

Two and three vector correlations in the rotationally inelastic scattering of state-selected NO(X)

A thesis submitted for the degree of Doctor of Philosophy

Physical and Theoretical Chemistry



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September 8, 2016

Abstract

In this thesis, an experimental and theoretical study of two and three vector correlations in the inelastic scattering of NO(X) with various rare gas atoms is presented. Vector correlations for a selection of rare gas systems were determined experimentally, and the observations were interpreted using a variety of classical and quantum mechanical models. The experiment is able to provide state-to-state resolution of the dynamics by means of an electrostatic hexapole and $(1 + 1')$ resonantly enhanced multi-photon ionisation (REMPI).

The simplest vector correlation of interest is the differential cross section (DCS), given by the $\mathbf{k}-\mathbf{k}'$ correlation. The DCSs were determined experimentally for the NO(X)–Kr and NO(X)–Xe collision systems, both characterised by the relatively deep ($\approx 140 \text{ cm}^{-1}$) attractive well and large extent of the attractive potential. The agreement between the experimental angular distributions and quantum mechanical DCS is very good for both systems. Classical calculations fail to correctly reproduce the form and magnitude of the DCS for either system, reflecting the inherently quantum mechanical nature of the collision. The classical calculations do however provide mechanistic insight into regions where the attractive part of the potential plays an important role in determining the dynamics.

In order to investigate narrow angular features in the forward scattered direction, several experimental improvements to molecular beams and the detection ion-optic stack were made. Investigation into these structures revealed a strong contribution from molecular diffraction into the classical shadow of the NO(X), and the simple Fraunhofer model revealed a preference for scattering from an individual $m \rightarrow m'$ sub-state. Such measurements are in a region of the DCS where scattering is forbidden classically, and reveal the purely quantum nature of the collision interaction in the forward scattered direction.

The low order $\mathbf{k}-\mathbf{k}'$ correlation was then extended by using linearly or circularly polarised laser excitation. The interaction of the light with the molecular dipole allows the measurement of the $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ correlation. When linearly polarised light was used for the excitation laser, two of the rank two $\rho_q^{\{2\}}(\theta)$ renormalised polarisation dependent differential cross sections (PDDCSs), which describe rotational alignment, were obtained. With circularly polarised light, the rank one $\rho_1^{\{1\}}(\theta)$ renormalised PDDCSs describing rotational orientation were determined. The collision induced alignment in NO(X)–Xe scattering was found to be well reproduced by classical and impulsive theories, highlighting the fact that the alignment is dominated by the propensity for the projection of $\mathbf{j}$ onto the kinematic apse to be conserved. The attractive part of the potential does augment the alignment renormalised PDDCSs, and this is most evident in states with strong features of the attractive part of the potential such as ℓ -type rainbows. The orientation is more strongly influenced by the attractive part of the potential and is also influenced by parity. In addition to the parity effect, there exist two limiting classical mechanisms which govern the orientation, one caused by attraction and the other repulsion.

Finally, the bond axis of the NO(X) can be oriented by means of hexapole state selection combined with adiabatic orientation using a set of guiding rods. The integral steric effect, an $\mathbf{r}-\mathbf{k}$ correlation, was measured for the NO(X)–Kr and NO(X)–Ar spin-orbit changing systems. There are large oscillations in the sign of the steric asymmetry which occur for scattering with the various rare gases. There are also large differences between the rare gases as the potentials become more attractive, and more isotropic. The steric asymmetry is well reproduced by quantum mechanics, however, a classical mechanism becomes dominant at high Δj .

Acknowledgements

Firstly, thanks must be given to my supervisor, Mark Brouard for his innumerable insightful comments, skilled guidance and unwavering support over the last few years. Without his tireless enthusiasm, sharp wit and the occasional short, none of this work would have been possible.

Secondly, thanks must be paid to all the members of the Brouard group whom I have had the great pleasure of getting to know over the years. I've been fortunate enough to work with extremely talented and passionate individuals, truly standing on the shoulders of giants. Particular thanks must go to Dr Helen Chadwick for teaching me how to use a mallet and enjoy crêpes, Cde Garreth McCrudden and Cde Dr Bethan Nichols for our fantastic cultural exchanges in eastern Europe (and my dining room), Dr Balázs Hornung for the words of wisdom and their translations, and lastly but not least, Dr Ed Halford for organising my social life for three years.

Many thanks must also go to the other members of the Brouard group who have also been particularly great, Dr Alexa Lauer for indulging me and facing her fear of roller-coasters, Dr Scott Seamons for his political insights, Eleanor Squires for knowing when to just hit STOP, James Pickering for keeping me strong (after we went to the gym that one time), and for fuelling my obsession with Kerbal Space Program, and of course Anna Hackett Boyle for providing her care, support, and a sense of calm and tranquillity that the office has now lost forever.

None of the experimental work presented in this thesis would have been possible without the enormous skill, expertise, patience and dedication of the staff in the PTCL and CRL workshops, particularly Andy Green, Charlie Jones, Phil Hurst, Nev Baker, Alan Roper and Jude Nettleton. A debt is also owed to the maintainers of all the open-source software used in our lab, gnuplot, L^AT_EX, gcc, GNUutils, the Kernel, CentOS, cygwin, texmaker, Notepad++, X.org, chromium, synergy, gimp, imagemagick, imageJ, VLC, 7z, and many others.

I also owe great personal thanks to Prof. Steven Stolte who has always been an excellent mentor and guide through the world of reaction dynamics (as well as the suburbs of Holland). Thanks must also be given to Bas van de Meerakker, David Parker, Jolijn Onvlee, Alex Von Zastrow and Sjoerd Vogels whose friendship and hospitality have made the collaboration between Nijmegen and Oxford so fruitful and enjoyable.

Finally, thanks must also be given to Oxford University Rifle Club and its members for helping me shoot straight these last few years, to my mother and father for their continued and invaluable help and support and to Dr. Peter Dean for his generous financial contributions.

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- [2] M. Brouard, H. Chadwick, S. D. S. Gordon, B. Hornung, B. Nichols, F. J. Aoiz, and S. Stolte, “Stereodynamics in NO(X)+Ar Inelastic Collisions,” *The Journal of Chemical Physics*, vol. 144, pp. 224301, 2016.
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List of Future Publications

- [1] H. Chadwick, S. D. S. Gordon, B. Hornung, B. Nichols, M. Brouard, and S. Stolte, “Three vector correlations in the inelastic scattering of state-selected NO(X) by Xe,” *Physical Chemistry Chemical Physics*, vol. xx, no. xx, p. in draft, 2016.
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Introduction

The field of chemistry seeks to understand and predict the behaviour of matter, and matter–field interactions. Such an undertaking requires knowledge of an exceptionally broad range of processes, from the complex interactions of dust in the interstellar medium, to the processes that replicate cells in living organisms. Regardless of the scale of the process, the interactions between the atoms and molecules themselves are always governed by quantum mechanics. Quantum theory itself turns out to be successful in describing all manner of physical processes. Despite its predictive power, the counter-intuitive nature of quantum mechanics has often precluded it from providing mechanistic insight, and the quantum–classical correspondence remains a subject of debate [1]. Furthermore, for many systems it is not useful to consider using quantum mechanical models, in the words of Paul Dirac:

“The underlying physical laws necessary for the mathematical theory of a large part of physics and *the whole of chemistry* are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.”

The models Dirac envisaged have been developed over the last several decades with the aim of understanding the dynamics of molecular systems, without explicitly solving the complete Schrödinger equation of that system. A multitude of approximations are now available and they provide a highly rigorous and mechanistically meaningful view of a multitude of systems from the atto-scale to the meso-scale. In order to ensure the approximate methods still have excellent predictive power, experiments must be performed and comparisons drawn between them and theory. Furthermore, mechanistic insight can be gained from approximate models, which enables ever more sophisticated control of molecular systems, leading to entirely new fields of research and the development of new experimental techniques.

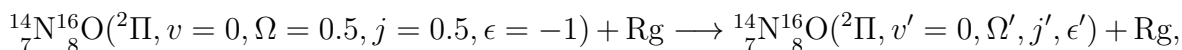
This thesis will explore a subset of chemistry that is referred to as dynamical stereochemistry, or stereodynamics. The goal of stereodynamics is to obtain fundamental understanding of the processes that govern the dynamics of chemical reactions. The experimental techniques used to achieve these goals must be developed, and the theoretical methods applied in order to contrive a deep understanding of the processes involved in the scattering interaction. Increasingly more sophisticated experimental and theoretical methods have led to a far more detailed understanding of simple gas-phase collisions. Vector correlations that conveniently characterise such collisions have also been defined; these quantities are observable, and their measurement by means of a crossed molecular beam apparatus will be presented in this thesis. The experimental data presented will be rationalised using various classical and quantum mechanical models that give mechanistic insight into the dynamics during the collision interaction.

