure 6.2: z -axis integral steric asymmetries, S_z , as a function of Δj for the $|j', \Omega', \varepsilon' = +1, e\rangle \leftarrow |j = 0.5, \Omega = 0.5, E\rangle$ transitions of NO(X) scattering with Ar, N₂, and O₂, from left to right. Spin-orbit conserving ($\Delta\Omega = 0$) and changing ($\Delta\Omega = 1$) transitions are shown in the top and bottom rows, respectively. The experimental, CC QM and QCT data are shown by black lines (with circles), red dotted lines (with squares), and green dashed lines (with diamonds), respectively. In each case the collision energy is shown in the bottom right hand corner of the plot. The experimental data of Nichols *et al.* [96, 97] for the spin-orbit conserving scattering of NO with Ar are shown for completeness.

[201]. Furthermore, the CC QM scattering calculations treated the system as if it were for the collision of a $^2\Pi$ molecule with a spherical atom [194, 196, 353] (*i.e.* a three atom system), and consequently the N₂ was treated as a structureless ‘atom’ with no possibility for rotational excitation during the collision process. Whilst the experimental values do not resolve the co-product pair, and consequently S_z may be considered an average over all final N₂ rotational states, the theoretical values do not correspond to the same averaging process.

The agreement between the experimental and QM values on the spin-orbit conserving manifold, for the scattering of NO with N₂, is noticeably better for collisions with odd Δj (which show a preference for ‘N-end’ collisions) than those with even Δj (preference for ‘O-end’ collisions). By calculating the normalised difference between the experimentally measured value of S_z and the CC QM value, $(S_z^{\text{expt}} - S_z^{\text{QM}}) / (S_z^{\text{expt}} + S_z^{\text{QM}})$, it is possible to quantify the level of disagreement; a negative value corresponds to an overestimation of the effect by the CC

QM calculations. For odd Δj transitions the average normalised difference is approximately -1%, whilst a value of approximately -31% is obtained for even Δj . That is, for collisions in the $-z(\text{N})$ orientation the agreement with theory is much better than in the $+z(\text{O})$ orientation. The agreement on the spin-orbit changing manifold between the experimental and QM data is very poor; this is also a consequence of inaccuracies in the PES, the diatom-atom nature of the QM calculations, and the larger errors expected in the PES for scattering on V_{diff} .

Several similarities are observed for scattering with different collision partners. On the spin-orbit conserving manifold there are two features which dominate the steric effect for all three systems; the presence of a regular Δj dependent oscillation, and a strong preference for $-z(\text{N})$ scattering at high Δj . These are signatures of the NO molecule rather than the collision partner [95], hence their appearance for all systems. The Δj dependent oscillations have been shown by Stolte and coworker, using the Quasi Quantum Treatment (QQT) of scattering [39, 174, 179, 275, 350], to arise from interfering trajectories from the ‘N-end’ and ‘O-end’ of the molecule. The hard shell nature of the QQT model, which approximates the Δj dependent oscillations very well [95, 179, 275, 350], also shows that the oscillations are largely due to scattering from the repulsive core of the molecule. Further investigation as to the repulsive origin of the integral steric effect [95, 219], by considering scattering on only the repulsive part of the potential, has provided further evidence of this.

A strong preference for $-z(\text{N})$ scattering at high Δj (on the spin-orbit conserving manifold) is observed for all systems.[‡] Both the QM and classical calculations predict this feature, suggesting a classical origin, which has previously been described by a classical ‘torque-like’ argument [96, 97]. Aoiz *et al.* [181] used QCT calculations for the collisions of NO with He to show that the asymmetry of the summed potential allows trajectories approaching the ‘N-end’ of the NO molecule to penetrate further into the repulsive part of the PES. Consequently, ‘N-end’ collisions peak at lower scattering angles, resulting in larger ICSs than for collisions at the ‘O-end’ of the molecule; an effect which becomes more pronounced for higher Δj .

[‡]There has been considerable discussion about the sign of S_z [219, 354, 355], due to some inconsistencies between experimental and theoretical calculations [90, 134, 355]. This is now resolved, and it is generally accepted that S_z is positive for collisions resulting in large Δj . In both this thesis, and other recent work [95–97], the experimental data and all experimental calculations are self-consistent.

The spin-orbit changing manifolds of all the systems also show evidence of the same Δj dependent oscillations and a preference for $-z(\text{N})$ scattering at high Δj that was observed for the spin-orbit conserving transitions. However, overall S_z is more positive, corresponding to a greater preference for collisions at the ‘N-end’ of the molecule. The average value of S_z for the collision of NO with Ar at $E_{\text{coll}} = 651 \text{ cm}^{-1}$ is $\bar{S}_z = 0.068$ and 0.209 for spin-orbit conserving and changing scattering, respectively. This shows that, whilst S_z shows on average a preference for scattering at the ‘N-end’ of the molecule on both spin-orbit manifolds, the magnitude of the preference is much larger for spin-orbit changing scattering. For collisions with Ar this has been shown to arise due to the nature of the difference potential (see Figure 2.3), which is assumed to govern spin-orbit changing transitions under Hund’s case (a) [95]. Whilst the V_{sum} potential is dominated by a slightly asymmetric ellipsoidal repulsive wall, the V_{diff} potential shows significant anisotropy between the ‘N’- and ‘O’-ends of the molecule. The difference potential is largely attractive, but at the ‘O-end’ of the molecule there is a repulsive wall, which explains the overall preference for scattering in the $-z(\text{N})$ orientation.

6.2.1 Energy Dependence

The QM data shown in Figure 6.2 is fixed at the mean experimental collision energy. However, experimentally the collision energy is more accurately described by a Gaussian distribution (due to spreads in the velocities of both collision partners), and one may expect to observe some dependence of the steric effect on the collision energy. Figure 6.3 shows the QM integral steric effect as a function of collision energy, as well as the value after averaging over a Gaussian spread of energies with a FWHM $35/100 \text{ cm}^{-1}$ about the mean collision energy ($E_{\text{coll}} = 650/845 \text{ cm}^{-1}$) for scattering with Ar/N₂. On the spin-orbit conserving manifold S_z is almost independent of the collision energy, however at higher final Δj and for spin-orbit changing transitions a much stronger effect is observed. Gordon [240] observed the same trend for scattering with the other rare gases. In general, S_z shows a stronger collision energy dependence for those states which show poorer agreement between experiment and theory (*e.g.* $\Delta j = 14$, $\Delta \Omega = 0$ for NO + Ar) in Figure 6.2. This (at least partially) explains the poorer

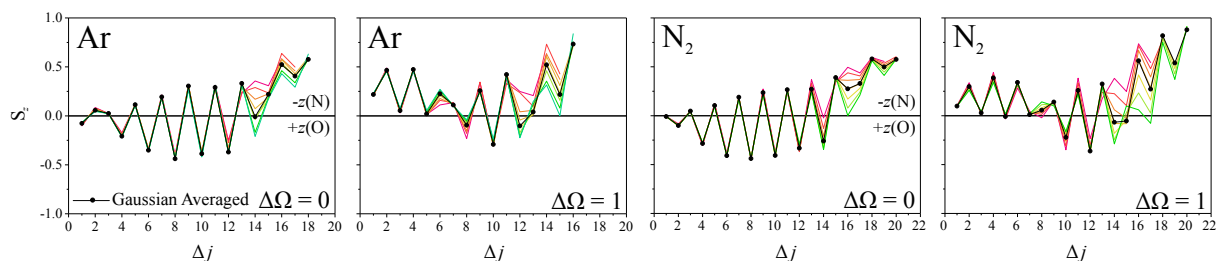


Figure 6.3: Collision energy dependence of S_z for the $|j', \Omega', \epsilon' = +1, e\rangle \leftarrow |j = 0.5, \Omega = 0.5, E\rangle$ transitions of NO + Ar (left) and N₂ (right) at $E_{\text{coll}} = 651 \text{ cm}^{-1}$ and 845 cm^{-1} , respectively. Collision energies vary between 530 cm^{-1} and 740 cm^{-1} , in steps of 30 cm^{-1} for collisions with Ar and are coloured on a scale from red to green. Similarly, collision energies vary between 700 cm^{-1} and 1000 cm^{-1} , in steps of 50 cm^{-1} for collisions with N₂. The black line (with circles) denotes the QM calculations averaged over a Gaussian distribution of collision energies with a FWHM of 35 cm^{-1} and 100 cm^{-1} for Ar and N₂, respectively.

agreement between the experimental and QM data observed for spin-orbit changing transitions, which are more strongly energy dependent, compared to transitions on the spin-orbit conserving manifold. Similar features are observed for scattering with N₂. However, the disagreement between the QM calculations and the experimental values observed in Figure 6.2 cannot simply be accounted for by a difference in collision energy and, as discussed above, other sources for this disparity must be considered.

The dependence on collision energy at high Δj for both spin-orbit manifolds can be rationalised simply; as the collision energy reaches the energetic threshold for scattering into a specific $|j', \Omega', \epsilon'\rangle$ state, only collisions at the ‘N-end’ of the NO molecule may induce such scattering as the extent of the NO molecule is greater at the ‘N-end’, and allows greater RET transfer than for an equivalent collision at the ‘O-end’ of the molecule. However, as the collision energy is further increased over the threshold, collisions at both ‘ends’ of the molecule are able to induce the required RET to access the state (*i.e* less ‘head-on’ collisions are required which can be accessed when scattering off either end of the molecule). This corresponds to a reduction in the absolute magnitude of S_z , since there is a weaker preference for scattering from a specific ‘end’ of the molecule. As the energy available for the collision is further increased the transition becomes less ‘classical’ in nature, since there is sufficient energy to access the rotational state of interest. Correspondingly, the quantum mechanical mechanism (which is washed out at high

Δj by the classical ‘torque’ effect) becomes more important and the Δj dependent oscillation becomes more prominent for the state of interest.

6.2.2 Attractive Effects

For low Δj transitions, Brouard *et al.* [95, 240] have shown that the absence or presence of oscillations in S_z is a subtle indicator of the balance between the attractive and repulsive parts of the potential for collisions of NO with the rare gases. Comparison between the full PES and the ‘soft’ PES, in which the attractive components have been removed as described in Section 2.4, allows inference of the effect of the attractive part of the potential on the scattering outcome. Figure 6.4 shows the QM values of S_z calculated on the full and ‘soft’ potentials for scattering of NO with He, Ar, and Xe into the final e Λ -doublet on the spin-orbit conserving manifold. Deviations between the two PESs are observed for all systems at high Δj due to the process of truncating the potential, which can lead to small deformations in the repulsive core of the potential.[§]

Scattering with He occurs on a largely repulsive PES (see Figure 2.2); consequently, S_z does not change upon removal of the attractive part of the potential, and regular Δj dependent oscillations are observed down to $j' = 1.5$. Meanwhile, removal of the attractive part of the potential has a more significant effect for scattering with Ar and Xe. This is particularly noticeable for low $\Delta j (< 4)$ transitions (shaded in green in Figure 6.4), where the Δj dependent oscillations are not regular on the full potential, and show a general preference for $-z(\text{N})$ scattering. This preference is attributed to the larger extent of the (attractive) potential at the ‘N-end’ of the molecule compared to the ‘O-end’. Regular oscillations may be recovered by removal of the attractive part of the potential.

By considering the regularity of the Δj dependent oscillations at low Δj in a specific system, information about the potential may be inferred. The oscillatory behaviour in the experimental spin-orbit conserving data for N_2 (also shown in Figure 6.4) is not regular, and a $-z(\text{N})$

[§]It should be noted that for intermediate Δj S_z does not depend strongly on the presence of the attractive part of the potential. This is consistent with the steric effect arising from scattering from the repulsive core of the NO molecule, as discussed by both Alexander and Stolte [219] and Brouard *et al.* [95].

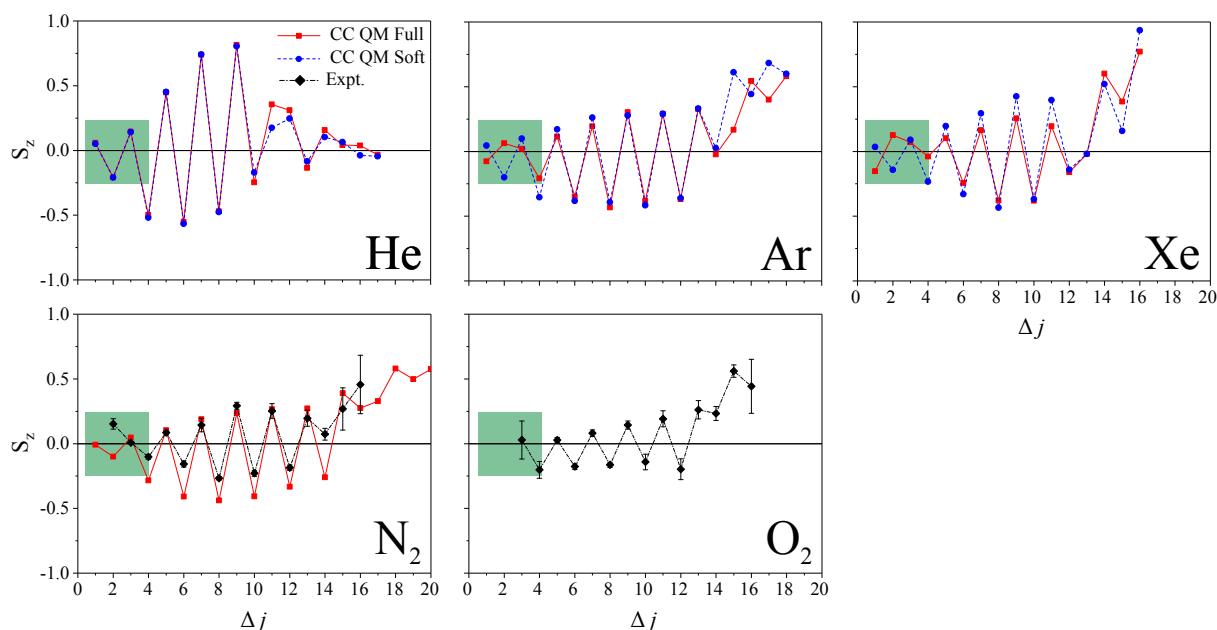


Figure 6.4: Effect of the attractive part of the potential on the z -axis integral steric asymmetry for spin-orbit conserving transitions to the final e Λ -doublet. Top row: CC QM data for NO scattering with He, Ar ($E_{\text{coll}} = 651 \text{ cm}^{-1}$), and Xe, from left to right. Bottom row: experimental data for N₂ (left) and O₂ (right). Calculations on the full and ‘soft’ (truncated) potential are shown by red lines (with squares) and blue dashed lines (with circles), respectively; the experimental data is shown for N₂ and O₂ by black dashed-dotted lines (with diamonds). The region of interest is highlighted by green shading.

preference is observed below $\Delta j = 4$, suggesting that the potential is more attractive than the 2D averaged PES predicts. Although it is also possible that the observed structure may arise due to averaging over the final state of the diatomic collision partner, rather than due to attractive effects. For collisions with O₂ the experimental data show oscillatory behaviour down to the lowest rotational states recorded ($\Delta j > 2$). However, since this effect is only seen for the very lowest rotational transitions, nothing may be inferred from the data with confidence. Furthermore, the implications of the additional PESs which describe collisions with the open shell O₂ molecule are unclear.

6.2.3 Absolute Magnitude

The absolute magnitude, $|S_z|$, of the integral steric effect for scattering of NO with the rare gases for low and intermediate Δj is largest in repulsive systems (*e.g.* He), and decreases as the PES becomes both more attractive and more isotropic in nature (*e.g.* Xe) [95, 240].

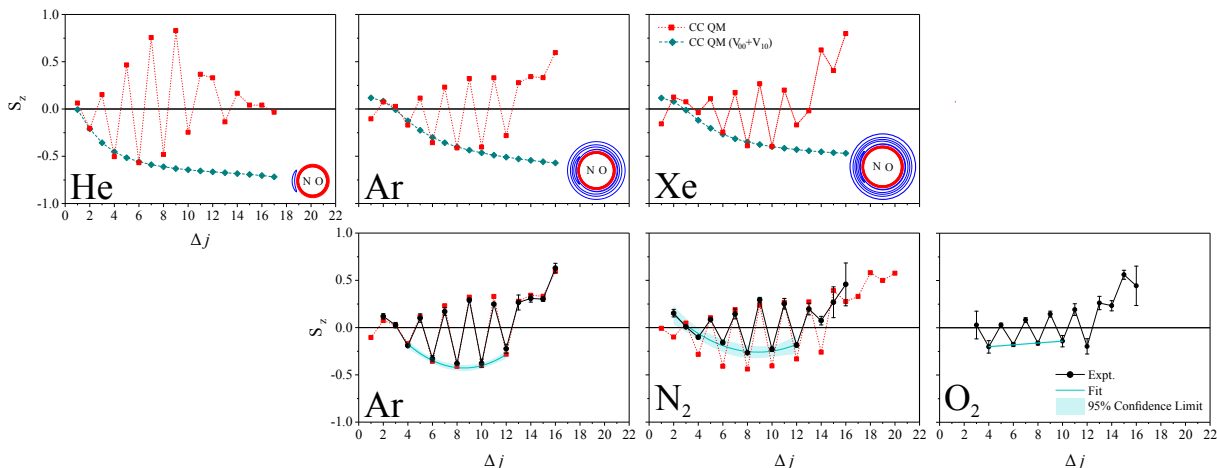


Figure 6.5: z -axis integral steric asymmetries, S_z , as a function of Δj for the $|j', \Omega' = 0.5, \varepsilon' = +1, e\rangle \leftarrow |j = 0.5, \Omega = 0.5, E\rangle$ collisions of NO(X). Top panel: CC QM data for scattering with He, Ar ($E_{\text{coll}} = 532 \text{ cm}^{-1}$), and Xe, from left to right, on the full (red dotted lines with squares) and $V_{00} + V_{10}$ (teal dashed line with diamonds) potentials. The $V_{00} + V_{10}$ potential is shown in each case. Bottom panel: CC QM (full potential) and experimental (black line with circles) data for scattering with Ar ($E_{\text{coll}} = 532 \text{ cm}^{-1}$), N_2 , and O_2 , from left to right. A fit to the experimental points in the purely quantum regime is shown by a blue line in the bottom panels; the corresponding shaded area shows the 95% confidence limit. The experimental data for the spin-orbit conserving scattering of NO with Ar are from References [96, 97].

Brouard *et al.* [95] have shown that whilst the Δj dependent oscillations arise due to the near-homonuclearity of the repulsive part of the PES, $|S_z|$ is characteristic of the lowest order heteronuclear term ($\lambda = 1$) in the expansion of the potential.

The top panel of Figure 6.5 shows the QM values of S_z calculated on both the full potential and a potential composed of only the $V_{00} + V_{10}$ terms in the expansion for scattering with He, Ar, and Xe. In each case it is clear that the points on the $V_{00} + V_{10}$ potential approximately bounds S_z . The preference for $+z(\text{O})$ scattering (on the $V_{00} + V_{10}$ potential) arises due to the attractive well observed at the ‘O-end’ of the NO molecule. For more attractive systems (*i.e.* going from He to Ar to Xe) the isotropic V_{00} term in the potential becomes longer ranged and the PES becomes more isotropic, giving rise to a smaller value of $|S_z|$. That is, the differences between the ‘N-end’ and ‘O-end’ of the NO molecule become less pronounced in the more attractive systems, and therefore the relative magnitude of S_z becomes smaller. The (experimental) mean value of $|S_z|$ (for $4 \leq \Delta j \leq 12$ where the oscillations are regular) is 0.26 ± 0.03 , 0.19 ± 0.03 , and 0.15 ± 0.05 for Ar, N_2 and O_2 , respectively; suggesting that the potentials become more

isotropic (and potentially attractive) upon going from Ar to N₂ to O₂ (*cf.* He ($4 \leq \Delta j \leq 11$) and Xe which have (QM) means of 0.47, and 0.21, respectively).

The profile of S at intermediate Δj is subtly different for scattering with the different collision partners. Figure 6.5 also shows the experimental integral steric asymmetry for spin-orbit conserving collisions of NO with Ar, N₂ and O₂; in each case the data in the (repulsive) quantum mechanical region have been fitted to a quadratic of the form $S_z = a\Delta j^2 + b\Delta j + c$ to allow qualitative analysis of the profile of S_z . Only the fit through the negative points are shown here; however one may also use the positive points, which would result in a sign inversion. For collisions with both Ar and N₂, the fit is clearly quadratic, similar behaviour is also observed for other rare gas collision partners [97]. For collisions with O₂, however, the fit to the quadratic results in $a \approx 0$ and the trend is linear; as Δj increases $|S_z|$ becomes increasingly positive, corresponding to an increasingly strong preference for scattering at the ‘N-end’ of the molecule. Since in this region the value of S_z is known to arise from repulsive scattering [97, 219], it is likely that the differences manifest in the repulsive core of the potential, whilst the reduced magnitude of S_z compared to scattering with N₂ and Ar arises from the attractive part of the potential (*cf.* scattering with Kr and Xe [95]).

Differences in $|S_z|$ between the three systems are also observed for scattering on the spin-orbit changing manifold (see Figure 6.2). The most obvious of these is observed for $\Delta j \leq 5$; for scattering with Ar, Δj dependent oscillations are observed (albeit with a general preference for $-z(\text{N})$ scattering), whilst for collisions with both N₂ and O₂ there is no significant steric effect observed, $S_z \approx 0$. This suggests that the potential is more isotropic in nature for these diatomic collision partners, with only subtle differences at either end of the molecule. A slight preference for $-z(\text{N})$ scattering is observed, suggesting that the potentials for collisions with both O₂ and N₂ are more repulsive at the ‘O-end’ of the molecule than at the ‘N-end’ (*cf.* scattering with Ar). Of course, it is also possible that this behaviour arises from averaging over all final rotational states of the diatomic collision partner. Since very similar trends are observed for collisions with the closed shell N₂ and open shell O₂, it is unlikely that this effect arises due to the presence of the unpaired electrons in the O₂ molecule, *i.e.* the extra PESs play

no significant role (atleast after averaging over all final N'_{O_2}). As was observed on the spin-orbit conserving manifold, the mean value of $|S_z|$ (for $2 \leq \Delta j \leq 13$) is smaller for N₂ (0.11 ± 0.06) and O₂ (0.11 ± 0.05) than Ar (0.20 ± 0.07).

6.3 Differential Steric Effects on the Spin-Orbit Changing Manifold: NO + Ar

Whilst steric effects in the scattering of NO with the rare gases have been relatively widely studied both theoretically and experimentally [92, 95–97, 134, 219, 230, 240, 354], experimental measurements on the spin-orbit changing manifold have been minimal [92, 95], with only a few theoretical studies [92, 95, 134, 219]. Due to the large-spin orbit energy ($\sim 123 \text{ cm}^{-1}$ [188] for low Δj) and small integral cross sections, spin-orbit changing collisions are more challenging to study experimentally. As such, until now, studies of the steric effect on the spin-orbit changing manifold have been limited to integral effects. The differential steric effect for the collision of NO with Ar is presented for the first time here.

Figure 6.6 shows the experimental and fitted ion images for the bond orientation resolved $|j', \Omega' = 1.5, \epsilon' = +1, e\rangle \leftarrow |j = 0.5, \Omega = 0.5, E\rangle$ transitions of NO with Ar. Further, complementary, experimental ion images at a collision energy of $E_{\text{coll}} = 532 \text{ cm}^{-1}$ are shown in Appendix B. The general agreement between the experimental images and the fits is good; all of the features in the experimental images are captured in the fit. For each final rotational state, the colour scale (where red is the maximum intensity, and black is zero intensity) is equivalent for the $+z(\text{O})$ - and $-z(\text{N})$ -orientations to preserve any intensity differences observed between the two ion images. The ion images are broadly similar to those obtained for bond-orientation resolved scattering on the spin-orbit conserving manifold [96, 97]. The most significant difference is the presence of intensity around the entire (crushed) Newton sphere for all rotational states, which is less apparent on the spin-orbit conserving manifold.

The majority of the general trends observed in the ion images may be explained using similar arguments to those used when the bond axis is not oriented before the collision [35, 39].

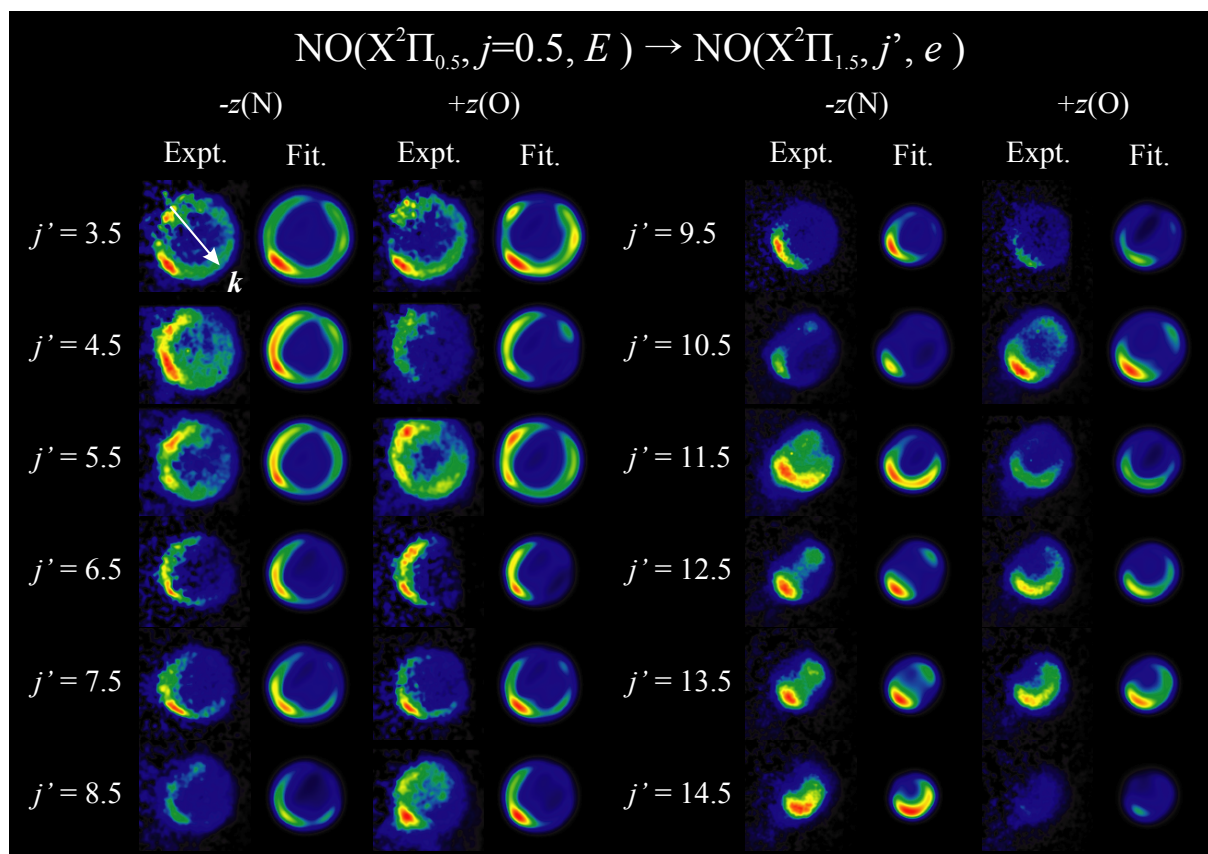


Figure 6.6: Experimental (left) and fitted (right) ion images for the bond orientation resolved spin-orbit changing collisions of NO with Ar at $E_{\text{coll}} = 651 \text{ cm}^{-1}$, into final rotational states defined by $|j', \Omega' = 1.5, \epsilon' = +1, e\rangle$. The $-z(\text{N})$ and $+z(\text{O})$ orientations are shown in panels 1/3 and 2/4, respectively. The relative velocity vector is shown in the $-z(\text{N})$ ion image for $j' = 3.5$.

The radius of the ion images becomes smaller with increasing final rotational state, j' , as a greater proportion of the initial translational velocity is converted into rotational energy, and the outgoing translational velocity is reduced. The distribution of intensity around the (crushed) Newton sphere also varies with increasing j' . For low rotational states, the intensity is predominantly forwards and sideways scattered, becoming increasingly sideways and then backwards scattered as the rotational energy transfer (RET) increases. This is easily rationalised according to the types of collision undergone. RET is small for ‘glancing blow’ type collisions which result in only a small deflection from the incoming trajectory (forwards scattering), whilst much larger RET may be achieved for more direct, ‘head-on’ type, collisions which undergo large deflection angles (backwards scattering).

Intensity is observed for scattering into all angles, *i.e.* there is intensity around the entire (crushed) Newton sphere, with peaks superimposed over this intensity. This is different to that observed for scattering on the spin-orbit conserving manifold [96, 97], in which the ion images are dominated by intense peaks. Since under Hund's case (a), which holds for low and intermediate j' , spin-orbit changing scattering can be approximated to occur on only the difference potential, it is helpful to consider the shape of the potential. The difference potential (shown in Figure 2.3) is much less hard shell in nature than the sum potential (on which spin-orbit conserving scattering may be considered to occur). V_{diff} is largely attractive, with a small repulsive lobe at the 'O-end' of the NO molecule. The extent of the attractive part of the potential at the 'N-end' of the molecule is greater than that at the 'O-end'. For small RET, resulting in low j' , the attractive part of the potential is sampled by 'glancing-blow' type collisions, which leads to forwards and sideways scattering for all j' . For large RET, resulting in high rotational states, the rotation of the NO molecule is more accurately described by the intermediate case between Hund's case (a) and (b), and scattering over both the summed and difference potentials must be considered. The repulsive wall on the V_{sum} potential becomes important for 'head-on' type collisions to higher rotational states; which results in more backwards scattering.

Clear differences in the intensity of the $+z(\text{O})$ and $-z(\text{N})$ ion images (for a single rotational state) are observed. In general, the $-z(\text{N})$ ion images are more intense (*i.e.* there is a preference for scattering from the 'N-end' of the molecule). To describe this overall preference it is more convenient to consider the integral steric asymmetry, S_z , according to Equation (6.1), and shown in Figure 6.2. As discussed in Section 6.2, the Δj dependent oscillations in S_z arise due to quantum interference between scattering from both molecular orientations [97, 219]. Generally, the steric is positive ($S_z > 0$), which corresponds to scattering preferentially occurring off of the 'N-end' of the molecule. It is important to note that whilst the average intensities of the oriented ion images vary, shown by $S_z \neq 0$, the distribution of the intensity around the (crushed) Newton sphere, which corresponds to the angular scattering distribution, is very similar for both orientations (*i.e.* the same number of peaks are observed

in the $\pm z$ -orientations). This is consistent with the mixing of the initial Λ -doublet states in the electric field, according to Equation (5.5), and the intensity observed in ion images for spin-orbit conserving scattering [96, 97].

6.3.1 Bond Orientation Resolved Differential Cross Sections

The experimentally determined bond orientation resolved DCSs, $d\sigma_{\pm z(\text{N/O})}(\theta)$, are shown in Figure 6.7, alongside the CC QM (field dependent) isotropic and orientation resolved DCSs. In general the agreement between the QM and experimental DCSs is good. The agreement is, however, particularly poor for $j' = 7.5$ due to the overlap of the intensity in the ion image with the position corresponding to a velocity of zero in the LAB frame. These NO molecules remain in the detection volume much longer than molecules scattered into other portions of the Newton sphere, resulting in a higher detection efficiency for such molecules. Any small errors in the calculation of the LAB frame detection efficiency factors will result in a poor description of slow moving molecules, and as such the fit to the experimental data. This effect is also observed (although to a lesser extent) for $j' = 6.5$ and 8.5 , where the highest intensity in the ion image also overlaps LAB origin.

The angular scattering distributions show some differences between collisions in the $\pm z$ orientations. However, the broadness of the peaks means that the differences are subtle (aside from the relative intensity of the DCSs which corresponds to the integral steric effect). As in the case for scattering on the spin-orbit conserving manifold [96, 97], collisions at both ends of the molecule result in the same number of peaks in the DCS, however the relative intensity of the two peaks varies between $+z(\text{O})$ and $-z(\text{N})$ collisions. This effect is particularly prominent for intermediate values of j' (*i.e.* between 9.5 and 11.5), where the two peaks in the DCS show a large difference in intensity depending on the end of the molecule at which the scattering event occurs. Take, for example, $j' = 10.5$: for scattering off both ends of the molecule, there are two peaks in the DCS, however, for ‘N-end’ collisions the first peak is more intense, whilst for collisions at the ‘O-end’ the peak at larger scattering angles is much more intense and appears as a shoulder on the lower angle peak in the DCS. In the spin-orbit conserving case these

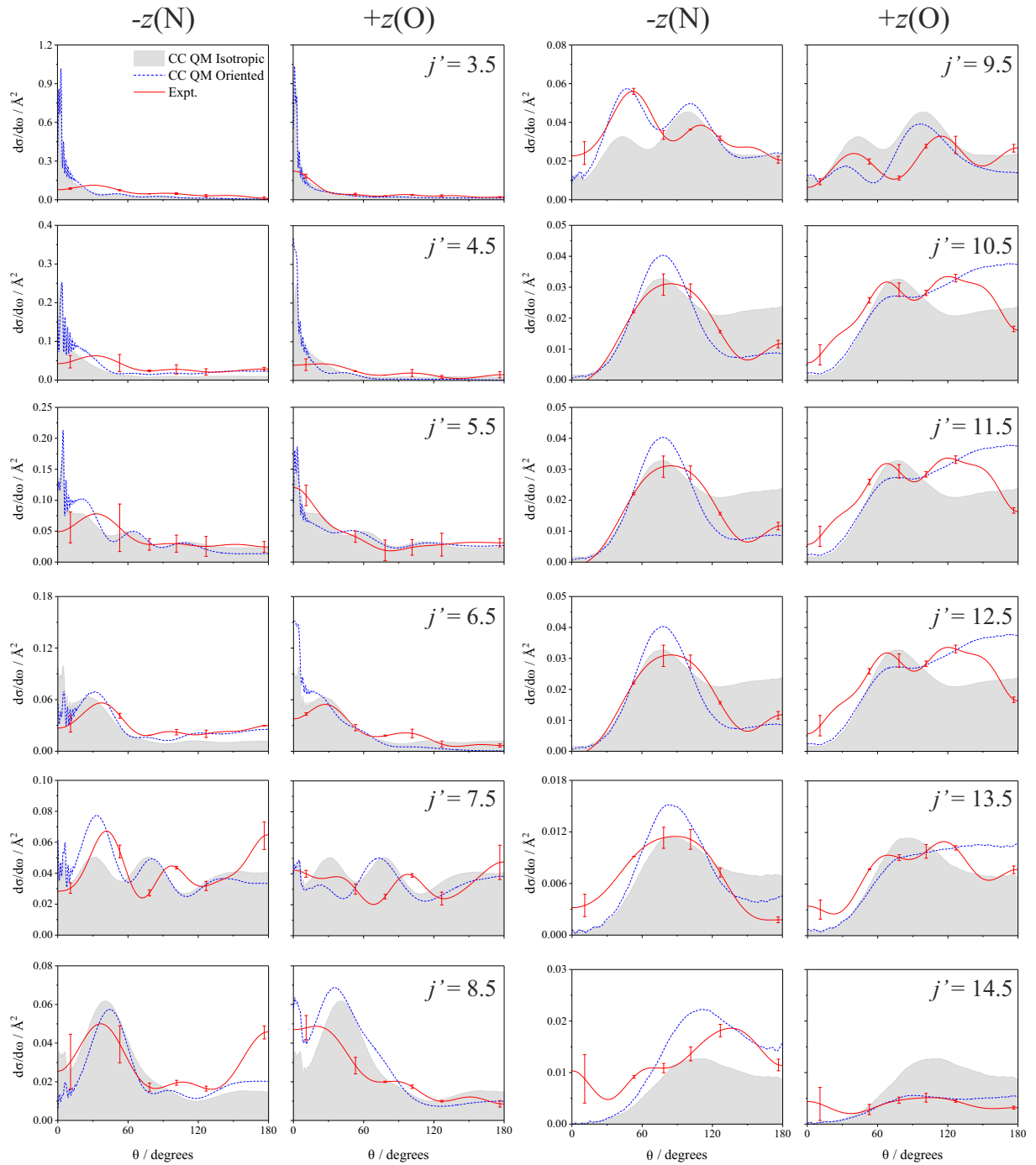


Figure 6.7: Experimental fitted (red lines) and QM (blue dashed lines) oriented DCSs for the spin-orbit changing collisions of NO with Ar at $E_{\text{coll}} = 651 \text{ cm}^{-1}$, into the final rotational states defined by $|j', \Omega' = 1.5, \epsilon' = +1, e\rangle$. Collisions in the $-z(\text{N})$ and $+z(\text{O})$ orientations are shown in panels 1/3 and 2/4, respectively. The QM isotropic DCS is shown shaded in gray. Error bars are calculated from the fits to the fast and slow sides of the image, as well as the full image, and correspond to a 95% confidence interval. QM data has been averaged over collision energy, weighted by a Gaussian of FWHM 35 cm^{-1} .

oscillations in the DCS have been shown to arise due to quantum interference from scattering at the two ‘ends’ of the molecule [96, 97]. Note that, as in the unoriented case [75], the DCSs for the oriented spin-orbit changing transitions are largely more uniform than the corresponding spin-orbit conserving DCSs, with the oscillations in the angular distributions superimposed over the top of the general structure.

6.3.2 Bond Orientation Moments

The renormalised $R_0^{(1)}(\theta)$ moments give a clearer picture of the differences in the angular scattering distribution for scattering at the two ends of the NO molecule. Figure 6.8 shows the experimental and QM renormalised bond orientation moments for the $|j', \Omega' = 1.5, \epsilon' = +1, e\rangle \leftarrow |j = 0.5, \Omega = 0.5, E\rangle$ transitions. The experimental values are calculated from the experimental DCSs according to Equation (5.55). In general, the experimental and QM moments follow the same trends, although not all of the features observed in the QM data are reproduced by the experimental data, in part because of the current resolution of the experiment. Differences in the absolute magnitude of the moment reflect differences between the experimental and QM integral steric effect shown in Figure 6.2. The agreement is less good than in the case of the oriented DCSs in Figure 6.7, due to the enhancement of errors when taking the normalised difference of scattering in the two orientations. Whilst the experimental oriented DCSs for $j' = 7.5$ did not show good agreement with the QM data, the renormalised moment is a relatively good representation. This may be rationalised, since any errors in the LAB frame detection efficiency factors are the same for both orientations (see Chapter 5), and will cancel when calculating the renormalised moment.

The renormalised $k = 1, q = 0$ moment may be understood in terms of differences between scattering occurring at the ‘N-end’ and ‘O-end’ of the molecule, according to Equation (5.54).[¶] A negative value of $R_0^{(1)}/R_0^{(0)}$ corresponds to a preference for scattering from the ‘O-end’ of the molecule, whilst a positive value corresponds to preferential scattering off the ‘N-end’. For $j' =$

[¶]Note that the limits of the renormalised $R_q^{(k)}(\theta)$ moments are field dependant, according to $\pm 1/|\alpha\beta|$. As such, at the experimental field the limits are ± 1.24 , whilst at an infinite field the limits are ± 1 .

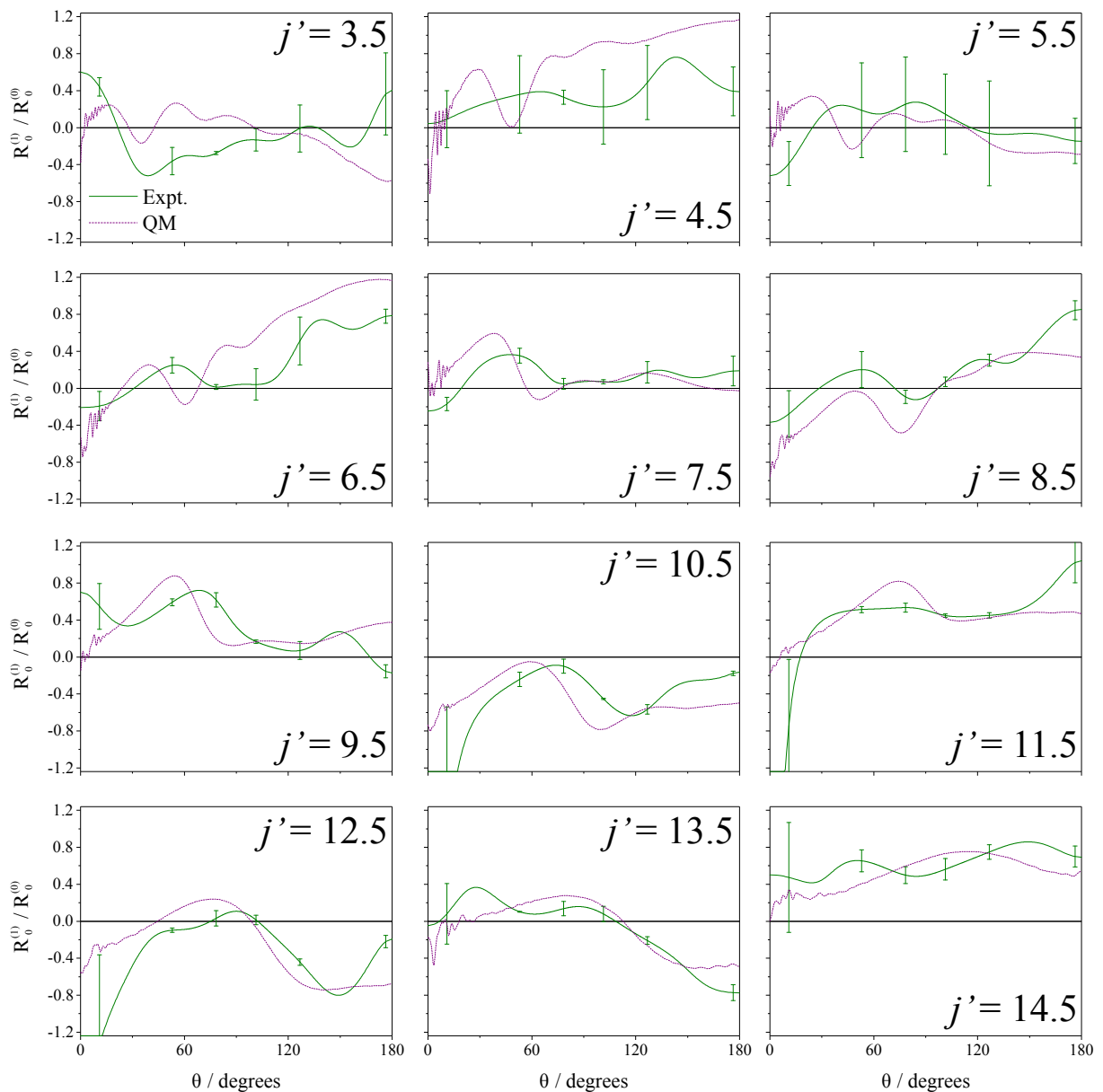


Figure 6.8: Experimental (green lines) and CC QM (purple dashed lines) renormalised $R_0^{(1)}(\theta)$ moments for the spin-orbit changing collisions of NO with Ar at $E_{\text{coll}} = 651 \text{ cm}^{-1}$, into final rotational states defined by $|j', \Omega' = 1.5, \varepsilon' = +1, e\rangle$. Error bars were propagated from the errors in the DCSs in Figure 6.7, and correspond to a 95% confidence interval. QM data has been averaged over collision energy and weighted by a Gaussian of FWHM 35 cm^{-1} .

10.5 to 12.5, the value of the renormalised moment is approximately -1.24 for small scattering angles; this arises when the experimental $-z(\text{N})$ DCS goes to zero in this region, leading to an absolute preference for scattering off the ‘O-end’. The general preference for scattering from the ‘N-end’ of the NO molecule, observed in both the experimental ion images and (more subtly) in the extracted DCSs, corresponds to a positive value of the renormalised r -PDDCS. The Δj

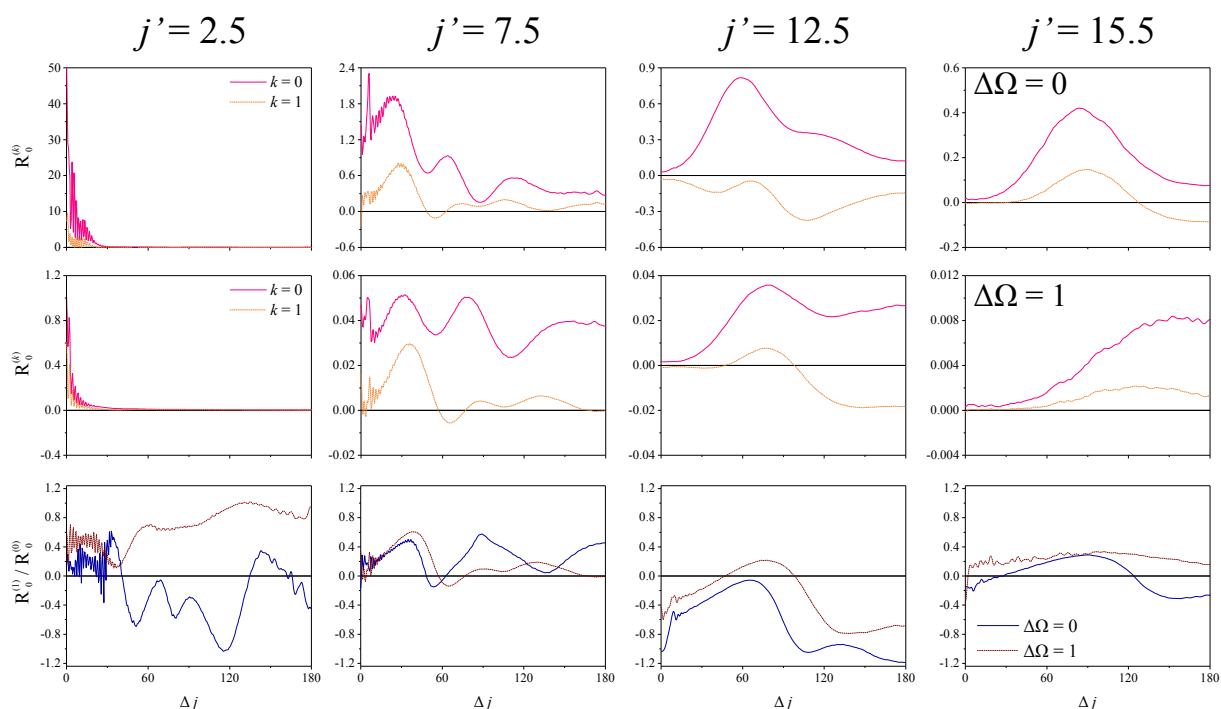


Figure 6.9: CC QM r -PDDCSs for the spin-orbit conserving (top) and changing (middle) manifolds. The $R_0^{(0)}(\theta)$ and $R_0^{(1)}(\theta)$ moments are shown by pink and teal (dashed) lines, respectively. The bottom row shows the renormalised $R_0^{(1)}(\theta)$ moment on the spin-orbit conserving (navy line) and changing (maroon dashed line) manifolds. Scattering is shown into the final e Λ -doublet, with final rotational state $j' = 2.5, 7.5, 12.5$, and 15.5 from left to right.

dependent oscillations observed in the integral steric effect in Figure 6.2 are also observed in the renormalised r -PDDCS. For example, the overall preference is for scattering from the ‘N-end’ of the molecule ($-z$) for $j' = 9.5$, but scattering from the ‘O-end’ ($+z$) for $j' = 10.5$.

6.3.3 Effect of Spin-Orbit Manifold on the r -PDDCS

A comparison between the r -PDDCSs for scattering (into the final e Λ -doublet) on the spin-orbit conserving and changing manifolds is shown in Figure 6.9, for several final rotations states: $j' = 2.5, 7.5, 12.5$, and 15.5 . The $R_0^{(0)}(\theta)$ moment describes the ‘isotropic’ scattering according to Equation (5.39); note that this moment depends on the field strength. Meanwhile, the $R_0^{(1)}(\theta)$ moment describes the effect of orientation of the NO bond axis with respect to the initial relative velocity vector, $\mathbf{k}$, and does not depend on the field strength. When renormalised, the $R_0^{(1)}(\theta)$ moment takes a value of $1/|\alpha\beta| = -1.24$ for collisions at only the ‘O-end’ of the molecule

(+z), and a value of $1/|\alpha\beta| = +1.24$ for collisions at only the ‘N-end’ (−z), corresponding to k parallel and antiparallel to the electric field, respectively.[¶]

As discussed previously in terms of unoriented scattering [35, 39], scattering through all angles is observed much more on the spin-orbit changing manifold than on the spin-orbit conserving manifold. On average the spin-orbit changing $R_0^{(0)}(\theta)$ moment is more backwards scattered than the corresponding spin-orbit conserving moment, as has previously been observed in the DCS for field free scattering [39]. This arises as collisions must overcome the spin-orbit energy ($\sim 120\text{cm}^{-1}$ [188] at low Δj). The V_{diff} potential, which is considered to govern spin-orbit changing transitions under Hund’s case (a), is complex, making simple connections between scattering and the underlying PES difficult. The V_{sum} potential is dominated by a repulsive core, whilst V_{diff} is much more attractive in nature (see Section 2.2). One may therefore assume that attractive collisions play an important part in spin-orbit changing transitions. However, Eyles *et al.* [39] have shown (for unoriented collisions) that there is little evidence for ‘far-side’ scattering (a typically attractive behaviour) and no evidence of glory scattering (also an attractive mechanism). This is also a consequence of the more ‘head-on’ collisions required to access the spin-orbit changing manifold, which do not typically (strongly) probe the attractive part of a potential. This implies that spin-orbit changing scattering is less strongly dependent on the attractive potential than first assumed. The Δj dependent oscillations in S_z (shown in Figure 6.2), which are known to arise from interference between repulsive collisions [95, 219], also suggest that the steric effect cannot be completely described by the largely attractive difference potential only.

The $R_0^{(1)}(\theta)$ moment also shows similarities between scattering on the spin-orbit conserving and changing manifolds. However, the moment is generally more positive for the spin-orbit changing transitions, implying a stronger general preference for collisions at the ‘N-end’ of the molecule (−z). The similarities in structure on the two manifolds suggests that similar arguments may be used to understand the differential steric effects on both manifolds.

The renormalised r -PDDCS provides information about the effect of bond orientation on the scattering process, independent of the overall scattering distribution. The renormalised

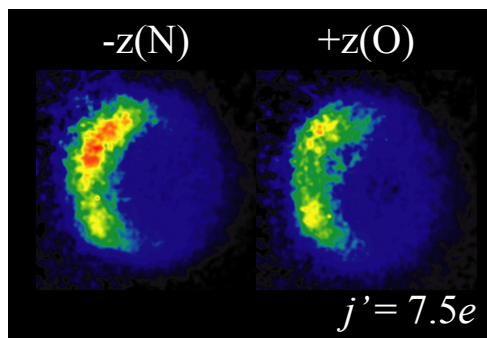


Figure 6.10: Experimental ion images for the bond orientation resolved spin-orbit conserving scattering of NO with O₂, resulting in the final rotational state, $|j'_{\text{NO}} = 7.5, \Omega' = 0.5, \epsilon' = +1, e\rangle$, averaged over all N'_{O_2} . The $-z(\text{N})$ and $+z(\text{O})$ orientations are shown on the left and right, respectively.

moment, therefore, depends only on the effects of bond orientation and allows comparisons between the two manifolds without the added complications of differences in the scattering distribution. At intermediate and large values of j' , the renormalised moments for scattering on the spin-orbit conserving and changing manifolds are very similar. As was clear from the $R_0^{(1)}(\theta)$ moment, the renormalised moment is generally more positive on the spin-orbit changing manifold than the corresponding moment on the conserving manifold, as discussed in terms of the integral steric effect above. Scattering into $j' = 2.5$, however, shows considerable differences between the two manifolds; the renormalised moment has many more peaks and troughs on the spin-orbit conserving than on the spin-orbit changing manifold, suggesting that orientation for these transitions depends more strongly on the orientation of the NO molecule before the collision. This is relatively simple to understand, since strong attractive effects (such as glory scattering and ℓ -type rainbows) are known to be observed on the spin-orbit conserving manifold, but are less important on the spin-orbit changing manifold [39]. That is, to access the spin-orbit changing manifold the spin-orbit energy must be overcome, this requires more ‘head-on’ collisions which do not typically probe the attractive part of the potential.

6.4 Future Work

The integral steric asymmetry for the scattering of NO(X) with diatomics, shown in Figure 6.2, is resolved in the final rotational state of the NO partner only. Consequently, S_z is averaged

Collision Partner	Scheme	via	λ / nm
O ₂ [24, 253, 356]	(2 + 1)	$3d\pi^3\Sigma_{1,g}^-$	~ 225
N ₂ [357, 358]	(2 + 2)	$a'\Pi_g$	283 – 285
N ₂ [359, 360]	(2 + 1)	$a''^1\Sigma_g^+$	~ 202
NO [361]	(1 + 1')	$A^2\Sigma^+$	$\sim 226/308$

Table 6.2: REMPI schemes for diatomic collision partners.

across all accessible final rotational states of the collision partner: j'_{N_2} and N'_{O_2} , for nitrogen and oxygen, respectively. To extract information about the correlations between the co-product pairs, $(j'_{\text{NO}}, j'_{\text{N}_2}/N'_{\text{O}_2})$, it is necessary to analyse the experimental ion images according to the ‘onion peeling’ method in Chapter 4. The extracted state-to-state resolved angular distributions can then be integrated to give the experimental ICS (see Equation (2.35)) for each orientation, and consequently S_z may be extracted. It is important to recognise that these are only relative cross-sections, which can only be compared within a single j'_{NO} state, since the experimental method does not produce information about the absolute cross-section.

Experimental ion images recorded with initial orientation of the NO bond axis along the $\pm z$ -axes are shown in Figure 6.10 for the $|j' = 7.5, \Omega' = 0.5, \epsilon' = +1, e\rangle \leftarrow |j = 0.5, \Omega = 0.5, E\rangle$ transition of NO with O₂. As described for the spin-orbit changing transitions of NO(X) scattering with Ar in Section 6.3, subtle differences are observed for orientation of the NO bond axis along $\pm z$ prior to the collision. The orientation largely manifests as the different relative intensities of the peaks in the two orientations, as observed for collisions with Ar [96, 97]. However, the resolution of the image is not good enough to allow extraction of the pair-correlated oriented DCSs and it is likely that experimental improvements, such as those discussed in Chapter 4, will be required to allow good enough resolution to experimentally measure these effects.

In an equivalent manner to the averaging of the collision partner rotation over all accessible states for a single j'_{NO} , one can imagine state selectively recording S_z as a function of the final rotational state of the collision partner (*i.e.* $j'_{\text{N}_2}/N'_{\text{O}_2}$), and averaging over all final NO rotational states. Such an experiment does not solve the problem of extracting information

about the relationship between the rotational states of NO and the collision partner, but provides complementary information to that obtained *via* detection of NO. REMPI schemes for the detection of both N₂ and O₂ are shown in Table 6.2. Note that the detection of both diatoms use single colour REMPI, and require more photons ($3h\nu$ or $4h\nu$) than for detection of NO ($2h\nu$). The REMPI scheme for O₂ is known to produce both O₂⁺ and O⁺ ions [253, 356], however the detector may be gated over the mass peak for O₂⁺ ($m/z = 32$) ensuring detection of only these ions. No strong evidence exists that the N⁺ ion is created in either of the schemes listed in Table 6.2.

6.5 Summary

In this chapter the results of orienting the NO bond axis parallel or antiparallel to the z -axis prior to the scattering event has been discussed. The first part of the chapter focused on the integral steric effect, S_z , observed for scattering of NO with diatomic collision partners, N₂ and O₂, in comparison to scattering with the atomic He, Ar, and Xe. Signatures of the NO molecule were observed in all systems (for both spin-orbit manifolds): Δj dependent oscillations due to the near homonuclearity of the molecule, and a strong preference for $-z(\text{N})$ scattering at high Δj due to a classical mechanism. Whilst the agreement between QM calculations and experimental data for collisions with Ar was very good, the agreement was much worse for collisions with N₂, suggesting that the 2D averaged PES used in calculations does not describe the interaction very well, potentially due to averaging over all N₂ orientations, the restriction of the complex to planarity, and treatment of the scattering as a ‘3-atom system’ (*cf.* NO + Ar). Comparison of the systems suggested that the PESs for collisions with both N₂ and O₂ are more isotropic and attractive in nature than for collisions with Ar.

The second part of the chapter focused on the bond orientation resolved spin-orbit changing collisions of NO(X) with Ar. The agreement between the experimental DCSs and QM calculations was relatively good, although, the particularly poor agreement for several intermediate states ($6 \leq \Delta j \leq 8$) was attributed to the overlap of the strong intensity over the

position where the LAB frame velocity is approximately zero. The bond orientation resolved DCSs showed that, as in the spin-orbit conserving case, the number of peaks observed in each orientation is the same. However the relative intensity of the peaks varies; this is particularly clear for states with $9 \leq \Delta j \leq 11$. The experimental renormalised $R_0^{(1)}(\theta)$ moments were also in good agreement with QM calculations. Comparison between the renormalised moments for scattering on the spin-orbit conserving and changing manifolds, showed that (except at very low Δj) the bond-axis dependence of scattering is very similar on both manifolds. Finally, future work was presented with the aim to further explore the ‘end-on’ steric effect in the scattering of NO with other diatoms.

Chapter 7

x -Axis Bond Orientation in the Collisions of NO(X) with Atoms

Orientation of the bond axis of a diatomic molecule parallel or antiparallel to the relative velocity vector (the scattering frame z -axis), which results in collisions at either ‘end’ of the diatom, has been relatively well studied; the majority of studies have focused on scattering with OH(X) [64, 91, 93, 94] or NO(X) [90, 92, 95–97, 134, 219, 230, 275, 362]. Such collisions were described in Chapter 6. Comparatively less work has been done relating to collisions at the ‘side’ of the diatom, with the majority of studies [328, 329, 333, 363] focusing on (‘head-on’ vs ‘side-on’) alignment rather than orientation. It is important to distinguish between these two types of polarisation [13]; whilst orientation refers to the bond axis lying either parallel or anti-parallel to a specific reference axis, alignment refers to the bond axis lying either parallel or perpendicular to the axis.

Figure 7.1 shows cartoons depicting alignment and orientation with respect to the z - and x -axes of the scattering frame. For orientation parallel/anti-parallel to the z - and x -axis collisions can be considered to be ‘end-on’ and ‘side-on’, respectively. The parallel orientation corresponds to collisions on one ‘end’/‘side’ of the molecule, and the anti-parallel orientation to collisions on the other ‘end’/‘side’. Alignment with respect to the x -axis, however, corresponds to ‘end-on’ *versus* ‘side-on’ collisions (and *vice versa* for alignment with respect to the z -axis). Alignment, thus distinguishes only whether the collision partner will be directed towards the ‘end’ or ‘side’ of the molecule, and not whether it will be directed towards the ‘N-end’ or ‘O-end’ in the case of the ‘end-on’ collisions (and correspondingly which ‘side’ in ‘side-on’

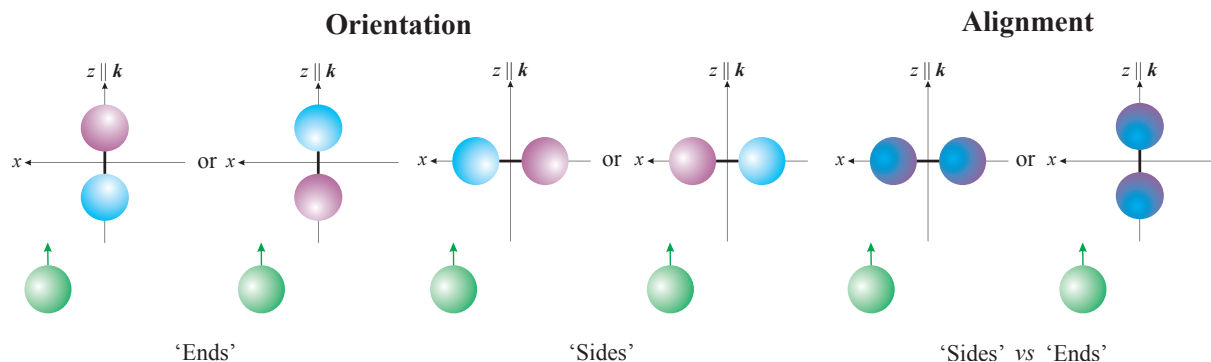


Figure 7.1: Cartoons depicting z -axis and x -axis orientation (left and center, respectively) and x -axis alignment (right) of a heteronuclear diatomic in the scattering frame.

collisions). In the ground rotational state of the NO molecule ($j = 0.5$) it is possible only to orient the bond axis and not align it [186].

Studies resulting in ‘side-on’ collisions have primarily probed the effect of alignment of the bond axis (*i.e.* ‘sides’ *versus* ‘ends’). Loesch *et al.* [329] studied the reactive asymmetry for the reaction of $\text{Sr} + \text{HF}(\nu = 1, j = 1) \rightarrow \text{SrF}(\nu', j') + \text{H}$, in which the bond axis of HF was aligned prior to the collision. The different alignments were shown to preferentially populate different final vibrational states. Subsequent studies [333] showed that the ‘side-on’ geometry was favoured at lower collision energies, and the ‘end-on’ geometry at higher energies. Similar studies on the $\text{Li} + \text{HF}(\nu = 1, j = 1, m = 0) \rightarrow \text{LiF} + \text{H}$ system [328], observed a preference for collisions at the ‘side’ of the molecule (side-on:end-on 1.76:1). The reaction $\text{KRb} + \text{KRb} \rightarrow \text{K}_2 + \text{Rb}_2$ has been studied by de Miranda *et al.* [363] in the ‘side-by-side’ geometry by use of an optical lattice trap to confine the polar molecules in a ‘quasi-two-dimensional’ geometry. A strong suppression of the reaction (by approximately two orders of magnitude) of the reaction was observed in this geometry when compared to the unpolarised case.

In this chapter, the effects of orientation of the NO bond axis along the $\pm x$ -axis on the inelastic scattering of NO with the rare gases will be discussed. Firstly, mechanisms of near- and far-side scattering with respect to ‘side-on’ collisions will be examined. This will be followed by a brief description of the experimental and theoretical methods used. The experimental integral and differential steric effects will then be discussed in terms of the integral steric asymmetry, the bond orientation resolved DCSs and the r -PDDCSs. The dependence of the bond orientation

resolved scattering as a function of the strength of the orientation field will then be discussed. Features observed in the orientation resolved DCSs and *r*-PDDCSs will be rationalised using QCT and QM calculations. Comparison between orientation along the $\pm x$ - and $\pm z$ -axes will then be given, including discussion of the static electric field direction which maximises the DCS. Finally, future work will be discussed.

7.1 Scattering Mechanisms: Near- and Far-side Scattering

In the case of orientation along the *z*-axis, discussed in Chapter 6, the two bond axis orientations, $+z$ and $-z$, could be related directly to approach of the collision partner at the ‘O-end’ and ‘N-end’ of the molecule, respectively. That is, only a single axis need be specified to define the two scattering geometries. The situation is somewhat more subtle when considering orientation along the $\pm x$ -axis, as orientation along a given direction does not correspond directly to scattering off a specific region of the NO molecule. In order for the steric effect to be non-zero it is necessary, not only to specify the initial relative velocity vector, $\mathbf{k}$, but also the final relative velocity vector, $\mathbf{k}'$; *i.e.* to define the $\mathbf{k}\mathbf{k}'$ (scattering) plane which defines the direction of the *x*-axis.

The specification of the scattering plane allows resolution of the two *x*-axis orientations. However, unlike in ‘end-on’ scattering, near-side and far-side scattering give rise to preferences for scattering at opposite ends of the NO molecule for a single bond axis orientation. Figure 7.2 shows a schematic of near- and far-side scattering in both the $+x$ and $-x$ orientations. Near-side scattering describes trajectories which scatter directly from the side of the molecule that they approach; this type of scattering may be either attractive or repulsive in nature. Meanwhile, far-side scattering occurs when the collision partner interacts with the attractive part of the potential and is drawn around the end of the molecule onto its far side (relative to the initial direction of approach). This type of scattering only occurs for collisions which probe the attractive part of the PES, and only for the highest partial waves (and correspondingly large classical impact parameters).

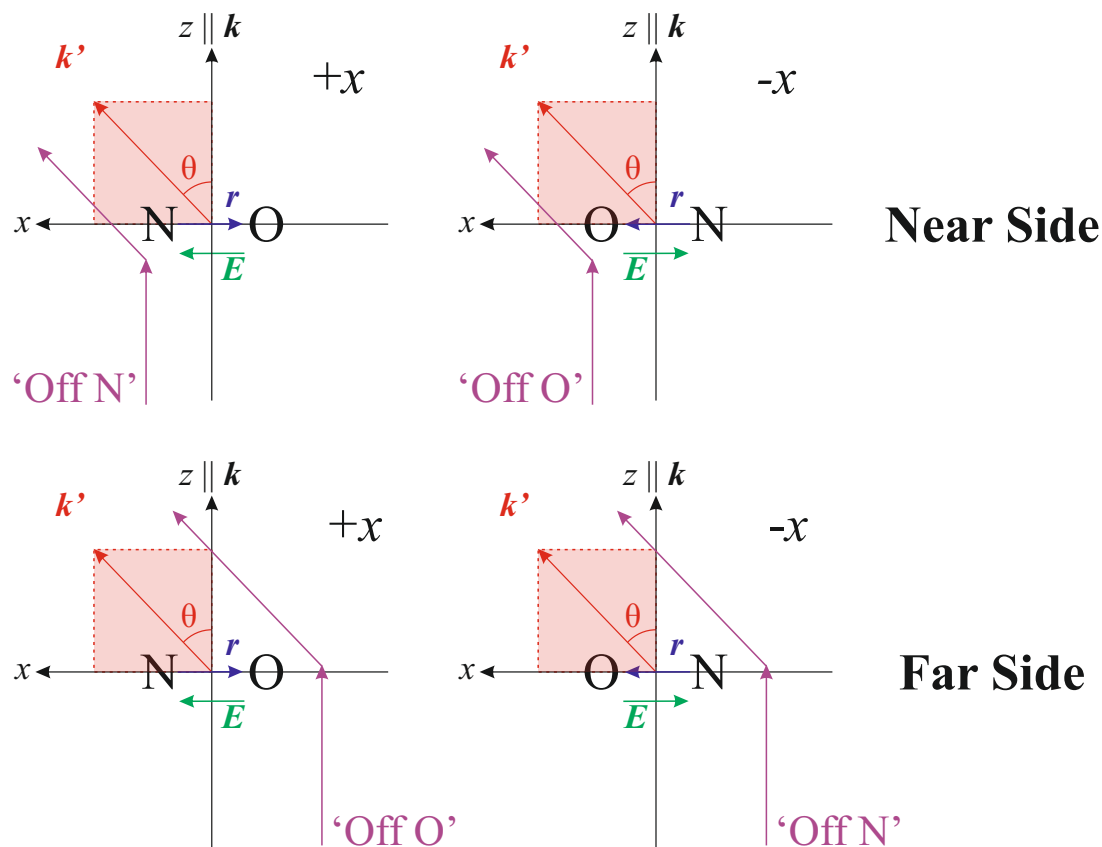


Figure 7.2: Schematic showing near-side (top) and far-side (bottom) scattering in the $+x$ (left) and $-x$ (right) orientations in the scattering (k, k') frame.

For the majority of final rotational states accessed by collisions between NO and Ar, scattering is largely repulsive in nature, and it may be assumed that very little far-side scattering occurs. Therefore, $+x$ and $-x$ collisions describe scattering from the ‘N-end’ and ‘O-end’ of the molecule, respectively. It is only for transitions into the very lowest final rotational states that far-side collisions become an important mechanism for scattering (which will be discussed in detail in Chapter 8). If the scattering were purely far-side in nature then the $+x$ - and $-x$ -orientations would correspond to scattering off the ‘O-end’ and ‘N-end’ of the molecule, respectively. It should be noted that the transitions for which this occurs depends on how attractive the PES is for the system of interest. Unless otherwise stated, the $+x$ - and $-x$ -orientations will be considered to denote (near-side) scattering off the ‘N-end’ and ‘O-end’ of the molecule, respectively. It is important to remember that this is a simplified picture; repulsive collisions may lead to (near-side) scattering both ‘off N’ and ‘off O’ in both orientations.

7.2 Experimental and Theoretical Methods

The experimental apparatus used to measure ‘side-on’ (x -axis) collisions was discussed in detail in Chapters 3 and 5. All the experimental data were recorded and analysed using the methods discussed in Section 5.4.2, at the experimental collision energy of 651 cm^{-1} . Data were recorded for the $|j', \Omega' = 0.5, \varepsilon' = +1, e\rangle \leftarrow |j = 0.5, \Omega = 0.5, E\rangle$ transitions of the scattering between NO and Ar. Since, at the experimental field strength, transitions into both final Λ -doublets are approximately equivalent [96, 97], only the e final Λ doublet states were recorded. All data were recorded with vertical (V) polarisation (*i.e.* polarisation parallel to the time-of-flight axis) of the excitation laser using a Rochon polariser, on the $Q_{21} + R_{11}$ mixed branch. Extraction of the r -PDDCSs, orientation resolved DCSs and integral steric asymmetry from the recorded ion images was done according to the methods presented in Section 5.4.2, accounting for the effect of collision induced polarisation by applying the relevant kinematic apse correction (see Section 3.5.2) during the analysis.

CC QM and QCT calculations were undertaken according to the methods described in Chapter 2 and extended in Chapter 5 to account for initial bond-axis orientation. QM calculations were performed on the V_{sum} and V_{diff} PESs of Alexander [175, 195] (described in Section 2.2), at the mean experimental collision energy ($E_{\text{coll}} = 651\text{ cm}^{-1}$), using the HIBRIDON suite of codes [226]. Rotational levels up to $j' = 20.5$, both Λ -doublet levels ($\varepsilon = \pm 1$) and spin-orbit manifolds ($\Omega = 0.5, 1.5$) were included in the scattering wave function. To ensure convergence of the calculations, the maximal partial wave was set as $J = 180.5$, corresponding to the classical impact parameter $b = 7.0\text{ \AA}$. Observables were calculated using the methodologies presented in Section 5.3.2. QCT calculations were run using approximately 1×10^6 trajectories on the V_{sum} potential, as described in Section 2.5.1, and the observables calculated using the methods outlined in Section 5.3.1. Both CC QM and QCT calculations were run at several orientation field strengths, corresponding to different (field dependent) mixing parameters, α and β (see Equation (5.6)); at the infinite field $|\alpha_{\infty}| = |\beta_{\infty}| = 1.0$, whilst

at the experimental field (9.2 kV cm^{-1}) $|\alpha_{\text{expt}}| = 0.64$ and $|\beta_{\text{expt}}| = 1.26$. Remember that in the absence of a field $|\alpha| = 0$ and $|\beta| = \sqrt{2}$, and the field free f Λ -doublet is recovered.

Experimentally, there is a distribution of collision energies; to allow comparison between the QM calculations and experimental data (presented in Section 7.3.2), it is therefore necessary to account for the collision energy spread. The QM calculations were performed (as described above) over a range of collision energies between $E_{\text{coll}} = 530 \text{ cm}^{-1}$ and $E_{\text{coll}} = 740 \text{ cm}^{-1}$, with a spacing of $E_{\text{coll}} = 30 \text{ cm}^{-1}$. The QM observables were then weighted according to a Gaussian energy distribution with a FWHM of 35 cm^{-1} and a mean value of $E_{\text{coll}} = 651 \text{ cm}^{-1}$.

QCT: Accounting for the Initial Bond Axis Distribution

The methods for calculating the QCT r -PDDCSs and bond orientation resolved DCSs implicitly accounts for the initial bond axis distribution (see Chapters 2 and 5). When extracting other information from the QCT trajectories, such as the deflection function (the scattering angle as a function of the impact parameter) or position of closest approach, it is necessary to account for the initial distribution of the bond axis which occurs experimentally for any given static field direction; this requires expression of the LAB frame bond axis distribution in the scattering frame.

Since the bond-axis, $\mathbf{r}$, is parallel to $\boldsymbol{\mu}$, Equation (5.14) may be rewritten

$$P(\Theta_{rE}) = 1 - |\alpha\beta| P_1(\cos \Theta_{rE}) , \quad (7.1)$$

where Θ_{rE} is the angle between the bond axis, $\mathbf{r}$, and the static electric field, $\mathbf{E}$, and $\alpha\beta$ are the field dependent mixing parameters in Equation (5.6). The bond axis distribution in the scattering frame may then be calculated using the spherical harmonic addition theorem [186]

$$P_{l=1}(\cos \theta_{ij}) = \frac{4\pi}{2l+1} \sum_{m=-1}^1 Y_{lm}^*(\theta_r, \phi_r) Y_{lm}(\theta_E, \phi_E) , \quad (7.2)$$

where the angles (θ_r, ϕ_r) and (θ_E, ϕ_E) are the angles between the scattering frame z -axis and $\mathbf{r}$ and $\mathbf{E}$, respectively. Expanding Equation (7.2), with $l = 1$ and $m = \pm 1, 0$, gives

$$P_1(\cos \Theta_{rE}) = \cos \theta_r \cos \theta_E + \sin \theta_r \sin \theta_E \cos(\phi_r - \phi_E), \quad (7.3)$$

which may be substituted into Equation (7.1) and used to weight each QCT trajectory by the probability of the initial bond axis orientation (θ_r, ϕ_r) , for any specific orientation field direction (θ_E, ϕ_E) , when calculating QCT deflection functions or positions of closest approach.

7.3 Experimental Steric Effects in NO + Ar Scattering

7.3.1 The Integral Steric Effect

In much the same way as for orientation along the $\pm z$ -axis (presented in Chapter 6), the steric effect for orientation of the NO bond axis along the $\pm x$ -axis can be described by the integral steric asymmetry, according to

$$S_x = \frac{\sigma_{-x} - \sigma_{+x}}{\sigma_{-x} + \sigma_{+x}}, \quad (7.4)$$

where $\sigma_{\pm x}$ are the ICSs for scattering in the $\pm x$ -orientations. For x -axis orientation, S_x is directly proportional to the renormalised $r_1^{(1)}$ moment (although the sign is inverted), according to Equation (5.65). A positive value of S_x corresponds to a preference for scattering in the $-x$ configuration, that is scattering ‘off O’ for near-side scattering or scattering ‘off N’ for far-side scattering. Meanwhile, a negative value of S_x corresponds to a preference for $+x$ scattering; scattering ‘off N’ and ‘off O’ for near- and far-side scattering, respectively.

The experimental integral steric asymmetry for the (spin-orbit conserving) collision of NO with Ar is shown in Figure 7.3, alongside CC QM and QCT calculations. The agreement between the experimental and QM values is very good, however, agreement with the QCT calculations is poor except at high values of Δj . Such collisions are repulsive (near-side) in nature, and therefore a preference for $+x$ scattering corresponds to a preference for scattering off of the ‘N-end’ of the molecule. This is consistent with a classical mechanism dominating

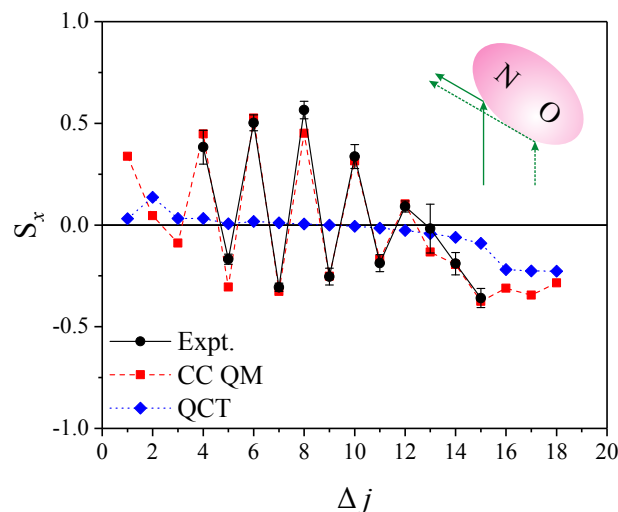


Figure 7.3: x -axis integral steric asymmetry, S_x , for the spin-orbit conserving collisions of NO with Ar into the final e Λ -doublet. Experimental, CC QM and QCT data are shown by black lines (with circles), red dashed lines (with squares), and blue dotted lines (with diamonds), respectively. Errors were propagated from the errors in the experimental ‘emphr-PDDCSs in Figures 7.6 and 7.7.

for high RET collisions, which may be rationalised in a very similar manner to that for z -axis orientation (as discussed in Chapter 6): Aoiz *et al.* [181] have shown that the asymmetry of the V_{sum} potential is such that trajectories which approach the ‘N-end’ of the diatom may penetrate further into the repulsive part of the potential, resulting in more forward peaked DCSs, and consequently larger ICSs when compared to scattering from the ‘O-end’ of the molecule.

In both the experimental and QM data, Δj dependent oscillations are observed. For ‘end-on’ collisions these oscillations have been shown to arise from the near-homonuclearity of the NO molecule, which results in interference between trajectories scattering from the ‘N-end’ and ‘O-end’ of the molecule. This was first demonstrated by Stolte *et al.* [179, 275] using the Quasi quantum treatment (QQT), which treats the NO molecule as a hard shell (and consequently as a completely repulsive system). It is perhaps surprising that these oscillations are observed in S_x , where the collision partner approaches perpendicular to the bond axis. However, it is possible to envisage a pair of trajectories scattering into the same final angle but impinging on different ‘ends’ of the NO molecule. A cartoon of such a process is shown in Figure 7.3. Interference between these pathways gives rise to the Δj dependent oscillations in S_x in much the same way as for S_z . Further insight into the integral steric asymmetry may be obtained by comparing scattering in the x - and z -orientations; this will be discussed in Section 7.6.

7.3.2 The Differential Steric Effect

Whilst the integral steric effect provides information about the overall preference for scattering in a specific geometry, further insight is gained by considering the angular scattering distribution, *i.e.* the differential steric effect. Figure 7.4 shows the experimental ion images for the $\pm x$ -axis bond orientation resolved $|j', \Omega' = 0.5, \epsilon' = +1, e\rangle \leftarrow |j = 0.5, \Omega = 0.5, E\rangle$ transitions of NO with Ar. The colour scale for both the $\pm x$ -orientations is kept the same, as to retain any differences in intensity between the two orientations. Some differences between the $+x$ and $-x$ ion images are observed; multiple peaks are present in the $+x$ -orientation for odd Δj , but only single peaks for even Δj . A single peak is observed for all states in the $-x$ -orientation. At high $\Delta j (= 15)$ the ion images become very backwards scattered and a single peak is observed for both the $\pm x$ -orientations; this is consistent with the classical mechanism observed at high Δj in S_x , and will be discussed in more detail in Section 7.5. For all rotational states the $+x$ -orientation is typically more forwards scattered than the $-x$ -orientation; this will also be returned to in Section 7.5.

The data analysis method in Section 5.4.2 uses the relationship between the summed and difference ion images with the $R_0^{(0)}(\theta)$ and $R_1^{(1)}(\theta)$ moments, respectively. The experimental summed and difference ion images are shown in Figure 7.4, alongside the fitted images resulting from the data analysis process. The difference ion images are shown on a scale in which red and blue correspond to negative (preference for $+x$) and positive (preference for $-x$) intensity, respectively; black represents zero intensity. The summed ion images (which are proportional to the $R_0^{(0)}(\theta)$ moment), show similar trends to the orientation resolved images. As one would expect, they appear intermediate between the two images, with a weak double peaked structure observed for odd Δj transitions. Unlike the $\pm x$ ion images, the summed images would be symmetric about k' if the instrument function (described in Section 3.5.1) was accounted for. The fits to the experimental images are good, reproducing all of the observed features.

The fits to the experimental difference ion images, which are proportional to the $R_1^{(1)}(\theta)$ moment, also show good agreement; reproducing all of the experimentally observed features.

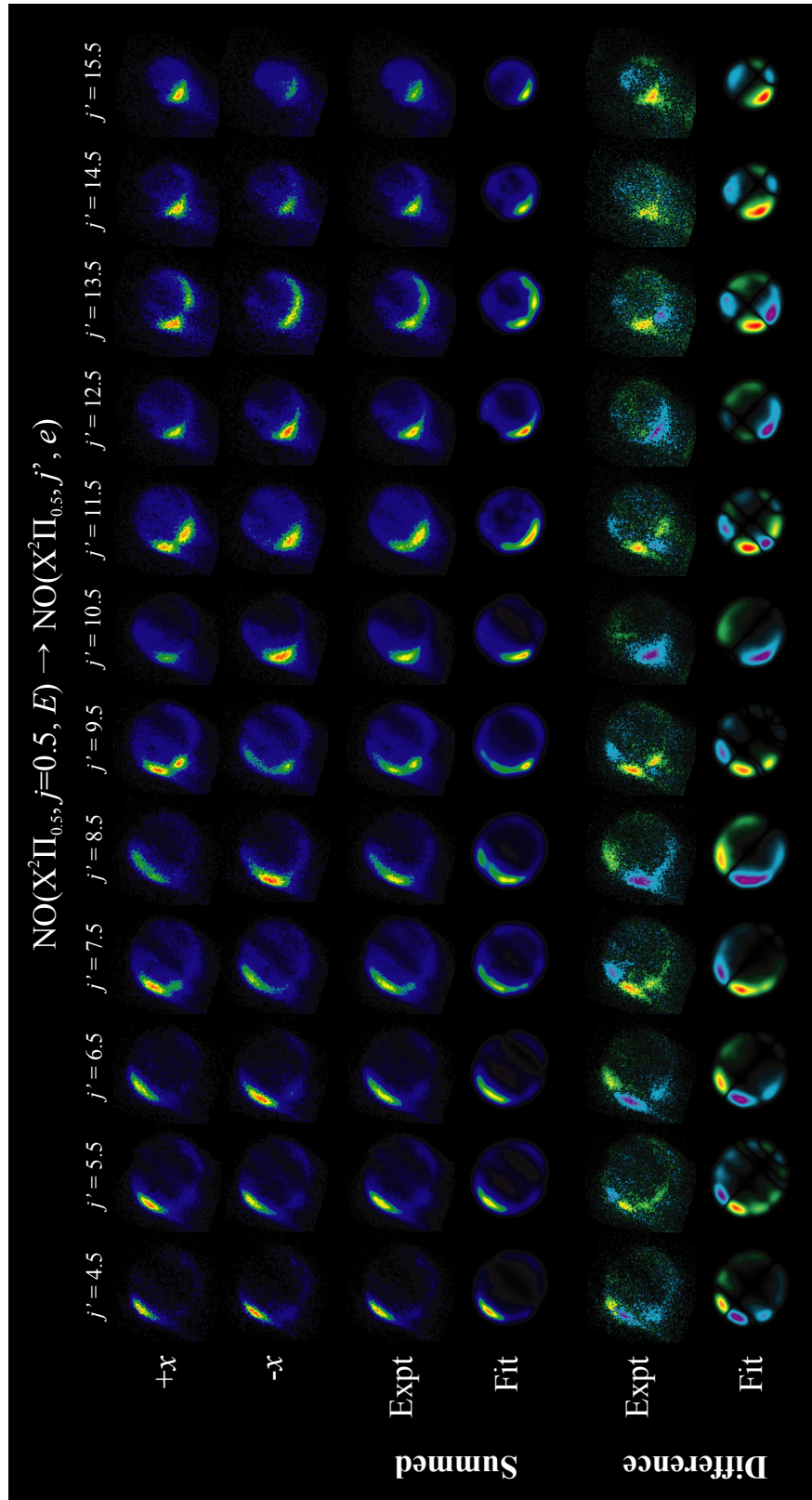


Figure 7.4: Experimental ion images for the bond orientation resolved spin-orbit conserving collisions of NO with Ar, into the final rotational states defined by $|j', \Omega' = 0.5, \epsilon' = +1, e\rangle$, for $j' = 4.5$ to 15.5 (from left to right). The $+x$ and $-x$ images are shown in panels 1 and 2, respectively. The experimental summed and difference images are shown in panels 3 and 5, respectively, and the corresponding fitted images in panels 4 and 6, respectively.

A node in both the experimental and fitted ion images is observed along the center-line of the image (along k), corresponding to scattering along the time-of-flight (TOF) axis (*i.e.* orientation along the y -axis). Remember that the $\pm x$ labels on the experimental images denote the orientation on the slow side of the image only, and that scattering on the fast side of the image corresponds to $\mp x$ scattering (see Section 5.4.2); this accounts for the inversion of the sign about the node in the difference image. Since the slow side of the image is much more intense than the fast side, the following discussion will focus on the orientation corresponding to scattering into the slow side of the image. As observed in the $\pm x$ images, a propensity is observed for odd and even Δj , which is particularly prominent for intermediate Δj . For even Δj , only a single strong peak is observed in the difference image, with positive intensity corresponding to a preference for the $-x$ orientation. Meanwhile, for odd values of Δj a double peak is observed in the difference image, with negative intensity (a $+x$ preference). For high values of Δj , as for the orientation resolved ion images, the propensity dissipates and a strong preference for $+x$ scattering is observed in the backwards direction, consistent with the classical mechanism discussed in terms of the integral effect in Section 7.3.1.