1.1 Molecular Collisions

In order to unravel the dynamics of a molecular collision (an event in which colliding moieties approach close enough that the internal states of one or both change), it is desirable to tightly constrain all of the scalar and vector properties that govern the interaction. In many systems, it is not possible to fully specify the initial or final states, or to constrain or measure all of the vector properties of interest. Any observation

of such systems results in averaging over multiple degrees of freedom and dynamical information is irretrievably lost. The dynamics of a relatively simple atom–diatom collision have remained of considerable interest, as for these systems, the vector and scalar properties can be tightly constrained and the internal states controlled.

There are a number of possible processes that can take place during the collision of an atom and a diatom. For example, there may be a reaction (reactive scattering), the internal states of one or both moieties may be changed (inelastic scattering), or the collision may deflect the species without the internal states changing (elastic scattering). In this thesis, the rotationally inelastic scattering of ground-state nitric oxide, NO(X), with a variety of rare gas (Rg) atoms will be presented. All¹ the collisions presented in this thesis are of the form



with $v=0$ the vibrational quantum number, Ω the spin-orbit quantum number, j the rotational quantum number, and ϵ the spectroscopic index which quantifies the system parity. A convention that will be used throughout has also been introduced: the vectors or quantities associated with the scattered products will be denoted by a ' symbol. The kinetic energy of the atom and molecule colliding is converted *via* rotational energy transfer (RET) from translational energy into rotational energy of the NO(X). This causes the rotational angular momentum, $\mathbf{j}$, to change during the course of the collision. This process may also cause the particles to deflect from their initial trajectories (defined by the vector $\mathbf{k}$), resulting in a change in relative velocity to a new value, $\mathbf{k}'$. Since the direction of the particles as they approach one another is known (by the geometry of the experiment), if one measures the correlation between these vector properties, information about the collision interaction itself can be obtained.

The state-to-state differential and integral cross sections are very important in the chemistry of combustion, when radical species interact, or in the chemistry in the interstellar medium. Furthermore, the nascent product distribution after a chemical

¹With the exception of the integral steric asymmetry of NO(X) scattering with O₂(X), presented in Chapter 8.

reaction or photochemical process is often non-Boltzmann. In order for the system to return to thermodynamic equilibrium, energy must be transferred between the product molecules, one of the dominant mechanisms is *via* inelastic collisions. Knowledge of the mechanisms governing inelastic collisions is therefore highly important to further our fundamental understanding of elementary chemical processes.

1.2 Vector and Scalar Quantities

Molecular beam methods have become a staple of investigations into gas-phase reaction dynamics. The simplicity and directness of the method allows a great deal of dynamical information to be obtained. Herschbach devised a theoretical scheme more than thirty years ago [2] in which the averaging over impact parameter, inherent to molecular scattering, could potentially be undone [3]. The language used to describe inelastic collisions is that of vector correlations. They consist of a hierarchy of vector properties, as shown in Fig. 1.1. One may be interested in measuring any of these quantities as they each provide rich information about the dynamics. Each correlation quantifies the relationships between two or more vector quantities. Determining a vector correlation is thus, in part, a matter of quantifying the change in cross section as a function of angle between them. Additional information is obtained by correlating more vectors with one another, however in practice this has proven to be an exceptionally difficult task, and only a few measurements of a complete three vector correlation have been made [4–6], and only one of the complete four vector correlation [7].

In general, atom–diatom collisions involve four vectors whose directions, or polarisations can be measured or controlled [2,8,9], as shown in the idealised collision interaction shown in Fig. 1.2. These vectors are the internal angular momenta of reagents and products, $\mathbf{j}$ and $\mathbf{j}'$, and the initial and final relative velocity vectors, $\mathbf{k}$ and $\mathbf{k}'$, respectively. Here, the vectors or quantities relating to scattered products are denoted by a “’” symbol; this notation will be used throughout the thesis. In molecular beam experiments, the scattering angle plays a central role, and is defined as $\cos \theta = \mathbf{k} \cdot \mathbf{k}'$.

Previous studies of inelastic scattering of NO(X) with rare gases have focused on

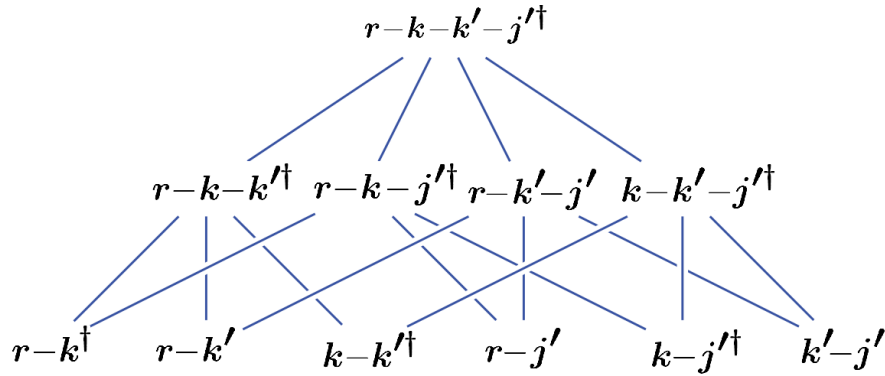


Figure 1.1: The hierarchy of vector correlations described by Barnwell [2]. The lowest level contains the two vector correlations that give the least detailed information about the collision and at the top is the four vector correlation that gives the most detailed information. Vector correlations with a dagger ($\dagger$) denote those presented experimentally and/or theoretically in this thesis.

the measurement of differential cross sections [10–14] which correlate the change in magnitude of the scattering cross section as a function of the scattering angle θ and therefore represent a low-order two vector $\mathbf{k}-\mathbf{k}'$ correlation, as depicted in Fig. 1.1. The differential cross section provides rich information about the collision interaction; for example, observation of ℓ -type rainbows in the angular distribution provides information on the attractive region of the potential, whilst rotational rainbows are affected by the anisotropy of the potential surface [12, 15–18].

Recent work has focused on collision-induced polarisation in which either the alignment [19–21] or the sense of rotation [19, 22] of the scattered NO(X) is determined. These measurements are sensitive to a multipole of the full three vector $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ correlation, and can be used to recover information about reaction dynamics that would otherwise be lost by the averaging over the impact parameter [3]. Such measurements have been performed on the NO(X)–Xe collision system, described in Chapter 4 and the NO(X)–Kr collision system described in Chapter 5.

Control of the bond axis of NO(X) defines the vector $\mathbf{r}$, and allows measurement of a quantity called the steric asymmetry which is related to the $\mathbf{r}-\mathbf{k}$ correlation and measures the preference for rotational excitation by either the N-end or O-end of the molecule. Such measurements are compared and contrasted between different systems in Chapter 6. The steric asymmetry for a process can provide information on the geometric requirements for a collision, for example, investigation of the OH(X)–Ar

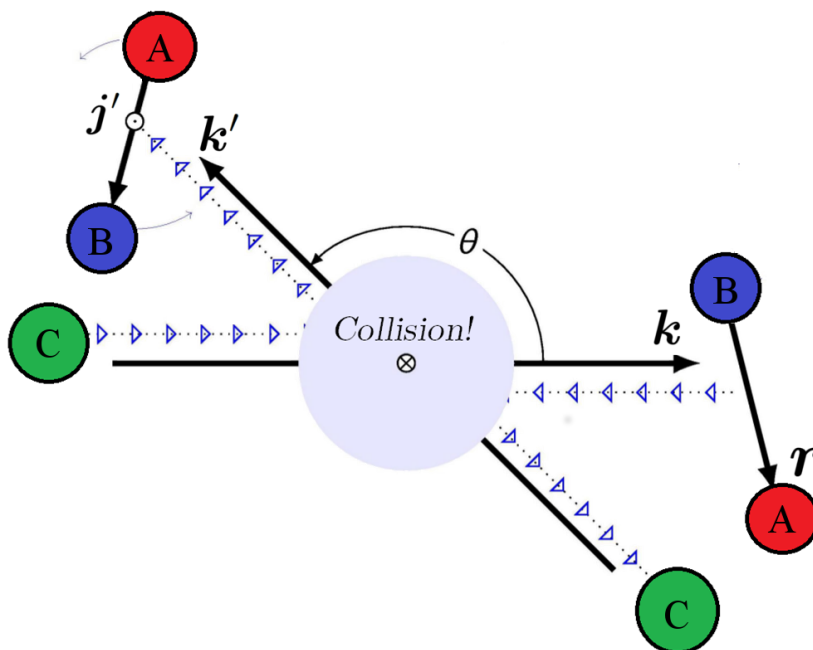


Figure 1.2: A cartoon of an idealised molecular collision involving the atoms A (red), B (blue) and C (green). The diatom AB and atom C approach one another and collide. The vectors $\mathbf{k}$, $\mathbf{k}'$, $\mathbf{r}$ and $\mathbf{j}'$ which fully specify the collision interaction are shown along with the scattering angle $\cos \theta = \mathbf{k} \cdot \mathbf{k}'$. Adapted from [8].

collision showed that collisions with the H end of the molecule resulted in larger rotationally inelastic cross sections than collisions with the O-end for all but the lowest rotational states [23]. Investigations of the steric asymmetry in the NO(X)–He [24] and NO(X)–Ar [25] collision systems have also been undertaken, revealing strong quantum interference effects giving way to classical behaviour at higher j' .