Orientation Resolved Differential Cross Sections

The experimental DCSs extracted from the ion images in Figure 7.4 are shown in Figure 7.5, alongside the CC QM DCSs (which have been averaged over the experimental Gaussian distribution of collision energies as described in Section 7.2). In general, the agreement between the QM and experimental data is good, and the majority of the calculated features are observed in the experimental data. Note the shape of the experimental data in the forwards scattered regions of the DCSs for the $-x$ -orientation with $5 \leq \Delta j \leq 9$: whilst the experimental data increases for low angle scattering, it is not peaked in nature and is likely due to the resolution ($\sim 15^\circ - 20^\circ$) of the experimental data. It should be noted that the relatively poor agreement for $j' = 9.5$ and 10.5 is due to the main intensity in the image overlapping the LAB origin, where the NO molecules have zero velocity in the LAB frame. Due to their low velocity, the NO molecules remain in the detection region longer than molecules elsewhere. As such, any

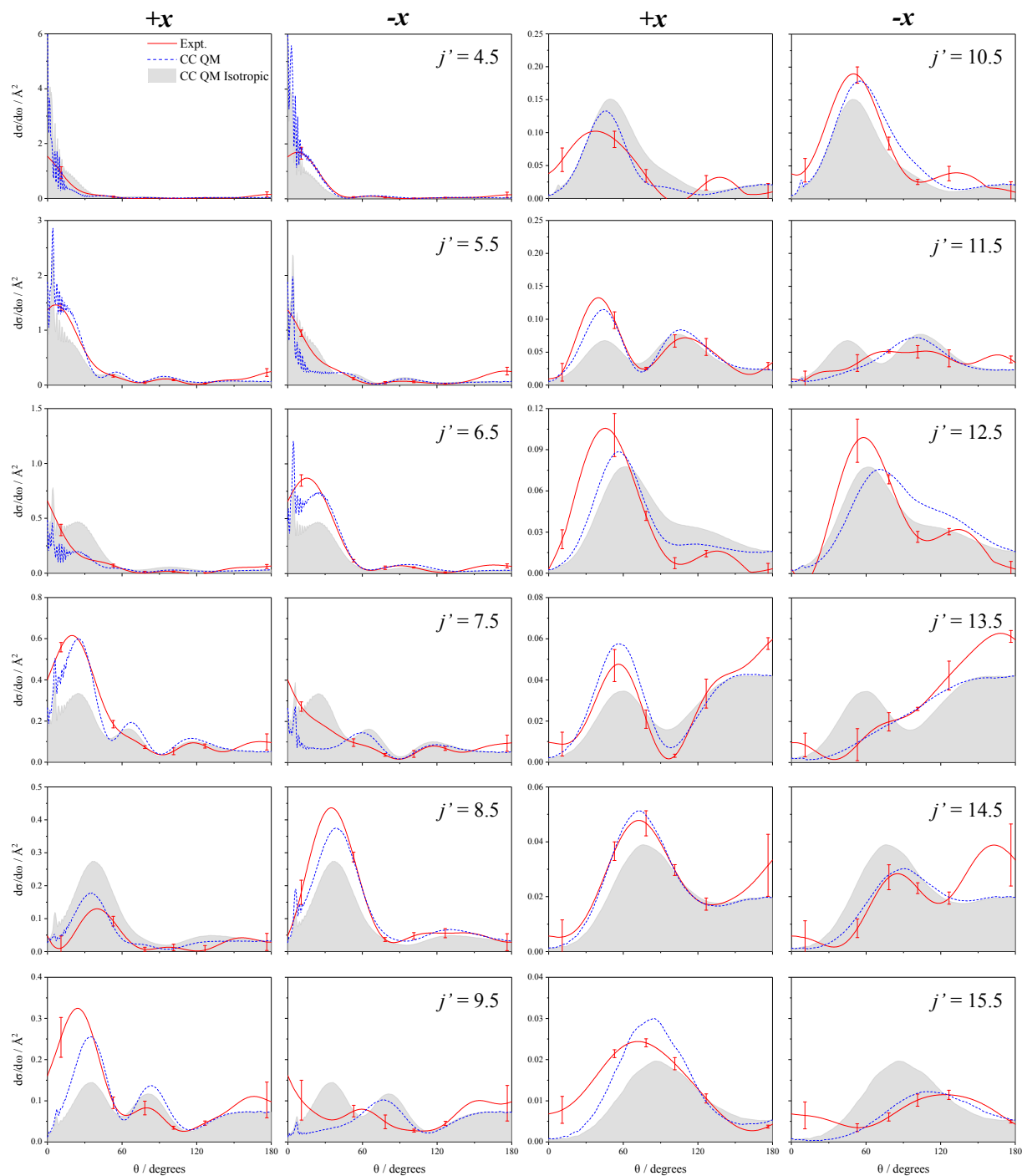


Figure 7.5: Experimental (red lines) and QM (blue dashed lines) x -axis oriented DCSs for the collisions of NO with Ar, into the final rotational states defined by $|j', \Omega' = 0.5, \epsilon' = +1, e\rangle$. Collisions in the $+x$ - and $-x$ -orientations are shown in panels 1/3 and 2/4, respectively. The QM (field dependent) isotropic DCS is shaded in gray. Error bars are propagated from the errors in the experimental r -PDDCSs in Figures 7.6 and 7.7. QM data have been averaged over a Gaussian distribution of collision energies with a FWHM of 35 cm^{-1} .

minor errors in the LAB frame detection efficiency factor (see Section 3.5.1), will lead to a poor representation in this region, and consequently a poor fit.

The oscillation in the preference for $+x$ (odd Δj) and $-x$ (even Δj) scattering, observed in the ion images and integral steric effect, is also observed in the DCSs, although for some states it is difficult to visualise due to the dependence on the scattering angle. The ‘isotropic’ (field dependent) DCS lies between the $\pm x$ -orientation resolved DCSs; this is expected since the oriented DCSs are essentially a deviation from the isotropic DCS (see Equation (5.56)). As in the experimental ion images, a double peak is observed for odd Δj in the $+x$ -orientation, whilst a single peak is observed for even Δj . A single peak is observed for all states in the $-x$ -orientation. This effect is also observed for low Δj transitions, although the propensity is more subtle (as the integral steric effect is relatively small in this region). For states with odd Δj the experimental data shows a strong preference for forwards scattering in the $+x$ -orientation, which is almost completely suppressed in the $-x$ -orientation; this is in good agreement with the QM calculations. It is not immediately apparent why this ‘peak propensity’ occurs; a detailed analysis will be given in Section 7.5.

Bond Orientation Moments

The experimental and CC QM bond orientation moments, $R_1^{(1)}(\theta)$ and $R_0^{(0)}(\theta)$, are shown in Figures 7.6 and 7.7 for even and odd Δj transitions, respectively. The agreement is generally good, with the majority of the features in the r -PDDCSs reproduced. However, the states for which agreement was poor in the DCSs also show relatively poorer agreement in the r -PDDCS (for the same region). Remember that during the experimental analysis (Section 5.4.2) the bond orientation moments are extracted from the summed and difference images, and the DCS subsequently calculated. As such, any errors in the experimental r -PDDCS will be manifested in the DCSs (in Figure 7.5). Note that the second peak in the $R_0^{(0)}(\theta)$ moment for $\Delta j = 7$ and $\Delta j = 9$ appears only as a shoulder on the more forwards scattered peak; this is likely due to the experimental resolution and small errors in the instrument function.

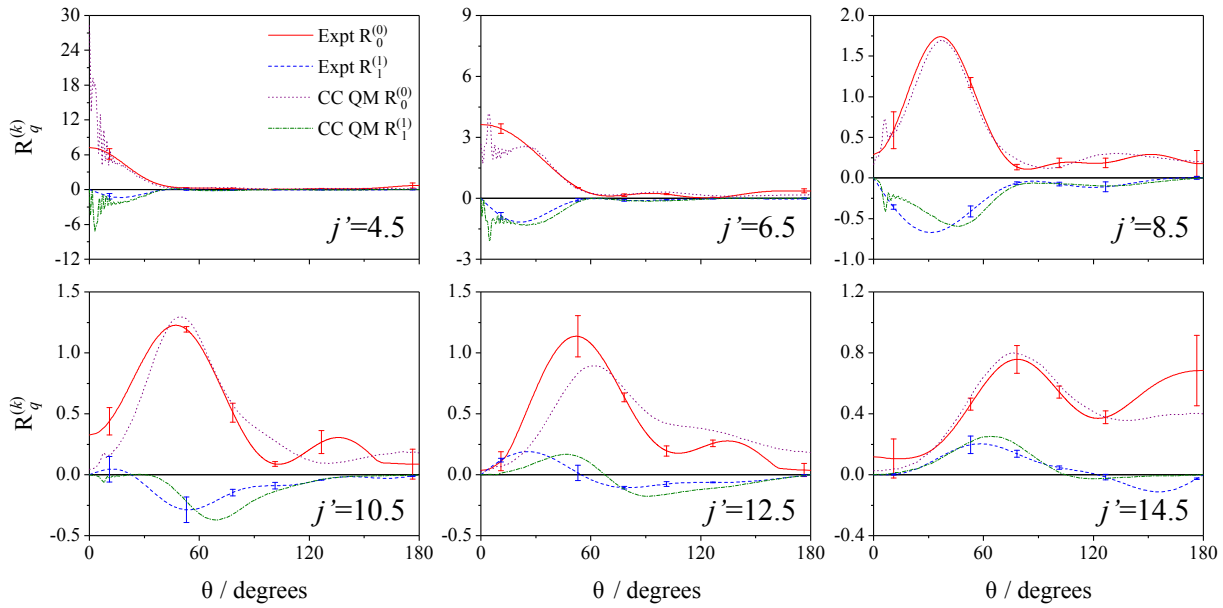


Figure 7.6: Experimental and QM r -PDDCSs for the collisions of NO with Ar, into the final rotational states defined by $|j', \Omega' = 0.5, \epsilon' = +1, e\rangle$, for even Δj . The experimental $R_0^{(0)}(\theta)$ and $R_1^{(1)}(\theta)$ moments are shown by red and blue (dashed) lines, respectively. The error bars were calculated as the standard deviation of analysing the slow, fast and whole experimental image. The CC QM $R_0^{(0)}(\theta)$ and $R_1^{(1)}(\theta)$ moments are shown by purple (dotted) lines and green (dashed-dotted) lines, respectively. The QM data has been averaged over a Gaussian distribution of collision energies with a FWHM of 35 cm^{-1} .

It is worth remembering that the $R_0^{(0)}(\theta)$ moment depends directly on a mixture of the field free Λ -doublets and consequently, α and β (see Equation (5.38a)). Therefore, the $R_0^{(0)}(\theta)$ moment depends on the strength of the electric field employed for orientation of the NO bond axis. Much as in the case of the bond orientation resolved DCSs a double peak is observed for odd Δj transitions but only a single peak for even Δj transitions.

The $R_1^{(1)}(\theta)$ moment is independent of the mixing parameters, and consequently the moment does not depend on the strength of the orientation field (as opposed to the renormalised moment, $R_1^{(1)}(\theta)/R_0^{(0)}(\theta)$, which is field dependent). Rather, the moment provides information about the preference for scattering into a specific angle as a function of the initial orientation of the NO bond axis along the $\pm x$ -axis. Positive and negative values of the moment correspond to a preference for the $+x$ - and $-x$ -orientations, respectively. An oscillations in the (average) sign of the moment is observed (positive and negative for even and odd Δj , respectively); this corresponds to the Δj dependent oscillations in S_x observed in Section 7.3.1, although the sign is inverted (see Equation (5.65)). The $R_1^{(1)}(\theta)$ moment has a (generally) larger magnitude in the

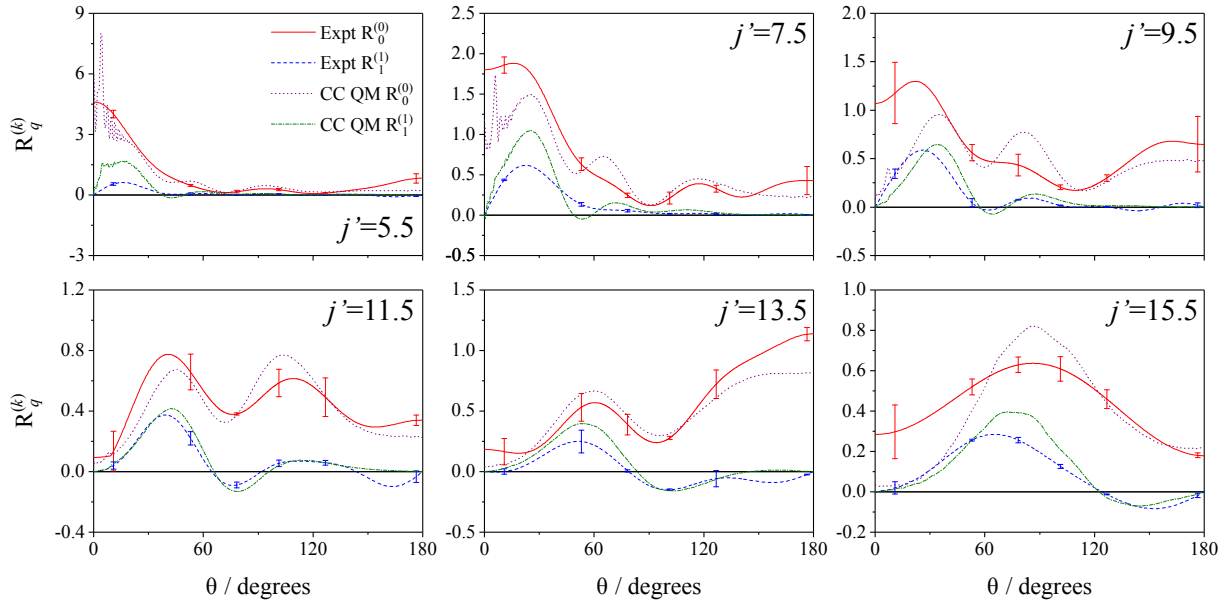


Figure 7.7: Experimental and QM r -PDDCSs for the collisions of NO with Ar, into the final rotational states defined by $|j', \Omega' = 0.5, \varepsilon' = +1, e\rangle$, for odd Δj . The experimental $R_0^{(0)}(\theta)$ and $R_1^{(1)}(\theta)$ moments are shown by red and blue (dashed) lines, respectively. The error bars were calculated as the standard deviation of analysing the slow, fast and whole experimental image. The CC QM $R_0^{(0)}(\theta)$ and $R_1^{(1)}(\theta)$ moments are shown by purple (dotted) lines and green (dashed-dotted) lines, respectively. The QM data has been averaged over a Gaussian distribution of collision energies with a FWHM of 35 cm^{-1} .

forwards scattered direction ($\theta < 90^\circ$) than for scattering into higher angles, this is concordant with the large steric effect in the forwards scattered region of the orientation resolved DCSs, which will be discussed further in Section 7.5.

7.4 Field Strength Dependence

In the presence of a static electric field, the initial wave function is a superposition of the field free e and f states according to [219, 230]

$$|jm_E \bar{\Omega} E\rangle = \frac{1}{\sqrt{2}} [\alpha |jm_E \bar{\Omega} e\rangle + \beta |jm_E \bar{\Omega} f\rangle] , \quad (7.5)$$

where α and β are field dependent mixing parameters in Equation (5.6). Since the magnitude of the mixing parameters depends on the field strength applied, the ratio of the initial e and f states in the superposition also depends on the field strength. As such, it is informative to consider how the experimental field (9.2 kV cm^{-1}), in which $|\alpha| = 0.64$ and $|\beta| = 1.26$, varies from an

infinite field where the superposition contains equal contributions from both the initial e and f states (*i.e.* $|\alpha| = |\beta| = 1$).

7.4.1 The Integral Steric Effect

The CC QM values of S_x for the scattering of NO with Ar into the final e state are shown as a function of the electric (orientation) field in Figure 7.8. Remember that when no field is applied $S_x = 0$ as the field free $f \rightarrow e$ state is recovered. As the field strength tends towards zero the magnitude of S_x becomes smaller as the bond axis distribution, see Equation (5.4), becomes more isotropic. At the highest field strengths S_x is approximately equivalent to the infinite field case, although the agreement is better for even Δj than odd. The difference between S_x at infinite field and the experimental field can be examined quantitatively by calculating the normalised difference, $(S_x^\infty - S_x^{\text{expt}}) / (S_x^\infty + S_x^{\text{expt}})$. A positive value corresponds to $S_x^\infty > S_x^{\text{expt}}$, and a negative value *vice versa*. The average normalised difference across all states is $\sim 8\%$; for scattering with even and odd Δj the value is $\sim 2\%$ and $\sim 13\%$, respectively. The largest differences are observed at low and high Δj .

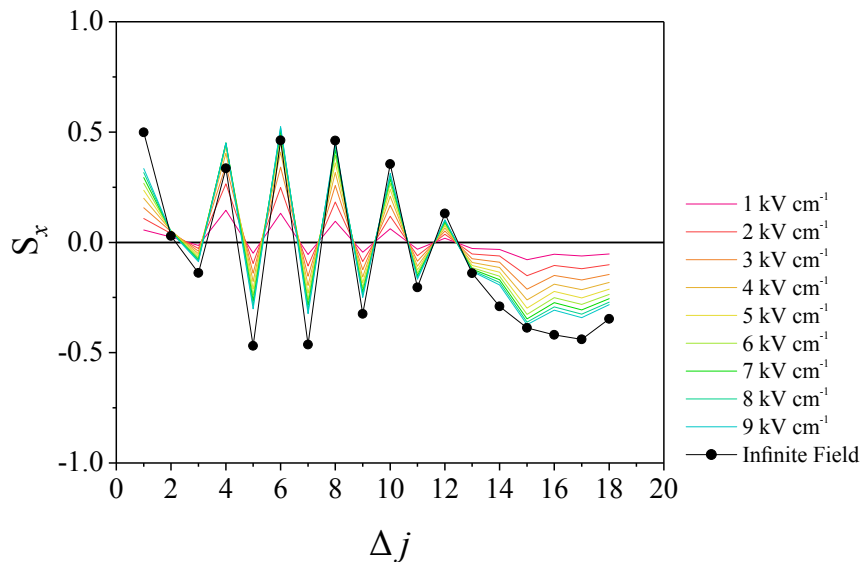


Figure 7.8: Effect of electric (orientation) field strength on the x -axis integral steric asymmetry for the collision of NO with Ar into the final states defined by $|j', \Omega' = 0.5, \epsilon' = +1, e\rangle$. S_x at the infinite field is shown by a black line with circles. A range of electric field strengths is shown from 1 kV cm^{-1} (red) to 9 kV cm^{-1} (blue) in steps of 1 kV cm^{-1} .

7.4.2 The Differential Steric Effect

Figure 7.9 shows CC QM x -axis orientation resolved DCSs at the experimental and infinite fields for the scattering of NO with Ar into the final $|j', \Omega' = 0.5, \epsilon'\rangle$ states where $j' = 7.5$ to 12.5. Note that these (intermediate) rotational states have been chosen for clarity, but the trend prevails for all but very high Δj where the DCSs are very backwards scattered in nature. Only the final e state is plotted at infinite field, as scattering into either Λ -doublet is approximately equivalent in this limit. At infinite field, where there is a 1 : 1 superposition of the initial Λ -doublet states in Equation (7.5), there are two major trends observed in the DCSs. Firstly, a Δj dependent oscillations is observed in the overall preference for scattering in the $+x$ -orientation for odd Δj and the $-x$ -orientation for even Δj . This feature corresponds to the oscillation in the integral steric effect observed in Section 7.3.1 for intermediate values of Δj . The second trend is the presence of multiple peaks in the $+x$ -orientation, whilst only a single peak is observed in the $-x$ orientation. Note that the lowest scattering angle peak in the $+x$ -orientation is more forward scattered than the single peak in the $-x$ -orientation (*i.e* for $j' = 11.5$ at $\theta \approx 45^\circ$ and 67° , respectively). This trend is observed for all states, and its origin will be discussed in more detail in Section 7.5.1.

Consider now the CC QM DCSs calculated at the experimental field; as in the infinite field case a single peak is observed in the $-x$ -orientation for all states; however, the multiple peaks in the $+x$ -orientation are no longer observed for all states. For scattering into the e final state, multiple peaks are observed in the $+x$ DCS for odd Δj transitions, whilst only a single peak is observed for even Δj transitions. For scattering into the final f state the trend is reversed; multiple peaks are observed for even Δj , whilst a single peak is observed for odd Δj .

The trends observed in the experimental field may be rationalised by considering the relative magnitude of the mixing parameters in the superposition in Equation (7.5). As the strength of the field tends to zero, the DCSs for both the $+x$ - and $-x$ -orientation evolve into those observed in the field free state. That is, for transitions to the final e Λ -doublet the $f \rightarrow e$ DCS is recovered. In the field free (unoriented) case it is well known that parity conserving

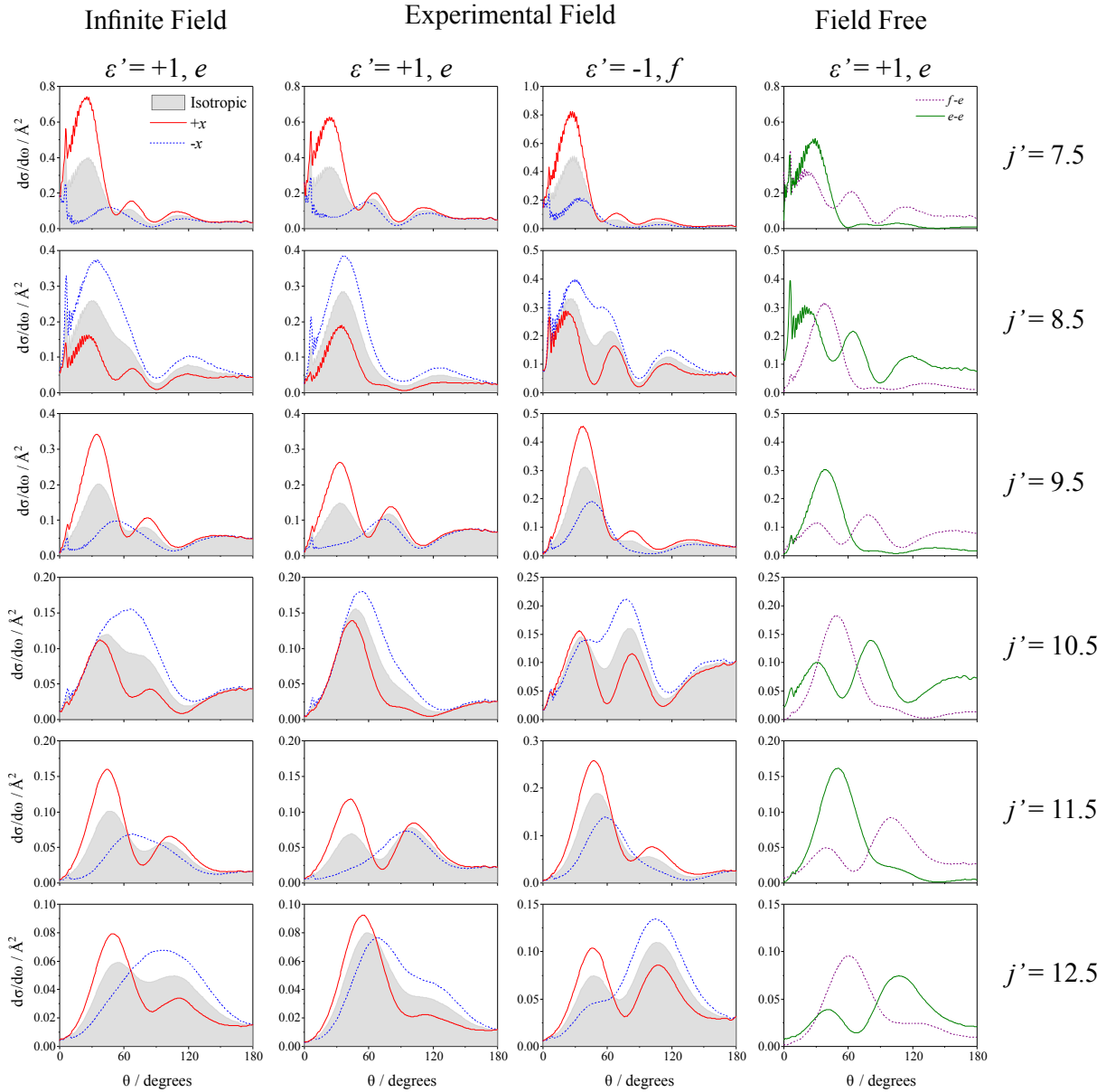


Figure 7.9: CC QM x -axis bond orientation resolved DCSs for the scattering of NO with Ar into final states with $|j', \Omega' = 0.5, \epsilon'\rangle$, for $j' = 7.5$ to 12.5 (from top to bottom). The far left panel shows the DCSs at infinite electric field for scattering into the final e Λ -doublet. The middle panels show the DCSs at the experimental field for transitions into both the e and f final states in the middle left and middle right panels, respectively. The $+x$ - and $-x$ - orientations are shown by red (solid) lines and blue (dashed) lines, respectively, and the isotropic (field dependent) DCS is shown shaded in grey. The far right panel shows the field free DCSs for scattering into the final e Λ -doublet; the $f \rightarrow e$ and $e \rightarrow e$ transitions are shown by purple (dashed) lines and green (solid) lines, respectively.

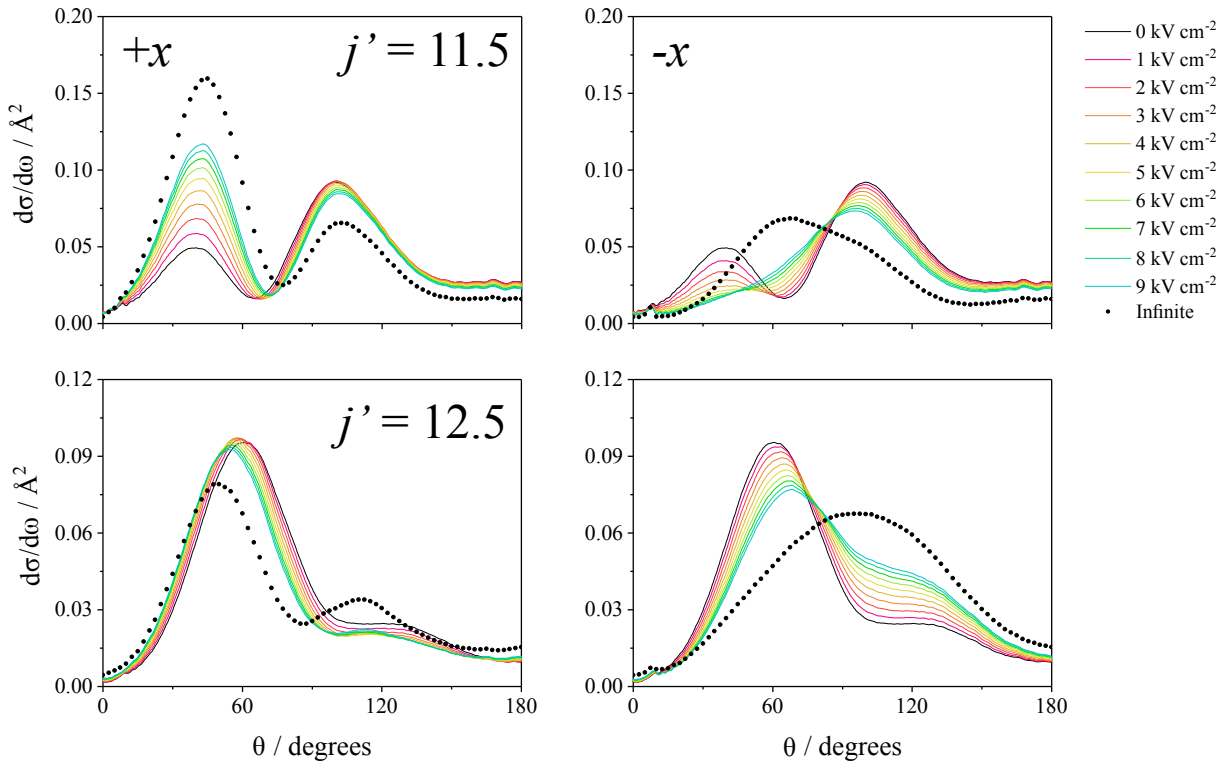


Figure 7.10: CC QM x -axis bond orientation resolved DCSs for the scattering of NO with Ar into final states with $|j', \Omega' = 0.5, \epsilon' = +1, e\rangle$, for $j' = 11.5$ (left) and $j' = 12.5$ (right). The electric field strength varies from 1 kV cm^{-1} (red line) to 9 kV cm^{-1} (blue line) in steps of 1 kV cm^{-1} . The infinite field and field free cases are shown by black circles and black lines, respectively.

and changing transitions result in multiple and single peaks in the DCS, respectively [39, 75, 96]. The field free DCSs for transitions to the final e state are also shown in Figure 7.5. At the experimental field strength, the ratio of the contributions from the initial f and e states is approximately 2:1, and therefore the $f \rightarrow e$ state contributes twice as much to the total scattering amplitude as the $e \rightarrow e$ state. Transitions with $f \rightarrow e$ and odd Δj are parity conserving whilst even Δj transitions are parity changing. Therefore, the stronger contribution of the parity conserving scattering amplitude gives rise to multiple peaks in the $+x$ -orientation for odd Δj , but a single peak for transitions with even Δj . For scattering into the final f state, similar analysis means that multiple peaks are observed in the $+x$ -orientation for even Δj (where the $f \rightarrow f$ transition is parity conserving) but only a single peak is observed for odd Δj transitions (where the $f \rightarrow f$ transition is parity changing).

Figure 7.10 shows the $+x$ - and $-x$ -orientation resolved CC QM DCSs for transitions to $j' = 11.5e$ and $j' = 12.5e$ as a function of the strength of the electric (orientation) field. The

black circles correspond to the infinite field DCSs plotted in Figure 7.9, whilst the black lines correspond to the field free $f \rightarrow e$ DCS. As described above, the field free transitions with odd Δj (parity conserving) are double peaked, but transitions with even Δj (parity changing) are single peaked. For odd Δj as the orientation field is increased from zero towards infinity the forwards scattered peak becomes more intense for $+x$ scattering and less intense for $-x$ scattering. As the intensity of the peak is reduced in the $-x$ -orientation, the position of the remaining peak is also shifted to lower scattering angles when compared to the field free case. Note that the field dependence is much stronger for the forwards scattered peak than the more backwards scattered peak (for both $\pm x$ -orientation), and is also stronger for the $+x$ -orientation than the $-x$ -orientation. Meanwhile, for even Δj the double peak in the $+x$ -orientation is suppressed for all but the infinite field (due to the dominance of the parity changing scattering amplitude). The $-x$ -orientation shows a strong shift towards higher scattering angles (opposite to the shift observed for odd Δj) as the field is increased towards infinity. Whilst the field dependence is of similar magnitude in the $-x$ -orientation for both odd and even Δj transitions, the dependence is much stronger for odd Δj transition in the $+x$ -orientation.

7.4.3 Effect on Experimental Ion Images

The effect of incomplete mixing of the Λ -doublet states in the electric (orientation) field is also observed in the experimental ion images (Figure 7.4). Figure 7.11 shows the simulated ion images for the states shown in Figure 7.9 at both experimental and infinite fields. Simulations were performed using the methods described in Section 3.5 and extended for bond axis orientation in Section 5.4.2, using the CC QM DCS calculated according to the methods in Section 7.2. The additional peak in the $+x$ -orientation has been highlighted by a white circle for clarity. The images in rows 1/2 (experimental field) and 3/4 (infinite field) of the figure are weighted (in each individual state) such that their relative intensities are preserved (*i.e.* the integral steric effect is included in the ion images). The bottom rows (5/6) have been normalised to unity, effectively removing any integral steric effects from the ion images.

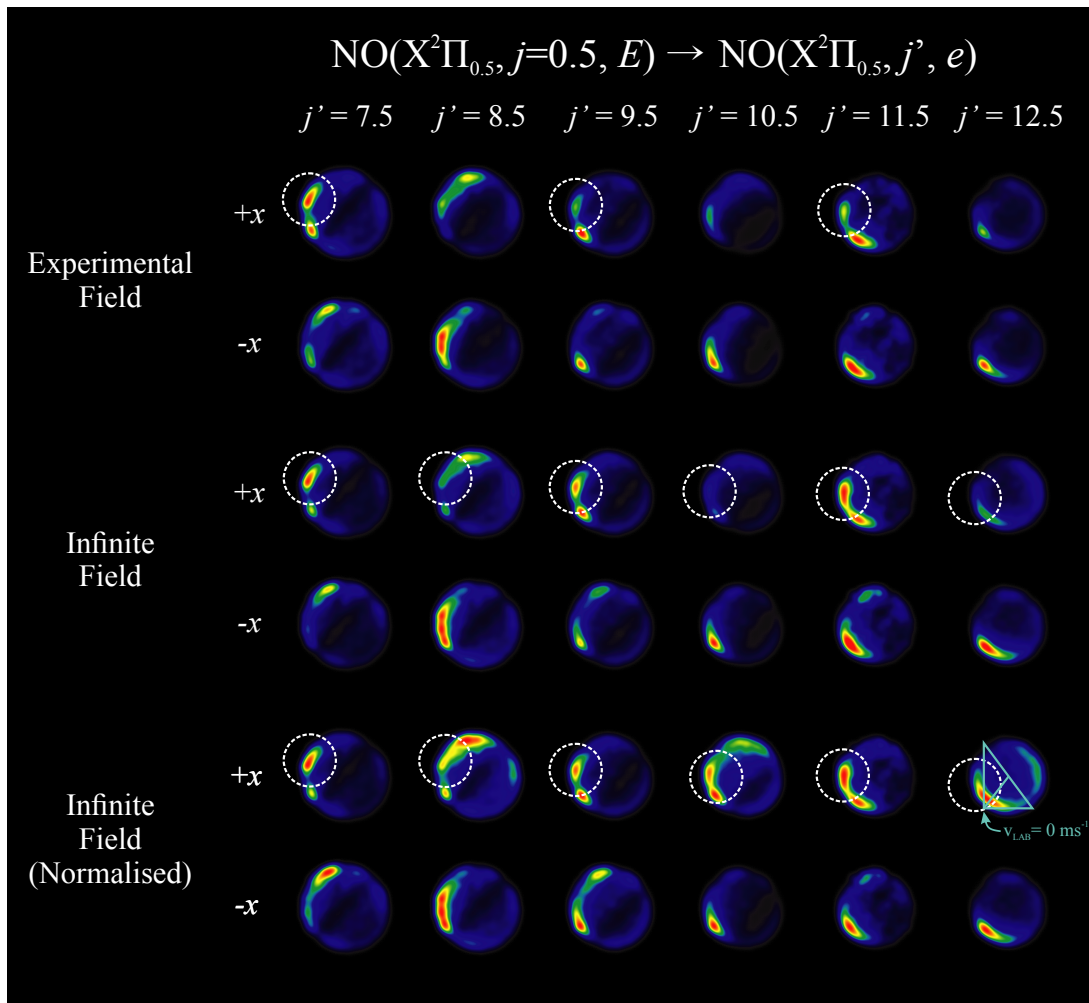


Figure 7.11: CC QM simulated ion images for the $|j', \Omega' = 0.5, e' = +1, e\rangle \leftarrow |j = 0.5, \Omega = 0.5, E\rangle$ transitions for the scattering of NO with Ar, for $j' = 7.5$ to 12.5 (from left to right). Simulations are shown at the experimental field (top), at infinite field (middle) and at infinite field normalised such as to remove the integral steric effect (bottom). The $+x$ - and $-x$ -orientations are shown in rows 1/3/5 and 2/4/6, respectively. The white dashed rings show the extra peak which is present in the $+x$ -orientation, the Newton triangle for the process is shown in blue.

As observed in the experimental ion images in Figure 7.4; the CC QM simulations at the experimental field show a double peak in the $+x$ -orientation for transitions with odd Δj , and a single peak for even Δj . A single peak is observed for all images in the $-x$ -orientation. At first glance, the simulations at the infinite field are very similar to those at the experimental field; with odd Δj and even Δj transitions in the $+x$ -orientation having double and single peaks, respectively. At first this seems counter-intuitive, since double peaks are observed for all states in the DCSs in Figure 7.9. After normalisation of the ion images to unity (to remove the integral steric effect) the propensity for double peaks in the $+x$ -orientation and single peaks in the

$-x$ -orientation is recovered. Note that the double peak is not particularly clear for $j' = 12.5$, this arises as the both peaks coincides with the position where NO has zero velocity in the LAB frame (shown by the Newton triangle in Figure 7.11); the strong probability of detection in this region washes out any structure. In the $\pm x$ -orientation resolved DCSs in Figures 7.5 and 7.10 the $+x$ -orientation is more forward peaked than the corresponding $-x$ -orientation; this is not observed in all of the simulated ion images. This may also be explained by the position at which the NO molecules have zero velocity in the LAB frame, which for several states coincides with the higher scattering angle peak, resulting in a different ratio of intensities between the two peaks than expected.

7.5 Theoretical Analysis of the Differential Steric Effect

As shown by the integral steric effects in Section 7.3.1, some of the effects of initial bond orientation may be attributed to classical mechanisms (high Δj) and some only to quantum mechanical mechanisms (intermediate Δj). Figure 7.12 shows the fixed collision energy CC QM and QCT bond orientation resolved DCSs for the $|j', \Omega' = 0.5, \varepsilon = +1, e\rangle \leftarrow |j = 0.5, \Omega = 0.5, E = \infty\rangle$ transitions of NO + Ar. For clarity, the following calculations were all run at infinite field to remove any effects arising from the incomplete mixing of the field free states in the orientation field, as discussed in Section 7.4. The QCT calculations are inherently closed shell, and so cannot be resolved in the Λ -doublet of the final state. Classically some angles cannot be accessed for scattering into higher final states, resulting in a forbidden region in the oriented DCSs (and r -PDDCSs). Simulations of the experimental ion images are also shown in Figure 7.12 using both the QM and QCT r -PDDCSs; for each Δj the $\pm x$ -images are plotted on the same intensity scale so as to conserve the relative intensities of the images (*i.e.* the integral steric asymmetry).

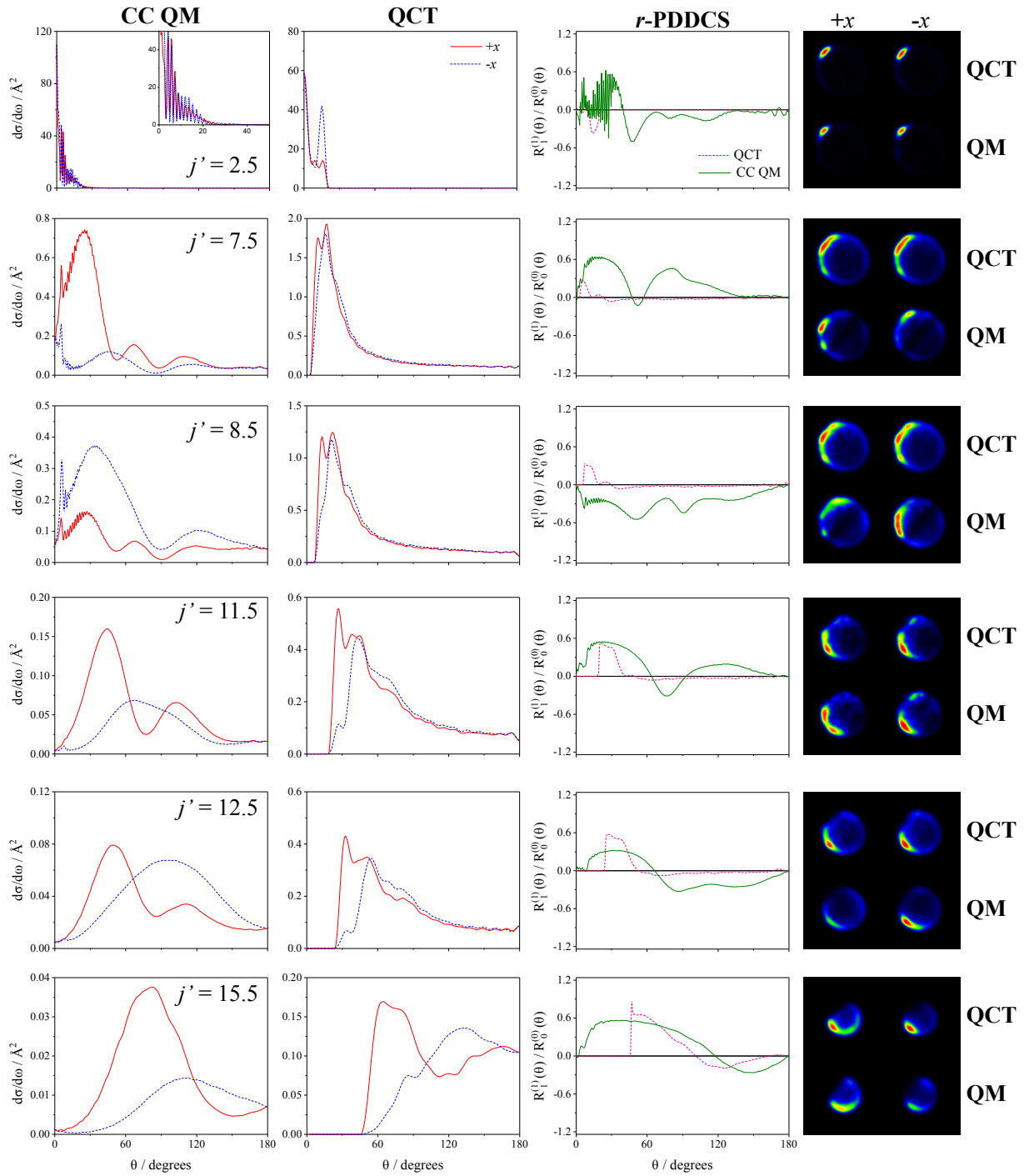


Figure 7.12: Comparison of QM (left) and QCT (center left) bond orientation resolved DCSs for the $|j', \Omega' = 0.5, \varepsilon' = +1, e\rangle \leftarrow |j = 0.5, \Omega = 0.5, E = \infty\rangle$ transitions of NO with Ar at infinite field; the $-x$ - and $+x$ -orientations are shown by blue (dashed) lines and red lines, respectively. The inset for $j' = 2.5$ shows the same DCSs but has been scaled for clarity. The QM and QCT renormalised $R_1^{(1)}(\theta)$ moments are shown in the (center) right panel, by green lines and pink (dashed) lines, respectively. QCT (top) and QM (bottom) ion image simulations are shown in the far right column for the $+x$ - (left) and $-x$ -orientations (right).

Low Rotational Energy Transfer

At low $\Delta j (= 2)$, the DCSs and corresponding (simulated) ion images are very forwards scattered. In the QCT data a secondary peak is observed in the DCS (at $\theta \approx 30^\circ$) which is much stronger in the $-x$ -orientation than the $+x$ -orientation. In the QM DCSs fast oscillations are superimposed over the structure in the DCS (and renormalised r -PDDCS); these are known as ‘diffraction oscillations’ and will be discussed in detail in Chapter 8 in terms of the steric effect, along with other features in the forwards scattered region of the DCS. The QM renormalised $R_1^{(1)}(\theta)$ moment has several peaks and troughs and depends strongly on the scattering angle. In comparison, the QCT renormalised moment has only a single peak, at the angle corresponding to the secondary maximum in the DCS. The QM and QCT simulations are very similar; this arises from the strongly forwards scattered nature of the DCS which dominates the image. A secondary maximum is not observed due to the experimental resolution of the ion image (which is accounted for during the simulation process), as well as the strong intensity at very low scattering angles.

Intermediate Rotational Energy Transfer

At intermediate Δj , the presence of multiple peaks in the QM DCSs for the $+x$ -orientation, but single peaks in the $-x$ -orientation, was initially observed when considering the infinite field data in Section 7.4.2. The effect of the incomplete mixing of the field free states in the presence of the experimental field was used to rationalise the observed experimental data in Figure 7.5. It is not immediately obvious why this ‘peak propensity’ occurs. Figure 7.12 shows two pairs of consecutive odd/even transitions ($\Delta j = 7/8$ and $11/12$); a double peak in the QM data is observed in the $+x$ -orientation of all the states, whilst a single peak dominates in the $-x$ -orientation. For the $\Delta j = 7/8$ pair a further peak is observed in both orientations at larger scattering angles, however, due to its relatively small magnitude it is of less interest. For odd Δj the double peak is clearer due to the (overall) preference for scattering into the $+x$ -orientation, whilst for even Δj the peaks are somewhat less clear as the preference for $-x$ -orientation leads to an increased magnitude of the single peaked DCS relative to the double peaked one. Irrespective

of the integral steric effect, the $+x$ -orientation is more forwards scattered than the corresponding $-x$ -orientation.

The general agreement between the QM and QCT data is poor in this region. Single peaks are observed in both the QCT $+x$ - and $-x$ -orientations for all Δj transitions. Notice that a (secondary) higher angle peak is observed in the $+x$ -orientation which coincides with the (primary) peak in the $-x$ -orientation. Similarly, a small shoulder is observed in the $-x$ -orientation which coincides with the (primary) peak in the $+x$ -orientation. This arises due to the bond axis distribution (see Figure 5.4) created in the orientation field, in which features associated with collisions off either ‘end’ of the molecule have a small (but non-zero) probability of occurring in the ‘side-on’ orientation (the probability of scattering from the other ‘side’ of the molecule is very low, see Equation (5.14)).

In the QCT calculations $S_x^{\text{QCT}} \approx 0$, and consequently the $\pm x$ -orientations have DCSs of similar magnitude. Meanwhile, the strong Δj dependent oscillation in S_x^{QM} results in a strong preference for scattering in a specific $\pm x$ -orientation. This difference is also observed in the simulated ion images; whilst the QCT $\pm x$ -images are of similar intensity, the QM images show a much stronger steric preference. Due to the oscillation of S_x^{QM} as a function of Δj , the double peak in the $+x$ ion image is not visible for even Δj transitions (due to the much weaker intensity of the image relative to the $-x$ image); if the ion images are normalised such as to remove the integral steric effect, the double peaks in the $+x$ may be recovered, as shown in Section 7.4.3. In the QCT simulations, differences between the two orientations are observed only as a subtle increase in the intensity in the forward scattered direction of the $+x$ ion image; this arises due to the small angular separation of the peaks which is not resolved at the current experimental resolution (accounted for in the simulation). The origins of the single/double peak propensity observed for the $+x/-x$ -orientations in the QM calculations will be discussed in more detail in Section 7.5.1.

The QM and QCT renormalised $R_1^{(1)}(\theta)$ moments are also shown in Figure 7.12. The renormalised moment does not depend on the angular scattering distribution, and as such allows direct comparison of the steric effect without the complication of underlying differences in the

angular scattering distribution. For intermediate values of Δj the agreement between the QCT and QM data is poor. In this region, the integral steric effect is known to arise from quantum mechanical interference and consequently the quasi-classical integral steric effect is close to zero ($S_x^{\text{QCT}} \approx 0$). The QCT moment in this region is largely positive, corresponding to a slight preference for the $+x$ -orientation as observed in the integral steric asymmetry in Figure 7.3. The QM moment shows an oscillation in preference for $\pm x$ -orientation as a function of Δj ; positive ($+x$) and negative ($-x$) for odd and even Δj , respectively. This is in-line with the oscillation in S_x arising from quantum interference, as discussed in Section 7.3.1. As Δj increases from 7 to 12, the moment becomes more backwards scattered (consistent with the more ‘head-on’ collisions required for transitions into higher rotational states). In general, the QCT moment peaks in a similar region to the QM moment.

Large Rotational Energy Transfer

Collisions resulting in high $\Delta j (= 15)$ are largely ‘head-on’ in nature resulting in mainly backwards scattered DCSs. The QCT and QM DCSs are in good qualitative agreement, suggesting a largely classical mechanism for scattering. In both cases only a single peak is observed in both the $\pm x$ -orientations, with the $+x$ DCS being more forward scattered than the $-x$ DCS. The $+x$ DCS is generally larger than the $-x$ DCS, as expected from the integral steric effect discussed in Section 7.3.1. The agreement is also good for the renormalised $R_1^{(1)}(\theta)$ moment, and the simulated ion images. A subtle difference between the intensity of the $\pm x$ ion images is observed between the QCT and QM simulations, due to $S_x^{\text{QM}} > S_x^{\text{QCT}}$.

Figure 7.13 shows the classical deflection function and position of closest approach for the $\pm x$ -orientations (calculated as described in Section 7.2); in these plots the intensity is directly proportional to the scattering probability. The deflection functions show significant differences between the $+x$ - and $-x$ -orientations; the highest probability for scattering in the $-x$ -orientation occurs around $\theta = 60^\circ$, which is concordant with that observed in the DCS. Meanwhile, in the $-x$ -orientation the greatest probability of scattering occurs in the region between $\theta = 90^\circ$ and 120° . The impact parameters which result in scattering into these angles are larger in the

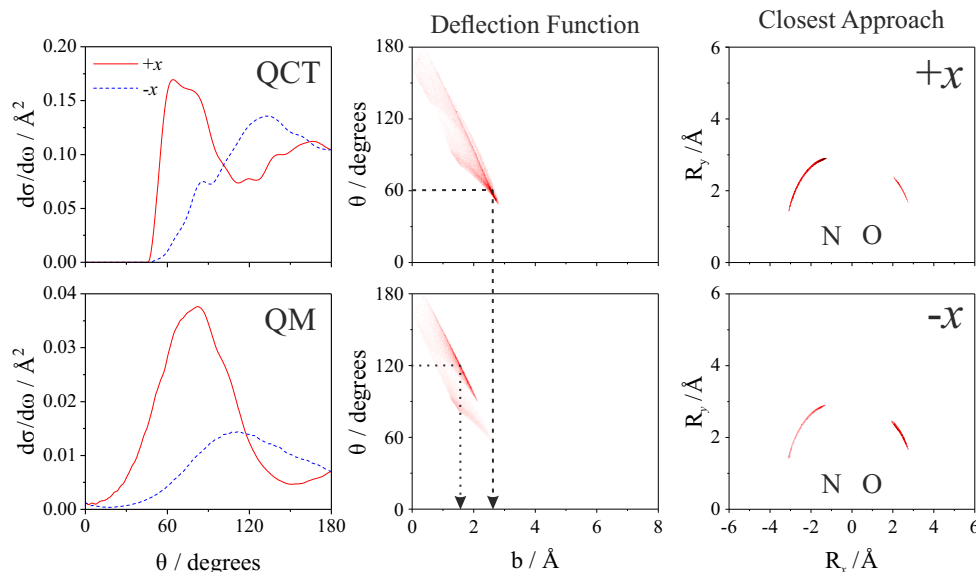


Figure 7.13: QM (bottom left) and QCT (top left) bond orientation resolved DCSs for the scattering of NO with Ar resulting in the $|j' = 15.5, \Omega' = 0.5, \epsilon' + 1, e\rangle$ state. The $+x$ - and $-x$ -orientations are shown by red lines and blue (dashed) lines, respectively. The middle right and right panels show the classical deflection function and the position of closest approach for the $+x$ - and $-x$ -orientations (top and bottom), respectively; the intensity is proportional to the probability of such an event occurring. All calculations were run at infinite field.

$+x$ -orientation than the $-x$ -orientation. Since scattering for high Δj is largely repulsive the $+x$ - and $-x$ -orientations describe scattering ‘off N’ and ‘off O’, respectively. Trajectories may penetrate further into the potential at the ‘N-end’ of the molecule than at the ‘O-end’, meaning that more ‘glancing’ collisions ‘off N’ (larger impact parameters) can result in scattering into the same angle as more ‘head-on’ collisions ‘off O’.

It is also useful to consider where these collisions actually impinge on the molecule, that is their position of closest approach as a function of the initial orientation of the NO molecule. Positions of closest approach are observed at both the ‘N-end’ and ‘O-end’ of the molecule; this is expected, since the initial bond axis distribution is somewhat broad. In the $+x$ -orientation the intensity is strongest for $R_x < 0$ (corresponding to the ‘N-end’ of the molecule), whilst the intensity is strongest for $R_x > 0$ (‘O-end’) for the $-x$ -orientation. This is consistent with the preference for repulsive scattering ‘off N’ and ‘off O’ in the $+x$ - and $-x$ -orientations, respectively. The range of positions of closest approach is much smaller for scattering at the ‘O-end’ of the molecule than at the ‘N-end’. This occurs as ‘O-end’ collisions require smaller impact parameters (more head on collisions) to induce transitions into high rotational states,

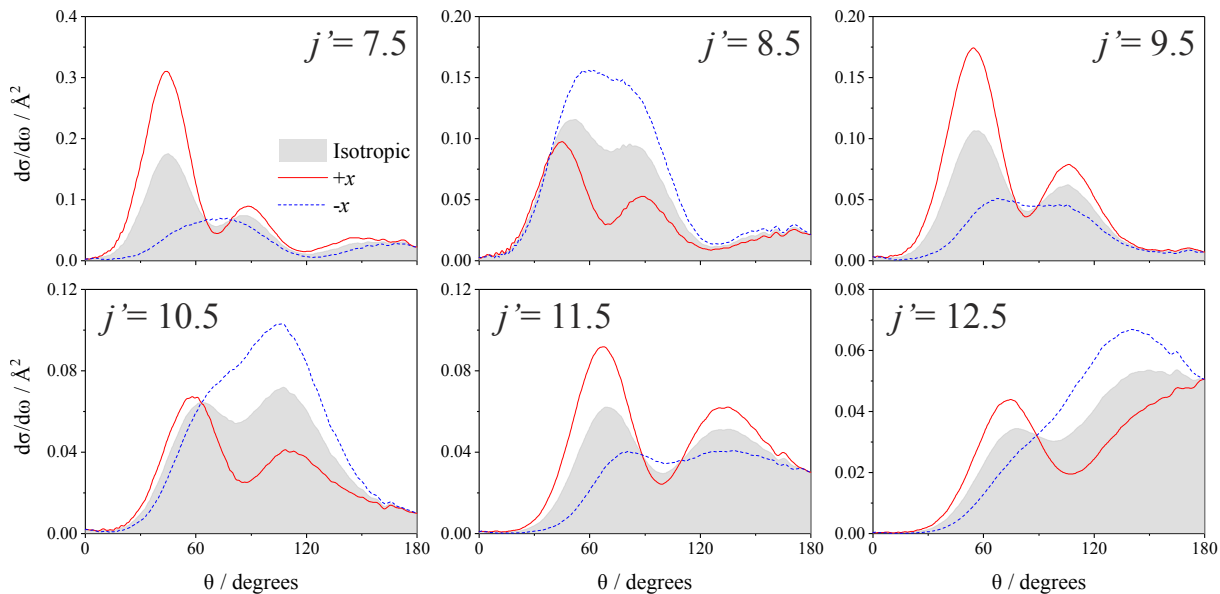


Figure 7.14: QM x -axis bond orientation resolved DCSs for the $|j', \Omega' = 0.5, \epsilon' = +1, e\rangle \leftarrow |j = 0.5, \Omega = 0.5, E = \infty\rangle$ transitions of NO + Ar on a ‘soft’ (truncated) PES. The $+x$ - and $-x$ -orientations are shown by red and blue (dashed) lines, respectively. The isotropic (field dependent) DCSs are shown by grey shading.

than collisions at the ‘N-end’ of the molecule. Further to this, the $-x$ -orientation has positions of closest approach closer to the ‘end’ of the molecule of interest than the $+x$ -orientation. This is necessary, since classically the torque of a collision further from the molecules center of mass will result in a larger transfer of translational to rotational energy during the collision.

7.5.1 Peak Propensity

The dynamics behind the propensity for a double peak in the $+x$ -orientation and a single peak in the $-x$ -orientation is not initially obvious. There is not a direct classical counterpart (*i.e.* only a single peak is observed for each orientation in the QCT DCSs, with secondary structure arising from the initial bond axis distribution), pointing towards a quantum mechanical origin. Calculations of the z -axis integral steric asymmetry have shown that the Δj dependent oscillations in S_z [95, 219] arise from scattering at the repulsive core of the NO molecule, and are only subtly modified by the attractive part of the potential (see Section 6.2.2 for orientation along the $\pm z$ -axis). Figure 7.14 shows the DCSs for several intermediate rotational states calculated on the ‘soft’ (truncated) PES under infinite field conditions. Note that in each case

the peaks are shifted towards higher scattering angles, relative to calculations on the full PES in Figure 7.12, due to the more ‘head-on’ nature of repulsive collisions. The peak propensity observed on the full potential is also observed for these purely repulsive collisions: with a double peak for $+x$ scattering and a single peak for $-x$ scattering. The oscillation in the sign of the steric effect is retained on the repulsive potential. This suggests that the origin of the propensity for single/double peaks in the $-x/+x$ -orientations also arises from the repulsive part of the potential only.

Rotational (or orientational) rainbows [25, 32, 39, 75, 173, 181, 271, 364, 365] originate from repulsive behaviour as a result of the anisotropy of the PES [366], where scattering with different initial conditions (such as bond axis orientation, or impact parameter) which lead to the same final outcome (such as j' , or scattering angle) may interfere. This effectively corresponds to the minimum scattering angle at which there is sufficient incoming translational energy to reach the rotational state of interest [271]. Classically, angles below this value, θ_R , are forbidden, whilst in the QM case this simply results in a maximum in the DCS, due to extrema in the scattered molecule’s angular momentum as a function of initial orientation [77].

In classical mechanics, for an atom-diatom (hard-shell) collision, the rainbow angle occurs at [189, 252]

$$\theta_R = 2 \sin^{-1} \left(\frac{\Delta j}{\Delta j_{\max}^n} \right), \quad (7.6)$$

where

$$\Delta j_{\max}^n = 2k(A_n - B), \quad (7.7)$$

and A_n ($A_N = 3.45 \text{ \AA}$ and $A_O = 3.28 \text{ \AA}$) and B ($= 2.85 \text{ \AA}$) are the major and minor semi-axes of the molecule, respectively; $n = N$ or O correspond to either the ‘N-end’ or ‘O-end’ of the molecule, respectively. k is the initial relative velocity of the system. It is clear that the rainbow is predicted to occur at different angles for collisions at the ‘N-end’ and ‘O-end’ of the molecule; for $\text{NO} + \text{Ar}$ scattering into $\Delta j = 8$, $\theta_R \approx 30^\circ$ and $\theta_R \approx 42^\circ$, respectively. In the QCT DCSs in Figure 7.12, a single rotational rainbow is observed in each of the $\pm x$ orientations, corresponding to scattering ‘off N’ and ‘off O’, respectively. The peak for the $-x$ -orientation

is always observed at larger scattering angles than the corresponding $+x$ -orientation peak, *i.e.* more ‘head-on’ collisions are required to access a specific rotational state for collisions ‘off O’ due to the shape of the potential. This is consistent with the different values of θ_R calculated from Equation (7.6).

It has already been noted that the QCT and QM DCSs are in poor agreement for all but the very highest Δj , and the multiple peaks in the QM DCS cannot simply be justified by the presence of classical (QCT) rotational rainbows. However, the structures can be rationalised on the basis of QM rotational rainbows, which arise due to wave-particle duality, whereby interference is allowed between particles which have different initial conditions scattering into the same final scattering angle [39, 75, 96]. Nichols *et. al.* [96, 252] have used a ‘four-path’ model to qualitatively describe the oscillations in the DCS for ‘end-on’ (z -axis) orientation of NO prior to scattering with Ar. This hard shell model is restricted to four limiting paths: collisions at the two ends and two sides of the molecule, which are allowed to interfere. The DCS is then a function of the relative phase shifts associated with scattering from the ‘N-end’ and ‘O-end’ of the molecule and scattering on the (‘flatter’) side. In the z -axis orientation it has been shown that the peaks observed in the orientation resolved DCSs are directly related to interference between scattering from the two ends of the NO molecule [96, 97]. This is in agreement with the Quasi Quantum Treatment of Stolte and coworkers [174, 275].

For orientation along the $\pm x$ -axis, in which the collision partner approaches the ‘side’ of the NO molecule, one may imagine a similar type of analysis to that of the ‘four-path’ model. The phase shift between two interfering trajectories leading to the same scattering angle, but scattering from the ‘end’ and the ‘side’ of the molecule, as shown in Figure 7.15, may be written [39, 75, 189]

$$\Delta\phi_n = \sqrt{\Delta j_\theta^n^2 - j'^2} - j' \cos^{-1} \left(\frac{j'}{\Delta j_\theta^n} \right), \quad (7.8)$$

where

$$\Delta j_\theta^n = \Delta j_{\max}^n \sin \left(\frac{\theta}{2} \right), \quad (7.9)$$

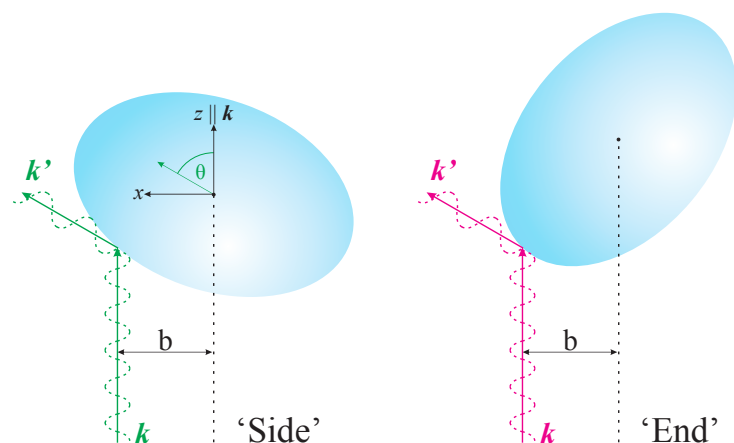


Figure 7.15: Cartoon describing the interference between two trajectories (shown in green and pink) scattering into the same scattering angle, θ , but with different initial bond axis orientations, *i.e.* trajectories for collisions at the ‘side’ (left) and ‘end’ (right) of the diatom.

and $\Delta j_{\max}^n$ is defined in Equation (7.6). The DCS for scattering between a single ‘end’ of the molecule and the ‘side’ may then be written [39, 75, 189]

$$\frac{d\sigma_n}{d\omega} \propto 2 + 2 \cos \Delta\phi_n. \quad (7.10)$$

The dependence of the phase shift $\Delta\phi_n$ on the anisotropy of the (hard shell) potential, $(A_n - B)$, implies that the number of oscillations in the DCS also depends on the anisotropy of the potential, and consequently, the number of peaks in the DCS is expected to be different for scattering off the ‘N-end’ and ‘O-end’ of the molecule.

Figure 7.16 shows the ‘2 path model’ DCSs for scattering into $j' = 7.5, 8.5, 11.5$, and 12.5 . Note that angles below θ_R , see Equation (7.6), are classically forbidden. It is also important to

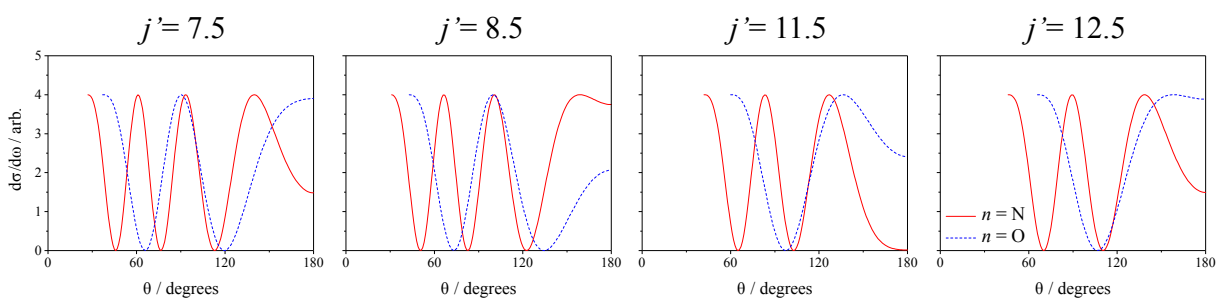


Figure 7.16: Two path model DCSs for the scattering of NO with Ar into final states with $j' = 7.5, 8.5, 11.5$, and 12.5 , from left to right. Paths at the ‘N-end’ ($n = N$) and ‘O-end’ ($n = O$) are shown by the red and blue (dashed) lines, respectively.

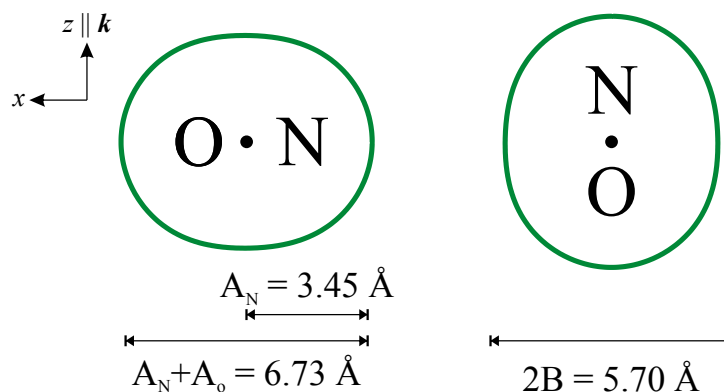


Figure 7.17: Schematic of scattering in the ‘side-on’ (left) and ‘end-on’ (right) geometries, shown for the hard shell contour of the NO + Ar V_{sum} potential (see Figure 2.3) at the experimental collision energy.

remember that the model only predicts the angular scattering distribution and not the absolute magnitude of the DCS (as the geometric cross section is neglected) [39, 75, 189]. For each state the number of peaks observed in the DCS is larger for scattering ‘off N’ ($A_N - B$) than for scattering ‘off O’ ($A_O - B$), as the anisotropy of the potential is larger. This is consistent with more oscillations in the $+x$ -orientation than the $-x$ -orientation, as observed in Figure 7.12.

7.6 Comparison of x - and z -Axis Orientation

For orientation of the NO bond axis in a ‘side-on’ configuration prior to collision with Ar it has been shown that scattering into small angles ($\theta < 90^\circ$) depends strongly on whether the bond axis is parallel or anti-parallel to the x -axis. This dependence arises from the larger impact parameter collisions possible for near-side scattering ‘off N’ ($+x$) compared to scattering ‘off O’ ($-x$), due to the shape of the potential. Figure 7.17 shows the hard shell potential for NO + Ar scattering with the relevant major and minor semi-axes (A_n and B , respectively); the NO molecule has two major semi-axes, which describe the ‘N-end’ ($A_N = 3.45 \text{ \AA}$) and ‘O-end’ ($A_O = 3.28 \text{ \AA}$) of the molecule (it is this anisotropy which leads to the strong dependence of the DCS on the x -axis orientation).^{*} In the ‘side-on’ geometry the maximal impact parameter depends on the magnitude of A_n , whilst in the ‘end-on’ geometry it depends on $B = 2.85 \text{ \AA}$.

^{*}These values differ from those used previously by Eyles *et al.* [39, 75], due to a difference in collision energy. For the collisions of NO with Ar at $E_{\text{coll}} = 532 \text{ cm}^{-1}$ semi-axes of $A_N = 3.53 \text{ \AA}$, $A_O = 3.37 \text{ \AA}$, and $B = 2.95 \text{ \AA}$, were reported.

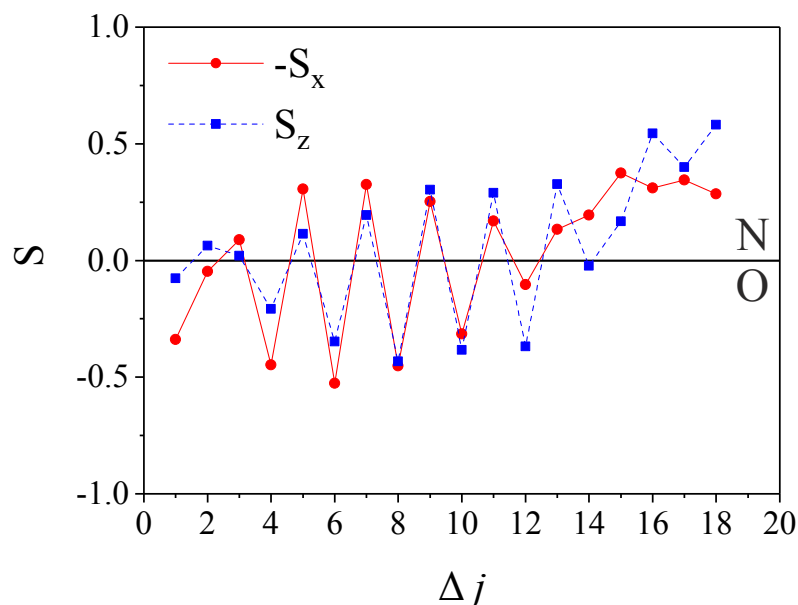


Figure 7.18: CC QM integral steric asymmetry, S , at infinite field, for the spin-orbit conserving scattering of NO with Ar into the final e Λ -doublet, with initial bond orientation along the $\pm x$ - (red lines with circles) and $\pm z$ -axis (blue dashed lines with squares). S_x is multiplied by a factor of -1 such that a positive value of S (for a near-side collision) corresponds to scattering off of the ‘N-end’ of the molecule.

Since $B < A_n$, a larger range of impact parameters may be accessed for collisions with the ‘side’ of the model than the ‘end’. Of course, this hard shell model is not an accurate representation of the potential, not least because attractive contributions are removed, but it does provide insight into the differences between the scattering geometries in ‘side-on’ and ‘end-on’ collisions. Direct comparison of orientation along the $\pm x$ - and $\pm z$ -axes therefore provides direct information about the anisotropy of the potential.

7.6.1 The Integral Steric Effect

Figure 7.18 shows the QM integral steric asymmetry for scattering in the $\pm x$ - and $\pm z$ -orientations. Due to the definition of S_z and S_x , in Equations (5.48) and (7.4), respectively, it is necessary to plot $-S_x$ to facilitate comparisons between scattering in the ‘end-on’ and ‘side-on’ geometries. The general features of the integral steric asymmetry are similar for both the x - and z -orientations; there are Δj dependent oscillations for intermediate Δj , and a strong preference for scattering into a specific orientation at high Δj . For collisions in the $\pm z$ -orientation the large positive value of S at high Δj corresponds to a preference for scattering

in the $-z(\text{N})$ orientation, whilst for the $\pm x$ -orientation the preference is for $+x$ scattering. Since scattering at high Δj is dominated by repulsive forces, it is reasonable to assign scattering in the $+x$ -orientation to scattering ‘off N’. The preference for scattering from the ‘N-end’ of the molecule at high Δj in both geometries is consistent with the classical argument given in Sections 6.2 and 7.3.1.

The origin of the Δj dependent oscillations in both S_x and S_z was discussed in Sections 6.2 and 7.3.1. Differences between S_z and $-S_x$ are subtle, and are mainly observed in the magnitude of the asymmetry. At low and intermediate $\Delta j (< 7.5)$, the magnitude of S_x is (generally) larger than S_z ; this may be attributed to the strong preference for forwards scattering observed in the $+x$ -orientation (compared to the $-x$ -orientation) due to large impact parameter collisions. The preference for orientation with respect to the z -axis is smaller since, for large impact parameter collisions resulting in forwards scattering, the potential sampled in the two orientations is less anisotropic than for orientation with respect to the x -axis. Conversely, for larger $\Delta j (> 9.5)$ (below the ‘classical’ regime), a stronger preference is observed for orientation with respect to the z -axis than the x -axis. This occurs as the potential sampled for collisions with smaller impact parameters (which access these rotational state) are more anisotropic at the ‘ends’ of the molecule than the ‘sides’. There is an intermediate region ($\Delta j = 8$ and 9), where these two effects cancel out, resulting in $|S_x| \approx |S_z|$. Further insight into the importance of forwards/backwards scattering in the $\pm x/\pm z$ orientations is discussed with reference to the maximised DCSs in Section 7.6.3.

In both the $\pm z$ - and $\pm x$ -orientations, the Δj oscillations are not regular at low Δj , which has been attributed to the attractive part of the potential, see Section 6.2.2 and References [95, 219]. The preference for $-z(\text{N})$ scattering and $+x$ scattering (near-side scattering ‘off O’ and attractive far-side scattering ‘off N’), arises from the importance of the attractive part of the potential for such collisions. This was described in detail in Section 6.2.2 for z -axis orientation, and will be revisited in terms of the differential steric effect in Chapter 8. Further insight into differences between the x - and z -axis integral steric effects are discussed in Appendix C.

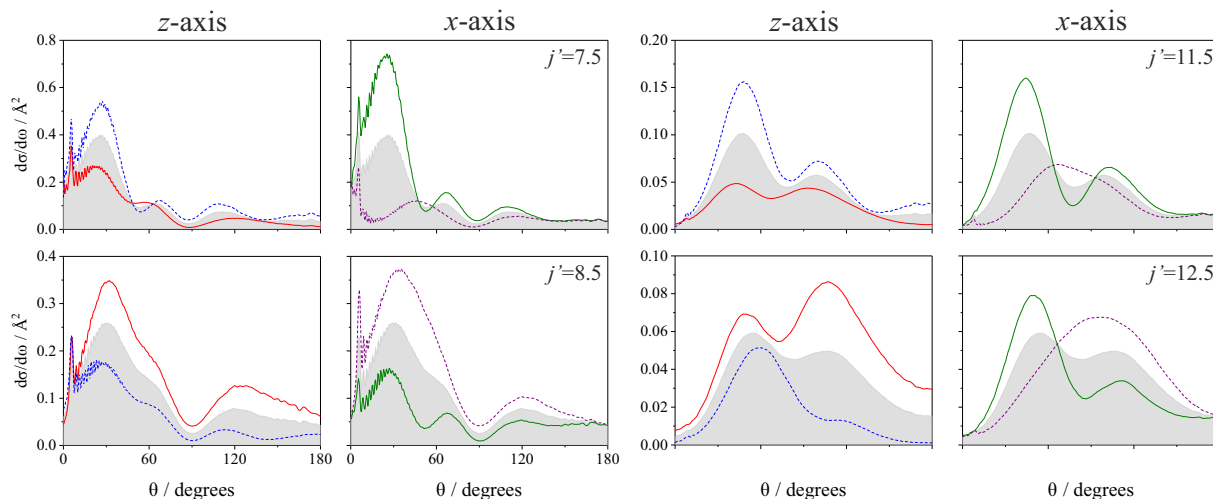


Figure 7.19: CC QM z - (1/3) and x -axis (2/4) bond orientation resolved DCSs for the scattering of NO with Ar into the $|j', \Omega' = 0.5, \epsilon' = +1, e\rangle$ states at infinite field, with $j' = 7.5/11.5$ and $8.5/12.5$ in the top and bottom rows (left/right), respectively. The $+z$, $-z$, $+x$, and $-x$ orientations are shown by red, blue (dashed), green, and purple (dashed) lines, respectively. The isotropic (field dependent) DCSs are shown by gray shading.

7.6.2 The Differential Steric Effect

Whilst the differences observed in the integral steric asymmetry for orientation along the $\pm z$ - and $\pm x$ -axes provide direct information about the general preferences for scattering, more detailed mechanistic information is ascertained from the oriented DCSs. Figure 7.19 shows the $\pm x$ - and $\pm z$ -orientation resolved DCSs for the $|j', \Omega' = 0.5, \epsilon' = +1, e\rangle \leftarrow |j = 0.5, \Omega = 0.5, E = \infty\rangle$ transitions of NO with Ar at an infinite orientation field. It is immediately obvious that orientation along the $\pm z$ - and $\pm x$ -axes gives rise to qualitatively similar angular distributions. This is understandable, since the oriented DCSs are deviations from the $R_0^{(0)}(\theta)$ moment; this will be discussed with respect to the renormalised $R_q^{(1)}(\theta)$ moments in Figure 7.20. The features at low Δj will be described in great detail in Chapter 8, and no discussion is given here.

Throughout this chapter the strong preference for scattering in the $+x$ -geometry in the forwards region of the DCS has been mentioned. In Section 7.5.1, this was attributed to the strong anisotropy in the potential when the collision partner approaches with large impact parameters towards the ‘side’ of the molecule. Unlike for orientation with respect to the x -axis, a double peak is observed in both the $\pm z$ -orientations; although in some cases (*e.g.* $\Delta j = 8$

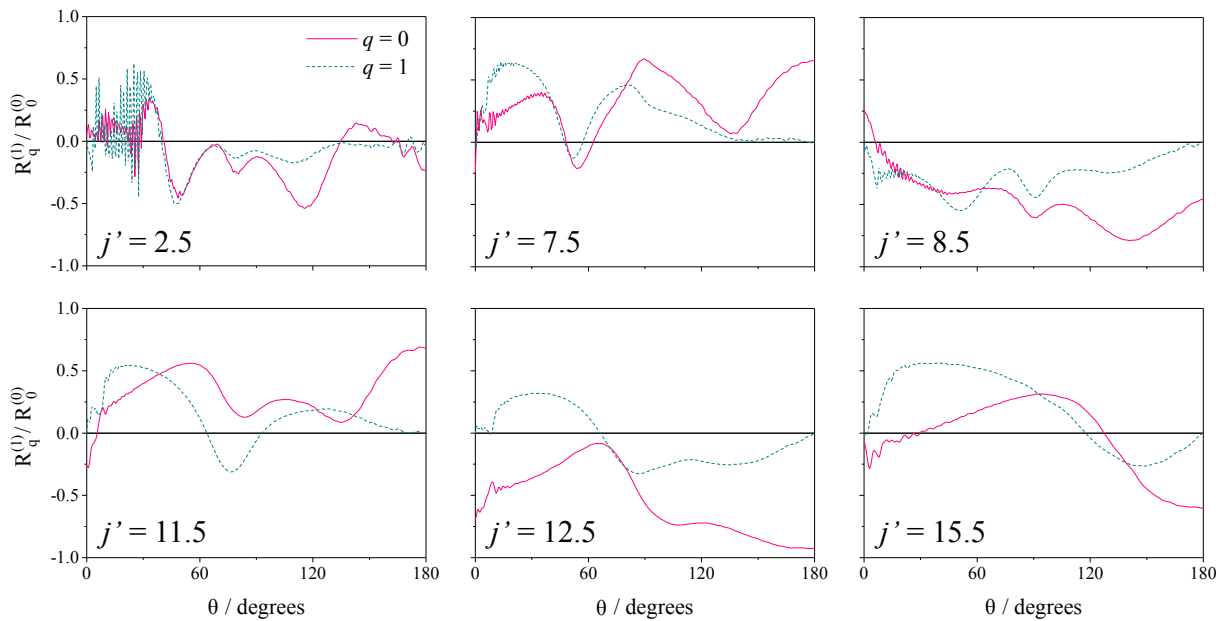


Figure 7.20: Infinite field CC QM renormalised r -PDDCSs for the scattering of NO with Ar into the $|j', \Omega' = 0.5, \epsilon' = +1, e\rangle$ states, with $j' = 2.5/11.5$, $7.5/12.5$, and $8.5/15.5$ from left to right (top/bottom). The renormalised $R_0^{(1)}(\theta)$ and $R_1^{(1)}(\theta)$ moments are shown by pink and teal (dashed) lines, respectively.

and 12) this is only present as a shoulder on the more forwards scattered peak. This shows that forward scattering is much more sensitive to orientation with respect to the x -axis than the z -axis. This is, in itself, not surprising, as the anisotropy between the two ends of the molecule is much larger when approaching the ‘side’ of the molecule as opposed to the ‘end’ for large impact parameter collisions. Indeed, a much wider range of impact parameters are possible in the $\pm x$ -orientation than in the $\pm z$ -orientation, resulting in the very pronounced forwards peak in the DCS for the $+x$ -orientation.

Bond Axis Orientation Moments

Figure 7.20 shows the renormalised $R_q^{(1)}(\theta)$ moments for $q = 1$ (x -axis) and $q = 0$ (z -axis). Since the moments have been renormalised, the features show only the effects of bond orientation and are independent of any underlying differences in the angular distribution. However, it is important to remember that due to the dependence of the $R_0^{(0)}(\theta)$ moment on the field dependent mixing parameters, α and β , the renormalised r -PDDCSs depend on the

strength of the orientation field.[†] Any differences in magnitude correspond to differences in the integral steric effect discussed in Section 7.6.1. For (largely) repulsive collisions (those with $j' > 2.5$) a positive value of the renormalised r -PDDCS corresponds to a preference for scattering ‘off N’ ($-z$ and $+x$), whilst a negative value corresponds to a preference for scattering ‘off O’ ($+z$ and $-x$).

The renormalised bond orientation moments with $q = 0$ and $q = 1$ are largely comparable, following the same trends for all states. It is unsurprising that the renormalised moments are so similar for orientation along both axes, since the mechanisms for scattering are largely comparable for collisions at the ‘side’ and ‘end’ of the molecule. It should be noted, that due to the factor of $\sqrt{2}$ in the $R_1^{(1)}(\theta)$ moment term in Equation (5.25), the bond axis resolved DCSs depend more strongly on the $R_1^{(1)}(\theta)$ term than the $R_0^{(1)}(\theta)$ term, even if the moments themselves take similar values. On average the ‘end-on’ moment takes larger values for large scattering angles, this can be rationalised simply by the increased classical torque achieved in ‘end-on’ collisions (which are further from the center-of-mass of the NO molecule) as opposed to ‘side-on’ ones. In general, the $q = 1$ moment is more forwards scattered than the $q = 0$ moment, arising from the larger impact parameters possible in the ‘side-on’ orientation, as well as the increased anisotropy in the potential compared to scattering in the ‘end-on’ geometry.

7.6.3 DCS Maximisation

It is possible to calculate the maximum possible DCS for any experimental orientation of the static field, $\mathbf{E}$, by finding the stationary points of Equation (5.25) (which describes the bond axis resolved DCS as a function of the direction of the electric field), for which a full derivation is given in Appendix D. The stationary points with respect to ϕ_E occur when $\phi_E = 0^\circ$ and 180° , using these values the stationary points with respect to θ_E may be calculated [367, 368]

$$\tan \theta_E = \mp \frac{\sqrt{2}R_1^{(1)}(\theta)}{R_0^{(1)}(\theta)}, \quad (7.11)$$

[†]The renormalised $R_q^{(1)}(\theta)$ moments have limits which depend on the field dependent mixing parameters according to $\pm 1/|\alpha\beta|$. At infinite field this corresponds to limits of ± 1 , as in Figure 7.20, however, at the experimental field the limits are ± 1.24

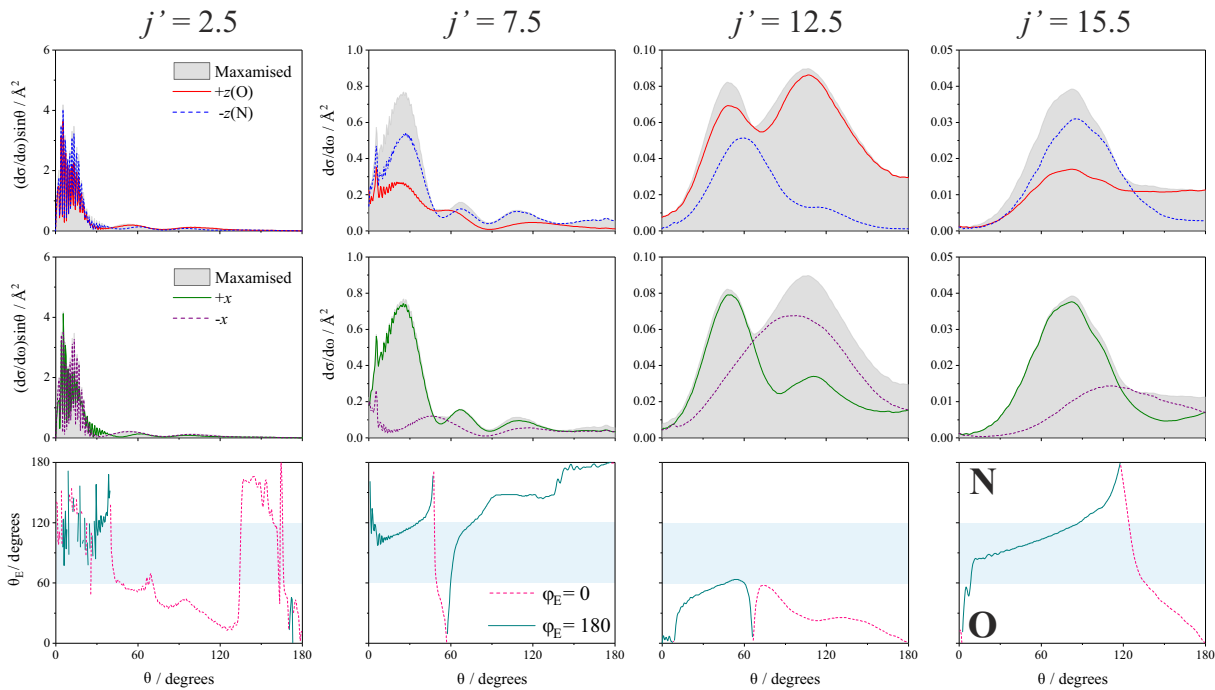


Figure 7.21: Infinite field maximised CC QM DCSs (grey shading) for transitions into the $|j', \Omega' = 0.5, \epsilon' = +1, e\rangle$ state, where $j' = 2.5, 7.5, 12.5$, and 15.5 from left to right. The $+z$ (O) and $-z$ (N) oriented DCSs are shown in the top panel by red lines and blue (dashed) lines, respectively. The $+x$ and $-x$ oriented DCSs are shown in the middle panel by green lines and purple (dashed) lines, respectively. The DCS for scattering into $j' = 2.5$ have been multiplied by a factor of $\sin \theta$ to facilitate comparison. The bottom panels shows the value of θ_E which maximises the DCS as a function of scattering angle; ϕ_E takes the limiting values of 0 and 180° , which are denoted by pink (dashed) and teal lines, respectively. The region in which collisions may be considered to occur at the ‘sides’ of the molecule has been highlighted in blue.

where the $\mp$ signs define the solutions for $\phi_E = 0^\circ$ and 180° , respectively. These angles may then be substituted into Equation (5.25) to calculate the maximised DCS. Remember that there will be a distribution of $\mathbf{r}$ for any field direction (see Figure 5.4).