1.3 Experimental Considerations

In order to study the vector properties of molecular collisions, all external factors that influence the internal states must be removed in order to exert maximum control over the colliding species. This is achieved by using a vacuum apparatus with moderately high vacuum (5.0×10^{-8} mbar). As discussed in the preceding sections, maximum information on the dynamics underlying a collisional process can be gained when the fully quantum state resolved vector correlations for the process are determined. In this section a brief overview of some of the experimental methods that can be employed to select the initial, and determine the final, quantum states and vector properties will be

given. A much more detailed explanation of the experiment is provided in Chapter 3.

1.3.1 Reagent State Selection

A multitude of methods has been devised over the past decades in order to prepare ensembles of state-pure systems. With the advent of the laser, populations can be efficiently transferred from one specific rovibrational level to another, allowing state-selection of both electronic [26] and vibrational [27] states. Recently, Zare has reported a new population transfer scheme that not only allow 100% population transfer from a specific rovibrational level [28], but also magnetic sub-state control [29, 30].

Use of magnetic and electric fields is also of considerable value when preparing a state-selected ensemble. The Stark and Zeeman energies of a molecule depend on the quantum numbers of specific states, so can be used to guide and focus molecules in a very similar way to how ion optics control the motion of ions using the Coulomb force. These methods have been extensively developed over the last thirty years and are now at a stage where exploitation of the Stark and Zeeman effects can lead to complete control of not only the state distributions, but also the velocities of polar molecules [31, 32].

Apart from the internal states, control or measurement of the vector properties outlined above must also be achieved in order to obtain the clearest picture of the collision interaction. The initial relative velocity is defined by the direction of the molecular beams. The beams themselves are pulsed and release a large number of molecules per pulse, typically with a number density of $10 \times 10^{13} \text{ cm}^{-3}$, the beam of molecules then expands into the vacuum at supersonic speeds. The speed and direction of each beam is thereby fixed, allowing specification of the initial relative velocity, $\mathbf{k}$.

The bond axis direction may be defined in many different ways. Absorption of light is an inherently anisotropic process, and can be used to polarise both ground state or excited state molecules. Following the early work of Zare and co-workers [33], Wang *et al.* have recently used optical preparation with an infrared laser to pre-align CHD_3 molecules to unravel the steric preferences of the reaction of CHD_3 with Cl [34]. The bond axis distribution can also be polarised by the absorption of two or more

photons [35]. A different way of using photons to align a molecular ensemble is to use an intense, non-resonant and polarised laser field to generate a strong, localised electric field; thereby exploiting the molecular AC Stark effect. The control of molecular alignment [36–38] and orientation [39,40] through intense laser pulses has received much attention recently in the literature, and has been the subject of several reviews [41,42]. These methods, though extremely powerful and general, have yet to be applied to crossed molecular beam scattering experiments.

In Chapter 6 of this thesis, hexapole state-selection is coupled with a static electric field to almost adiabatically orient the NO(X) [25,43], thereby allowing control of $\mathbf{r}$.

1.3.2 Product State Selection and Detection

In order to detect the final relative velocity of the scattered products in conjunction with other vector quantities, several schemes have been used, including rotatable detectors and electron ionisation. An alternative approach was made possible by the advent of velocity mapped [44] ion imaging [45] coupled with resonantly enhanced multi-photon ionisation (REMPI). In this scheme, a narrow bandwidth laser is used to selectively ionise a particular quantum state of the scattered products after collision. The newly formed ions are manipulated by a weak DC electric field in the interaction region which focuses them onto a position sensitive detector such that ions with the same velocities are focussed onto the same point on the detector. The detector itself consists of charged multi-channel plates (MCPs) which emit large numbers of electrons when impacted by an ion. The electrons are then accelerated towards a scintillating phosphor screen that emits light upon electron impact. The flashes of light are recorded by a CCD camera and transferred to a computer for processing. Alternatively, MCPs can be combined with delay line detectors, in which an ion impact generates a current that takes a certain time to reach the sink depending on the position of the impact [46–48]. The velocity mapping technique has been widely used to study both inelastic and reactive scattering systems as well as other processes such as photodissociation [49,50] and the Coulomb explosion of large molecules [51,52].

In order to determine the direction in which $\mathbf{j}'$ lies, laser induced fluorescence (LIF)

detection can be employed. In the Zeeman Quantum Beats variation of this method, the fluorescence emitted from molecules in electronically excited states is monitored as the molecules radiate back to the ground state. The intensity of this fluorescence is related to the population of the excited state. The orientation or alignment of $\mathbf{j}'$ can be determined by monitoring the polarisation of the emitted light as a function of time [53–56].

Instead of the LIF scheme outlined above, which would be cumbersome to use in conjunction with velocity mapped ion imaging, a REMPI scheme is used instead. In this scheme, a polarised 226 nm laser is used to promote NO(X) to the NO(A) state, and the NO(A) state is subsequently ionised by a 308 nm laser. The determination of polarisation information is possible due to the correlation between the transition dipole moment of a molecule and the direction of the angular momentum vector [57]. Classically, the absorption probability of a photon depends on the angle between the electric vector of the light and the transition dipole moment by

$$P(\theta_{\mu E}) \propto \cos^2 \theta_{\mu E}, \quad (1.1)$$

where $\theta_{\mu E}$ is the angle between the transition dipole of the molecule $\boldsymbol{\mu}$ and the electric vector of the light, $\mathbf{E}$. If the distribution of $\mathbf{j}'$ is anisotropic, then the chance of absorption of a photon will be dependent on the direction of its polarisation. Linearly polarised light is employed to determine the alignment of $\mathbf{j}'$, the plane of rotation in Chapter 4. Circularly polarised light is used to determine the orientation of $\mathbf{j}'$ in Chapter 5.

1.4 Theoretical Considerations

A large body of rigorous theoretical work [58–60] has been produced on rotational energy transfer in the NO(X) collision systems. This ranges from *ab initio* potential energy surfaces [61,62] to models that simplify the description of a collision [63–65], in order to provide intuitive insights into the forces at play during the collision.

1.4.1 The Potential Energy Surface

The collision and subsequent scattering of two species can be thought of as the coupled movement of the species across a surface, with the coordinates given by the degrees of freedom of the system. The surface describes the potential energy of the system at various geometries. Due to the number of degrees of freedom in the NO(X) rare gas collision system, some of these can be fixed at a specific value. For the calculations presented in this work, the potential energy surfaces (PESs) were obtained from *ab initio* calculations assuming that the bond length of the NO(X) molecule is fixed at its equilibrium value [61]. Calculations performed at various different bond lengths have been found to make an imperceptible effect on the calculated observables [61]. All of the NO(X) + Rg surfaces are comprised of two surfaces (described in detail in Chapter 2) of A' and A'' symmetry. This is due to the two possible π^* orbitals that the unpaired electron may reside in. In the absence of an external molecule or field these two orbital energies are degenerate, but the approach of a rare gas atom lifts the degeneracy.

The low lying spin-orbit state in NO(X) leads to a breakdown in the Born-Oppenheimer approximation. The process must then be considered to occur over multiple diabatic potential energy surfaces which are coupled. Collisions of NO(X) with rare gases have therefore become a benchmark system for the treatment of non-adiabatic effects.

By performing state-selected experiments, different regions of the potential surfaces can be probed. Aspects of observed vector correlations can be linked to specific features of the potential energy surface, such as the attractive well or the anisotropy of the potential. Furthermore, different vector correlations are sensitive to different parts of the potential, as will be explained throughout the thesis.

1.4.2 Theoretical Dynamics

Once the potential energy surfaces have been determined, scattering calculations can be employed in order to predict the phenomena and enable comparison to experimental quantities. Calculations treat the system either classically, semi-classically or quantum

mechanically by solving the associated equations of motion. As will be seen in this thesis, the quantum mechanical and classical mechanics calculations often agree almost quantitatively. However, regions where quantum effects are dominant in the differential cross sections and higher order vector correlations can cause significant differences.

The central maxim of the classical calculations is the trajectory. For a given set of initial conditions, the particles are allowed to propagate over the potential energy surface according to the Hamiltonian equations of motion. Depending on the initial starting conditions, and regions of the potential energy surface sampled, the scattering outcome from any individual trajectory may differ significantly from one with similar initial conditions. Given the number of possible initial conditions, it is necessary to perform a large number of trajectory calculations in order to fully sample the parameter space. Vector correlations can then be obtained from analysis of the trajectories. The classical calculations are advantageous as all the momenta and positions can be specified simultaneously. However, difficulties arise when comparing to experiment and quantum calculations; the rotational states calculated in the QCT are not quantised and must be binned into the nearest quantum state. Additionally, since the classical theory contains no phase information, no interference effects are observed, nor is tunnelling through barriers possible in classical calculations.

Quantum mechanical calculations enable a rigorous treatment of the scattering problem from first principles and have repeatedly been shown to provide quantitative agreement to experimental results. The treatment of NO(X) rare gas systems is now well established, however the addition of a fourth atom, as described in Chapter 8, leads to the scattering calculations becoming far too difficult to perform.