Figure 7.21 shows the maximised DCS for the collisions of NO with Ar leading to scattering in several final rotational states, along with the x - and z -axis bond orientation resolved DCSs (for $j' = 2.5$ all of the DCSs are multiplied by a factor of $\sin \theta$ to facilitate comparison). The static field direction, θ_E , as a function of scattering angle, θ , is also shown; ϕ_E is restricted to 0° and 180° , and the value is denoted in the figure by teal (dashed) and pink lines, respectively. Whilst there is a distribution of bond axis orientations, (θ_r, ϕ_r) for any specified direction of E , it may be roughly approximated that geometries with $60^\circ < \theta_E < 120^\circ$ are ‘side-on’ geometries

(shaded in pale blue), whilst $0^\circ \leq \theta_E \leq 60^\circ$ and $120^\circ \leq \theta_E \leq 180^\circ$ correspond to ‘O-end’ and ‘N-end’ geometries, respectively.

For forwards and sideways scattering the maximised DCS is quantitatively similar to scattering in the ‘side-on’ geometry. That is, the maximised DCS is essentially equivalent to the $\pm x$ DCS for each state. Meanwhile, for backwards scattering the maximised DCS is quantitatively more similar to scattering in the ‘end-on’ geometries. This can be simply interpreted, since approach at the ‘side’ of the NO molecule allows a wide range of large and intermediate impact parameters, resulting in ‘glancing-blow’ type collisions and small angle scattering. Meanwhile, collisions at the ‘end’ of the molecule occur with smaller impact parameters due to the shape of the potential (see Figure 7.17), resulting in more backwards scattering. The angle at which the maximised DCS becomes ‘end-on’ in nature occurs at smaller scattering angles as j' increases; this arises due to the increased torque arm for collisions at the ‘end’ of the molecule, compared to a corresponding collision with the ‘side’ of the molecule. It is important to note that whilst ‘end-on’ type of collisions are important for large scattering angles, the region does not depend strongly on the orientation of the bond axis. On the other hand, the orientation of the bond axis provides considerable control over the magnitude of lower angle scattering.

The electric (orientation) field directions, (θ_E, ϕ_E) , that maximise the DCS as a function of θ are also shown in Figure 7.21. The polar angle, θ_E , does not vary smoothly as a function of scattering angle, and distinct regions are observed where $\phi_E = 0^\circ$ (‘off O’) and 180° (‘off N’). Note that whilst a lot of structure is observed for scattering into the $j' = 2.5$ state, the relative magnitude of the DCS (and consequently the scattering probability) is very small for scattering into angles greater than 60° . As such, whilst present, the effects of the varying bond orientation angle can be disregarded. Strong oscillations are observed in the forwards scattered region of the maximised DCS for $j' = 2.5$; θ_E also varies strongly with scattering angle, suggesting a strong dependence of the DCS on the bond axis orientation (with a preference for ‘side-on’ geometries). This region of the DCS will be discussed in more detail in Chapter 8, for orientation of the bond axis along both the $\pm x$ - and $\pm z$ -axes.

The (average) preference for ‘N-end’ or ‘O-end’ scattering corresponds to the preference observed in the integral steric effect shown in Figure 7.20 (*i.e.* $-z(\text{N})$ for $j' = 7.5$ but $+z(\text{O})$ for $j' = 12.5$). As discussed above, the value of θ_E tends towards either 0° for ‘O-end’ collisions or 180° for ‘N-end’ collisions at large scattering angles. For $j' = 7.5$ and $j' = 12.5$, a sharp change in the bond orientation angle is observed, at $\theta = 57^\circ$ and $\theta = 67^\circ$, respectively. This sudden change in the (azimuthal) angle which maximises the DCS suggests that the scattering mechanism(s) in this region depend very strongly on the initial bond axis orientation.

The extrinsic bond axis distributions for the static field direction which maximise the DCS may be calculated according to [367, 368]

$$P_{\max}(\theta_r, \phi_r | \theta) = \frac{1}{4\pi} \left[1 - \left(\frac{R_0^{(1)}(\theta)}{S(\theta)} \right) \cos \theta_r \pm \left(\frac{\sqrt{2}R_1^{(1)}(\theta)}{S(\theta)} \right) \sin \theta_r \cos \phi_r \right], \quad (7.12)$$

where the $\pm$ sign accounts for orientations in which $\phi_E = 0$ and 180° , respectively, and

$$S(\theta) = \sqrt{R_0^{(1)}(\theta)^2 + 2R_1^{(1)}(\theta)^2}. \quad (7.13)$$

This arises directly from the stationary points calculated in Equation (7.11), and is derived in full in Appendix D. Figure 7.22 shows the maximised DCSs for the scattering of NO with Ar into $j' = 7.5e$ and $j' = 8.5e$, alongside mechanistic sketches of the geometries which maximise the DCS at several pertinent scattering angles. Since the stationary points of the bond axis resolved DCS occur when ϕ_E takes values of 0° or 180° (see Appendix D), it is sufficient to sketch the collision geometries in the xz plane (shown in panel 1 for $j' = 7.5$). In each sketch, the most probable bond axis orientation, which is anti-parallel to the orientation field (green arrow), is shown by a black arrow; the extrinsic bond axis distribution is superimposed over the sketch (shown by the shaded region). The bond axis distribution shows the range of bond axis orientations that may be sampled for for a specific electric field direction. It is clear from these distributions that experimentally a large range of orientations are sampled, and whilst the largest probability arises for scattering off a specific ‘end’ of the molecule, collisions at the other ‘end’ of the molecule will also contribute.

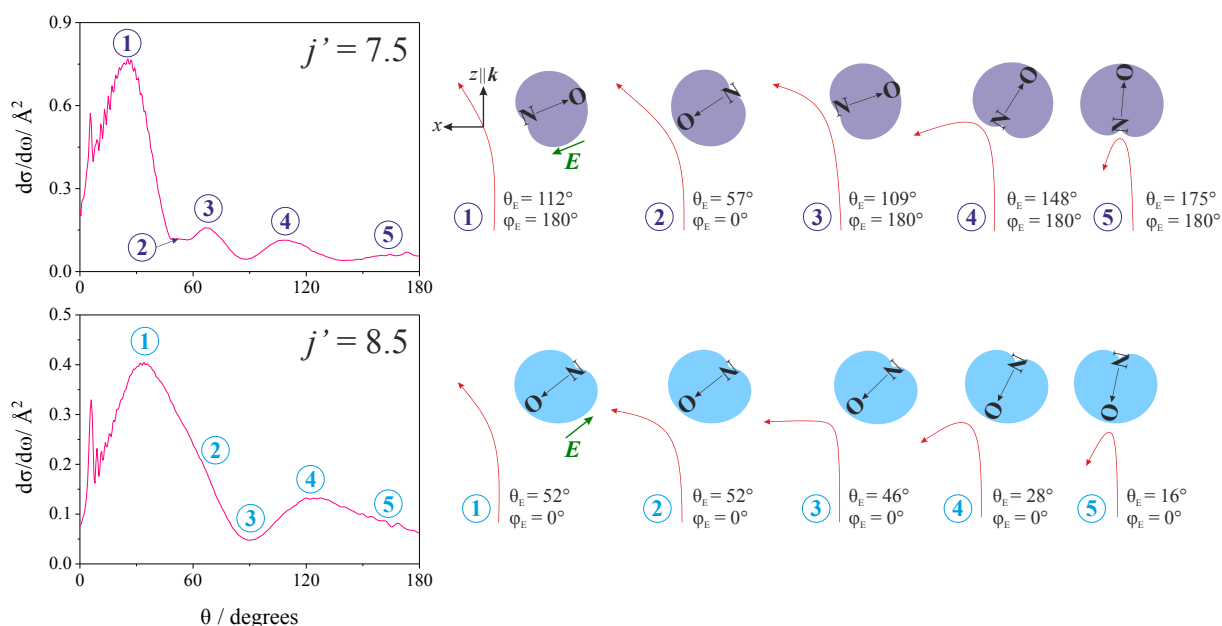


Figure 7.22: CC QM maximised DCSs (left) for transitions in to the $|j', \Omega' = 0.5, \varepsilon' = +1, e\rangle$ states, where $j' = 7.5$ (top) and $j' = 8.5$ (bottom). Mechanistic sketches of the scattering event are shown to the right, for pertinent cases. The extrinsic bond axis distributions, calculated according to Equation (7.12), are shown by the shaded areas.

From the sketches it is clear that the collisions occur ‘off N’ for $j' = 7.5$ and ‘off O’ for $j' = 8.5$, this is consistent with the Δj dependent oscillation in S_x , discussed in Section 7.6.1. For the forwards and sideways scattered regions of the DCS (1, 3 and 4 for $j' = 7.5$ and 1 to 4 for $j' = 8.5$) the scattering geometries are ‘side-on’ in nature. This is consistent with the maximised DCS in Figure 7.21 being of x -axis character for such scattering angles. Similarly, the more backwards scattered region (5) corresponds to ‘end-on’ geometries, as was observed in the maximised DCS. At position 2 in the maximised DCS for $j' = 7.5$ there is a scattering geometry which does not follow the general trend of ‘side-on’ collisions for forwards/sideways scattering and ‘end-on’ geometries for backwards scattering. At this trough in the maximised DCS an ‘O-end’ collision is observed, although it is not easy to rationalise this preference. This region of the DCS corresponds to the sharp change in θ_E in the plot of θ_E vs θ in Figure 7.21, in which the value of ϕ_E also changes. This rapid transition between scattering at the two ends of the molecule over a range of only $\sim 10^\circ$, suggests that the mechanism for scattering depends very strongly on the initial bond-axis orientation in this region.

7.7 Future Work

The initial experimental and theoretical study of ‘side-on’ collisions in the inelastic scattering of NO(X) with Ar described here presents two potential avenues for future work: firstly, the effect of initial x -axis orientation on the spin-orbit changing transitions of NO with the rare gases, and secondly extension of both experimental and theoretical methods to the full four vector correlation.

7.7.1 Spin-Orbit Changing Transitions

As discussed in Chapter 6, experimental measurement of spin-orbit changing transitions is more difficult than for their spin-orbit conserving counterparts, due to the large spin-orbit energy (approximately 123 cm^{-1} for low Δj [188]) and the much smaller ICSs of such transitions. However, the current experimental apparatus has been used to record such transitions for initial z -axis orientation with a sufficiently high signal-to-noise ratio; these were presented in Chapter 6. Since collisions at the ‘side’ of the molecule have been shown to probe the anisotropy between the two ‘ends’ of the molecule more strongly than collisions occurring at either ‘end’, a strong effect is expected for spin-orbit changing collisions which sample the strongly anisotropic V_{diff} PES (on which spin-orbit changing transitions are considered to occur under Hund’s case (a)).

Figure 7.23 shows the CC QM integral steric asymmetry for the spin-orbit changing scattering of NO with Ar resulting in the e Λ -doublet for orientation of the NO bond axis with respect to both the x - and z -axis. Note that S_x is multiplied by a factor of -1 such that collisions ‘off N’ correspond to a positive value for both S_x and S_z . A comparison between the two orientations for scattering on the spin-orbit conserving manifold was given in Section 7.6.1 and will not be repeated here. On the spin-orbit changing manifold, significant differences are observed between $-S_x$ and S_z . The irregularity of the Δj dependent oscillations observed for both orientations, has been attributed to the more anisotropic nature of the difference potential on which spin-orbit changing collisions are considered to occur for spin-orbit changing

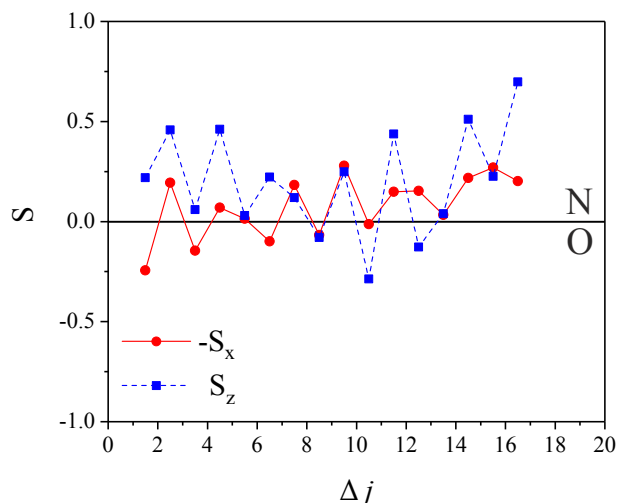


Figure 7.23: ‘End-on’ and ‘side-on’ CC QM integral steric asymmetry (at infinite field) on the spin-orbit changing manifold, resulting in the final e Λ -doublet. Orientation of the NO bond axis along the $\pm x$ - and $\pm z$ -axis are shown by red lines (with circles) and blue dashed lines (with squares), respectively. S_x is multiplied by a factor of -1 to facilitate comparison.

scattering under Hund’s case (a) (see Chapter 6 and References [95, 362]). Whilst a general preference for ‘N-end’ collisions ($S_z > 0$) is observed for ‘end-on’ collisions, the trend is more nuanced in the ‘side-on’ case. $-S_x$ shows a preference (on average) for $+x$ scattering, the magnitude of which increases as a function of Δj , corresponding to an increasing preference for (near-side) scattering ‘off N’. The differences are likely due to the larger anisotropy probed by the collision partner in the $\pm x$ -axis orientation than in the $\pm z$ -orientation.

The differential steric effect is also of interest when considering scattering on the spin-orbit changing manifold. Figure 7.24 shows the x -axis bond orientation resolved DCSs for the scattering of NO with Ar into several final rotational states. Similar trends are observed to those discussed throughout this chapter with respect to the spin-orbit conserving manifold. For low RET transitions the differences between the DCSs are subtle, since no ℓ -type rainbows are expected on the spin-orbit changing manifold [362] to distinguish the two orientations. A preference for scattering ‘off N’ ($+x$) is observed for high RET due to the larger extent of the potential at the ‘N-end’ of the molecule.

The intermediate transitions also show similar trends to those observed for x -axis orientation on the spin-orbit conserving manifold, although the features are generally broader. A double peak is observed in the $+x$ -orientation, but only a single peak is observed in the $-x$ -orientation,

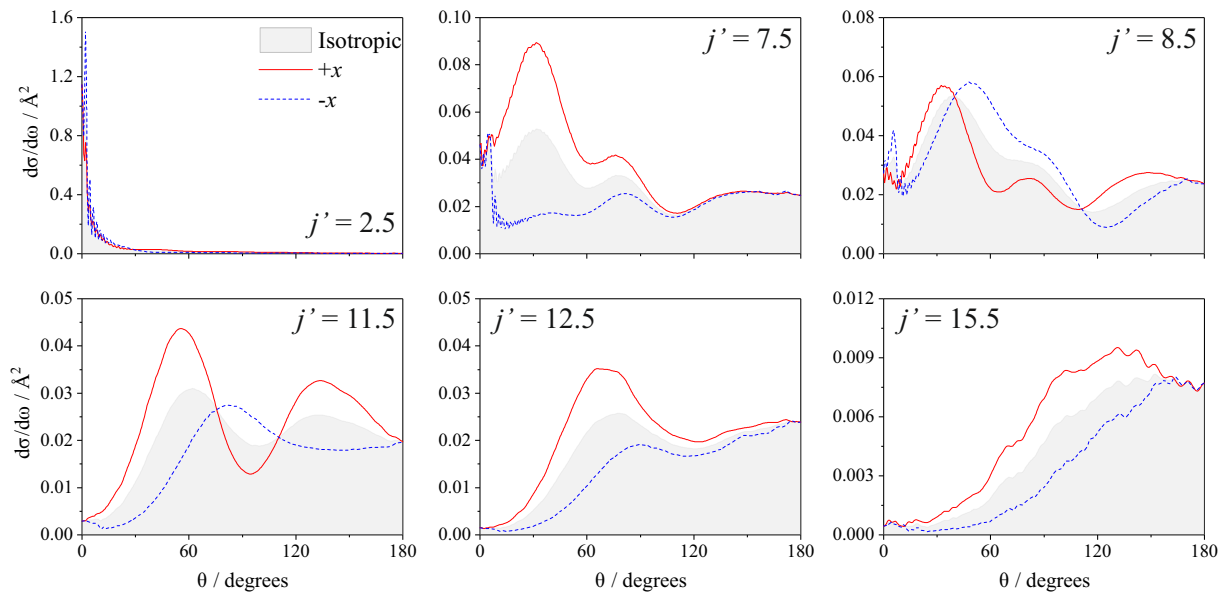


Figure 7.24: CC QM bond orientation resolved DCSs for the scattering of NO with Ar for the $|j', \Omega' = 1.5, \epsilon' = +1, e\rangle \leftarrow |j = 0.5, \Omega = 0.5, E = \infty\rangle$ transitions. The $+x$ - and $-x$ -orientations are shown by red lines and blue (dashed) lines, respectively. The isotropic DCS is shown by gray shading.

much as in the spin-orbit conserving case. The $-x$ DCS is more backwards scattered than the corresponding $+x$ DCS, arising from the more ‘head-on’ nature of collisions required to achieve such rotational states for (repulsive) collisions off the ‘O-end’ of the molecule. These similarities suggests a similar mechanism is at play for scattering on both spin-orbit manifolds; arising due to the larger impact parameters possible for collisions in the $+x$ -orientation than the $-x$ -orientation, which probe the anisotropy of the PES more strongly than for orientation with respect to the z -axis.

7.7.2 The Four Vector Correlation

The four vector $\mathbf{r} - \mathbf{k} - \mathbf{k}' - \mathbf{j}'$ (or $\mathbf{j} - \mathbf{k} - \mathbf{k}' - \mathbf{j}'$) correlation completely describes the scattering process for the collision of a diatom with an atom [13]. To experimentally probe this correlation it is necessary to combine the apparatus used to record the $\mathbf{k} - \mathbf{k}' - \mathbf{j}'$ (the collision induced orientation/alignment of the rotational angular momentum) [79, 83–88] and $\mathbf{r} - \mathbf{k} - \mathbf{k}'$ (initial bond orientation) [96, 97] correlations. Measurement of the collision induced alignment (CIA) provides information about the plane in which molecular rotation occurs after

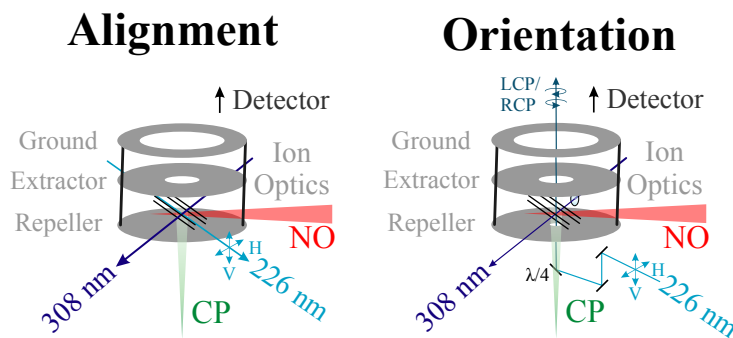


Figure 7.25: Experimental geometries to perform collision induced alignment (left) and orientation (right) measurements with initial bond axis orientation.

the collision, whilst the collision induced orientation (CIO) describes the sense of rotation (*i.e.* clockwise or counter-clockwise).

Initial reports of the measurement of the four vector correlation for the elastic and inelastic scattering of Li_2 with Ar and Xe were reported by Collins *et al.* [99] using a two-colour sub-Doppler optical-optical double resonance experiment. More recently, Perreault *et al.* [100] have studied the rotationally inelastic scattering of HD with D_2 , in which the $\text{HD}(v = 1, j = 2, m = 0)$ state was prepared *via* Stark-induced adiabatic Raman passage (SARP), with the bond axis aligned preferentially parallel or perpendicular to the initial LAB frame relative velocity. The $\mathbf{j} - \mathbf{k} - \mathbf{k}' - \mathbf{j}'$ vector correlation was then measured, showing a strong preference (3:1) for scattering in the perpendicular *versus* parallel alignment. The measurement of the full four vector correlation was made possible by the very low temperatures achieved in the molecular beam (with a collision temperature of $T_{\text{coll}} \approx 1$ K), which restricted scattering to s ($\ell = 0$) and p ($\ell = 1$) partial waves only. Whilst theoretical descriptions of several three vector correlations exist ($\mathbf{k} - \mathbf{k}' - \mathbf{j}'$ [231, 369, 370], $\mathbf{j} - \mathbf{k} - \mathbf{j}'$ [182, 370] and $\mathbf{r} - \mathbf{k} - \mathbf{k}'$ [339, 368]), only a few of these have been extended to the full four vector correlation *e.g.* the Fraunhofer model [370] used in Chapter 8.

To measure the CIA it is sufficient to use the orientation geometry (described in Chapter 5 and reproduced in Figure 7.25) with the addition of a PEM (photoelastic modulator) to switch between horizontal (H) and vertical (V) polarisation of the 226 nm radiation axis, *i.e.* polarisation perpendicular or parallel to the time-of-flight axis, respectively. Such experiments

(and corresponding theory) without initial orientation of the NO bond axis have been reported for several NO + Rg systems [79, 86–88, 149, 371].[‡]

Measurement of the CIO is more complicated, as the measurement step requires the use of circularly polarised light propagating perpendicular to the plane of the molecular beams (*i.e.* along the TOF axis). This is experimentally more challenging than the corresponding alignment set-up, requiring both a PEM and quarter wave plate to generate alternating left- and right-hand circularly polarised light (as shown in Figure 7.25). The distortion of the velocity mapping field by the static orientation field (along the TOF axis), requires that a cylindrical lens be placed in the path of the 308 nm laser to reduce blurring along the TOF axis by only ionising molecules scattered in the plane of the molecular beams [240, 252]. CIO has been previously studied for unoriented collisions of NO with both Ar [83, 150] and Kr [84].

Whether measuring the CIO or CIA with initial bond axis orientation, the number of acquisition channels required for the measurement is doubled from 4 (initial bond orientation only) to 8 (initial bond orientation and CIA/CIO). This would significantly increase the time taken to converge the ion images for each state, and at the current repetition rate (10 Hz) of the experiment this would be challenging.

Figure 7.26 shows the CC QM $\rho_0^{\{2\}}(\theta)$ (alignment along $\mathbf{k}$ *i.e.* the scattering frame z -axis) and $\rho_{1-}^{\{1\}}(\theta)$ (orientation parallel or antiparallel to y) with initial orientation of the NO bond axis along the z -axis prior to the collision of NO + Ar for the $|j', \Omega' = 0.5, \epsilon' = +1, e\rangle \leftarrow |j = 0.5, \Omega = 0.5, E = \infty\rangle$ transitions. There is currently no full QM description of the four vector correlation for a $^2\Pi$ diatom with an atom. However, calculations of the j' -PDDCS as a function of orientation of the NO bond axis along the $\pm z$ -axis prior to the collision [230] are possible due to the symmetry of the system.

It is clear that orientation of the NO bond axis along the $\pm z$ -axis prior to the scattering event has very little effect on the $\rho_0^{\{2\}}(\theta)$ alignment moment. Indeed the $\pm z$ -orientation resolved moments are very similar to those observed in the unoriented case. This in itself is not surprising, since the collision induced alignment for unoriented scattering of NO with

[‡]Some initial bond orientation resolved CIA measurements have been undertaken for the scattering of NO with Ar [252]; however, the quality of the images was poor.

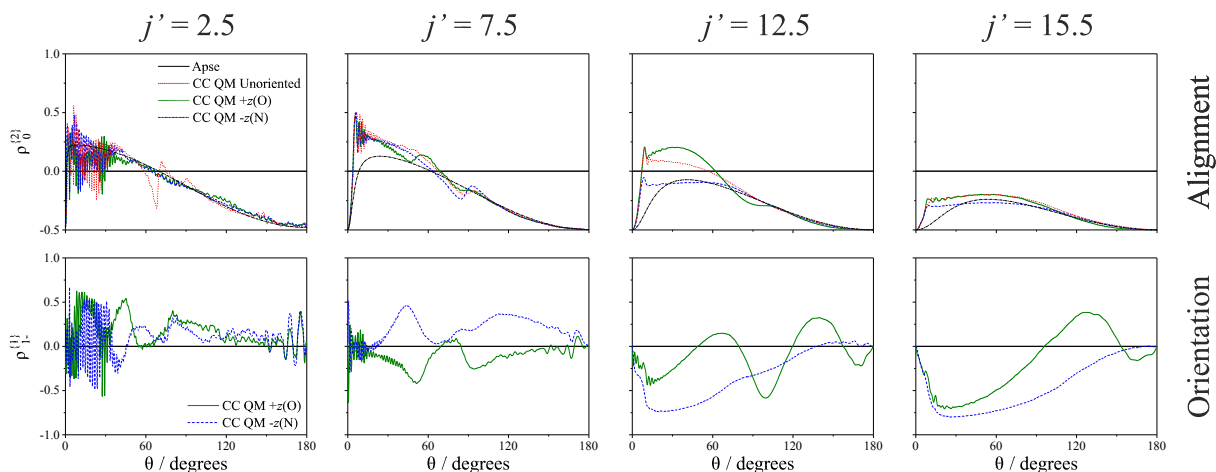


Figure 7.26: Infinite field bond orientation resolved j' -PDDCSs for NO + Ar scattering into final states defined by $|j', \Omega' = 0.5, \epsilon' = +1, e\rangle$, where $j' = 2.5, 7.5, 12.5$, and 15.5 from left to right. The $\rho_0^{\{2\}}(\theta)$ (top) and $\rho_{1-}^{\{1\}}(\theta)$ (bottom) moments correspond to alignment and orientation of the final rotational angular momentum, respectively. The apse model (for alignment) is shown by a black (dashed-dotted) line, the unoriented CC QM moments by a red (dotted) line, and the $+z$ (O) and $-z$ (N) resolved moments shown by green and blue (dashed) lines, respectively.

Ar has been shown previously to be well described by the classical kinematic apse model [86, 87], in which the NO molecule is treated as a rigid ellipse. The $\rho_0^{\{2\}}(\theta)$ moment is positive/negative when j' is parallel/perpendicular to $\mathbf{k}$. As j' increases the moment becomes (on average) more negative, corresponding to alignment of j' perpendicular to the scattering plane (‘frisbee-like’ rotation [79, 86–88]). For lower j' (and in the forwards scattered region at higher j') the moment is more positive, corresponding to rotation in-the-plane of the molecular beams (‘propeller-like’ rotation [86, 87]). QCT calculations by Nichols [252] have shown that scattering from the ‘sides’ of the NO molecule results in predominantly positive alignment (‘propeller-like’ rotation), whilst negative alignment (‘frisbee-like’ rotation) largely occurs from collisions at the ‘ends’ of the molecule. This suggests that larger differences in the alignment moments may be observed for scattering with the NO bond axis oriented along the $\pm x$ -axis than the $\pm z$ -axis.

Collision induced orientation, on the other hand, is known to have both classical and quantum mechanical mechanisms [82–84], and is expected to depend more sensitively than the alignment on initial bond axis orientation. The $\rho_{1-}^{\{1\}}(\theta)$ orientation moment in Figure 7.26 depends strongly on the initial orientation of the NO bond axis. A positive/negative value of

the moment corresponds to j' lying preferentially parallel/anti-parallel to the scattering frame y -axis [83, 84, 252]. For low j' , the moment oscillates between positive and negative, with the sign of the oscillations being opposite for $+z(\text{O})$ and $-z(\text{N})$ orientation. These oscillations are known to be quantum mechanical in nature [83, 84, 252]. At higher j' these oscillations have a lower frequency (due to the increased outgoing de Broglie wavelength) and become more negative (on average) as collisions become more repulsive in nature [83, 252]. Whilst the moments for $\pm z$ -orientation are negative for low scattering angles and become increasingly positive as the scattering angle increases, the $+z(\text{O})$ moment is consistently more positive.

7.8 Summary

In this chapter the effects of bond axis orientation along the x -axis, in which the collision partner approaches the side of the NO molecule, on the inelastic scattering of NO with Ar have been discussed. Firstly, the mechanisms for ‘near-side’ and ‘far-side’ scattering were described. This was followed by a description of experimental and theoretical methods.

Good agreement between experimental and CC QM calculations of the integral steric effect, S_x , was observed and features attributed to the near homonuclearity of the NO molecule as previously described in the z -axis integral steric effect. Experimentally, both in the ion images and the extracted DCSs, a double peak was observed in the $+x$ -orientation for transitions with odd Δj , whilst only a single peak was observed for even Δj transitions. A single peak was observed for all Δj transitions in the $-x$ -geometry. It was shown that at infinite field strengths a double peak is observed for all Δj transitions in the $+x$ -orientation, and only a single peak in the $-x$ -orientation. The differences between the experimental and infinite fields was rationalised by the incomplete mixing of the initial Λ -doublet states at the experimental field, and the multiple/single peaks observed in the field free Λ -doublet states as a function of parity conservation. The experimental data were shown to be in relatively good agreement with the CC QM calculations, although small inconsistencies were observed for $j' = 9.5$ and $j' = 10.5$ due to the overlap of the experimental intensity and LAB zero.

For low and intermediate Δj , the double/single peaks observed in the DCS for the $+x/-x$ -orientations were attributed to rotational rainbows arising from interference between collisions at the ‘ends’ and ‘sides’ of the molecule. The increased number of peaks in the $+x$ -orientation (repulsive scattering ‘off N’) was rationalised by the larger anisotropy of the potential at the ‘N-end’ of the molecule than the ‘O-end’. This reflects the larger impact parameter collisions which may occur for collisions at the ‘N-end’ of the molecule. High RET collisions were shown to preferentially arise from collisions ‘off N’ in the repulsive regime, a largely classical effect arising due to the larger extent of the potential at the ‘N-end’ of the molecule.

A detailed comparison of x - and z -axis bond orientation showed that scattering at the ‘sides’ and ‘ends’ of the NO molecule are fundamentally similar. However, differences (particularly in the forwards scattered region) were shown to arise due to the larger impact parameter collisions possible in the x -axis orientation compared to those for orientation with respect to the z -axis, and the relative anisotropy (for scattering at the ‘N-end’ or ‘O-end’ of the molecule) of the potential in each configuration. Maximisation of the orientation resolved DCSs showed that forwards and sideways scattering are maximised by collisions with the ‘side’ of the NO molecule, as larger impact parameter collisions may occur with the ‘side’ of the molecule than the ‘end’. Backwards scattering was maximised by collisions at the end of the molecule; ‘head-on’ collisions which result in backwards scattering may more easily induce larger rotational energy than collisions with the (flatter) ‘side’ of the molecule due to the larger (classical) torque arm. It has been shown that exquisite control over the probability of scattering into a particular angle, especially in the forwards scattered direction, may be achieved by defining the direction of the orientation field. Finally, avenues for future work, including the measurement of bond axis orientation resolved DCSs for spin-orbit changing transitions and the four vector ($\mathbf{r} - \mathbf{k} - \mathbf{k}' - \mathbf{j}'$) correlation, were described.

Chapter 8

Diffraction Oscillations in Bond Oriented Inelastic Scattering

In many systems, the narrowest features in the DCS are very fast oscillations in the forward scattered region, known as diffraction oscillations [16, 17, 369, 372–374]. These oscillations are caused by molecular diffraction, in which the incoming ‘matter wave’ of one collision partner scatters off the other partner in much the same way as light diffracting off an object [80, 240, 375]. The diffraction oscillations are purely quantum mechanical in nature, and have no classical analogue. A simplified illustration of such behaviour is shown in Figure 8.1.

Whilst the forward scattered region of the DCS has been theoretically calculated and modelled [369, 376, 377], only specific systems have been amenable to the measurement of diffraction oscillations experimentally [17, 76, 265, 266, 372, 374, 378–380]. The relatively recent advent of Stark decelerated crossed molecular beam experiments has allowed the group of van de Meerakker [80, 123, 263, 272, 273, 366, 375] to experimentally measure diffraction oscillations in the inelastic collisions of NO(X) with a variety of collision partners. By Stark decelerating the packet of NO radicals, and therefore obtaining fine control of the velocity and angular spreads of the NO($X^2\Pi_{0.5}$, $j = 0.5$, f) molecules in the molecular beam, resolution of the velocity-mapped ion image is increased. This is particularly true in the case of counterpropagating beams [80, 123]. The diffraction oscillations are known to be very sensitive to the PES upon which scattering occurs [263]; this sensitivity to the underlying PES is expected to lead to observable differences for scattering from the ‘ends’ and ‘sides’ of the NO molecule.

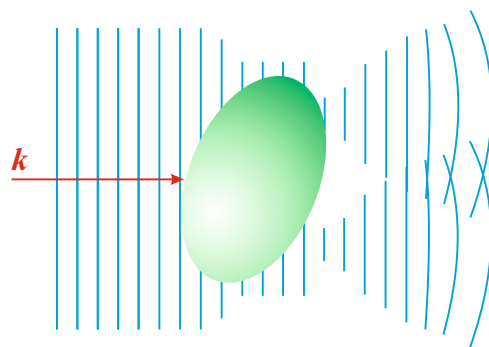


Figure 8.1: Illustration of diffraction.

In this chapter, the effect of initial bond axis orientation on the forward scattered region of the DCS will be investigated theoretically. A brief discussion of the field free case will be given, before extension to field dependent ‘isotropic orientation’. Orientation with respect to the z -axis will be discussed in terms of the r -PDDCSs, repulsive scattering, and the effects of both ℓ -type and rotational (orientational) rainbows on the observed scattering distribution. The importance of the anisotropy in the potential for $\text{NO}(\text{X}) + \text{Rg}$ scattering will be discussed in detail. This will be followed by a comparison with orientation with respect to the x -axis. Finally, the question of experimental measurements will be addressed.

8.1 Theoretical Methods

The CC QM calculations presented here were calculated according to the methods described in Chapter 2 and extended, for initial bond axis orientation, in Chapter 5. Calculations were run at the fixed collision energies in Table 3.1, on the relevant V_{sum} and V_{diff} PES surfaces described in Section 2.2, using the HIBRIDON suite of codes [226]. Rotational levels up to $j' = 20.5$, both Λ -doublets ($\epsilon = \pm 1$) and spin-orbit manifolds ($\Omega = 0.5, 1.5$) were included in the wave function. Partial waves up to and including $J = 142.5$ (He), 180.5 (Ar), and 290.5 (Xe) were used to ensure convergence. Observables were calculated using the methodology in Section 5.3.2 Calculations were run at the experimental field (9.2 kV cm^{-1}), with mixing parameters $|\alpha_{\text{expt}}| = 0.64$ and $|\beta_{\text{expt}}| = 1.26$. Any modifications made to the PES used are noted when the data are presented.

Rg	$k / \text{\AA}^{-1}$	$A_N / \text{\AA}$	$A_O / \text{\AA}$	$B / \text{\AA}$	$R / \text{\AA}$	$\Delta\theta$	$\Delta\theta_N$	$\Delta\theta_O$
He	10.93	2.88	2.78	2.37	2.67	6.16 (4.90)	5.72	5.95
Ar	26.20	3.45	3.28	2.85	3.19	2.15 (1.60)	1.99	2.09
Xe	27.09	3.77	3.67	3.24	3.56	1.87 (1.40)	1.76	1.81

Table 8.1: Hard shell parameters for the scattering of NO with He, Ar, and Xe; the major (A_N and A_O) and minor (B) semi-axes. The effective radius, R , is the average of the major and minor semi-axes of the hard shell according to $R = (A_N + A_O + B) / 3$. The angular spacing, $\Delta\theta$, is shown for the averaged case, as well as for each major semi-axis ($\Delta\theta_N$ and $\Delta\theta_O$), where $R = A_N$ and $R = A_O$, respectively; the QM separation, for $\Delta\theta$, is shown in brackets.

8.2 The Field Free Case

Semi-classically, the angular spacing, $\Delta\theta$, between diffraction oscillations, may be obtained according to a hard shell model [263, 265]

$$\Delta\theta = \frac{\pi}{kR}, \quad (8.1)$$

where k is the magnitude of the collision wave vector and R is the radius of the ‘target’.* The NO molecule may be modelled as a hard shell ellipse with major and minor semi-axes of A and B , respectively. Since NO is heteronuclear two major semi-axes may be defined; A_N and A_O , corresponding to the distance between the center-of-mass of the molecule and the ‘N’ and ‘O’ nuclei, respectively. The effective radius, R , is taken to be the average of all radii, $R = (A_N + A_O + B) / 3$, and is shown in Table 8.1 for the collision of NO with He, Ar, and Xe at the experimental collision energies defined in Table 3.1.

Figure 8.2 shows the forward scattered region ($0^\circ \leq \theta \leq 20^\circ$) of the DCS for the unoriented scattering of NO(X) with He, Ar, and Xe into the $|j', \Omega' = 0.5, \epsilon' = -1, f\rangle$ state, where $j' = 1.5$, 3.5, and 6.5. Fast oscillations in this region of the DCS are clearly visible for all systems. As can be seen from Table 8.1, the semi-classical model consistently overestimates $\Delta\theta$, likely due to modelling the NO molecule as a hard shell ellipse (with no attractive contributions to the PES), and the approximation of the effective radius of the ellipse as a simple average [96, 366].

*This is equivalent to the angular spacing for Fraunhofer diffraction by a slit of infinite depth, where the slit is replaced by a ‘target’ of radius R , and k is related to the de Broglie wavelength, $\lambda = 2\pi/k$, of the system.

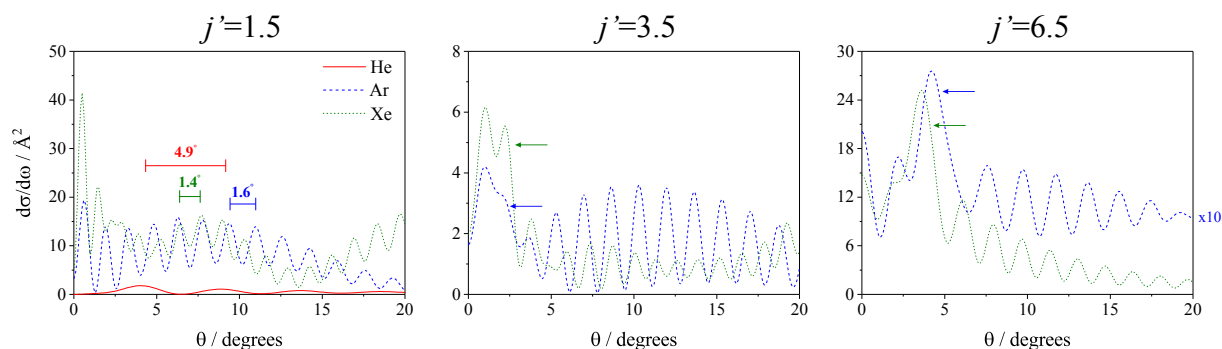


Figure 8.2: QM DCS for the unoriented scattering of NO with He, Ar, and Xe for the $|j', \Omega = 0.5, \varepsilon = -1, f\rangle \leftarrow |j = 0.5, \Omega = 0.5, \varepsilon = -1, f\rangle$ transitions, where $j' = 1.5, 3.5$ and 6.5 (from left to right). For $j' = 1.5$ the angular separation, $\Delta\theta$, is shown. For $j' = 3.5$ and 6.5 the arrows show the ‘irregular diffraction peak’; this peak is washed out by the presence of other structures for scattering with He and is not shown. The $j' = 6.5$ DCS for Ar has been multiplied by a factor of 10 for clarity.

The decrease in the value of $\Delta\theta$, in both the classical and QM calculations, on going from He to Ar to Xe is due to the increase in the effective size of the target.

In each DCS in Figure 8.2 a peak exists (shown by the blue and green arrows for scattering with Ar and Xe, respectively) which is mismatched with the regular oscillation pattern. The ($j' = 3.5$ and 6.5) DCSs for scattering with He are not shown as no significant ‘irregular’ peak is observed, as it is washed out by other features in the DCS. Onvlee *et al.* [366, 375] have been able to resolve this peak (along with the regular oscillations) in the DCS for NO + Ar scattering using a Stark decelerated NO molecular beam and counter propagating beams to achieve sufficient resolution; these techniques will be discussed further in Section 8.6. The origin of this peak has been attributed to the ‘side-on’ orientation of the NO bond axis with respect to the incoming collision partner [240, 366, 375]. This is in agreement with the Huygens-Fresnel principle [381], in which maximum diffraction is achieved when the anisotropy of the molecules shape is maximal.

8.3 Isotropic Orientation

In Chapter 5, (field dependent) ‘isotropic’ scattering was shown to be equivalent to the incoherent sum of the contributions from the initial e and f states, arising from the presence

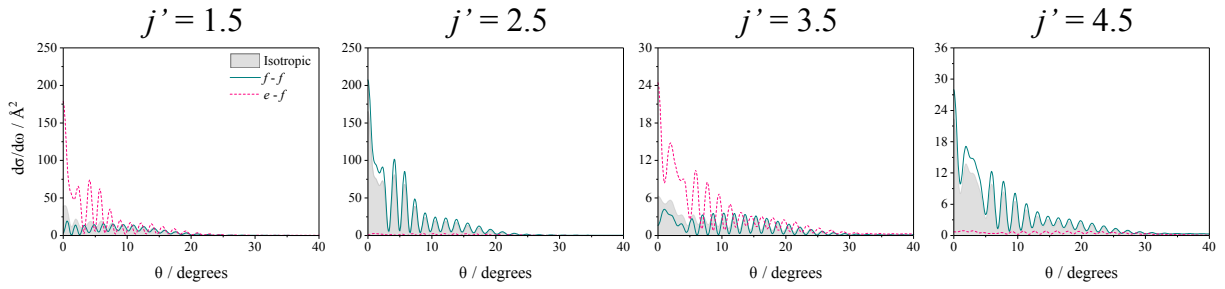


Figure 8.3: Λ -doublet resolved CC QM DCSs for the NO + Ar $|j', \Omega' = 0.5, \varepsilon' = -1, f\rangle \leftarrow |j = 0.5, \Omega' = 0.5, \varepsilon'\rangle$ transitions into $j' = 1.5 - 4.5$, from left to right. The initial f and e states are shown by teal and pink (dashed) lines, respectively. The isotropic DCS in the presence of a static electric field is shown by the grey shading.

of the electric field

$$R_0^{(0)}(\theta) \propto \frac{d\sigma_{\text{iso}}}{d\omega}(\theta) = \alpha^2 \frac{d\sigma_{\varepsilon' \leftarrow e}}{d\omega}(\theta) + \beta^2 \frac{d\sigma_{\varepsilon' \leftarrow f}}{d\omega}(\theta), \quad (8.2)$$

where α and β are the field dependent mixing parameters in Equation (5.6). Figure 8.3 shows the isotropic DCS (shaded in grey) and the Λ -doublet resolved DCSs in Equation (8.2), for scattering of NO with Ar into the final f Λ -doublet, in the diffraction dominated region of the DCS. In the field free (unoriented) case, the parity conserving DCS ($f \rightarrow f$ and $e \rightarrow f$ for even and odd Δj , respectively) has greater magnitude than the parity changing DCS. This may be rationalised simply by the near-homonuclearity of the NO molecule, leading to even (homonuclear) terms dominating in the Legendre expansion of the potential, which favour parity conservation [230, 382]. However, the relative magnitudes of the parity conserving and changing transitions depend on whether Δj is odd or even. For even Δj , in the field free case, the magnitude of the parity conserving transition is very large in comparison to the parity changing transition. Consequently, upon application of the static (orientation) field the isotropic DCS is approximately equivalent to the field free parity conserving DCS weighted by the relevant field dependent mixing parameter (β^2 for transitions from the initial f state). Meanwhile, odd values of Δj have parity conserving and changing transitions of more similar magnitude in the field free case, and therefore characteristics of both initial Λ -doublets are observed in the isotropic DCS.

8.3.1 The Fraunhofer Model

The Fraunhofer model, originally used to model inelastic nuclear scattering [383–385], was adapted by Faubel [373] for rotational energy transfer (RET). Further adaptation by Lemeshko and Friedrich [376] allowed the description of the scattering of an open shell diatom with a closed shell atom in the presence of a field. The model requires only information about the shape of the target (in this case the hard-shell potential of the NO molecule) in the form of the Legendre moments, along with the wave vector, $\mathbf{k}$, which describes the incoming matter wave. Two assumptions are made: firstly, the energy sudden approximation, allowing the inelastic scattering amplitudes to be written in terms of their elastic counterparts. Secondly, that the scattering amplitude may be replaced by the Fraunhofer diffraction amplitude. Onvlee *et al.* [375] have shown that the model may be used to accurately reproduce the diffraction patterns observed in the unoriented scattering of NO(X) with the rare gases.

In the presence of an electric field, the Fraunhofer scattering amplitude for a $^2\Pi$ molecule may be written [376]

$$\begin{aligned}
 f_{i \rightarrow f}(\theta) = & \frac{ikR_0}{4\pi} \sqrt{\frac{2j+1}{2j'+1}} \sum_{\substack{\kappa\rho \\ \kappa \neq 0 \\ \kappa+\rho \text{ even}}} D_{-\rho, \Delta m}^{\kappa *}(\phi_E, \theta_E, 0) \Xi_{\kappa 0} F_{\kappa \rho} J_{|\rho|}(kR_0\theta) \\
 & \times \langle jm, \kappa \Delta m | j' m' \rangle \langle j | \Omega, \kappa 0 | j' | \Omega' \rangle \\
 & \times \left\{ \begin{array}{l} \beta \left[(-1)^\kappa + (-1)^{\Delta j} \right] + \alpha \left[(-1)^\kappa - (-1)^{\Delta j} \right] \\ \alpha \left[(-1)^\kappa + (-1)^{\Delta j} \right] + \beta \left[(-1)^\kappa - (-1)^{\Delta j} \right] \end{array} \right\}, \quad (8.3)
 \end{aligned}$$

where the first and second row of the expression in curly brackets correspond to the f and e final states, respectively. The values of m and m' are the projection of the angular momenta, $\mathbf{j}$ and $\mathbf{j}'$, onto the wave vector, $\mathbf{k}$; Ω and Ω' are the projections of $\mathbf{j}$ and $\mathbf{j}'$ onto the internuclear axis; α and β are the field dependent mixing parameters in Equation (5.6); and $J_{|\rho|}(kR_0\theta)$ is a

Bessel function of the first kind. The function $F_{\kappa\rho}$ is [376]

$$F_{\kappa\rho} = \begin{cases} (-1)^\rho 2\pi \left(\frac{2\kappa+1}{4\pi}\right)^{1/2} (-i)^\kappa \frac{\sqrt{(\kappa+\rho)! (\kappa-\rho)!}}{(\kappa+\rho)!! (\kappa-\rho)!!} & \kappa + \rho \text{ even, } \kappa \geq \rho \\ 0 & \text{elsewhere .} \end{cases} \quad (8.4)$$

The shape of the object from which the incoming waves scatter is defined by the repulsive hard shell contour of the PES at the collision energy of interest, which may be described by the expansion of a series of spherical harmonics [376]

$$R(\theta, \phi) = \sum_{\kappa=0}^{\kappa_{\max}} \Xi_{\kappa 0} Y_{\kappa 0}(\theta, \phi) , \quad (8.5)$$

where $\Xi_{\kappa 0}$ are the expansion coefficients and $Y_{\kappa 0}(\theta, \phi)$ are spherical harmonics. The zeroth-order moment ($\kappa = 0$) corresponds to a sharp edged disk of radius, $R_0 = \Xi_{00}/\sqrt{4\pi}$, and higher order moments describe deviations from this shape.

The Fraunhofer model is not quantitative and cannot yield integral or differential cross sections [376]. Consequently, it is necessary to apply two scaling factors [240, 375] to the Fraunhofer DCS in order to allow comparison with the corresponding CC QM DCS. Before correction, the diffraction structure in the Fraunhofer DCS appears shifted relative to the QM structures (typically by $\ll 1^\circ$). To correct for this, the radius of the hard shell object is multiplied by a system dependent scaling factor (1.20 for Ar), to account for the finite range of the repulsive potential as well as any contributions from the attractive part of the potential [240, 375]. Secondly, a factor is required to scale the magnitude of the Fraunhofer DCS itself such that the intensity of the most prominent peak, known as the ‘irregular diffraction peak’ (shown by a green arrow in Figure 8.4), is equivalent in the QM and Fraunhofer DCS [240, 375]. This factor can be very large, and is indicated in each relevant plot.

Figure 8.4 shows the oriented Fraunhofer DCS and the CC QM isotropic DCS for NO + Ar scattering into several final states. The Fraunhofer model qualitatively describes the diffraction pattern observed in the isotropic QM DCS. Since the model depends only on the projection of a hard shell object onto the xy plane, attractive forces are not accounted for, leading to differences

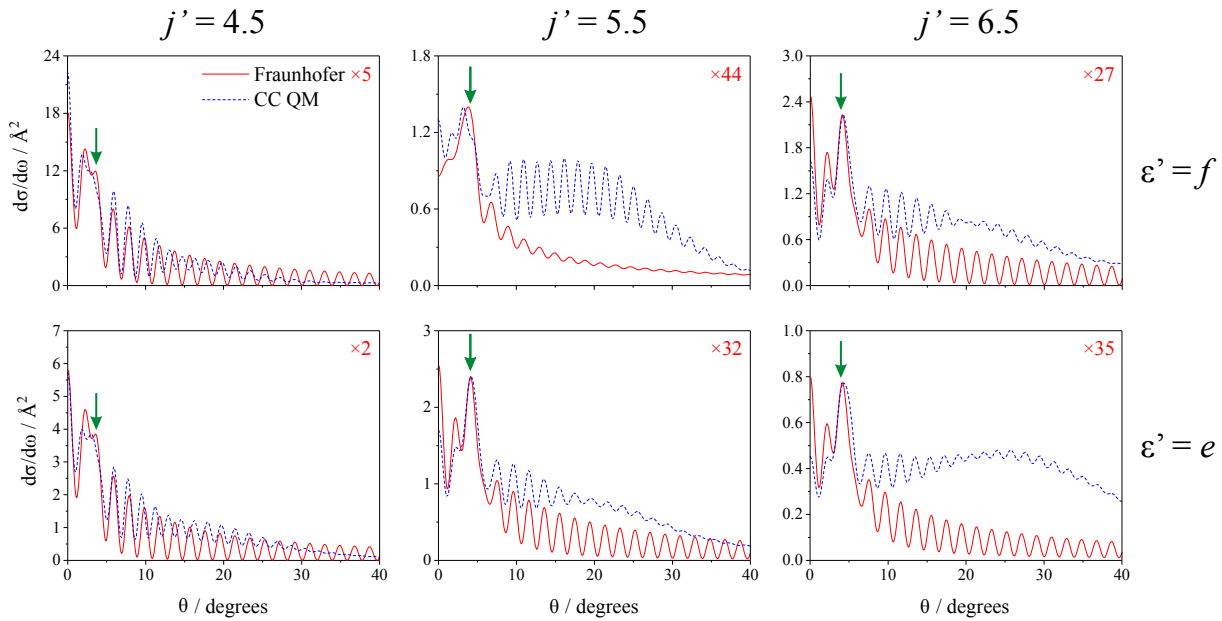


Figure 8.4: Oriented Fraunhofer (red) and isotropic CC QM (blue dashed) DCSs for the NO + Ar $|j', \Omega' = 0.5, \epsilon'\rangle \leftarrow |j = 0.5, \Omega = 0.5, E\rangle$ transition into $j' = 4.5 - 6.5$ (from left to right), for $\epsilon' = -1, f$ (top) and $\epsilon' = +1, e$ (bottom). The green arrow denotes the ‘irregular diffraction peak’ in each case. The Fraunhofer DCSs have been scaled by the factor shown in the top right of each panel.

in the absolute magnitude of the diffraction oscillations. The ‘irregular peak’ (see Section 8.2 for the field free case), which will be discussed further in Section 8.5, is very well described by the Fraunhofer model, indicating that it arises from diffractive scattering from the repulsive wall of the diatom. At larger scattering angles ($\theta > 30^\circ$) the model begins to break down, as the assumptions on which the Fraunhofer model is built begin to fail [375].

8.4 z-Axis Orientation

The CC QM z -axis oriented DCSs for the collision of NO with He, Ar, and Xe are shown in Figure 8.5 for the $|j', \Omega' = 0.5, \epsilon' = -1, f\rangle \leftarrow |j = 0.5, \Omega = 0.5, E\rangle$ transitions, where $j' = 1.5$ to 8.5. As in the unoriented case, irrelevant of which orientation is considered, the angular separation between peaks becomes smaller on going from He to Ar to Xe; the smaller ‘target’ size of He leads to a larger angular separation, see Equation (8.1). Note that the angular separation also depends on the de Broglie wavelength of the system, which enters into Equation (8.1) as the wave vector. It is clear that above a certain rotational transition, $j' = 3.5$ for the scattering of NO with He, diffraction oscillations are no longer an important feature in the

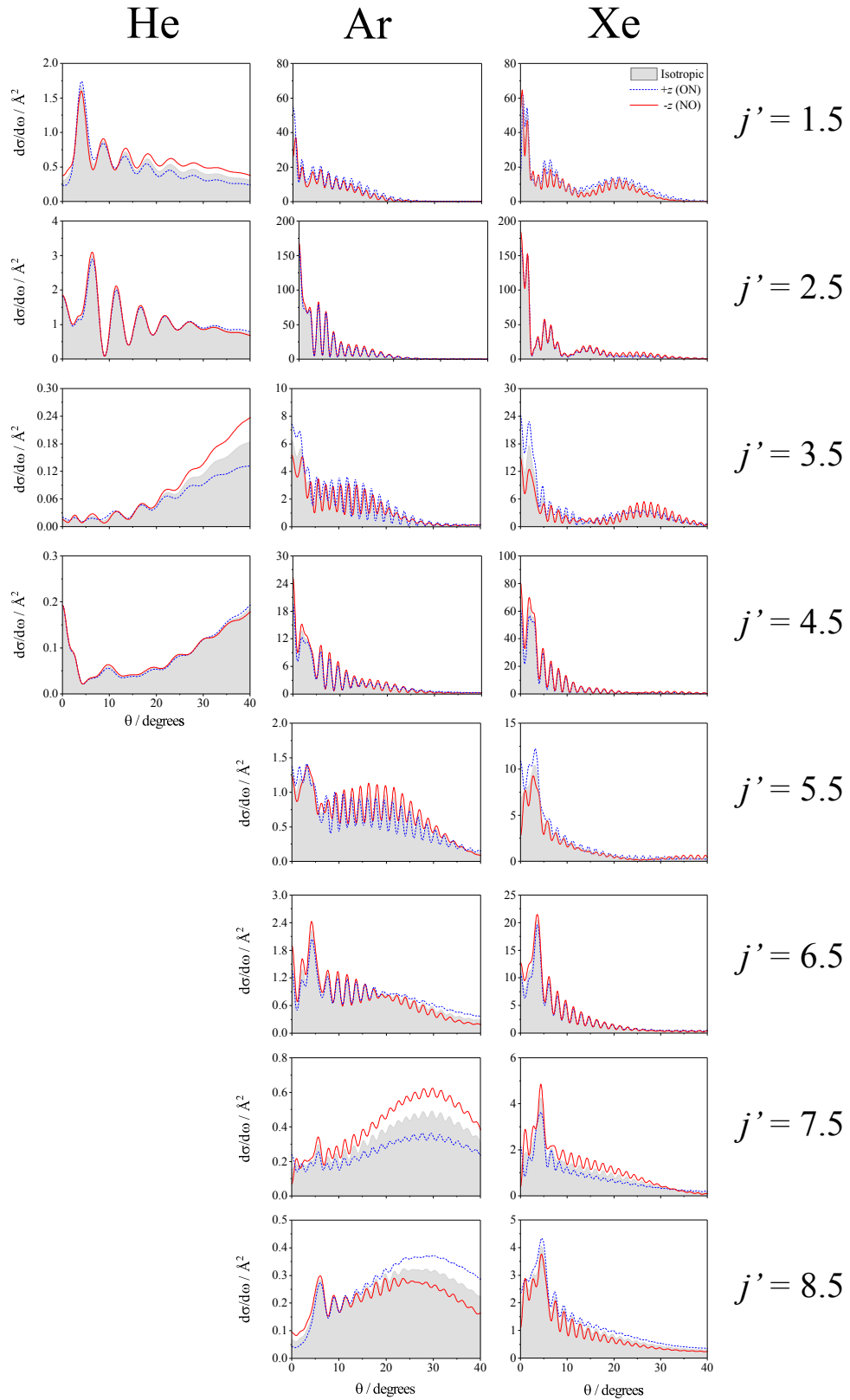


Figure 8.5: CC QM z -axis oriented DCSs in the forward scattered region for the $|j', \Omega' = 0.5, \varepsilon' = -1, f\rangle \leftarrow |j = 0.5, \Omega = 0.5, E\rangle$ transitions of NO scattering with He (left), Ar (middle) and Xe (right) at the collision energies defined in Table 3.1, where $j' = 1.5$ to 8.5 from top to bottom. For He no states above $j' = 4.5$ are shown, since these states show no evidence of oscillations in the DCS. The red and blue (dashed) lines denote collisions corresponding to $-z$ (N) and $+z$ (O) bond axis orientation, respectively. The (field dependent) isotropic DCS is shaded in grey.

forwards scattered region of the DCS. Such transitions are not shown for Ar and Xe as they occur at much higher values of j' , due to the increased well depths of these potentials (which is correlated with the polarisability of the collision partner) [306].

The semi-classical model in Equation (8.1) used to describe the spacing between diffraction oscillations may be extended to include information about the initial orientation of the diatom bond axis by replacing the average radius of the target, R , with the major/minor semi-axes of interest. If the collision partner approaches from either ‘end’ of the molecule (*i.e.* approach along the NO bond axis) the target is ‘circular’, with the same radius (equivalent to the minor semi-axis of the hard shell) for both ‘N-end’ and ‘O-end’ collisions ($R = B$), resulting in the same value of $\Delta\theta$ for both $\pm z$ -orientations. On the other hand, approach of the collision partner towards the ‘side’ of the molecule (*i.e.* perpendicular to the NO bond axis) results in an ellipsoidal target. Since NO is heteronuclear, the ellipse extends further at the ‘N-end’ of the molecule than the ‘O-end’, and the hard shell is described by two major semi-axes (shown in Table 8.1). Consequently, Equation (8.1) predicts different angular spacings for the two ‘side-on’ orientations, with the $+x$ -orientation (corresponding to repulsive ‘near-side’ scattering ‘off N’) having a larger effective radius ($R = A_N$) than the $-x$ -orientation ($R = A_O$), and correspondingly, a smaller angular spacing between the oscillations in the DCS. This will be discussed further when considering x -axis orientation in Section 8.5.

Several features due to the attractive parts of the potential in collisions with Ar and Xe are observed in the underlying shape of the DCS, over which the fast oscillations are superimposed, including glory scattering and ℓ -type rainbows [39, 77–79, 223, 306, 318, 374, 386]. They are not observed in collisions with He due to the largely repulsive nature of the PES (see Figure 2.3). The effect of such dynamics on the overall structure of the DCS will be discussed in more detail in Section 8.4.3. As in the ‘isotropic’ and field free cases, an ‘irregular diffraction peak’ [375] is observed which stands out against the more regular diffraction pattern; this will be discussed in more detail in Section 8.5.

A propensity is observed for all systems, depending on whether the transition leads to an odd or even value of Δj . Focus first on those transitions with an even value of Δj shown in

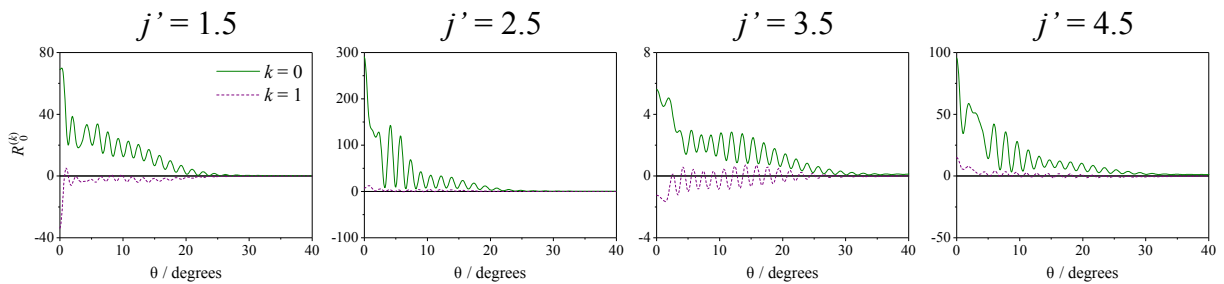


Figure 8.6: CC QM $R_0^{(0)}(\theta)$ (green line) and $R_0^{(1)}(\theta)$ (purple dashed line) moments, in the forward scattered region for the NO + Ar $|j', \Omega' = 0.5, \varepsilon' = -1, f\rangle \leftarrow |j = 0.5, \Omega' = 0.5, E\rangle$ transitions with $j' = 1.5 - 4.5$, from left to right.

Figure 8.5; the structure and magnitude of the oscillations is very similar for both the $+z$ - and $-z$ -orientations. The difference in magnitude is smallest for low Δj transitions, which is in-line with the small absolute magnitude of the integral steric effect for these states [95]. However, even for transitions to higher states, such as that into $j' = 8.5$, the structure is almost identical for both orientations and differs only in magnitude, as defined by the integral steric effect.

For transitions with an odd value of Δj , significant differences between the $+z$ - and $-z$ -orientations are observed. Firstly, in general, the difference in magnitude between the two orientations is much larger than for transitions with even Δj , and secondly, the structure of the oscillations differs (although sometimes subtly). In the region where the oscillations are most regular this corresponds to a shift of the peak for the $+z(\text{O})$ -orientation with respect to the $-z(\text{N})$ -orientation. In each case the $+z(\text{O})$ orientation occurs at smaller values of θ than the corresponding peak in the $-z(\text{N})$ orientation, whilst the peak in the isotropic DCS lies directly between the $\pm z$ -orientations. It is not immediately obvious why this occurs; calculations on various modified PESs in the following sections will be used to investigate the origin of this effect.

8.4.1 The $R_0^{(1)}$ Moment

For scattering in the ‘end-on’ geometry, the orientation resolved DCS in Equation (5.25), depends on only the $R_0^{(1)}(\theta)$ and $R_0^{(0)}(\theta)$ bond orientation moments. These moments are shown in Figure 8.6 for several NO + Ar transitions. The $R_0^{(0)}(\theta)$ moment is proportional to the (field dependent) isotropic DCS, described in Section 8.3, whilst the $R_0^{(1)}(\theta)$ moment

provides information about differences in scattering dynamics for initial orientation of the NO bond axis either parallel or anti-parallel to the z -axis (and is field strength independent). For odd Δj transitions, the oscillations in the $R_0^{(1)}(\theta)$ moment are shifted relative to the corresponding peaks in the isotropic DCS, which accounts for the shift of the oscillations in the oriented DCS with respect to the isotropic DCS. For transitions with even Δj , although a slight shift in peak position is observed between the two orientation moments, the effect is much smaller than for odd values of Δj . Furthermore, the relatively small magnitude of the $R_0^{(1)}(\theta)$ moment with respect to the $R_0^{(0)}(\theta)$ moments leads to negligibly small changes in the oriented DCS relative to the isotropic DCS.

8.4.2 Repulsive Scattering

In the unoriented case, the diffraction oscillations in the DCS may be largely described by scattering with the repulsive core of the NO molecule [240]. Upon bond-orientation it is important to see whether this holds, or whether an attractive mechanism becomes important. It is possible to confirm this *via* removal of the attractive part of the potential according to the method in Section 2.4. Full CC QM calculations are then run on the modified ('soft') potential; the results of which are shown in Figure 8.7 for the z -axis oriented scattering of NO with Ar. It should be noted that removal of the attractive part of the potential affects the observed angular scattering distribution, as the DCS becomes more backwards scattered due to the more 'head-on' nature of collisions with the repulsive wall of the potential.

It is clear that the diffraction oscillations are still present when only repulsive collisions are considered, suggesting that this behaviour largely arises from the repulsive part of the potential [240, 366, 375]. Despite the changes in the DCS due to the removal of the attractive part of the potential, it is clear that the position of the diffraction oscillation peaks for collisions at the 'N-end' and 'O-end' of the molecule, for all Δj transitions, are approximately equivalent to the isotropic peaks in the DCS. There is still a difference in magnitude between collisions at the two ends of the molecule, due to the inherent steric asymmetry of the collision, which is also known to derive from the repulsive part of the potential [95, 219]. The modification of the peak

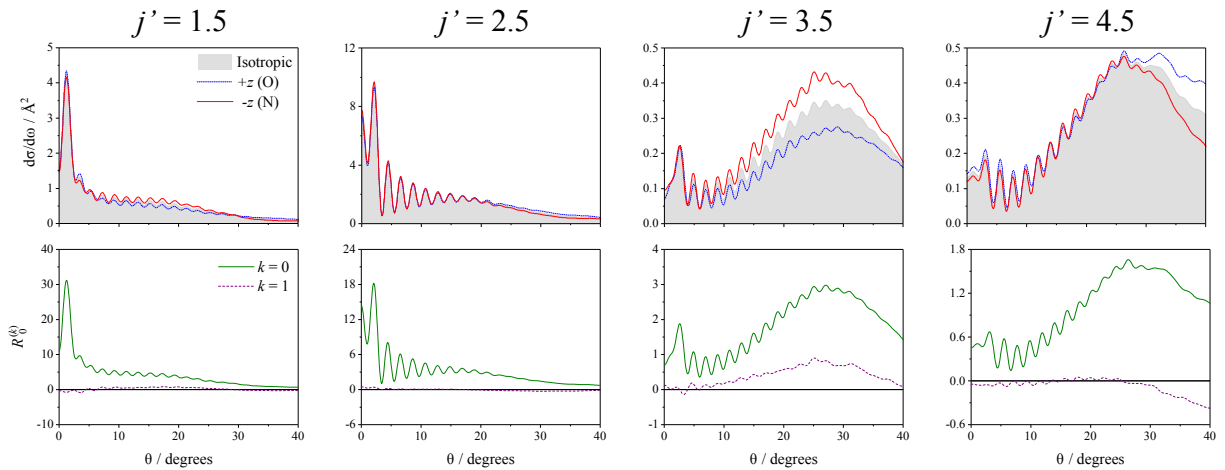


Figure 8.7: CC QM z -axis r -PDDCSs, calculated on the ‘soft’ potential, in the forward scattered region for the NO + Ar $|j', \Omega' = 0.5, \epsilon' = -1, f\rangle \leftarrow |j = 0.5, \Omega' = 0.5, E\rangle$ transitions where $j' = 1.5 - 4.5$ from left to right. The top row shows the bond axis resolved DCSs, where the red and blue (dashed) lines correspond to collisions in the $-z(N)$ - and $+z(O)$ -orientations, respectively. The grey shading corresponds to the isotropic DCS in the presence of a static electric field. The bottom row shows the $R_0^{(0)}(\theta)$ and $R_0^{(1)}(\theta)$ moments with green and purple (dashed) lines, respectively.

positions as a function of the attractive part of the potential suggests that whilst the diffraction pattern largely arises from scattering off of the repulsive core of the molecule, attractive effects play a significant role in the observed differences between the oscillations in the DCSs for each initial bond axis orientation.

The $R_0^{(1)}(\theta)$ and $R_0^{(0)}(\theta)$ moments calculated on the ‘soft’ potential are also plotted in Figure 8.7. The similarities between the $\pm z$ -orientation resolved DCSs can be understood in terms of the very small $R_0^{(1)}(\theta)$ moment, which results in only small modifications to the isotropic DCS. That is, on the ‘soft’ potential the DCS does not depend strongly on the initial orientation of the NO bond axis. Note that where differences in magnitude are observed between the $\pm z$ -orientations (*e.g.* $j' = 3.5$) the $R_0^{(1)}(\theta)$ moment has a larger magnitude, but the oscillations superimposed over the moment are very small in amplitude. The bond orientation moments can be compared to those on the full potential in Figure 8.6; where the relative magnitude of the $R_0^{(1)}(\theta)$ moment is much larger (for transitions with odd Δj), and the oscillations are of much more similar amplitude to those in the $R_0^{(0)}(\theta)$ moment. That is, the oscillations in the DCS depends more strongly on the bond axis orientation on the full potential than the soft one.

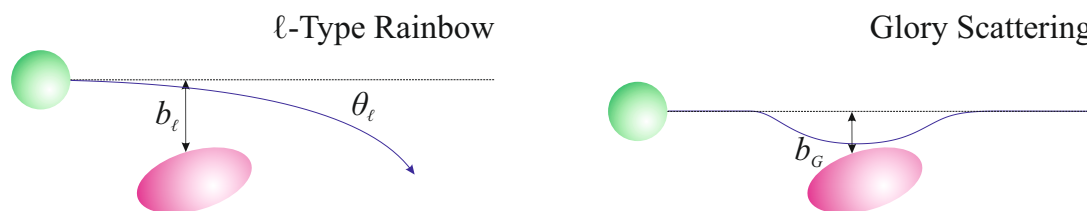


Figure 8.8: Schematic depicting ℓ -type rainbow scattering (left) and glory scattering (right). b_ℓ and b_G describe the classical impact parameter for which ℓ -type rainbow and glory scattering occur, respectively. θ_ℓ describes the rainbow angle, *i.e.* the scattering angle at which ℓ -type rainbow scattering occurs. Adapted from Reference [13].

8.4.3 Rainbow Scattering

Several different mechanisms give rise to the broad oscillatory features, which are overlaid by the diffraction oscillations, in the forward scattered region of the DCS for low and moderate rotational energy transfer collisions. These features are typically attributed to rainbow scattering [80]. The effects of such scattering dynamics have been studied in depth for unoriented collisions of NO(X) with the rare gases [25, 33, 35, 39, 75, 77–79, 195, 263, 271, 273, 275], including measurements with resolution of the superimposed diffraction oscillations [80, 366]. However, there has been less work related to rainbow scattering in initially bond oriented systems [97]. Rotational rainbows, which arise from the repulsive part of the potential, were discussed in Chapter 7 to rationalise the number of peaks observed in the $\pm x$ -orientation resolved DCSs. A detailed description of such rainbows is given in Section 7.5.1.

ℓ -type Rainbows

Whilst rotational rainbows (see Section 7.5.1) arise from the repulsive part of the PES, there also exists a rainbow in the DCS arising from the presence of the attractive part of the potential [79, 366], known as an ℓ -type rainbow. These rainbows arise due to trajectories which are deflected by the attractive part of the PES being amplified by constructive quantum interference, which leads to a build-up of scattering intensity in the DCS at the rainbow angle, θ_ℓ [79, 318, 366]. Also observed in atom-atom scattering [387], these trajectories originate from partial waves with $J > J_G$ (the glory partial wave, which corresponds to scattering with almost zero deflection), corresponding to ‘far-side’ collisions. Since these partial waves

Rg	$\varepsilon / \text{cm}^{-1}$	θ_ℓ
He	16.5	3.3°
Ar	70.7	12.4°
Xe	113.9	30.5°

Table 8.2: Parameters related to the ℓ -type rainbow, see Equation (8.6)), for the scattering of NO with the rare gases.

cannot induce large RET, the effect is most prominent for low Δj transitions. A schematic of both ℓ -type rainbow and glory scattering are shown in Figure 8.8.

Classically, the rainbow angle may be approximated by [366, 374]

$$\theta_\ell = \frac{2\varepsilon}{E_{\text{coll}}}, \quad (8.6)$$

where ε is the minimum of the isotropic potential (corresponding to the well depth of the V_{00} term in the expansion of the PES). The classical values of θ_ℓ are shown in Table 8.2 for collisions with He, Ar, and Xe at the collision energies in Table 3.1. As the rare gas collision partner becomes increasingly polarisable, from He to Xe, the well depth of the isotropic potential term becomes larger and as such θ_ℓ shifts to larger angles.

Structural Assignment

Figure 8.9 shows the z -axis oriented CC QM DCSs for the collision of NO with He, Ar, and Xe into several final rotational states with $\varepsilon' = -1, f$. The classical rainbow angles, θ_R and θ_ℓ , calculated according to Equations (7.6) and (8.6), are shown by black and green arrows, respectively. Assignment of the structures in the DCS is somewhat complicated by the overlap between rotational and ℓ -type rainbows (in particular for collisions with Ar), and the presence of strong glory scattering. Both types of rainbow are shifted from the classically predicted values. Structure arising from rainbow scattering is most clear for collisions with Xe, as the rotational and ℓ -type rainbows do not significantly overlap for the rotational states shown. It is important to note that no ℓ -type rainbow is observed in the QM DCSs for scattering with He, as the system is largely repulsive in nature (see Figure 2.3).

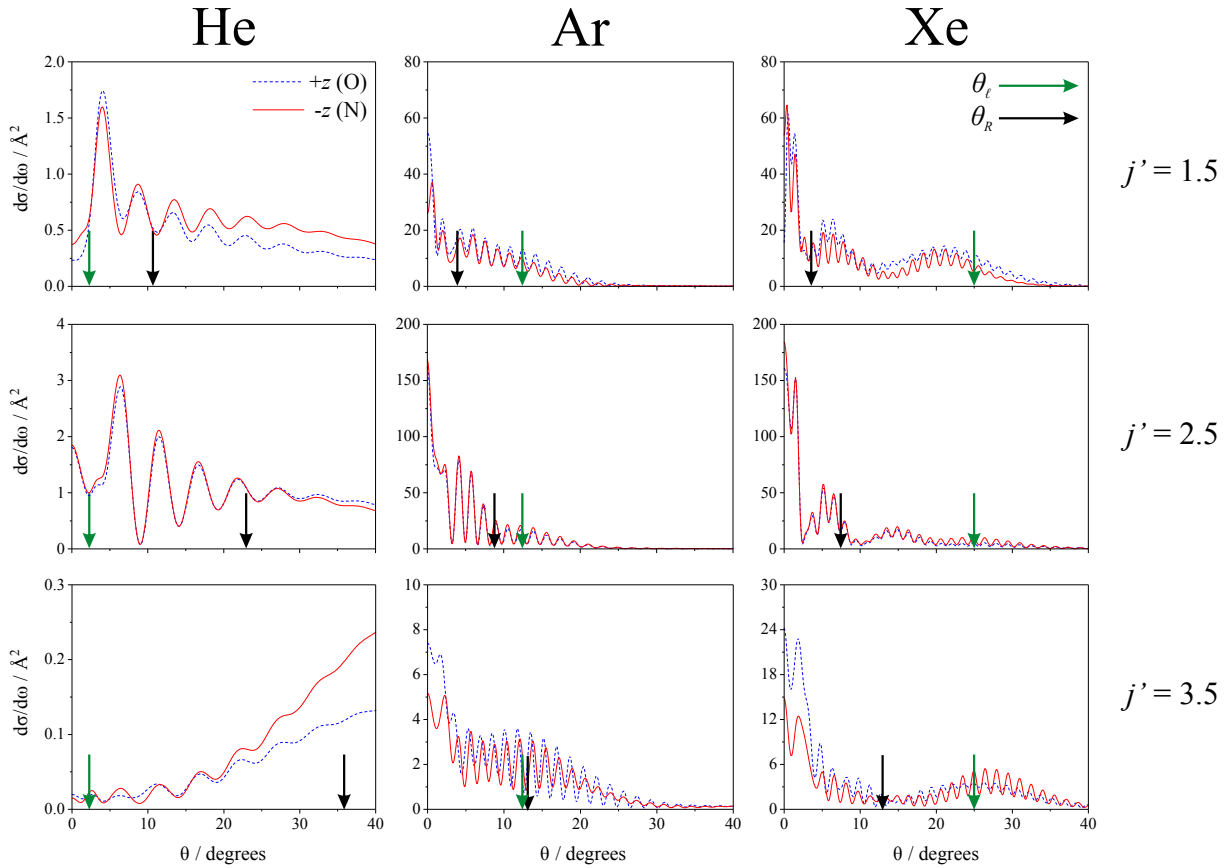


Figure 8.9: z -axis oriented CC QM DCS for the $|j', \Omega' = 0.5, \varepsilon' = -1, f\rangle \leftarrow |j = 0.5, \Omega' = 0.5, E\rangle$ transitions for scattering of NO with the rare gases, where Rg = He, Ar and Xe (from left to right), and $j' = 1.5 - 3.5$ (from top to bottom). The $+z$ (O)- and $-z$ (N)-orientations are shown by blue (dashed) and red lines respectively. The black and green arrows depict the classical value of θ_R and θ_ℓ , respectively.

The ℓ -type rainbow peak is observed to be stronger for odd Δj transitions than even ones; this may be explained in a similar manner to that for the unoriented case. In unoriented scattering the ℓ -type rainbow is only observed for parity changing transitions, and is suppressed by the presence of very strong glory scattering for parity conserving transitions [79]. Of course, upon bond orientation the initial state is a coherent superposition of the e and f Λ -doublet states and the concept of parity conserving and changing transitions does not exist. However, as discussed previously, the $f \rightarrow f$ transitions dominate the oriented DCS for even Δj transitions; these transitions are parity conserving, dominated by the homonuclear (even) terms in the potential and, as such, only a weak rainbow is expected. Meanwhile, for transitions resulting in an odd Δj state, both initial Λ -doublets contribute to the oriented DCS and a strong ℓ -type rainbow is observed.

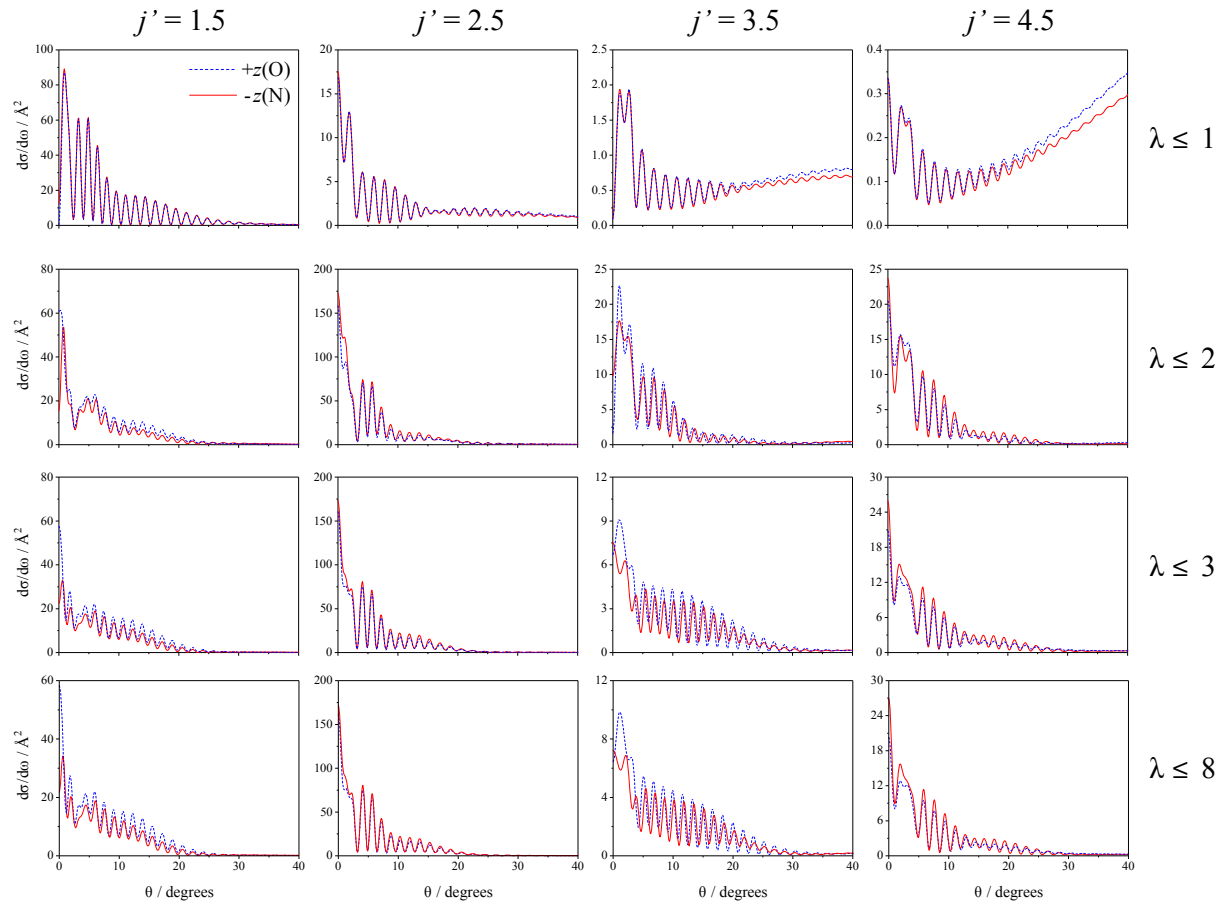


Figure 8.10: CC QM z -axis oriented DCSs, in the forward scattered region, for the scattering of NO with Ar on (V_{sum}) potentials of the form $V_{\lambda 0}$, with terms up to and including $\lambda = 1, 2, 3$, and 8 from top to bottom. Transitions described by $|j', \Omega' = 0.5, \varepsilon' = -1, f\rangle \leftarrow |j = 0.5, \Omega' = 0.5, E\rangle$ are shown for $j' = 1.5 - 4.5$ from left to right. Scattering for bond orientation along the $+z(\text{O})$ and $-z(\text{N})$ directions are shown by red and blue (dashed) lines, respectively.

8.4.4 Parity and Anisotropy in Orientation

Further insight may be gained into the origin of the differences observed in the oscillations for collisions at the two ends of the molecule, by considering the effects of different terms in the expansion of the potential, $V_{\lambda 0}$. Figure 8.10 shows the oriented QM DCS in the forward scattered region for the scattering of NO with Ar, in which the maximum number of terms in the potential has been modified from $\lambda = 1$ to $\lambda = 3$. For comparison, the DCS calculated on the V_{sum} potential including all terms in the potential ($\lambda \leq 8$) is also shown. The $\lambda \leq 1$ term includes only the $\lambda = 0$ and 1 terms of the potential: the isotropic zeroth order term and the first heteronuclear term. In this case the DCS is independent of orientation, and the peaks for the

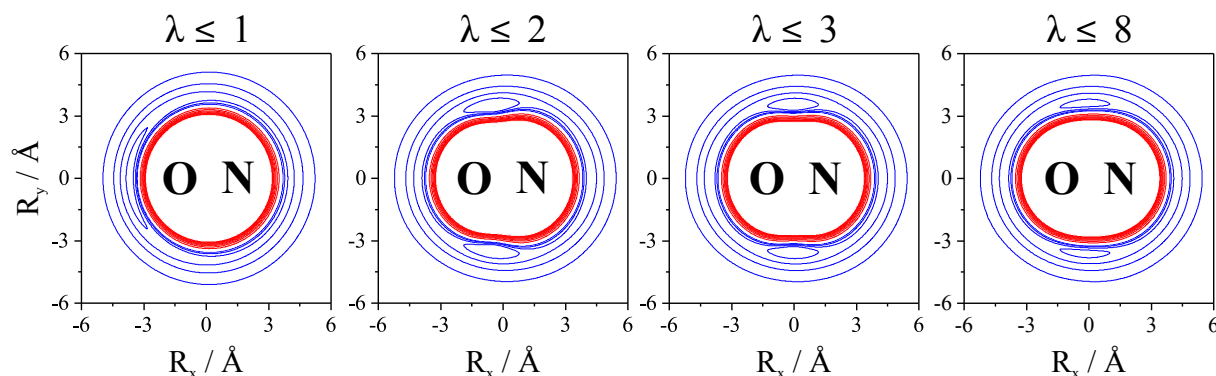


Figure 8.11: V_{sum} PES for the collision of NO with Ar, composed of up to and including the $V_{\lambda 0}$ term in the expansion of the potential, where $\lambda = 1, 2, 3$, and 8 , from left to right. Attractive and repulsive contours are shown by blue and red lines, respectively; attractive contours are separated by 100 cm^{-1} and repulsive contours by 25 cm^{-1} .

$+z$ - and $-z$ -orientations lie on top of each other. This is easy to rationalise based on the shape of the potential energy surface, shown in Figure 8.11, which is largely isotropic apart from a deep attractive well at the ‘O-end’ of the molecule. Transitions with low Δj are ‘glancing’ type collisions, leading to small θ , which occur for large impact parameter collisions. Since the DCS is largely isotropic, when the collision partner approaches toward either ‘end’ of the molecule it experiences similar interactions in the two z -axis orientations (*i.e.* the anisotropy observed between the ‘N-end’ and ‘O-end’ of the molecule is not probed). Note that some deviation in the magnitude of the $\pm z$ -orientations is observed for $\Delta j = 3$ and 4 ; this arises due to the non-zero integral steric effect for these states [95].