For the case of NO(X) scattering with a rare gas, comparison between the classical and quantum mechanical calculations proves a valuable tool for identifying features, such as interference effects, that are purely quantum mechanical in origin and have no classical analogue. Other models can also be devised and used to explain scattering phenomena, such as semi-classical interference effects. Such models are far from quantitative, but provide qualitative information about interference effects or other phenomena.

1.5 Outline

This chapter has discussed the motivations for performing state-selected scattering experiments of NO(X) with as many vector properties as possible experimentally constrained or observed. The theoretical background that underpins this work will be presented in Chapter 2, which will include descriptions of the angular-momentum coupling schemes in NO(X) as well as a more detailed description of the potential energy surfaces upon which the scattering process occurs. The quantum and classical calculations as well as the scattering theory necessary to calculate observable quantities will also be presented in Chapter 2.

Chapter 3 contains an in-depth description of the experimental apparatus and the experimental geometries used to obtain the data in this thesis. Experimental protocols used to accurately characterise the experiment are also presented. These are necessary in order to allow accurate comparisons to theory. The method of extracting observable quantities (such as DCSs presented in Chapters 4 and 5) from the experimental velocity mapped ion images is also discussed.

Inelastic scattering of NO(X) with Xe is investigated in Chapter 4. The state-to-state differential cross sections (representing the $\mathbf{k}\text{--}\mathbf{k}'$ correlation) were obtained for the entire range of energetically accessible transitions at a collision energy of 519 cm^{-1} . The data were recorded with a well defined horizontal or vertical laser polarisation. This allows the determination of the rank two renormalised polarisation dependent differential cross sections (PDDCSs), $\rho_{q+}^{\{2\}}(\theta)$, which quantify the $\mathbf{k}\text{--}\mathbf{k}'\text{--}\mathbf{j}'$ correlation from the experimental ion images. The features observed are rationalised based on the large and polarisable nature of the xenon atom and results are compared to previous measurements of the NO(X)–Ar and NO(X)–Kr collision systems.

The orientation of the angular momentum vector can also be determined. The rotational orientation is given by the rank one $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCS which quantifies the preference of NO(X) to be scattered rotating clockwise or counter-clockwise (as a function of scattering angle) after the collision. This effect is called the collision-induced orientation or CIO. The CIO has been shown to be exquisitely sensitive to the balance

of attractive and repulsive forces during a collision, and thus allows observation of the attractive and repulsive forces in detail. The origin and experimental investigation of the CIO will be described in Chapter 5 by making use of the orientation geometry described in Chapter 3. CIO was first investigated by Chandler and co-workers [22] in a ground-breaking experiment using Λ -doublet state-averaged NO(X) scattering with argon. Little work has been reported since, apart from some investigations in reactive scattering [66,67] and an extension of the work performed on argon with a state-selected beam of NO(X) [63,68].

A set of four rods with a strong DC electric field between them was then installed into the interaction region. These rods cause almost adiabatic orientation of the NO(X) molecule before interaction with the rare gas atom. These experiments, presented in Chapter 6 investigate the integral steric effect in detail, and a joint experimental and theoretical comparison between the different rare gas systems is presented. The integral steric asymmetry is rationalised in terms of quantum mechanical and classical effects, and is shown to be sensitive to several different parts of the potential.

The Fraunhofer theory of molecular collisions is presented in Chapter 7. The experimental apparatus characterised in Chapter 3 was used to attempt to observe diffraction oscillations in the low angle region. The diffraction oscillations were then analysed in order to understand the origin of an intense diffraction peak visible in most inelastic scattering differential cross sections.

A summary of the main findings of this thesis is then presented in Chapter 8, along with possible avenues for future research.

Theoretical Methods

In this chapter, an overview of the theoretical framework of the classical and the quantum mechanical calculations used in this thesis will be given.

The first part of this chapter will be dedicated to explaining the angular momentum coupling in the NO(X) molecule. Later, the potential energy surfaces (PESs) which designate the interaction of NO(X) with its collision partner will be described, followed by an explanation of how scattering calculations (whether they be quantum mechanical or classical) are performed on these surfaces. By running classical and quantum mechanical calculations upon the PES of interest, effects resulting from classical mechanics and effects resulting from quantum mechanical phenomena are distinguished.

Stereodynamics is the name given to the field involved in the study of the dependence of reactive or inelastic scattering processes on the polarisation of one or more of the reactants [69]. By using vector correlations, preferred relationships between two or more vectors can be quantified. Since vectors contain both magnitude and direction, a correlation between two vectors is in part, a matter of quantifying the angular distribution between them. It is also desirable to determine how the cross section for a process varies with the angle between two or more vector quantities. As this chapter, and subsequent chapters will demonstrate, these measurements are more challenging

than measuring the angular distribution alone.

2.1 The NO(X) Molecule

NO(X) is a stable, radical species. It contains an unpaired electron in the outermost π^* orbital, and it is therefore an open shell molecule and as such has a non-zero electronic angular momentum [57].

The ground state electronic configuration of the NO(X) molecule is

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

In the low j limit, its unpaired π^* electron makes a single quanta of angular momentum $L = 1$, which carries a projection quantum number of $|\Lambda| = +1$ onto the internuclear axis. The electron also possesses spin $S = 1/2$ which leads to a projection of $\Sigma = \pm 1/2$ onto the internuclear axis.

The coupling scheme between the molecular framework and the orbital momentum of the electron and spin in the low j limit is described by Hund's case (a) coupling as detailed by Zare [57]. $\mathbf{N}$ couples to Ω , the sum of the projections of the electronic (Σ) and spin (Λ) angular momentum. The resultant vector is called the total angular momentum and is denoted by the vector $\mathbf{j}$. The vectors of interest (neglecting nuclear spin) are shown in Fig. 2.1. The value of Ω can take one of two values depending on the relative signs of the Σ and Λ quantum numbers: these are $\Omega = 0.5$ or $\Omega = 1.5$, which lead to two separate spin-orbit states separating different series of j , one set in each spin-orbit state as shown in Fig. 2.2.

Without considering the effect of Λ -doubling, the molecular Hamiltonian can be factored into two terms, one for spin-orbit coupling and the other due to rotation [57]

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

$$\hat{H} = A(\mathbf{L} \cdot \mathbf{S}) + B(\mathbf{j} - \mathbf{S} - \mathbf{L})^2, \quad (2.3)$$

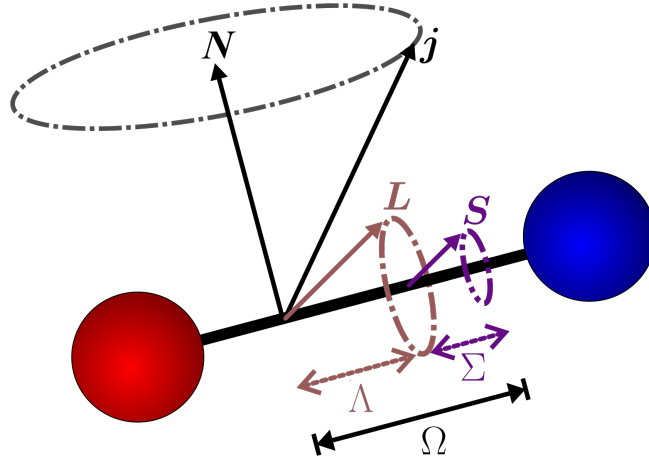


Figure 2.1: The Hund's case (a) coupling scheme for NO(X). The projection, Ω , of the electronic angular momentum couples to the angular momentum of the nuclear framework, $\mathbf{N}$, to create the resultant total angular momentum vector, $\mathbf{j}$.

where $A = 123.13 \text{ cm}^{-1}$ and $B = 1.6961 \text{ cm}^{-1}$ are the spin-orbit coupling and rotational constants for NO(X) respectively. These constants are necessary to calculate the NO(X) rotational energy [70]. From the Hamiltonian, the total energy can be calculated according to [57]

$$E(j) = B \left[\left(j - \frac{1}{2} \right) \left(j + \frac{3}{2} \right) \pm \frac{1}{2} X \right], \quad (2.4)$$

with

$$X = \sqrt{4 \left(j + \frac{1}{2} \right)^2 + Y(Y - 4)} \quad (2.5)$$

$$Y = \frac{A}{B}. \quad (2.6)$$

The $\pm$ sign in Eqn. (2.4) is used to distinguish between the F_1 (${}^2\Pi_{\frac{1}{2}}$) and F_2 (${}^2\Pi_{\frac{3}{2}}$) spin-orbit manifolds, which each have a distinct ladder of rotational energy levels separated by an energy equal to $A = 123.13 \text{ cm}^{-1}$.

Apart from the spin-orbit coupling, there exists another coupling in the nitric oxide molecule, known as the Λ -doubling. The interaction between the electronic angular momentum, $\mathbf{L}$, and the rotation of the nuclei induces a splitting in each rotational energy level, resulting in two closely spaced sub-levels. The energy difference between the two Λ -doublet components is very small, usually significantly less than 1 cm^{-1} . The energy spacing between the Λ -doublet components increases linearly with j for the F_1

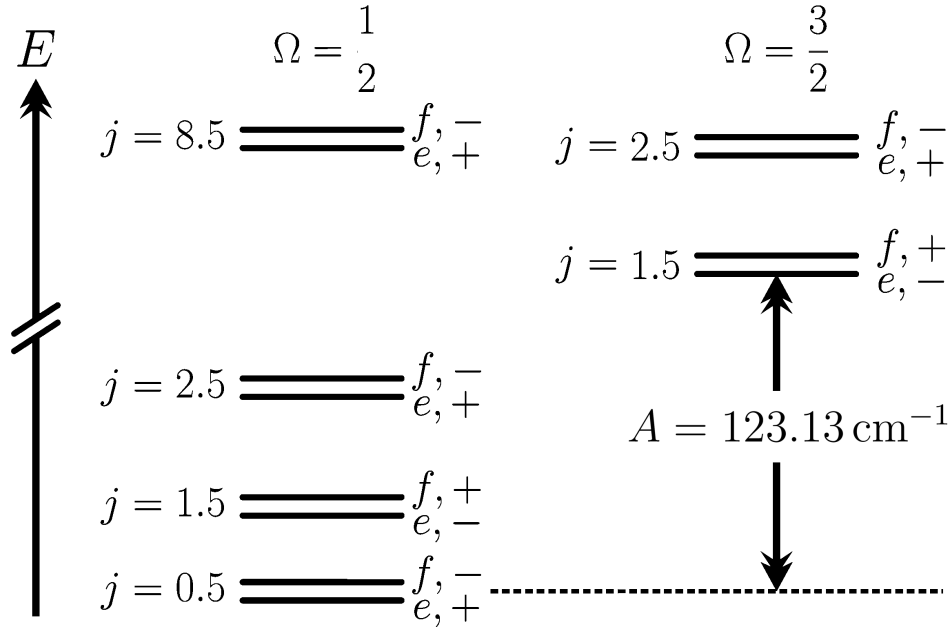


Figure 2.2: The energy levels of the first few rotational states in the ground spin-orbit (left) and excited spin-orbit (right) states of NO(X). The labels + and – correspond to states of positive or negative parity denoted by the spectroscopic index e or f .

manifold and with the third power of j for the F_2 manifold. The ground state Λ -doublet splitting is 0.01188 cm^{-1} and increases to 0.1767 cm^{-1} for $\Omega = 0.5, j = 16.5$, the highest rotational state considered in this thesis [71]. The Λ -doublet components are labelled either by e/f or by the spectroscopic index, ϵ , they are related by $\epsilon = -1 \equiv f$ and $\epsilon = +1 \equiv e$ [72].

As well as the labels e and f , the Λ -doublets are also given symmetry labels A' and A'' , which designate whether the electronic part of the NO(X) wavefunction is symmetric or antisymmetric with respect to reflection in the plane of rotation (in the high j limit [73]). The A' label refers to the state in which the unpaired electron is located in a π^* orbital in the plane of rotation, and A'' when the orbital is perpendicular to the plane of rotation. The degeneracy of the two Λ -doublets is lifted through interactions with high lying electronic states, especially those with Σ character, such as the A state.

The wavefunction of a Ω state can be expressed in terms of the Wigner D-matrices [57]

$$|j, m, \Omega\rangle = \sqrt{\frac{2j+1}{4\pi}} D_{m\Omega}^{j*}(\phi, \gamma, 0), \quad (2.7)$$

where m is the projection quantum number of $\mathbf{j}$ onto a space fixed z -axis. The

states defined in Eqn. (2.7) do not possess the required symmetry properties with respect to inversion through the plane of rotation, and as such, they are not the correct wavefunctions of the molecular Hamiltonian. The symmetric and antisymmetric combinations of the states in Eqn. (2.7) do have the correct symmetry properties, the correct wavefunctions are given thus

$$|j, m, \Omega, \epsilon\rangle = \frac{\sqrt{2}}{2} \left(|j, m, \Omega\rangle + \epsilon |j, m, -\Omega\rangle \right), \quad (2.8)$$

where ϵ is the spectroscopic index. The spectroscopic index (and hence the e/f levels) is related to the system parity by

$$\epsilon = p * (-1)^{j-(\frac{1}{2})}. \quad (2.9)$$

As j increases, Hund's case (a) no longer accurately describes the angular momentum coupling scheme in NO(X), as $\mathbf{L}$ and $\mathbf{S}$ are no longer strongly coupled to the internuclear axis. In this case, it is more accurate to employ the Hund's case (b) wavefunctions, given as

$$|F_1, j, m, \epsilon\rangle = a|j, m, \Omega = 0.5, \epsilon\rangle + b|j, m, \Omega = 1.5, \epsilon\rangle, \quad (2.10a)$$

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

with the mixing coefficients a and b given by:

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

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

with X and Y as defined in Eqn. (2.5). For a rotational state with $j' = 16.5$, the values of the mixing coefficients are $a = 0.976$ and $b = 0.222$.

Table 2.1: A comparison of the attractive well depths of the NO(X)-Rg system and their polarisabilities. The well depth of the V_{sum} surface (see Eqn. (2.12)) is calculated from CCSD(T) calculations for He, Ne and Ar and RCCSD(T) calculations for Kr and Xe. Polarisability data was obtained from [81].

Rare gas	polarisability / a_0^3	V_{sum} Well depth / cm^{-1}
He	1.3838	27.70 [82]
Ne	2.6648	58.05 [78]
Ar	11.0840	115.98 [78]
Kr	16.8000	139.30 [82]
Xe	27.0600	141.70 [82]

2.1.1 NO(X) + Rg Systems

The interaction of NO(X) with a collision partner is described by a number of non-degenerate PESs. For NO(X) scattering with a rare gas, the collision can be thought of as occurring on two coupled PESs. As discussed in Section 2.1, the NO(X) molecule has an electron which can either lie in or out of the plane of rotation. Upon approach of the spherical rare gas atom in a non-linear geometry, the symmetry of the NO(X) which is normally of point group $C_{\infty v}$ is reduced to C_s . The only symmetry operation possible on a C_s point group is reflection in the triatomic plane, so the electronic states are labelled A' or A'' depending on whether the sign changes or not upon reflection [74].

A number of PESs for the NO(X) rare gas system have been constructed with varying accuracy over the last few decades [61, 62, 75–78]. In the studies presented in Chapter 4 of this thesis, the PESs of Kłos *et al.* [62] are utilised to study the collision-induced alignment of scattering of NO(X) with Xe. In Chapter 5, the surfaces of Wen *et al.* are employed to study the collision-induced orientation of scattering of NO(X) with Kr [77]. Each of the surfaces utilised (with the exception of the NO(X)–He [75] surface used in Chapter 6) have been calculated with coupled cluster techniques [79]. The NO(X) bond length was kept fixed at the equilibrium bond distance of $r_e = 115.09$ pm, and as such all vibrational motion and centrifugal distortion was neglected in the present studies.

The two degrees of freedom which describe the system are the distance between the centre-of-mass of the atom and diatom, labelled $\mathbf{R}$; and the angle γ , called the Jacobi angle, which represents the angle between $\mathbf{R}$ and the bond axis vector $\mathbf{r}$ [80].

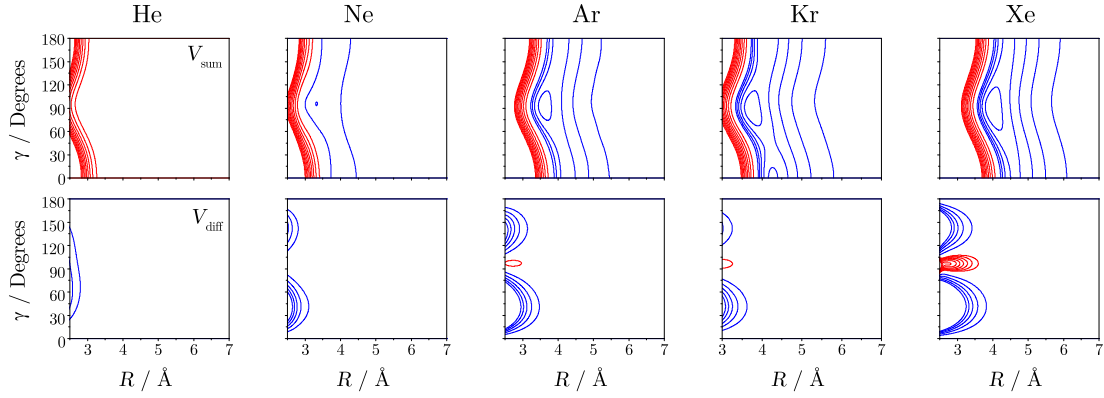


Figure 2.3: Plots of the V_{sum} (top panels) and V_{diff} (bottom panels) potentials for the NO(X)–Rg systems. A clear progression is seen from helium to xenon as the attractive part of the potential (blue, spacing 15 cm^{-1}) becomes increasingly important. The extent of the repulsive wall (red, spacing 100 cm^{-1}) is also shown as a function of system. $\gamma = 0^\circ$ corresponds to the linear Rg–NO geometry and $\gamma = 180^\circ$ to the linear Rg–ON geometry.