The addition of the second, $\lambda = 2$, term (which is homonuclear in character) to the potential leads to a very subtle shift in position of the oscillations with respect to one another for collisions in both the $\pm z$ -orientations. Whilst the PES in this case is overall more homonuclear in character, the potential is wider (perpendicular to the bond axis) at the ‘N-end’ of the molecule than the ‘O-end’ (*i.e.* the potential is ‘egg-like’ in shape). Consequently, the collision partner feels a different potential for scattering in the $\pm z$ -orientations, resulting in a shift of the $\pm z$ oscillations in the DCS relative to one another. Addition of the third, $\lambda = 3$, term (which is heteronuclear in character), leads to a nearly homonuclear potential energy surface, although the heteronuclear character of the diatomic remains as both the attractive and repulsive parts of the potential extend further at the ‘N-end’ of the molecule. As in the case where $\lambda = 2$ is

	Even Δj	Odd Δj
ε -conserving	p -conserving	p -changing
ε -changing	p -changing	p -conserving

Table 8.3: Affects of ε and Δj on the overall parity of an inelastic scattering event for NO(X) with the rare gases.

the maximum term in the PES expansion, the potential is ‘egg’ shaped (although more subtly), and the oscillations in the $\pm z$ -orientations are shifted with respect to one another (for odd Δj). In this case the DCS is qualitatively similar to the full DCS, and addition of extra terms to the already near-homonuclear potential results only in slight modifications to the overall shape and intensity of the DCS.

It is useful to consider the concept of direct scattering [219, 230], which at low Δj , may be employed to understand the form of the field free DCS. In the direct scattering model, the DCS can be described by a single term in the potential energy surface coupled according to [230]

$$\varepsilon \varepsilon' (-1)^{\Delta j + \lambda + 1} = -1, \quad (8.7)$$

and calculation of the DCS using any other terms results in a negligibly small quantity. For ε -conserving and changing transitions, the direct scattering model is coupled by $\lambda = \Delta j$ and $\lambda = \Delta j + 1$, respectively. These terms, alongside the potentials discussed above, may be used to rationalise the difference in magnitude between the ε -conserving and changing transitions for odd and even Δj , observed in Figure 8.5.

Even Δj transitions are governed by even (homonuclear) terms in the potential, for which ε -conserving transitions are parity-conserving. The relevant parities for different types of transition are shown in Table 8.3. For a truly homonuclear molecule, parity-changing transitions are forbidden, and as such the even Δj (parity changing) transitions in this near homonuclear system, are very small in magnitude (although not strictly forbidden). However, for odd Δj transitions, which are governed by odd (heteronuclear) terms in the potential, there are no such constraints and therefore the magnitude of the ε -conserving and changing transitions are much more similar.

Of course, in the case of bond orientation, there is no longer a concept of an ε -conserving or changing transition, due to the coherent superposition of the Λ -doublet states in the static bond orientation field, and the direct scattering model does not hold. As such, for each transition there will be contributions from both ε -conserving and ε -changing transitions. However, for even Δj transitions, ε -changing transitions are overall parity changing, and their magnitude is very small. Therefore, the *r*-PDDCS will be dominated by the ε -conserving transition (weighted by the appropriate mixing parameter); that is the even terms in the expansion of the potential will be dominant, according to Equation (8.7). Since even terms in the potential account for homonuclear behaviour, it is unsurprising that no differences in the position of the oscillations are observed for scattering from the two ends of the NO molecule. Meanwhile, for odd Δj transitions which are controlled by both even and odd terms in the potential the situation is more complex, with the differences brought about by the heteronuclear term giving rise to a shift between the peaks in the two orientations.

8.5 *x*-Axis Orientation

Consider orientation of the NO molecule along the $\pm x$ -axis, as discussed in Chapter 7, in which the collision partner hits the ‘side’ of the NO molecule. It has been suggested by Onvlee *et al.* [375] that the ‘side-on’ orientation is particularly important in defining the angular distribution in the forward scattered region of the DCS where the diffraction oscillations dominate, as this is where the phase difference between waves from the two extremes of the molecule is the greatest [366, 375]. In Chapter 7 a strong preference for forward scattering was observed in the $+x$ -orientation (which almost maximised the DCS); this was attributed to the stronger anisotropy probed in the potential during ‘side-on’ collisions.

Figure 8.12 shows the diffraction oscillations for both the *x*-axis (‘side-on’ collision) and *z*-axis (‘end-on’ collision) geometries. Note the same propensity for the relative shifting of the oscillations in the $+x$ - and $-x$ -orientations, as that discussed in terms of orientation along the *z*-axis in Section 8.4. For transitions with even Δj , the DCS for both *x*-axis orientations

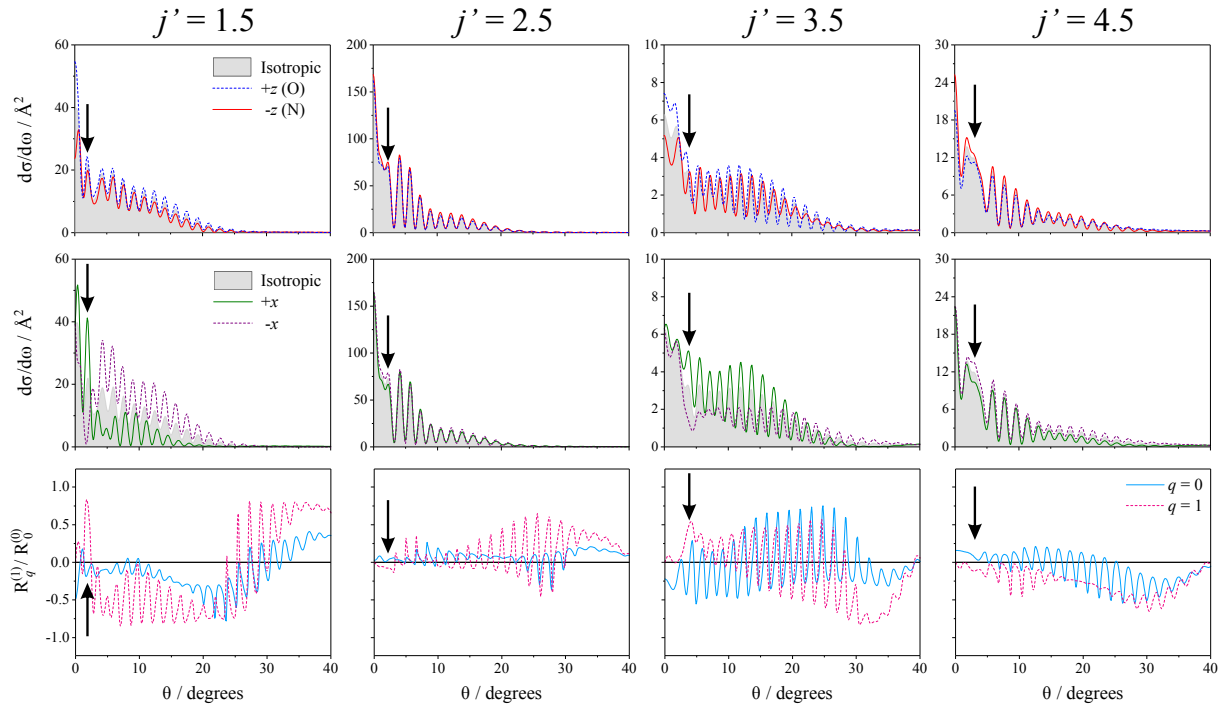


Figure 8.12: CC QM oriented DCS in the forward scattered region for the $|j', \Omega' = 0.5, \varepsilon' = -1, f\rangle \leftarrow |j = 0.5, \Omega = 0.5, E\rangle$ transitions of NO scattering with Ar, where $j' = 1.5$ to 4.5 from left to right. The top and middle panels show orientation along the z - and x -axes, respectively. The red and blue (dashed) lines denote collisions corresponding to the $-z$ (N)- and $+z$ (O)-orientation, respectively, whilst the green and purple (dashed) lines correspond to the $+x$ - and $-x$ -orientation, respectively. In both cases the gray shading corresponds to the isotropic DCS. The bottom panel shows the renormalised $R_q^{(1)}(\theta)$ moments for $q = 0$ (turquoise) and $q = 1$ (pink dashed). In each state the black arrow corresponds to the position of the irregular diffraction peak.

is very similar to that observed for z -axis orientation, and both orientations are comparable to the isotropic DCS. This was shown (in Section 8.4) to arise from the small magnitude of the ε -changing term in the initial superposition of Λ -doublets in the presence of the orientation field, which leads to a small $R_q^{(1)}(\theta)$ moment and oriented DCSs which are similar to the isotropic case (see Figure 8.6).

Transitions to odd final states show considerable differences for orientation along the z - and x -axes; although a shift between the isotropic and oriented DCSs is observed in both orientations. Whilst orientation either parallel or antiparallel to the z -axis results in only a subtle difference in magnitude from the isotropic DCS, orientation along the x -axis shows large variations in magnitude between the two orientations. This is clear from the (generally) larger magnitude of the renormalised $R_1^{(1)}(\theta)$ moment in Figure 8.12 compared to the renormalised

$R_0^{(1)}(\theta)$ moment for transitions to odd Δj .[†] This suggests that in the forward scattered region of the DCS, collisions on the ‘side’ of the NO molecule more strongly affect the structure of the DCS than collisions which occur at either ‘end’ of the molecule. The effect of anisotropy on the relative magnitude of the shift for z - and x -axis orientation will be discussed further in Section 8.5.1.

ℓ -type Rainbows

An ℓ -type rainbow is observed for the $\Delta j = 1$ (and to some extent for the $\Delta j = 3$) transition in the ‘end-on’ geometry, this feature is also observed for collisions in the ‘side-on’ geometry. However, whilst a rainbow is observed for both the $+z$ - and $-z$ -orientations, the rainbow is much stronger in the $-x$ -orientation than in the $+x$ -orientation. As described in Section 8.4.3, ℓ -type rainbows arise from large classical impact parameter collisions, in which the incoming atom is directed around the ‘far-side’ of the NO molecule during the collision. For this attractive type scattering the x -axis orientations correspond to collisions ‘off N’ and ‘off O’ in the $-x$ - and $+x$ -orientations, respectively.

The preference for ℓ -type rainbow scattering in the $-x$ -orientation may be understood simply in terms of the fact that the extent of the attractive part of the potential is larger at the ‘N-end’ of the NO molecule, and therefore ‘far-side’ collisions are favoured in this orientation. The effect is less strong in the $\pm z$ -orientation, since the extent of the potential is smaller in this geometry, resulting in smaller impact parameter collisions, which are more ‘head-on’ in nature, and are consequently less likely to undergo ‘far-side’ scattering. The presence of the rainbow in both the $\pm z$ -orientations arises since the potential probed (at the side of the molecule) during the collision is very similar in both orientations. The large magnitude of the rainbow in the $-x$ -orientation (compared to the $\pm z$ -orientations) suggests that scattering onto the ‘far-side’ of the molecule is very strongly orientation dependent.

[†]The limits of the renormalised r -PDDCSs depend on the field strength as $\pm 1/|\alpha\beta|$, which at the infinite and experimental fields is ± 1 and ± 1.24 , respectively.

The ‘Irregular’ Diffraction Peak

A significant difference in the magnitude of the *x*- and *z*-axis steric effect is observed around the ‘irregular diffraction peak’ (see Section 8.2), a feature in the field-free DCS first measured experimentally for the NO + Ar system by Onvlee *et al.* [375]. This irregular feature in the DCS (marked by the black arrows in Figure 8.12), is much more sensitive to orientation of the bond axis along the $\pm x$ -axis than for orientation along the $\pm z$ -axis. Detailed analysis by Onvlee *et al.* [375] has suggested that collisions with the ‘side’ of the NO molecule are responsible for this ‘irregular diffraction peak’. This is supported by the much larger maximum in the renormalised $R_1^{(1)}(\theta)$ moment, at the location of the ‘irregular diffraction peak’ in comparison to that observed at the same angle in the $R_0^{(1)}(\theta)$ moment. The irregular diffraction peak shows a preference for $+x$ scattering. Since diffraction oscillations arise largely from the repulsive part of the potential [369, 373, 376], this corresponds to repulsive ‘near-side’ scattering ‘off N’, in contrast to the general preference for the scattering observed in the rest of the region. It should be noted that differences in the magnitude of the ‘irregular diffraction peak’ between the $\pm z$ - and $\pm x$ -orientations arises from the attractive part of the potential (see Figures 8.7 and 8.15); this is not trivial to rationalise.

8.5.1 Anisotropy in ‘Side-on’ Scattering

The increased anisotropy of the potential for scattering in the ‘side-on’ (*x*) geometry relative to the ‘end-on’ (*z*) geometry suggests that the shifting of the oscillations with respect to the (field dependent) isotropic DCS should be stronger in the $\pm x$ -orientation than the $\pm z$ -orientation. Such an effect was alluded to in terms of the hard shell semi-axes of the NO molecule in Section 8.4, with reference to the semi-classical model in Equation (8.1). In both ‘end-on’ orientations the shape of the hard shell is defined by the minor semi-axis (*B*), whilst in the ‘side on’ orientations the shape of the hard shell is defined by the major semi-axis (*A_n*), which depends on whether the collision occurs ‘off N’ or ‘off O’, *i.e.* there is a strong anisotropy in the shape of the ‘target’ in the ‘side-on’ geometry.

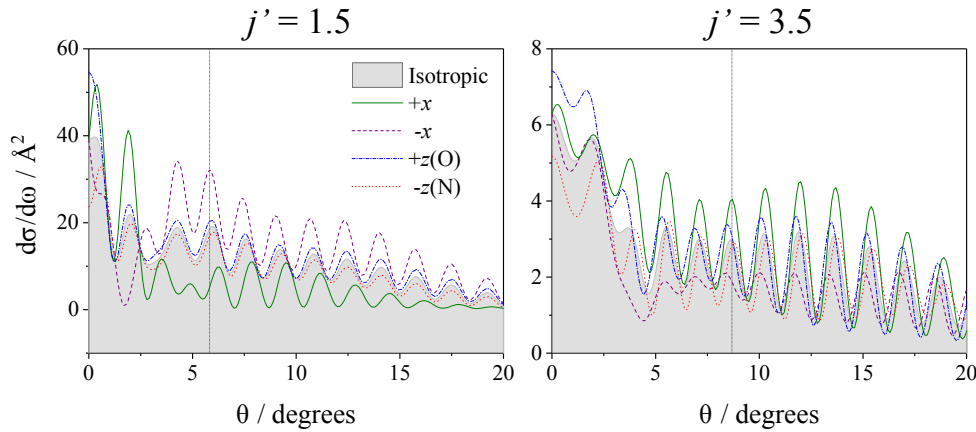


Figure 8.13: CC QM z - and x -axis oriented DCSs for the $|j', \Omega' = 0.5, \epsilon' = -1, f\rangle \leftarrow |j = 0.5, \Omega' = 0.5, E\rangle$ transitions of NO with Ar, where $j' = 1.5$ (left) and 3.5 (right). Scattering for bond orientation along the $+x$, $-x$, $+z(O)$, and $-z(N)$ directions are shown by green, purple (dashed), blue (dashed-dotted) and red (dotted) lines, respectively. The vertical line is simply to guide the eye.

Figure 8.13 shows the $\pm z$ - and $\pm x$ -orientations for $\Delta j = 1$ and $\Delta j = 3$; states with even Δj are excluded since no (significant) shift in the position of the oscillations is observed as a function of orientation. It is clear that the peaks in the $\pm x$ -orientation are shifted more with respect to one another than those in the $\pm z$ -orientation. This is consistent with the semi-classical model described in Equation (8.1), where a larger angular spacing is predicted for A_N than A_O (which defines the shape of the ‘target’). It is this anisotropy in the potential which results in the shift of the diffraction oscillations depending on the degree of anisotropy probed for a specific bond axis orientation (this was also discussed in detail in Chapter 7 with respect to the observation of multiple/single peaks in the $+x/-x$ -orientation resolved DCSs).

As in the case for orientation along the $\pm z$ -axis, in Section 8.4, it is important to discern whether the role of the attractive part of the potential is important in the shifting of the oscillations with respect to one another in the $\pm x$ -geometry. Figure 8.15 shows the bond axis resolved DCSs calculated on the ‘soft’ (truncated) potential; note that the DCSs on the ‘soft’ potential are shifted to higher scattering angles compared to the full DCS in Figure 8.12, due to the more ‘head-on’ nature of collisions on the repulsive potential. As was observed for the z -axis case (see Figure 8.7), removal of the attractive parts of the potential results in the oscillations peaking at the same angle in the $\pm x$ -orientations. Therefore, it is important to consider the effect of the attractive part of the potential for calculations on each of the potentials in Figure 8.13.

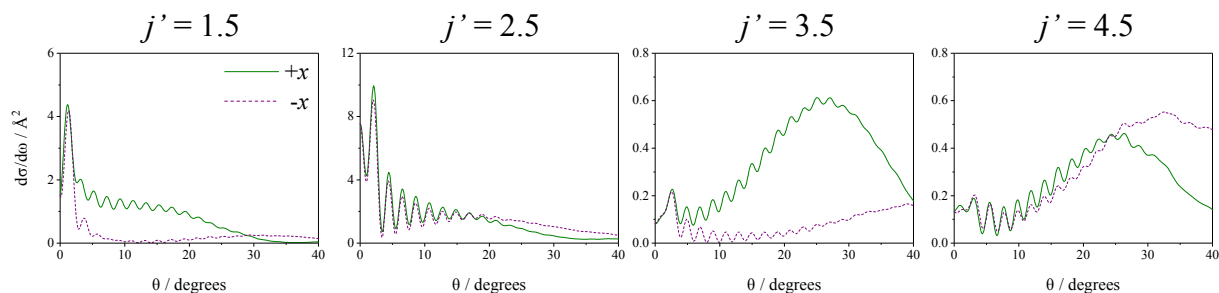


Figure 8.14: CC QM x -axis oriented DCSs, for the scattering of NO with Ar on the ‘soft’ (truncated) potential. Transitions described by $|j', \Omega' = 1/2, \epsilon' = -1, f\rangle \leftarrow |j = 1/2, \Omega' = 1/2, E\rangle$ are shown for $j' = 1.5 - 4.5$ from left to right. Scattering for bond orientation along the $+x$ and $-x$ directions are shown by green and purple (dashed) lines, respectively.

In the region of the ℓ -type rainbow, described with reference to Figure 8.12, the preference for scattering on the ‘soft’ and full potentials are very different. This is particularly obvious for $\Delta j = 1$, in which the preference for scattering is $+x$ on the ‘soft’ potential (*i.e.* repulsive ‘near-side’ scattering ‘off N’) but $-x$ on the full potential (*i.e.* attractive ‘near-side’ and ‘far-side’ scattering ‘off O’ and ‘off N’, respectively).

In much the same way as for the ‘end-on’ orientation discussed in Section 8.4.4, analysing the effects of the maximum term included in the expansion of the PES can provide mechanistic insight into scattering in the ‘side-on’ orientation. Figure 8.13 shows the bond orientation resolved DCSs obtained when the maximum term in the (V_{sum}) potential of the form $V_{\lambda 0}$ is $\lambda = 1, 2, 3$, and 8 (*cf.* Figure 8.10 for the ‘end-on’ orientation). For the potential expanded with a maximum term of $\lambda = 1$ ($V_{00} + V_{10}$) the ‘end-on’ DCSs were shown to be independent of the $\pm z$ -orientation. Orientation in the ‘side-on’ geometry, however, shows a significant shift in the oscillations in the $\pm x$ -geometries for both odd and even Δj . In the ‘end-on’ orientation, approach of the collision partner did not probe the anisotropy in the potential, resulting in almost identical scattering in both the $\pm z$ -orientations. This is consistent with the semi-classical model in Equation (8.1), for which the radius of the target, and consequently the angular separation between peaks, is the same in both orientations. In the ‘side-on’ geometry, however, the radius of the ‘target’ depends on whether scattering occurs ‘off N’ or ‘off O’, which have different semi-axes ($A_N > A_O$). The anisotropy of the $V_{00} + V_{10}$ potential is very large, with an attractive well at the ‘O-end’ of the molecule (consistent with the fact that the

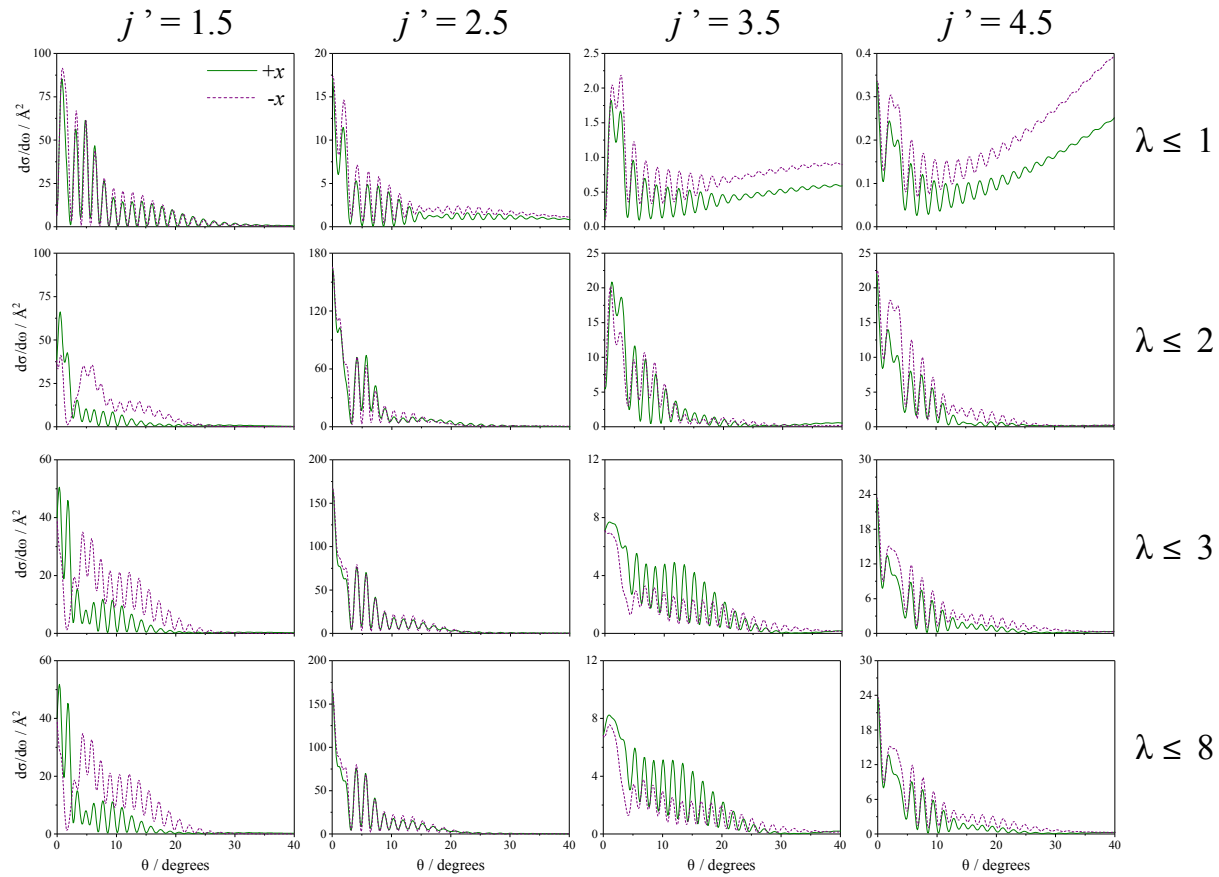


Figure 8.15: CC QM x -axis oriented DCSs, for the scattering of NO with Ar on potentials of the form $V_{\lambda 0}$, with terms up to and including $\lambda = 1, 2, 3$, and 8 from top to bottom. Transitions described by $|j', \Omega' = 0.5, \epsilon' = -1, f\rangle \leftarrow |j = 0.5, \Omega' = 0.5, E\rangle$ are shown for $j' = 1.5 - 4.5$ from left to right. Scattering for bond orientation along the $+x$ and $-x$ directions are shown by green and purple (dashed) lines, respectively.

relative shift of the oscillations arises from attractive behaviour). Unlike in the ‘end-on’ case, large impact parameter collisions (resulting in forwards scattering and low RET) probe this anisotropy in the potential, resulting in a shift of the oscillations relative to one another for ‘side-on’ collisions. The lack of a strong ℓ -type rainbow suggests that this behaviour arises from ‘near-side’ scattering. On the $V_{00} + V_{10}$ potential $\theta_{-x} > \theta_{+x}$, corresponding to ‘near-side’ scattering ‘off O’ occurring at larger scattering angles than ‘off N’.

Addition of the $\lambda = 2$ term to the expansion of the potential leads to restoration of the behaviour observed on the full potential. Oscillations peak in the same position for both $\pm x$ -orientations when Δj is even, but are shifted with respect to one another for odd Δj (but with $\theta_{+x} > \theta_{-x}$, unlike on the $V_{00} + V_{10}$ potential). The presence of an ℓ -type rainbow in the

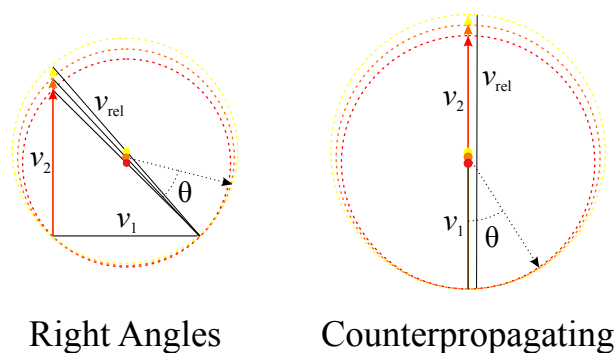
$-x$ DCS for $\Delta j = 1$, suggests the possibility for attractive ‘far-side’ scattering ‘off N’, similarly the lack of rainbow in the $+x$ DCS suggests that no significant ‘far-side’ scattering occurs ‘off O’. By the addition of the $\lambda = 3$ term the DCSs are almost the same as for scattering on the full potential, as was observed with respect to the ‘end-on’ geometry, and which may be rationalised in a similar manner.

8.6 Future Work: Experimental Measurement?

The angular resolution required to differentiate between the oscillations in the $\pm x/z$ -orientation resolved DCSs with respect to each other is less than 0.2° . The current experimental set-up provides an angular resolution in the region of $15\text{--}20^\circ$, which is not sufficient to resolve the diffraction oscillations in the DCS (whether oriented or unoriented). The resolution is largely limited by the velocity spreads in the molecular beams (discussed in Chapter 3), which leads to a range of collision energies and consequently significant blurring in the experimental ion images [123]. The presence of a static electric field in the interaction region for the orientation of the NO bond axis prior to the collision event also gives rise to blurring, resulting from imperfections in the velocity mapping due to the orientation field between the velocity mapping electrodes.

Several methods have been used in crossed molecular beam (CMB) studies to increase the angular resolution which is achievable, including use of Stark deceleration to control initial velocity [123, 263, 366, 375], counterpropagating beams [123, 366], and slice imaging [312]. As discussed in Chapter 4, whilst slice imaging may considerably increase the angular resolution achieved, using the current experimental apparatus such resolutions are still out of reach. It is important to note that none of these methods have been used simultaneously with an static electric field present in the interaction region.

Stark Deceleration Stark deceleration may be used to produce a packet of molecules with high density and a tunable velocity (with a narrow spread), as well as almost 100% quantum state purity [112, 388]. The reduction of the velocity spread of the molecular beam (compared



Right Angles

Counterpropagating

Figure 8.16: Newton diagram for two beams of particles with equal mass and velocity crossing at right angles (90°) and counterpropagating (180°). The beam with v_1 is assumed to have zero beam spread velocity, $\sigma_v = 0 \text{ m s}^{-1}$, whilst the other beam has a large velocity spread. The scattering angle, θ , in each case is assumed to be equivalent. Adapted from Vogels *et al.* [123].

to conventional methods), leads to a narrower distribution of collision energies being accessed experimentally, resulting in less apparent blurring in the ion image. Typically, only a single molecular beam is controlled using a decelerator, in which case the image resolution is determined only by the velocity spread of the second molecular beam [123]. The improvement in resolution achieved has allowed the group of van de Meerakker [123, 263, 273, 366, 375] to resolve the unoriented diffraction oscillations in several $\text{NO} + \text{Rg}$ systems with $< 0.1^\circ$ resolution.

Counterpropagating Beams Only a few examples exist of CMB apparatus used in conjunction with counterpropagating beams [121, 122]. However, the kinematics of such beams are more favourable for high resolution studies of the forward scattered region of the DCS than conventional beam setups (at right angles) [123]. Figure 8.16 shows the Newton diagrams corresponding to molecular beams in the perpendicular and counterpropagating geometries, for scattering into the same angle, θ . The larger size of the Newton sphere for the counterpropagating case corresponds to the higher relative velocity of the system. For simplicity, assume that molecules in each molecular beam have equal masses and velocities. The first (Stark decelerated) beam (with velocity v_1), has a close to zero velocity spread, whilst the second beam, with velocity v_2 , has a considerably larger velocity spread. Focusing on the forward scattered region of the Newton triangle, it can be shown that the spread in the velocity of the collision partner (from beam two) does not strongly affect the size of the resulting Newton

sphere (compared to the case when the beams cross at right angles). Vogels *et al.* [123] have used this method (in combination with Stark deceleration) to obtain the resolution necessary to study unoriented diffraction oscillations in the scattering of NO(X) with Ne and Ar.

8.7 Summary

This chapter has dealt with the effects of bond axis orientation on the forward scattered region of the DCS. For orientation of the bond axis along the $\pm z$ -axis, transitions with even Δj were shown to give rise to oriented DCSs very similar to the isotropic case. Meanwhile, transitions with odd Δj give rise to a shift of the oscillations in the two orientations with respect to the isotropic DCS, along with a more significant difference observed in the magnitude of the underlying structure. The origin of this effect was shown to arise from the attractive part of the potential, and several underlying rainbow features were discussed. The origin of the Δj propensity was shown to arise from the relative dominance of even and odd terms in the PES.

Orientation along the $\pm x$ -axis was shown to give rise to similar trends as those observed for orientation along the $\pm z$ -axis. However, significant variations between the two x -axis orientations were observed, specifically in relation to the strong preference for $-x$ -orientation (attractive scattering ‘off N’) in ℓ -type rainbow scattering, and for the $+x$ -orientation (repulsive/attractive scattering ‘off N’/‘off O’) in the region of the ‘irregular diffraction peak’. Finally, methods which may allow the experimental measurement of the features discussed in this chapter were reviewed.

Chapter 9

Conclusions

The primary aim of this thesis was to explore the vector correlations in the rotationally inelastic scattering of NO(X) with atoms and diatoms. The experiments presented here may be largely separated into two sections: those which focus on the two vector correlations in diatom-diatom scattering, and those whose which investigate the effect of initial bond axis orientation in the scattering of NO with the rare gases. The theoretical and experimental methods used throughout this thesis were presented in Chapters 2, 3, and 5. This includes a new quantum mechanical treatment of the scattering of symmetric tops in the presence of a static electric (orientation) field of arbitrary direction.

The inelastic scattering of NO(X) with O₂(X) at $E_{\text{coll}} = 550\text{cm}^{-1}$ was investigated in Chapter 4. This system represents a step forward in complexity from previous experiments measuring the fully state-to-state resolved DCS in the scattering of NO(X) with the rare gases [38–40, 88]. To extract the $(j'_{\text{NO}}, N'_{\text{O}_2})$ resolved angular distributions, a new modified onion-peeling method was used, which was shown to accurately reproduce the DCS in NO + Ar scattering as proof of concept. The state-to-state resolved angular distributions were rationalised in a similar way to those used for NO scattering with an atom. The co-product rotation was shown to be a trade-off between partitioning of energy between NO and O₂ and the nature of the collision. A consequence of this is the N'_{O_2} population peaking for intermediate rotational states for a specific j'_{NO} . Parity pairs were also observed in the state-averaged angular distributions, similar to those observed for collisions of NO with the rare gases [39]. Comparisons between scattering with Ar and O₂ showed qualitatively similar dynamics.

Chapter 6 discussed z -axis bond orientation, where the collision partner approached either the ‘N-end’ or ‘O-end’ of the NO molecule. In the first part of the chapter the integral steric asymmetry for scattering with O₂ and N₂ (averaged over all co-product final rotational states) was presented. Strong similarities between scattering with atoms and diatoms were observed, particularly the presence of Δj dependent oscillations, arising from the near-homonuclearity of the NO molecule. The agreement between experiments and QM calculations for N₂ was shown to be particularly poor, which was attributed to the assumptions made in the calculation of the PES, as well as treatment as a diatom-atom system during CC QM calculations. Ultimately, comparison of diatom and atom scattering suggested that the PESs for diatom-diatom scattering are more isotropic in nature. The implications of the additional PESs required to describe scattering with O₂(X) were unclear.

In the second part of Chapter 6 the z -axis differential steric effect was investigated for the spin-orbit changing collisions of NO(X) with Ar at $E_{\text{coll}} = 651 \text{ cm}^{-1}$ (with additional data at $E_{\text{coll}} = 532 \text{ cm}^{-1}$ presented in Appendix B). The agreement between the experimental and QM calculations was shown to be generally good. The same number of peaks were observed in the bond orientation resolved DCSs for scattering at the ‘N-end’ and ‘O-end’ of the molecule, although differences in relative intensity were observed, concordant with measurements made on the spin-orbit conserving manifold previously [96, 97]. An intuitive mechanism for the underlying structure was difficult to rationalise, due to the complexity of the V_{diff} potential which is considered to govern spin-orbit changing transitions in Hund’s case (a). Comparison of the renormalised $R_0^{(1)}(\theta)$ moments on the two spin-orbit manifolds showed striking similarities; the moments were slightly more backwards scattered on the spin-orbit changing manifold, consistent with the need to overcome the spin-orbit energy.

Measurement of the x -axis steric effect for the scattering of NO with Ar was presented for the first time in Chapter 7, in which the collision partner approaches either ‘side’ of the NO molecule. The importance of defining $\mathbf{k}'$, as well as $\mathbf{k}$, to unravel information about the $R_0^{(1)}(\theta)$ bond orientation moment was stressed. Indeed, without definition of the xz -plane no steric effect is observed. Despite the additional complexity of the need to separate near- and

far-side collisions, scattering preferences were attributed to collisions ‘off N’ and ‘off O’ in much the same way as for collisions at the ‘N-end’ and ‘O-end’ of the molecule in the z -axis steric effect. The agreement between experiments and theory was shown to be good for both the integral and differential steric effects. A strong propensity for single/multiple peaks in the $-x/+x$ -orientation resolved DCSs was observed, and rationalised by the presence of rotational rainbows, in which the increased anisotropy of the potential for ‘N-end’ collisions ($+x$) results in more oscillations in the DCS. The presence of the strong forwards scattered peak in the $+x$ -orientation, which was almost completely suppressed in the $-x$ -orientation, was attributed to the larger impact parameter collisions possible at the ‘N-end’ of the molecule.

Comparison between orientation with respect to the x - and z -axis showed the importance of scattering at the ‘side’ of the molecule in the forwards region of the DCS, attributed to the possibility for larger impact parameter collisions at the ‘side’ of the molecule than at the ‘end’. Added weight was given to the importance of ‘side-on’ scattering in the forwards direction, as such collisions were shown to maximise the DCS. The dependence of the DCS on initial bond axis orientation whilst strong in the forwards scattered direction was relatively weak in the backwards scattered direction. This unlocks the possibility of exquisite control over the angular distribution achieved by modification of the bond axis orientation prior to the collision event.

Chapter 8 focused on the effects of bond axis orientation on the forwards scattered region of the DCS, where diffraction oscillations are superimposed over other structures in the DCS. The ‘isotropic orientation’ of the molecule in the presence of a static electric field was shown to be in good agreement with that predicted by the Fraunhofer model, which describes diffraction from a molecular target. However, to fully unravel the complexities of the features in the DCS it was necessary to turn to full quantum mechanical calculations, which showed a surprising shift in the diffraction peaks in the $+z$ -orientation relative to the $-z$ -orientation for odd (but not even) Δj transitions. A similar effect was observed for orientation relative to the x -axis. Calculations on a variety of modified potentials showed the origin of the effect to be the anisotropy of the attractive part of the potential, as well as the relative dominance of odd and even terms in the

expansion of the PES. Orientation with respect to the x -axis was shown to have a much stronger effect on the DCS than z -axis orientation, particularly in the region of the ℓ -type rainbow and the ‘irregular diffraction peak’; this was attributed to the increased anisotropy sampled by collisions at the ‘side’ of the molecule.

Throughout the chapters in this thesis various avenues for future work have been considered. In Section 4.6 a method to increase the resolution of diatom-diatom scattering studies focused on the ability to retrieve a sufficiently narrow central slice of the nested Newton spheres using Post-extraction inversion slice imaging coupled with a time stamping camera. In a similar vein, Section 6.4 discussed the potential for measuring the integral steric asymmetry as a function of the co-product rotational state, as opposed to that of NO. Section 8.6 discussed the methods required to measure bond orientation resolved diffraction oscillations; the implications of the static electric field used to orient the NO bond axis prior to scattering suggest that such an experiment is still some way off. Having measured all moments of the r -PDDCS, Section 7.7 discussed the methods required to measure the full $\mathbf{r} - \mathbf{k} - \mathbf{k}' - \mathbf{j}'$ correlation; it is suggested that the effects of initial bond axis orientation will be much stronger for collision induced orientation (the sense of rotation) than for collision induced alignment (the plane of rotation).

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Appendices

A NO(X) + Oxygen: Further Details of the Data Analysis Method

An overview of the modified onion-peeling method used to analyse the experimental ion images for the scattering of NO with O₂ was given in Chapter 4. For completeness, some further discussion is presented here with reference to:

- the instrument function and flux density correction in Section A.1,
- extraction of angular distributions in Section A.2, and
- the collision induced alignment (CIA) correction in Section A.3.

A.1 The Instrument Function

The recorded experimental images in Chapter 4 are not a true representation of the $\mathbf{k} - \mathbf{k}'$ correlation; they represent a convolution of the total DCS, that is the angular distributions for each N'_{O_2} weighted by their relative contribution to the total population, with an instrument dependent function (as discussed in Section 3.5.1). The instrument function may be separated into two components: a flux-density correction and a collision induced alignment correction. The flux-density correction accounts for the position dependent detection efficiency of NO ions arriving with the same outgoing velocity, u'_{NO} , but different positions on the surface of the Newton sphere, defined by (θ, ϕ) . To fully determine this flux-density correction it is necessary to consider the geometric design of the experiment, the temporal and spatial profiles of the molecular beams, along with their velocity distributions and the temporal and spatial profiles of the detection lasers, along with their polarisation, as discussed in Section 3.5.

The instrument function must be determined from experimental measurements (including molecular beam profiles, and laser positions in the scattering chamber) according to a benchmark system with an accurately known DCS. In this case, the scattering of NO with Ar was used as the benchmark system, due to the plethora of data confirming the accuracy of experimental data in comparison to QM scattering theory [34, 35, 39, 75, 195, 263]. By analysing NO + Ar scattering, the correct parameters for simulating the instrument function, and for the onion-peeling algorithm may be obtained. The pixel-to-velocity ratio (a conversion factor specific to the experimental apparatus) was determined from the known NO + Ar collision energy, and the observed image radius. Information about the profile of the O₂ molecular beam was calculated from beam scans of the secondary molecular beam with trace NO in O₂; the speed was calculated from the collision energy (and its distribution) as discussed in Section 4.1.2. A Monte Carlo simulation of the instrument function may then be carried out according to the description in Section 3.5.1, accounting for the possibility of rotational excitation of the oxygen co-product.

Instrument Function Correction

The experimental image is corrected by dividing the raw experimental image through by the experiment dependent instrument function. Since the absolute intensity of the flux density simulation depends only on the number of Monte Carlo trajectories used in the calculation (enough as to converge the experimental simulation), the experimental image and flux density simulation were both normalised to their integrals to facilitate comparisons. Figure A.1 shows the ion images and the corresponding angular distributions, $I(\theta)$, for the flux density correction process for NO + O₂ scattering into $j' = 7.5e$: the raw experimental image, the instrument function (summed across all N'_{O_2}) and the resulting flux density corrected image. It is clear that the raw experimental ion image is not symmetric about the relative velocity vector, k , as required by the cylindrically symmetric nature of the scattering process; this is confirmed by the asymmetric angular distribution, $I(\theta)$. It should be noted that a scattering angle of 0° is read at $\theta_{\text{read}} = 185^\circ$ in the radial distributions, due to the computational nature of the ring reading

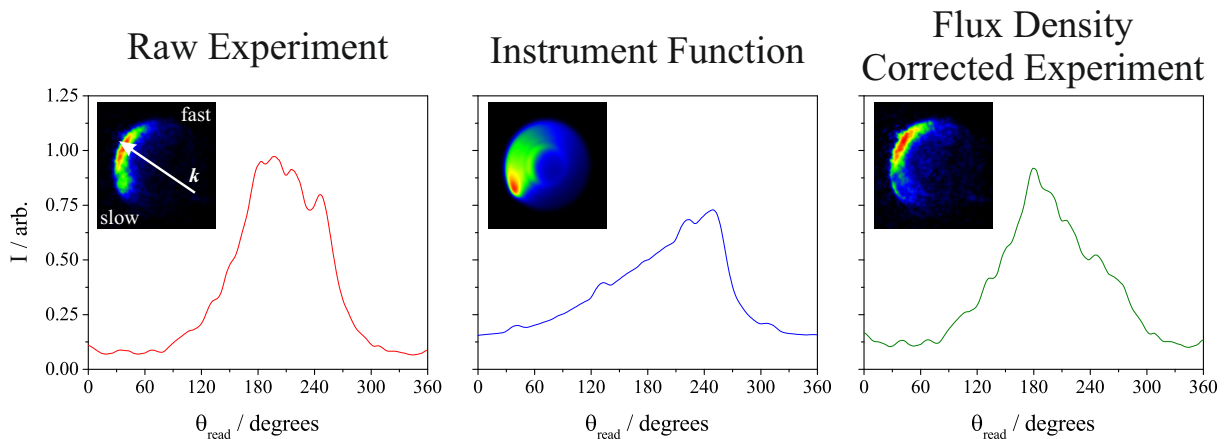


Figure A.1: The instrument function correction procedure for NO + O₂ scattering into $j'_{\text{NO}} = 7.5, e$. Angular distributions (integrated across all radii) are shown for the raw experiment, the simulated instrument function and the instrument function corrected experiment (from left to right). The corresponding ion image is shown in the top corner of each plot. The integrated area of each curve has been normalised to facilitate comparison.

process used to extract the angular distribution. The angular distribution is integrated across all possible radii, according to Equation 4.2.