Inelastic collisions of NO(X) with rare gases simultaneously take place on both the A' and A'' PESs [74]. In the theoretical treatment of the collision interaction it is customary to introduce linear combinations of these surfaces as defined in Eqn. (2.12) and Eqn. (2.13). The half-sum (V_{sum}) and half-difference (V_{diff}) potentials can also be given in terms of a series expansion, where the reduced rotation matrices are the basis functions [83] and, the radial expansion coefficients are denoted as $V_{\kappa 0}(R)$ for V_{sum} and $V_{\kappa 2}(R)$ for V_{diff}

$$V_{\text{sum}}(R, \gamma) = \frac{1}{2} [V_{A''}(R, \gamma) + V_{A'}(R, \gamma)] = \sum_{\kappa} V_{\kappa 0}(R) d_{00}^{\kappa}(\gamma) \quad (2.12)$$

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

In the case of the scattering of a pure Hund’s case (a) molecule, spin-orbit conserving collisions take place solely on the V_{sum} potential, whereas spin-orbit changing transitions take place solely on V_{diff} [74]. At high j' , due to the breakdown in Hund’s case (a) coupling, this assumption no longer proves to be accurate as demonstrated in Chapter 6.

The V_{sum} and V_{diff} potentials for each NO(X)-Rg system are shown in Fig. 2.3. The V_{sum} potentials display a characteristic repulsive wall and form a ‘stadium’ shape. The

repulsive wall increases in size as the collision partner increases in size; a reflection of the increased atomic radius of the rare gas. In Fig. 2.3, the blue attractive contours are spaced at 15 cm^{-1} for V_{sum} and 100 cm^{-1} for V_{diff} .

The NO(X) rare gas potentials are strongly repulsive at small $\mathbf{R}$ and exhibit varying degrees of attractiveness at larger separations related to the polarisability of the rare gas in question, this relationship is demonstrated in Table 2.1. As the size and polarisability of the rare gas atom increases, there is a significant increase in the well depth of the potential which leads to a marked increase in the magnitude of the inelastic scattering cross sections [19, 84]. Close inspection of the potentials in Fig. 2.3 shows that the extent of the N-end ($\gamma = 0$) of the NO molecule is slightly larger than that of the O-end ($\gamma = 180$). The V_{diff} potentials are significantly more attractive than the V_{sum} potentials and are much shorter range. This has a significant effect on the scattering, as shown by the integral and differential steric asymmetries in Chapter 6, and the spin-orbit changing transitions in the scattering of NO(X) with Xe presented in Chapter 4. The spin-orbit changing transitions exclusively occur on V_{diff} [76] in the limit of Hund's case (a). However, as will be demonstrated, the V_{diff} potential also plays an important role in high j' transitions upon the spin-orbit conserving manifold.

2.2 Theoretical Techniques

A number of theoretical dynamical techniques based upon the PESs detailed above can be employed. In the quasi-classical method, Hamilton's equations of motion are solved as the collision proceeds upon the *ab initio* PES. Throughout the classical calculations, the spatial co-ordinates of each moiety and the associated momenta are known throughout the interaction. In order to sample all the initial conditions, a large number of classical trajectories are employed in order for observables to be calculated.

Full close-coupled quantum mechanical (CC QM) scattering calculations can also be employed, these will also be described in this section.

Other theoretical methods will also be utilised. It is possible to make modifications to the PESs themselves, or use the contour of the PESs in order to perform hard-shell

calculations. These hard shell calculations can be formulated in either the quantum or classical regime. Such techniques will also be explored in this section.

2.2.1 Quasi-Classical Theory

Quasi-classical trajectory (QCT) calculations make use of long established trajectory methods first developed by Karplus [85]. The techniques applied in this thesis were developed by Aoiz *et al.* and have been described numerous times in the literature [12, 86, 87] and applied to a wide range of problems in physics [88–90] and chemistry [65, 91–94]. The QCT method assumes that the path of a particle across the interaction potential is purely classical. In brief, at each timestep, the changes in the particles positions and momenta are calculated and the trajectory is propagated to the next timestep, where again the changes in the positions and momenta are calculated. A single trajectory is insufficient to converge on the classical solution, instead several to tens of millions of trajectories are required in order to obtain accurate differential cross sections (DCSs) and polarisation dependent differential cross sections (PDDCSs).

The atom-diatom system consists of three atoms. The Cartesian representation of the molecular Hamiltonian contains nine pairs of positions and momenta and is described by [80]

$$\mathcal{H} = \sum_{i=1}^3 \frac{p_{x_i}^2}{2m_A} + \sum_{i=4}^6 \frac{p_{x_i}^2}{2m_B} + \sum_{i=7}^9 \frac{p_{x_i}^2}{2m_C} + V(x_1, x_2, \dots, x_9), \quad (2.14)$$

where the atom A has mass m_A , the co-ordinates (x_i) and linear momenta (p_i) of the atom A are indexed by $i = 1, 2, 3$, and those of atoms B and C are labelled by $i = 4, 5, 6$ and $i = 7, 8, 9$, respectively.

The kinetic components of the Hamiltonian are described by the first three sums, whereas the potential energy is described by the $V(x_1, x_2, \dots, x_9)$ term. Eqn. (2.14) contains the motion of the centre of mass and is equivalent to running the calculation in a space-fixed frame of reference. If the origin of this frame is placed in the centre of mass of the diatom, only six pairs of co-ordinates and momenta are required to describe the motion of the system. The Hamiltonian written in Eqn. (2.14) can be

parameterised in terms of Jacobi co-ordinates, each of which has a well defined physical meaning; the co-ordinates q_1, q_2 and q_3 describe the relative position of atom C with respect to atom B . This defines the bond axis vector $\mathbf{r}$ of the molecule. The q_4, q_5 and q_6 co-ordinates specify the position of atom A relative to the B – C centre of mass, this vector gives the equivalent $\mathbf{R}$ vector in the scattering picture. Another important quantity is the angle γ , the angle between $\mathbf{r}$ and $\mathbf{R}$, which can be calculated from the dot product of the two vectors:

$$\cos(\gamma) = \frac{\mathbf{r} \cdot \mathbf{R}}{||\mathbf{r}|| ||\mathbf{R}||} = \frac{R_x r_x + R_y r_y + R_z r_z}{|\mathbf{R}| |\mathbf{r}|} = \frac{q_1 q_4 + q_2 q_5 + q_3 q_6}{\sqrt{q_1^2 + q_2^2 + q_3^2} \sqrt{q_4^2 + q_5^2 + q_6^2}}. \quad (2.15)$$

The Hamiltonian from Eqn. (2.14) then becomes

$$\mathcal{H} = \sum_{i=1}^3 \frac{p_{q_i}^2}{2\mu_{BC}} + \sum_{i=4}^6 \frac{p_{q_i}^2}{2\mu_{A,BC}} + V(R, r, \gamma) \quad (2.16)$$

where μ_{BC} is the reduced mass of the diatom and $\mu_{A,BC}$ is the reduced mass of the entire system. The force acting on the system is determined by the potential energy, $-\frac{dV(\mathbf{R}, \mathbf{r}, \gamma)}{dq}$.

The trajectories are propagated over the V_{sum} PES by solving Hamilton's equations of motion with a suitably small time-step, as described in Equations (2.17) and (2.18)

$$\frac{dq_i}{dt} = \frac{\partial \mathcal{H}}{\partial p_i}, \quad (2.17)$$

$$\frac{dp_i}{dt} = -\frac{\partial \mathcal{H}}{\partial q_i} = -\frac{\partial \mathcal{V}}{\partial q_i} = -\left(\frac{\partial V}{\partial R} + \frac{\partial V}{\partial r} \frac{\partial r}{\partial q_i} + \frac{\partial V}{\partial \cos \gamma} \frac{\partial \cos \gamma}{\partial q_i} \right). \quad (2.18)$$

The propagation *via* Equations (2.17) and (2.18) should start with an infinite particle-diatom separation. In practice, the position is set as close as possible such that the initial interaction is almost zero and therefore negligible [95]. Similarly, the trajectory is terminated when $|\mathbf{R}|$ is beyond the interaction region and the interaction is no longer affected by the presence of the collision partner. The bond axis is maintained at its equilibrium bond length by the use of Lagrangian multipliers as the *ab initio* surfaces were calculated at the equilibrium bond length. The numerical methods which solve the spatial-temporal evolution of the system are the fourth order Runge-Kutta algorithms

followed by Hammond’s predictor-corrector algorithm [80, 96]. These propagate the atom on the surface by solving Equations. (2.17) and (2.18).

It is important to properly specify the initial conditions that the trajectory experiences, or otherwise sample them from a physically relevant distribution in order to correctly model the experiment. The total collision energy E_{coll} is one of the most important quantities, it is sampled from a Gaussian distribution based on the experimental collision energy distribution. The classical impact parameter, b , denotes the distance between the initial position of the atom and $\mathbf{k}$. It is sampled from a quadratic distribution between 0 and b_{max} such that $P(b) \propto 2\pi b$. b_{max} is chosen such that at $b > b_{\text{max}}$, rotationally inelastic scattering no longer occurs. This means that it is not possible to converge the elastic integral cross-sections in the QCT calculations, as increasing b_{max} will increase the number of trajectories considered to be elastic. b is allowed to take any value between these limits and therefore reflects the fact that classically, the orbital angular momentum ℓ is not quantised. The classical orbital angular momentum is related to the quantum orbital angular momentum by $|\ell| = \mu v_{\text{rel}} b = \hbar \sqrt{\ell(\ell + 1)}$.

The initial orientation of the NO(X) bond axis with respect to the relative velocity is defined by two angles θ_r and ϕ_r . When the O-end of the molecule points towards the incoming atom, the angle is defined such that $\theta_r = 0^\circ$. The initial value of $\cos \theta_r$ is sampled uniformly between 0 and π and ϕ_r is sampled between 0 and 2π .

Finally, the final rotational angular momentum of the molecule is determined. This is done by equating the moduli of the classical and quantum angular momentum $|\mathbf{j}| = \hbar \sqrt{j(j + 1)}$ and rounding to the nearest integer. The QCT neglects the contribution of the electronic angular momentum and therefore only includes the rotation of the nuclear framework. The scattering in this thesis is from the $j = 0.5f$ state of NO(X), which is equated to the classical $j = 0$ state as the NO(X) is treated as a closed shell. When the trajectory moves across the surface, the rotational angular momentum is allowed to vary continuously as is permitted in classical mechanics. As the trajectory is terminated, the rotational level to which the NO(X) has been excited based on $|\mathbf{j}| = \hbar \sqrt{j(j + 1)}$ is calculated. The direction of $\mathbf{j}'$ is also noted so the polarisation moments, introduced later may be calculated.

Calculation of Observable Quantities

By employing the QCT method it is possible to fully specify the initial and determine the final conditions of the triatomic system and calculate quantities of interest. The classical opacity function quantifies the scattering probability into a particular state as a function of impact parameter. The opacity function is given by

$$P_{f \leftarrow i}(b) = \frac{N_{f \leftarrow i}(b)}{N_i(b)}, \quad (2.19)$$

with $N_i(b)$ the number of classical trajectories with an initial state i at an impact parameter b and $N_{f \leftarrow i}(b)$ the number of trajectories in final state f at that b . The partial cross sections are obtained from the opacity functions by

$$\sigma_{f \leftarrow i}(b) = 2\pi b P_{f \leftarrow i}(b). \quad (2.20)$$

Integration over all b gives the integral cross section (ICS) for transitions from the initial i state to the final f state

$$\sigma_{f \leftarrow i} = \int_0^{b_{\max}} 2\pi b P_{f \leftarrow i}(b) db \quad (2.21)$$

$$= \pi b_{\max}^2 \frac{N_{f \leftarrow i}}{N_i}. \quad (2.22)$$

The DCSs are then obtained from the ICSs *via*

$$\frac{d\sigma_{f \leftarrow i}}{d\omega}(\theta) = \frac{1}{4\pi \sin \theta} \frac{d^2 \sigma_{f \leftarrow i}}{d\theta d\phi}, \quad (2.23)$$

where ω is the solid angle in steradians and θ is the scattering angle, defined as the angle between the incoming and outgoing wavevectors $\mathbf{k}$ and $\mathbf{k}'$ respectively.

2.2.2 Quantum Mechanical Scattering Theory

All close-coupled quantum mechanics (CC QM) calculations in this thesis were performed using the HIBRIDON [97] suite of codes which propagate the scattering wave

function by solving the close-coupled quantum mechanical equations of Victor & Dalgarno [98]. Their procedure couples the systems rotational and orbital angular momenta and constructs a set of coupled differential equations which are the matrix representation of the collision systems Schrödinger equation. The propagation method employed in HIBRIDON is the log-derivative propagator [99] at short range, where high accuracy is required, and the Airy propagator at longer range [100].

In these calculations, all information about the scattering is contained within the scattering matrix ($\hat{S}$ -matrix). The $\hat{S}$ -matrix transforms the incoming matter-wave into the outgoing matter-wave. Once the $\hat{S}$ -matrix is determined by the solution of the close coupled equations, it is possible to calculate any observable quantity of the system of interest from it. The plane wave which represents the incoming atom can be written in terms of increasing total angular momenta, J_{tot} . The scattering matrix is then defined as

$$\hat{S}|\Psi_{\text{in}}^{J_{\text{tot}}}\rangle = |\Psi_{\text{out}}^{J_{\text{tot}}}\rangle, \quad (2.24)$$

where, for pure, coherent states, the outgoing partial waves can be written as a linear combination of the ro-vibrational eigenfunctions of the system [101]

$$|\Psi_{\text{in}}^{J_{\text{tot}}}\rangle = \sum_i c_i |\psi_i^{J_{\text{tot}}}\rangle, \quad (2.25)$$

$$|\Psi_{\text{out}}^{J_{\text{tot}}}\rangle = \sum_f c_f |\psi_f^{J_{\text{tot}}}\rangle. \quad (2.26)$$

To ensure normalisation of the wavefunctions, the coefficients are constrained by

$$\sum_i |c_i|^2 = 1,$$

$$\sum_f |c_f|^2 = 1.$$

Rather than considering the scattering matrix operator, $\hat{S}$, it has been shown to be more convenient to apply the transition operator defined as $\hat{T} = \hat{S} - 1$ [102]. When

the transition operator, $\hat{T}$, is applied to the initial wavefunction, the result is

$$\hat{T}|\psi_{\text{in}}^{J_{\text{tot}}}\rangle = (\hat{S} - 1)|\psi_{\text{in}}^{J_{\text{tot}}}\rangle = |\psi_{\text{in}}^{J_{\text{tot}}}\rangle - |\psi_{\text{out}}^{J_{\text{tot}}}\rangle. \quad (2.27)$$

The square modulus of the transition matrix element $|\hat{T}_{if}^{J_{\text{tot}}}|^2$ then gives the probability of scattering from an initial state $|\psi_i\rangle$ to a final state $|\psi_f\rangle$ for a specific value of J [95]. This quantity is the quantum mechanical opacity function $P_{f \leftarrow i}(J_{\text{tot}})$.

The state-resolved opacity function $P_{f \leftarrow i}(J_{\text{tot}})$ is equivalent to the square modulus of the $\hat{T}$ matrix elements, $|T_{fi}^{J_{\text{tot}}}|^2$. The state resolved opacity functions and partial cross sections are related by

$$\sigma_{f \leftarrow i}^{\text{QM}} = \sum_{J_{\text{tot}}=0}^{J_{\text{max}}} \frac{\pi(2J_{\text{tot}} + 1)}{k^2(2j + 1)} [2 \min(J_{\text{tot}}, j) + 1] P_{f \leftarrow i}(J_{\text{tot}}), \quad (2.28)$$

where j is the rotational quantum number of the NO(X) and k is the wavevector defined as $\sqrt{2\mu E_{\text{col}}}/\hbar$. At a certain value of J_{tot} the opacity function will decrease to a negligibly small value, and adding any additional J_{tot} above this value to the summation will cease to affect the value of $\sigma_{f \leftarrow i}^{\text{QM}}$. This allows the value of J to be truncated at maximum total angular momentum J_{max} .

The scattering amplitude is a useful quantity from which all of the quantum observables can be calculated. In terms of $\hat{T}$ matrix elements, it is given by

$$f_{f \leftarrow i}(\theta) = \frac{1}{2ik} \sum_{J_{\text{tot}}=0}^{J_{\text{max}}} \frac{2J_{\text{tot}} + 1}{2j + 1} [2 \min(J_{\text{tot}}, j) + 1] P_{J_{\text{tot}}}(\cos \theta) \hat{T}_{fi}^{J_{\text{tot}}}, \quad (2.29)$$

where $P_{J_{\text{tot}}}(\cos \theta)$ is an associated Legendre polynomial, itself given by

$$P_q^k(x) = (-1)^q (1 - x^2)^{q/2} \frac{d^q P_k(x)}{dx^q}, \quad (2.30)$$

with $P_k(x)$ the un-associated Legendre polynomials given by

$$P_k(x) = \frac{1}{2^k k!} \frac{d^k (x^2 - 1)^k}{dx^k}. \quad (2.31)$$

By taking the square modulus of the scattering amplitude, the DCSs are obtained

$$\begin{aligned}
\frac{d\sigma_{f \leftarrow i}}{d\omega} &= |f_{f \leftarrow i}(\theta)|^2, \\
&= \frac{1}{4k^2} \sum_J \sum_{J_{\text{tot}'}} \frac{2J_{\text{tot}} + 1}{2j + 1} \frac{2J_{\text{tot}'} + 1}{2j + 1} [2\min(J_{\text{tot}}, j) + 1] \\
&\times [2\min(J_{\text{tot}'}, j) + 1] T_{fi}^{J_{\text{tot}}} T_{fi}^{J_{\text{tot}'}}* P_{J_{\text{tot}}}(\cos \theta) P_{J_{\text{tot}'}}(\cos \theta).
\end{aligned} \tag{2.32}$$

Whilst the individual $\hat{T}$ -matrix elements which correspond to individual partial waves are independent of one another, the double summation in Eqn. (2.32) leads to interferences between different partial waves. The DCSs quantify how the integral cross sections change as a function of angle between $\mathbf{k}$ and $\mathbf{k}'$. The DCS is given in dimensions of area per solid angle. The ICS can be obtained from the DCS by integrating over the scattering angle

$$\sigma_{f \leftarrow i}^{\text{QM}} = 2\pi \int_0^\pi \frac{d\sigma_{f \leftarrow i}}{d\omega} \sin \theta d\theta, \tag{2.33}$$

where $2\pi \sin \theta$ quantifies the volume element of the integral.