The simulated instrument function is a representation of the probability of detection, due to experimental parameters, for an NO molecule scattered on to each position on the detector. The instrument function shows clearly that the probability for detection is much higher on the ‘slow’ side of the ion image than the ‘fast’ side; this correlates well with where the scattered intensity is observed in the experimental image. ‘Fast’ and ‘slow’ refer to the LAB frame velocities of the scattered NO molecules; whereby molecules scattered into the bottom left corner of the Newton sphere have a smaller LAB frame velocity than those scattered through an identical angle into the top right corner, as discussed in Section 3.5. Molecules with a larger LAB frame velocity will pass through the detection volume more quickly, and therefore have a lower detection efficiency than molecules with a slower LAB frame velocity, which remain in the detection volume for longer.

The flux density corrected experimental image (and corresponding angular distribution), is more symmetric about the initial velocity vector than the raw experimental image. The symmetrisation process is not perfect, as some artefacts are observed (for example the intensity in the bottom left hand corner of the corrected image), suggesting that there are some

discrepancies in the determination of the instrument function. This is a particular problem for the $j'_{\text{NO}} = 7.5$ state, in which the intensity in the bottom left of the Newton sphere ($60^\circ < \theta < 100^\circ$) overlaps the origin of the Newton triangle, such that ions in this region have a LAB frame velocity very close to zero. As such any small imperfections in the calculation of the instrument function will become magnified upon division of the raw experimental data by the instrument function. This represents the worst case scenario, and most j'_{NO} states become almost perfectly symmetric after the flux density correction process.

A.2 Extraction of Angular Distributions

As detailed in Section 4.3.1, the angular distribution for each $(j'_{\text{NO}}, N'_{\text{O}_2})$ pair is extracted from the instrument function corrected experimental image by reading the intensity around a ring of a radius proportional to the outgoing energy of the state of interest, according to Equation (4.9). Since the scattering is azimuthally symmetric about the initial relative velocity vector, $\mathbf{k}$, the angular distribution may be extracted from either the ‘fast’ or ‘slow’ side of the ion image. Figure A.2 shows the extracted angular distributions for the scattering of NO + O₂ into the $|j'_{\text{NO}} = 7.5e, \Omega' = 0.5, N'_{\text{O}_2} = 1-5\rangle$ state, after division of the experimental data by the calculated instrument function. Due to the small energy difference between the lowest rotational states of O₂, only the average DCS may be extracted with certainty, as the Newton spheres of each state overlap on the detector. It is clear that the DCS extracted from the ‘fast’ and ‘slow’ side of the image are quantitatively similar, showing that the flux density correction has been well modelled for the experiment (since the azimuthal symmetry of the scattering is reconstructed). The ‘structure’ in the extracted DCS arises due to the nature of reading the intensity of the ion image from a pixelated detector, even after the inclusion of the interpolation routine described in Section 4.1.

The middle panel of Figure A.2 shows the average experimental angular distribution, compared to the angular distribution after fitting to a Legendre polynomial, according to

$$I(\theta) = \sum_n \frac{2n+1}{2} a_n P_n(\cos \theta) , \quad (\text{A.1})$$

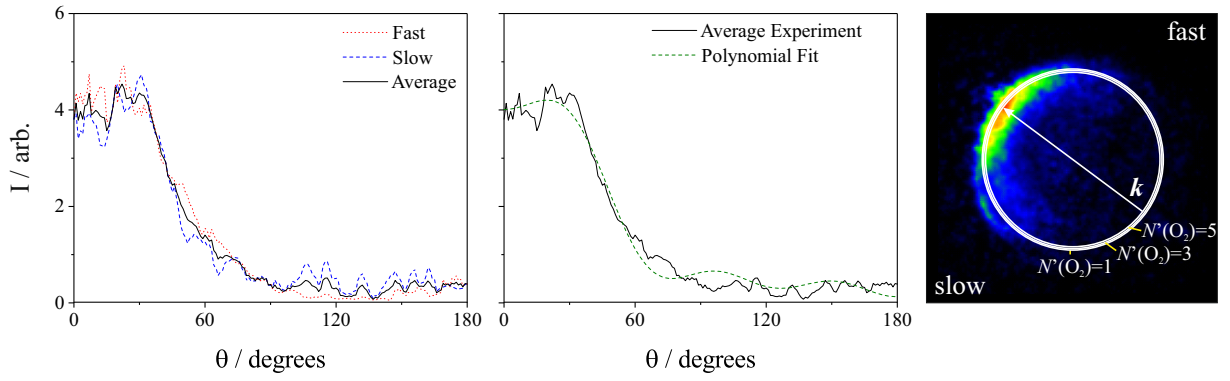


Figure A.2: Angular distributions, $I(\theta)$, for NO + O₂ scattering into the $|j'_{\text{NO}} = 7.5, \Omega' = 0.5, \epsilon' = +1, e\rangle$ state for $N'_{\text{O}_2} = 1 - 5$, which is extracted as a single averaged distribution. The left panel shows the distributions calculated from the fast (red dotted line) and slow (blue dashed line) sides of the instrument function corrected experimental ion image, alongside the average DCS (black line). The middle panel shows the averaged experimental angular distribution as read from the ion image (black line), alongside the fit to a Legendre polynomial up to and including $n = 6$. The right panel shows the experimental ion image, overlaid with circles corresponding to the radius of $N'_{\text{O}_2} = 1 - 5$, about which $I(\theta)$ was read.

where n is the order of the polynomial, a_n are the relevant expansion coefficients and $P_n(\cos \theta)$ is a Legendre polynomial. Once the angular resolution of the experiment has been taken into account, the experimental noise is removed from the extracted DCS. The small oscillations in the angular distribution at larger angles occur due to the Legendre fitting process, where higher order polynomials are included in the expansion to produce a good fit to the width of the main peak in the angular distribution.

It should be noted that the raw angular distribution, plotted in Figure A.2, has an arbitrary scale depending on the intensity of the experimental ion image from which it was extracted. As such the probability distribution for the final angular distribution, $P(\theta)$, is plotted henceforth, in which the integral of the angular distribution is normalised to one. To account for the presence of multiple N'_{O_2} states within the probability distribution for a specific j'_{NO} , the normalisation is done once all states have been extracted as to retain their relative populations. As such the relative intensity of N'_{O_2} gives information about the relative probability of transition into this state within a given NO rotational state, however no information is gained about the probability of transitions to different j'_{NO} .

A.3 Collision Induced Alignment Correction

Experimentally the 226 nm radiation used for the excitation step of the REMPI process is vertically polarised using a Rochon polariser. As such, the effect of this polarisation must be accounted for when simulating (and then fitting) experimental images, as discussed in Section 3.5.2. Since nothing is known about the collision induced alignment in NO + O₂, a small sub-set of data were recorded using both H and V polarised light (using a PEM) to investigate the prominence of such effects. Polarisation dependent ion images are shown in Figure A.3, for scattering of NO with Ar and O₂ into the final state $j' = 7.5e$, recorded on the mixed branch ($Q_{21} + R_{11}$). The normalised difference images, $(V - H) / (V + H)$, show positive and negative intensity in green and blue respectively. The rotational alignment of NO after collision with Ar has been well studied both experimentally and theoretically [86, 87]. Within the noise of the experimental image shown here (which were taken as a reference only), it is clear that the ion images recorded with H and V polarised light are different; particularly in the sideways scattered region, where the H polarised image is clearly more intense than the corresponding position on the V polarised image.

The normalised difference images, $(V - H) / (V + H)$, give qualitative information about the alignment of j' [86]: if the vertical transition probability is greater than the horizontal ($I_V > I_H$) then the intensity is positive (green), corresponding to the transition dipole moment lying preferentially out of the scattering plane, and j' lies preferentially in the scattering plane equivalent to ‘propeller’ like rotation. If $I_V < I_H$, then the intensity is negative (blue), corresponding to the transition dipole moment lying preferentially in the scattering plane, and j' lying preferentially perpendicular to the scattering plane corresponding to ‘frisbee’ like rotation. Within the noise of the normalised difference image, for the scattering of NO with Ar, it can be seen that in the forward scattered direction the intensity is mainly positive, corresponding to j' lying preferentially in the scattering plane (propeller-like behaviour), in the sideways scattered region the effect of polarisation is less clear (due to noise), this is in agreement with previous experimental data [86]. Equivalent ion images were taken for collisions with O₂, to try and

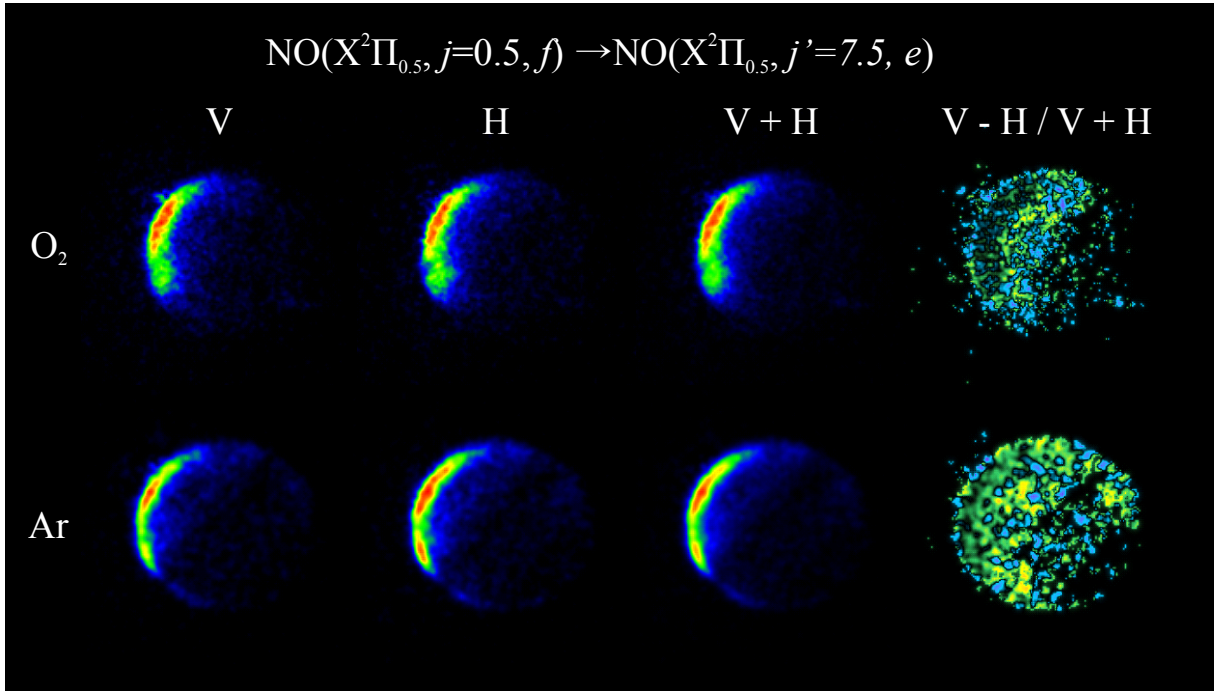


Figure A.3: Experimental ion images for scattering of NO(X) with Ar (bottom) and O₂ (top) into the final state $j' = 7.5e$ on the spin-orbit conserving manifold. Ion images are shown for V and H polarised light (left and middle left respectively), for the sum (V + H) of the polarisation dependent images (middle right) and for the normalised difference (V - H/V + H) (right). The normalised difference image is plotted in a different palette where green and blue correspond to positive and negative values of the CIA, respectively.

confirm the presence of alignment effects within the ion images, however within the resolution of the experiment there is no clear difference observed between the H and V polarised light. This is likely due to the washing out of features by the presence of overlapping N'_{O_2} states in the ion image, which may have different polarisation dependencies. The normalised difference image does show hints of polarisation effects, however these are difficult to resolve and rationalise within the noise of the image.

To confirm that within the resolution of the experiment the H and V polarised ion images are indistinguishable, the lowest $N'_{O_2} = 1 - 5$ angular distribution was analysed in each case, to show that the recovered angular distributions do not depend on the laser polarisation. Figure A.4 shows the results of the analysis process, averaged across $N'_{O_2} = 1 - 5$ (due to the restricted resolution for these states); within the experimental error (calculated from the standard deviation of the fast and slow sides of the image, and analysis of ± 1 pixel of the ring radius) there is no difference between the angular distributions extracted from different polarisations of the

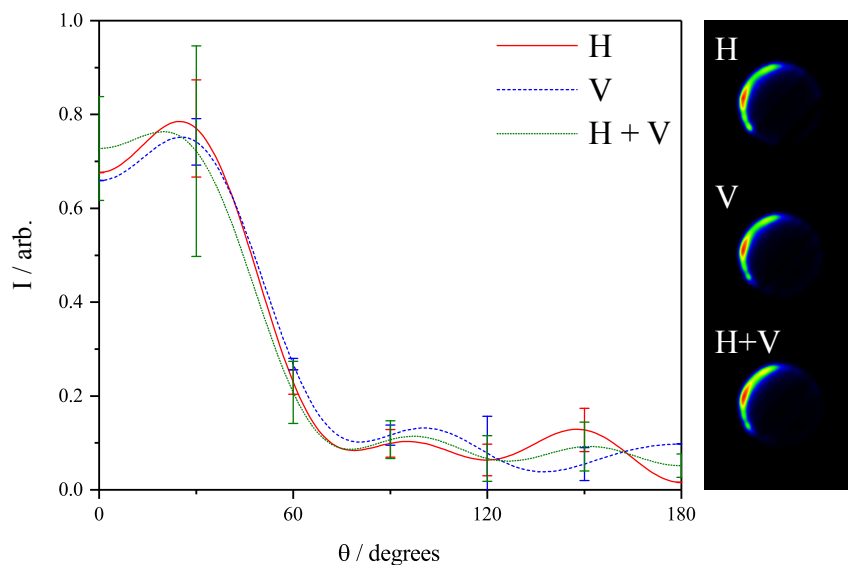


Figure A.4: Experimental angular distributions for the collision of NO + O₂ into $j'_{\text{NO}} = 7.5e$, averaged across the lowest oxygen rotational states $N'_{\text{O}_2} = 1 - 5$. The angular distribution is shown for H, V and H + V polarised detection by red, blue (dashed) and green (dotted) lines respectively. The back-simulated images for these rotational states are shown for H (top), V (middle) and H + V (bottom) polarised detection, using the shown angular distributions and an apse model correction to account for rotational polarisation.

detection laser. As such, it is assumed that the polarisation of the light used in the detection scheme does not significantly affect the resulting extracted angular distributions using the method outlined here.

It has been shown that the collision induced alignment (CIA) of NO(X) with He, Ne and Ar [86, 87, 96] may be approximated well by the classical (impulsive) apse model [87]. Since the scattering of NO(X) with O₂ is expected to show similarities to that of scattering with an Ar collision partner [59], it is assumed that the apse model will also fairly accurately model the CIA of the more complicated NO + O₂ system, as discussed below. The effects of including the apse model in the simulation of the lowest $N'_{\text{O}_2} = 1 - 5$, for scattering into $\Delta j = 7e$, is shown in Figure A.4. Given that the extracted angular distributions for these states are qualitatively equivalent for the different polarisations of the excitation laser, any differences observed in the simulations arise due to the inclusion of polarisation dependent effects from the apse model polarisation moments used. From these simulations, which have the same resolution as the experiment, it is clear that the addition of apse model polarisation moments does not significantly change the

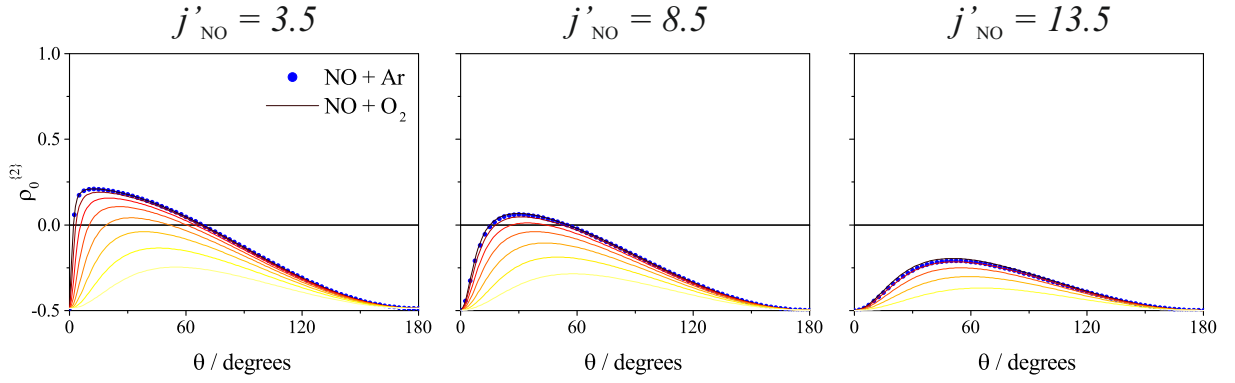


Figure A.5: Apse model $\rho_0^{\{2\}}(\theta)$ renormalised j' -PDDCSs, for the inelastic scattering of NO with Ar (blue points) and O₂ (lines), into the final rotational states $j' = 3.5, 8.5$ and 13.5 , from left to right. Increasing N'_{O_2} are shown on a scale from red ($N'_{\text{O}_2} = 1$) to yellow. Calculations were run at a fixed collision energy of 532 cm^{-1} and 550 cm^{-1} for Ar and O₂ respectively.

observed scattering in the ion image. As such the apse model is used to describe the rotational polarisation in the system for completeness, given the use of V polarised light experimentally.

The Kinematic Apse Model

The classical apse model described in Section 3.5.2, is easily expanded to include diatom-diatom collisions, by considering the potential for rotational excitation of the diatomic collision partner on the outgoing relative velocity, $\mathbf{k}'$. Figure A.5 shows the effect of increasing N'_{O_2} on the $\rho_0^{\{2\}}(\theta)$ moment of the renormalised j' -PDDCS, which describes the alignment of the the final rotational angular momentum with respect to the scattering frame z -axis, calculated using the apse model. As j'_{NO} increases, the $\rho_0^{\{2\}}(\theta)$ moment becomes increasingly more negative, corresponding to alignment of j' perpendicular to the scattering plane [86–88]. Similarly, for a given j'_{NO} , as the rotational excitation of the O₂ molecule increases the $\rho_0^{\{2\}}(\theta)$ moment becomes more negative, and less strongly peaked in the forward scattered direction.

B z -Axis Orientation: Spin-Orbit Changing Transitions of NO(X) + Ar

In Chapter 6, experimental results for the scattering of NO with Ar on the spin-orbit changing manifold after initial bond axis orientation along the $\pm z$ -axis were presented. The data in this appendix are complementary; recorded at $E_{\text{coll}} = 532 \text{ cm}^{-1}$ on the overlapping $Q_{21} + R_{11}$ branches for transitions resulting in the final e Λ -doublet.* CC QM calculations were run as described in Section 6.1, except the maximal partial wave was set to $J = 160.5$. The data here is qualitatively similar to that for collisions at $E_{\text{coll}} = 651 \text{ cm}^{-1}$ in Section 6.3, and as such no in depth discussion of the data will be provided. Figure B.1 shows the experimental and fitted ion images for the bond orientation resolved $|j', \Omega' = 1.5, \epsilon' = +1, e\rangle \leftarrow |j = 0.5, \Omega = 0.5, E\rangle$ transitions of NO scattering with Ar. Note that the images are stretched perpendicular to $\mathbf{k}$: this arises from imperfect velocity-mapping due to the presence of the orientation rods between the ion optics, and is accounted for in the analysis process. The experimentally determined and CC QM bond orientation resolved DCSs and renormalised $R_0^{(1)}(\theta)$ moments are shown in Figures B.2 and B.3, respectively.

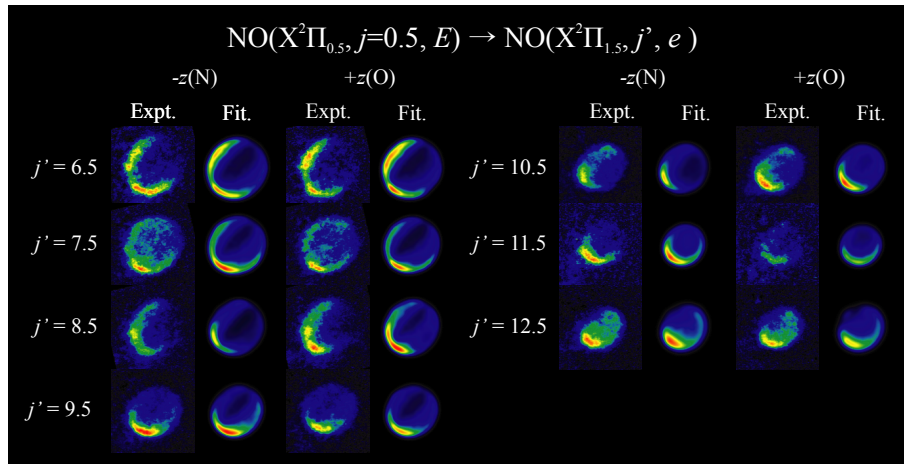


Figure B.1: Experimental (left) and fitted (right) ion images for the bond orientation resolved spin-orbit changing collision of NO with Ar at $E_{\text{coll}} = 532 \text{ cm}^{-1}$, into the final rotational states defined by $|j', \Omega' = 1.5, \epsilon' = +1, e\rangle$. The $-z(\text{N})$ and $+z(\text{O})$ orientations are shown in panels 1/3 and 2/4, respectively.

*The data here was recorded by Dr. Bethan Nichols and Dr. Sean Gordon.

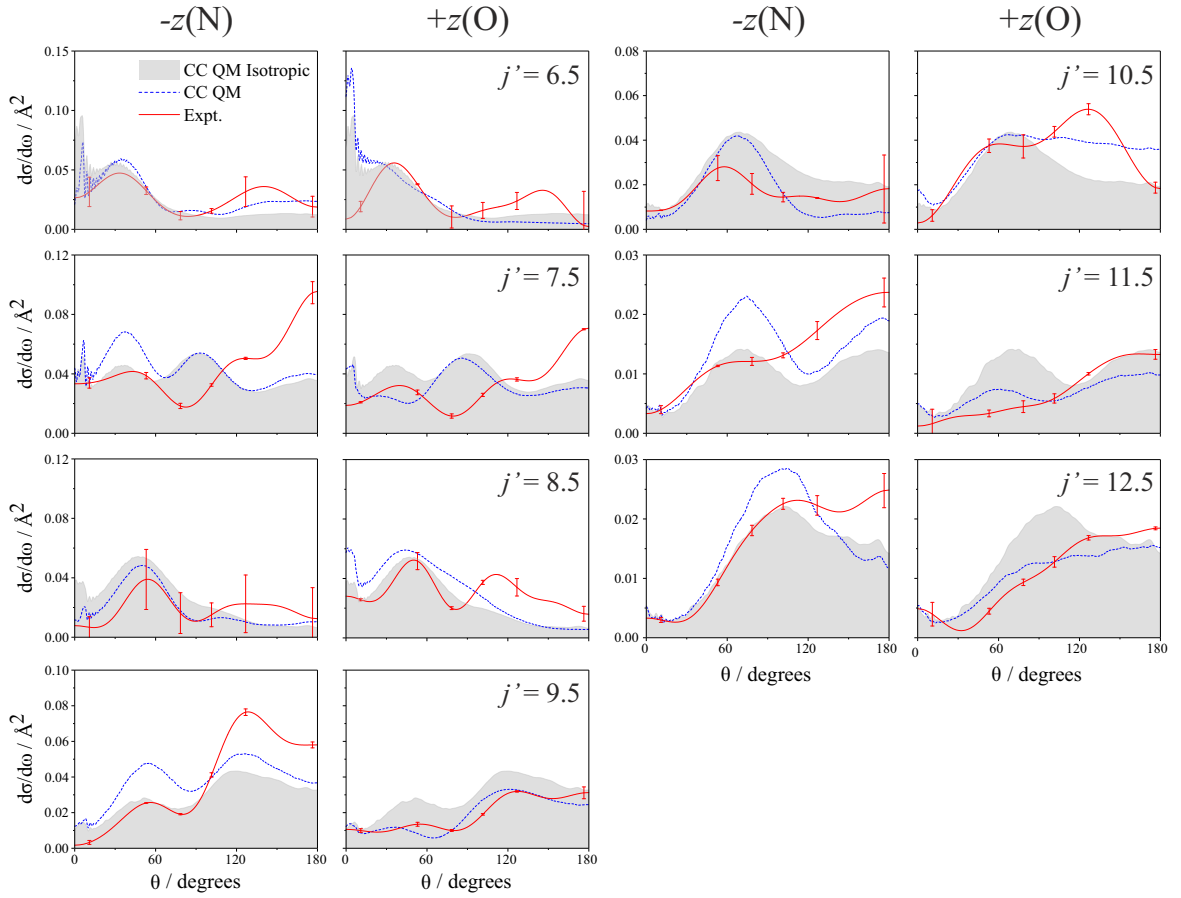


Figure B.2: Experimental fitted (red lines) and QM (blue dashed lines) oriented DCSs for the spin-orbit changing collision of NO with Ar at $E_{\text{coll}} = 532 \text{ cm}^{-1}$, into the final rotational states defined by $|j', \Omega' = 1.5, \epsilon' = +1, e\rangle$. Collisions in the $-z(\text{N})$ and $+z(\text{O})$ orientations are shown in panels 1/3 and 2/4, respectively. The QM isotropic DCS is shaded in gray. Error bars are calculated from the fits to the fast, slow and both sides of the image and correspond to a 95% confidence interval. The QM data have been averaged over collision energy weighted by a Gaussian of FWHM 35 cm^{-1} .

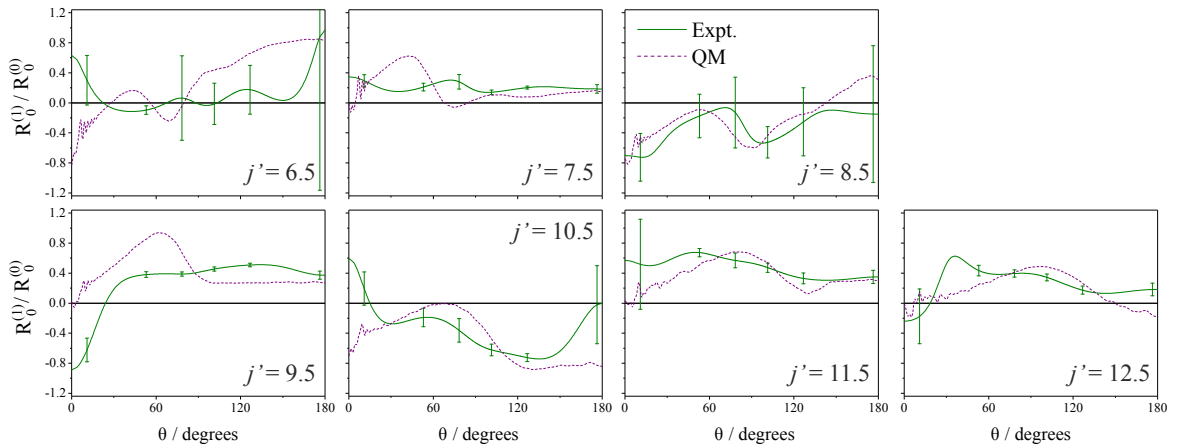


Figure B.3: Experimental (green lines) and CC QM (purple dashed lines) renormalised $R_0^{(1)}(\theta)$ moments for the spin-orbit changing collisions of NO with Ar at $E_{\text{coll}} = 532 \text{ cm}^{-1}$, into final rotational states defined by $|j', \Omega' = 1.5, \epsilon' = +1, e\rangle$. Error bars were propagated from the errors in the DCSs in Figure B.2, and correspond to a 95% confidence interval. The QM data have been averaged over collision energy weighted by a Gaussian of FWHM 35 cm^{-1} .

C x -Axis *versus* z -Axis Integral Steric Asymmetry

The QM integral steric asymmetry for scattering in the $\pm x$ - and $\pm z$ -orientations was presented in Section 7.6.1. The data is reproduced here for a more in-depth analysis. Due to the definition of S_z and S_x , in Equations (5.48) and (7.4), respectively, it is necessary to plot $-S_x$ to facilitate comparisons between scattering in the ‘end-on’ and ‘side-on’ geometries. The top (middle and right) panels of Figure C.1 shows calculations on both the full PES and also on the V_{sum} potential only; it is clear that for $\Delta j < 12$ considering scattering on the V_{sum} PES is sufficient. This is in-line with the fact that spin-orbit conserving transitions may be approximately described using only V_{sum} for a Hund’s case (a) molecule. For $\Delta j \geq 12$ calculations on the full and V_{sum} potential are no longer equivalent, as the NO molecule is better described by an intermediate case between Hund’s case (a) and (b), and scattering occurs across both the V_{sum} and V_{diff} potentials. For low and intermediate states it is therefore sufficient to consider scattering on the summed potential only.

It has been shown by Brouard *et al.* [95] that only terms up to and including $\lambda = 3$ in the expansion of the PES strongly effect the integral steric effect for orientation along the $\pm z$ -axis. As such, it is informative to consider the effects of varying the maximum term, λ , included in the expansion of the potential, in both orientation geometries. The bottom panel of Figure C.1 shows S_x calculated on the potentials with $\lambda = 1, 2$, and 3 . Consider first the case when $\lambda = 1$, which includes only the isotropic V_{00} term, and the heteronuclear V_{10} term. No Δj dependent oscillations are observed in S_x , due to the largely isotropic nature of the PES. For both orientation geometries S is negative (remember however that $-S_x$ is plotted and therefore S_x is positive), corresponding to a preference for $+z$ (O) and $-x$ (repulsive scattering off ‘O’), respectively. S_z decreases as a function of Δj , whilst $-S_x$ decreases until $\Delta j = 5$ before increasing again. The increasing preference as a function of Δj for ‘O-end’ scattering in the z -axis orientation may be easily understood by the only anisotropy observed in the potential, a deep attractive well at the ‘O-end’ of the molecule. For low Δj where large impact parameters (‘glancing blow’) collisions dominate, the anisotropy in the potential is not sampled (see the

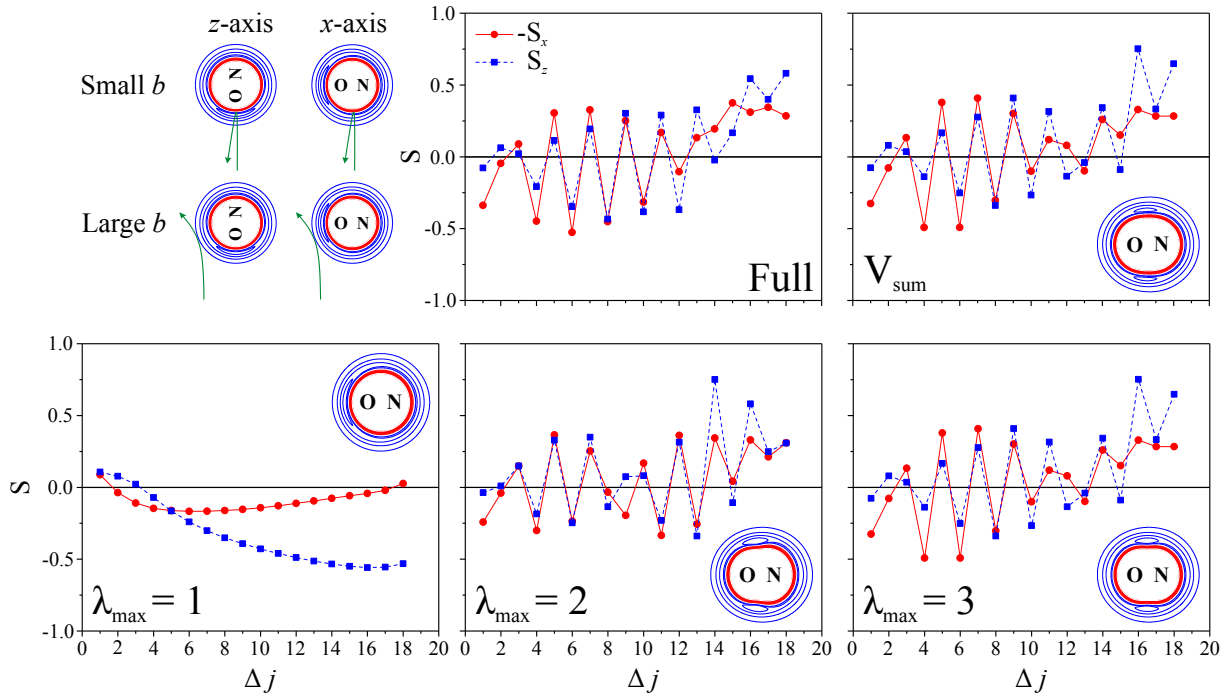


Figure C.1: CC QM integral steric asymmetry, S , at infinite field, for the spin-orbit conserving scattering of NO with Ar into the final e Λ -doublet, with initial bond orientation along the $\pm x$ - (red lines with circles) and $\pm z$ -axis (blue dashed lines with squares). S_x is multiplied by a factor of -1 such that a positive value of S (for a near-side collision) corresponds to scattering off of the ‘N-end’ of the molecule. The top left and right panels show calculations on the full potential and on the V_{sum} potential only, the bottom panels show calculations on the V_{sum} potential with terms larger than 1, 2, and 3 removed (from left to right). The inset in each panel shows the V_{sum} potential used for the calculations. The top left panel shows cartoons of x - and z -axis orientation for small and large impact parameter collisions on the potential with $\lambda = 1$.

cartoon in Figure C.1 for small and large impact parameter collisions). However, for more ‘head-on’ (small b) collisions, resulting in high Δj transitions, the well on the potential energy surface is strongly sampled and the large anisotropy between the ‘N-end’ and ‘O-end’ of the potential is observed as the large negative value of S_z .

The trend in the integral steric asymmetry, calculated on the potential where $\lambda = 1$, for x -axis orientation is slightly more complicated than in the ‘end-on’ geometry. Again, cartoons for small and large impact parameters are shown in Figure C.1. Now, large impact parameter (‘glancing-blow’) collisions, resulting in low Δj transitions, sample the potential well on the at the ‘O-end’ of the molecule, and the strong anisotropy between the two orientations results in the negative value of $-S_x$ (*i.e.* a preference for the $-x$ orientation). As the impact parameter becomes smaller (*i.e.* more ‘head-on’ collisions), the effect of the potential well becomes

weaker and the anisotropy between the two orientations becomes smaller, this results in a decrease in magnitude of the steric effect ($-S_x \rightarrow 0$). At the largest values of Δj the collisions have such small impact parameters that the potential is approximately equivalent in both the $\pm x$ orientations ($S_x \sim 0$). These preferences are directly opposite to that observed for orientation along the $\pm z$ -axis.

Upon addition of the $\lambda = 2$ term of the potential the Δj dependent oscillations in S are restored for both $\pm x$ - and $\pm z$ -orientations. The potential is now near homonuclear in character with an attractive well on its side; subtle differences in the extent and shape of the potential are observed at the two ends of the molecule. This is in agreement with prior work on z -axis orientation [95, 219], which has shown that it is the near homonuclearity of the NO molecule which gives rise to the oscillations in the steric preference. In the region for which the calculations on the V_{sum} potential are in agreement with calculations on the full PES ($\Delta j < 12$) the magnitudes of the S_x and S_z are approximately equal, unlike the differences observed in the full potential. Further addition of the $\lambda = 3$ term, restores the relative magnitudes of S_x and S_z to that observed on the full PES. Only relative minor differences in the absolute magnitude of S_x are observed suggesting that further additions to the expansion of the PES are relatively unimportant. The potential in this case is very similar to the full V_{sum} potential, and the near homonuclearity of the molecule is obvious.

D The Maximised Bond Axis Probability Distribution Function

In Chapter 7, the direction of the electric field which maximised the DCS were presented and discussed. Here the theoretical derivation of the extrinsic maximised probability distribution function in Equation (7.12) is presented. The extrinsic distribution, which accounts for the initial preparation of the internuclear axis in the scattering frame, is [367, 368]

$$P(\theta_r, \phi_r) = \frac{1}{4\pi} \sum_k \left(\frac{2k+1}{4\pi} \right) A_0^{(k)} \sum_{q=-k}^k C_{kq}(\theta_E, \phi_E) C_{kq}^*(\theta_r, \phi_r), \quad (\text{D.1})$$

where θ_E and ϕ_E are the polar and azimuthal angles that describe the direction of the orientation field in the scattering frame. When $j = 1/2$, $A_0^{(0)} = 1$ and $A_0^{(1)} = -1/3 |\alpha\beta|$, and the distribution may be written [367, 368]

$$P(\theta_r, \phi_r) = \frac{1}{4\pi} \left[1 + 3A_0^{(1)} \cos \theta_E \cos \theta_r + 3A_0^{(1)} \sin \theta_E \sin \theta_r \cos(\phi_E - \phi_r) \right]. \quad (\text{D.2})$$

The differential cross section, when the orienting field has a direction (θ_E, ϕ_E) , is

$$\begin{aligned} d\sigma(\theta | \theta_E, \phi_E) = \frac{\sigma_{\text{iso}}}{2\pi} & \left[R_0^{(0)}(\theta) + 3A_0^{(1)} R_0^{(1)}(\theta) \cos \theta_E \right. \\ & \left. - 3\sqrt{2} A_0^{(1)} R_1^{(1)}(\theta) \sin \theta_E \cos \phi_E \right], \end{aligned} \quad (\text{D.3})$$

according to Equation (5.25). The orientation resolved DCS in Equation (D.3) may be maximised with respect to θ_E and ϕ_E at each scattering angle. Maximisation with respect to ϕ_E results in [367, 368]

$$\left[\frac{\partial \sigma(\theta | \theta_E, \phi_E)}{\partial \phi_E} \right]_{\theta_E} = \frac{\sigma_{\text{iso}}}{2\pi} 3\sqrt{2} A_0^{(1)} R_1^{(1)}(\theta) \sin \theta_E \sin \phi_E = 0, \quad (\text{D.4})$$

which has solutions $\phi_E = 0^\circ$ and 180° . Maximising Equation (D.3) with respect to θ_E when $\phi_E = 0^\circ$ [367, 368]

$$\left[\frac{\partial \sigma(\theta | \theta_E, \phi_E)}{\partial \theta_E} \right]_{\phi_E=0} = \frac{\sigma_{\text{iso}}}{2\pi} 3A_0^{(1)} \left[-R_0^{(1)}(\theta) \sin \theta_E - \sqrt{2}R_1^{(1)}(\theta) \cos \theta_E \right] = 0, \quad (\text{D.5})$$

which has a solution

$$\tan \theta_E = -\frac{\sqrt{2}R_1^{(1)}(\theta)}{R_0^{(1)}(\theta)}. \quad (\text{D.6})$$

Similarly, maximising Equation (D.3) with respect to θ_E when $\phi_E = 180^\circ$ gives

$$\left[\frac{\partial \sigma(\theta | \theta_E, \phi_E)}{\partial \theta_E} \right]_{\phi_E=0^\circ} = \frac{\sigma_{\text{iso}}}{2\pi} 3A_0^{(1)} \left[-R_0^{(1)}(\theta) \sin \theta_E + \sqrt{2}R_1^{(1)}(\theta) \cos \theta_E \right] = 0, \quad (\text{D.7})$$

which has a solution

$$\tan \theta_E = \frac{\sqrt{2}R_1^{(1)}(\theta)}{R_0^{(1)}(\theta)}. \quad (\text{D.8})$$

To calculate the maximised extrinsic distribution, the solutions which maximise the bond orientation resolved DCS (Equations (D.6) and (D.8) for $\phi_E = 0^\circ$ and 180° , respectively) are substituted into Equation (D.2). After some algebraic manipulation the maximised extrinsic distribution can be written [367, 368]

$$P_{\text{max}}(\theta_r, \phi_r | \theta) = \frac{1}{4\pi} \left[1 + 3A_0^{(1)} \left(\frac{R_0^{(1)}(\theta)}{S(\theta)} \right) \cos \theta_r - 3A_0^{(1)} \left(\frac{\sqrt{2}R_1^{(1)}(\theta)}{S(\theta)} \right) \sin \theta_r \cos \phi_r \right], \quad (\text{D.9})$$

for $\phi_E = 0^\circ$, and

$$P_{\text{max}}(\theta_r, \phi_r | \theta) = \frac{1}{4\pi} \left[1 + 3A_0^{(1)} \left(\frac{R_0^{(1)}(\theta)}{S(\theta)} \right) \cos \theta_r + 3A_0^{(1)} \left(\frac{\sqrt{2}R_1^{(1)}(\theta)}{S(\theta)} \right) \sin \theta_r \cos \phi_r \right], \quad (\text{D.10})$$

for $\phi_E = 180^\circ$, where

$$S(\theta) = \sqrt{R_0^{(1)}(\theta)^2 + 2R_1^{(1)}(\theta)^2}. \quad (\text{D.11})$$

In the limit of complete orientation, $|\alpha| = |\beta| = 1$, there are therefore two solutions for $\theta_E = 0^\circ$:

$$P_{\max}(\theta_r, \phi_r | \theta) = \frac{1}{4\pi} \left[1 - \left(\frac{R_0^{(1)}(\theta)}{S(\theta)} \right) \cos \theta_r + \left(\frac{\sqrt{2}R_1^{(1)}(\theta)}{S(\theta)} \right) \sin \theta_r \cos \phi_r \right], \quad (\text{D.12})$$

and

$$P_{\max}(\theta_r, \phi_r | \theta) = \frac{1}{4\pi} \left[1 + \left(\frac{R_0^{(1)}(\theta)}{S(\theta)} \right) \cos \theta_r - \left(\frac{\sqrt{2}R_1^{(1)}(\theta)}{S(\theta)} \right) \sin \theta_r \cos \phi_r \right]. \quad (\text{D.13})$$

Similarly, for $\phi_E = 180^\circ$:

$$P_{\max}(\theta_r, \phi_r | \theta) = \frac{1}{4\pi} \left[1 - \left(\frac{R_0^{(1)}(\theta)}{S(\theta)} \right) \cos \theta_r + \left(\frac{\sqrt{2}R_1^{(1)}(\theta)}{S(\theta)} \right) \sin \theta_r \cos \phi_r \right], \quad (\text{D.14})$$

and

$$P_{\max}(\theta_r, \phi_r | \theta) = \frac{1}{4\pi} \left[1 + \left(\frac{R_0^{(1)}(\theta)}{S(\theta)} \right) \cos \theta_r - \left(\frac{\sqrt{2}R_1^{(1)}(\theta)}{S(\theta)} \right) \sin \theta_r \cos \phi_r \right]. \quad (\text{D.15})$$