2.2.3 Quantum Mechanical Hard Shell Scattering

The Quantum mechanical hard shell scattering formalism seeks to solve the scattering problem of two hard objects striking each other governed by quantum mechanics. These objects are assumed, as in the classical billiard-ball case, to have no attractive potential and at the moment of the collision, the repulsive wall is infinitely high. Due to effects relating to the temporal and spatial non-locality of the collision, as investigated by Hornung [63,103], much mechanistic insight can be gained from the quantum mechanical hard shell scattering problem. The scattering of hard shells with structureless atoms was first presented by Bosanac in terms of Jost functions [104] and was later reformulated by him to employ vanishing integrals of the scattering wavefunctions on the molecular surface of the target [105].

The method had been applied to several different closed-shell systems to obtain observable quantities such as the DCS and ICS [104–107]. It was later extended by

Hornung to allow for the determination of renormalised PDDCSs and other observables of interest [63, 103]. The quantum mechanical scattering of hard shells leads to a set of linear equations which must be solved, as detailed by Bosanac [103, 105]

$$-\frac{i(2J_{\text{tot}} + 1)}{2k_{j\Omega\epsilon}} X_{j'm'\Omega'\epsilon'}^{J_{\text{tot}}} = \sum_{jm} W_{j'm'\Omega'\epsilon',jm\Omega\epsilon}^{J_{\text{tot}}} F_{jm\Omega\epsilon,jm\Omega\epsilon}^{J_{\text{tot}}m}, \quad (2.34)$$

where $F_{jm\Omega\epsilon,j_0m_0\Omega_0\epsilon_0}^{J_{\text{tot}}m}$ are the partial scattering amplitudes, and $W_{j'm'\Omega'\epsilon',jm\Omega\epsilon}^J$ and $X_{j'm'\Omega'\epsilon'}^J$ are the coupling elements of the scattered and incident waves. The coupling matrix, $W_{j'm'\Omega'\epsilon',jm\Omega\epsilon}^J$, is defined in terms of the overlap integrals

$$W_{j'm'\Omega'\epsilon',jm\Omega\epsilon}^{J_{\text{tot}}} = \sum_{\ell} (2\ell + 1) \langle \ell 0, jm | J_{\text{tot}} m \rangle \langle \ell 0, jm' | J_{\text{tot}} m' \rangle B_{jm'\Omega\epsilon,j'm'\Omega'\epsilon'}^{(\ell)}. \quad (2.35)$$

The overlap integrals between the initial and final rotational wavefunctions determine the transition probability between the initial and final rotational states. The overlap integrals behave as an analogue to the potential matrix. The coupling matrix can be obtained by solving Eqn. (2.35) which is achieved with the LAPACK [108] routines ZGESVX and ZGELSS.

In order to achieve convergence of the observable quantities, partial waves up to $J = 150$ and rotational states up to $j = 20$ were included in the basis sets at the collision energies of the experiment. The hard shell calculations requires approximately 5 minutes to complete using an intel i5-3550 CPU.

2.3 Angular Momentum Polarisation

An area of particular interest in recent years has been polarisation effects [6, 19–21, 103, 109–115]. Polarisation effects describe the anisotropy of the rotational angular momentum vector $\mathbf{j}$ or $\mathbf{j}'$ with respect to another vector, usually $\mathbf{k}$, the initial wavevector. The collision itself in general causes an anisotropy in an initially isotropic distribution of the angular momentum vector. This effect can also be particularly large if the initial distribution of the angular momentum vector is anisotropic. These effects are referred to as collision-induced polarisation (CIP). The polarisation of the scattered NO(X)

molecule can be probed experimentally, as described in Chapter 3. It can also be calculated theoretically, and is described by either polarisation moments, or polarisation parameters. These quantities describe the *orientation* and *alignment* of a vector.

Of particular interest in this thesis is the orientation and the alignment of the angular momentum vector, the collision-induced orientation and collision-induced-alignment respectively. Classically, an oriented distribution of $\mathbf{j}'$ is one in which the direction of $\mathbf{j}'$ lies either parallel or antiparallel to a reference axis – corresponding to the NO(X) molecules rotating clockwise or anticlockwise with respect to the axis. In the case of alignment, $\mathbf{j}'$ lies preferentially along a specific reference axis, but with equal chance of pointing in the positive or negative direction.

The working equations for calculating the polarisation moments in classical and quantum mechanical models will be explained and correspondences between the quantum and classical theories will be highlighted.

2.3.1 Reference Frames

Experimentally, polarised light allows measurements of the renormalised j' -PDDCSs to be made. Throughout this thesis, j' -PDDCSs will be referred to as PDDCSs unless explicitly stated otherwise. This technique has successfully probed vector correlations involving the initial velocity $\mathbf{k}$, the final velocity $\mathbf{k}'$ and the angular momentum vector of the scattered NO(X), $\mathbf{j}'$. The $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ vector correlation contains $2j' + 1$ multipoles, labelled with rank k and order q . The experiment can be configured to probe the multipoles with rank $k = 2$ which describe alignment (Chapter 4) or rank $k = 1$ which describe orientation (Chapter 5). These quantities give additional insight into the dynamics of inelastic scattering and additionally provide the information necessary to produce stereodynamical portraits [116] of the angular momentum vector.

In order to characterise the distributions, careful choice of the reference frame must be made. The scattering frame is a convenient choice of axis for comparing experimental data [8]. In the scattering frame (left panel Fig. 2.4), the principal $\mathbf{z}$ axis is defined by the initial relative velocity $\mathbf{k}$, the scattering process takes place on the $+xz$ plane with the direction of the $\mathbf{x}$ axis constrained by the direction of $\mathbf{k}'$ so that $\mathbf{k}'$ lies in the

$+zx$ plane. The $\mathbf{y}$ axis is chosen to ensure that the reference frame is right handed. The scattering frame is shown pictorially in Fig. 2.4. The angle θ , called the scattering angle, gives the angle between the vectors $\mathbf{k}$ and $\mathbf{k}'$.

The angle Φ relates the scattering frame $\mathbf{x}$ axis to the direction of the laser frame defined by the laser propagation vector, $\mathbf{k}_{226}$. The angle Θ , gives the angle of the laser vector with respect to the scattering frame $\mathbf{z}$ axis. The equations used to determine the polarisation of $\mathbf{j}'$ and understand the $\mathbf{k}$ – $\mathbf{k}'$ correlation make use of this reference axis and the angles within it. The dotted region of the left hand panel of Fig. 2.4 contains the laser frame. The laser frame is expanded in the right hand panel of Fig. 2.4, and describes the axis in which the alignment parameters are defined. In the Fano-Macek formalism [117], the principal axis of the laser frame, $\boldsymbol{\zeta}$, is parallel to the laser propagation axis. The polarisation axis, $\boldsymbol{\xi}$, is defined so that the major component of $\boldsymbol{\varepsilon}$ is parallel to $\boldsymbol{\xi}$. The polarisation vector is given for linearly polarised light as $\boldsymbol{\varepsilon} = (0, 0, 1)$ and for circularly polarised light as $\boldsymbol{\varepsilon} = \frac{\sqrt{2}}{2}(0, \pm i, 1)$. The final axis, $\boldsymbol{\eta}$, is chosen to ensure that the frame is right handed.

The scattering plane itself is defined experimentally by the molecular beams. The angle $\Theta \approx 90^\circ$ to $\mathbf{k}$ in the steric and alignment geometries defined in Chapter 3. The intensity expressions for the polarisation are always given in the laser frame, but scattering takes place in the scattering frame, the transformation between the two is achieved by rotation of the scattering frame quantities into the laser frame by three Euler angles, $\Gamma_{V/H,R/L} = (\chi, \Theta, \Phi)$, where the angle χ depends on the laser polarisation of the experiment and is 90° for linearly polarised light and 45° for circularly polarised light.

2.3.2 Classical PDDCSs

In the scattering frame, the angular momentum direction after scattering is defined by two Euler angles, $\theta_{j'}$ and $\phi_{j'}$. The probability of the rotational angular momentum vector pointing along a direction $(\theta_{j'}, \phi_{j'})$ after a collision event is given by the equation

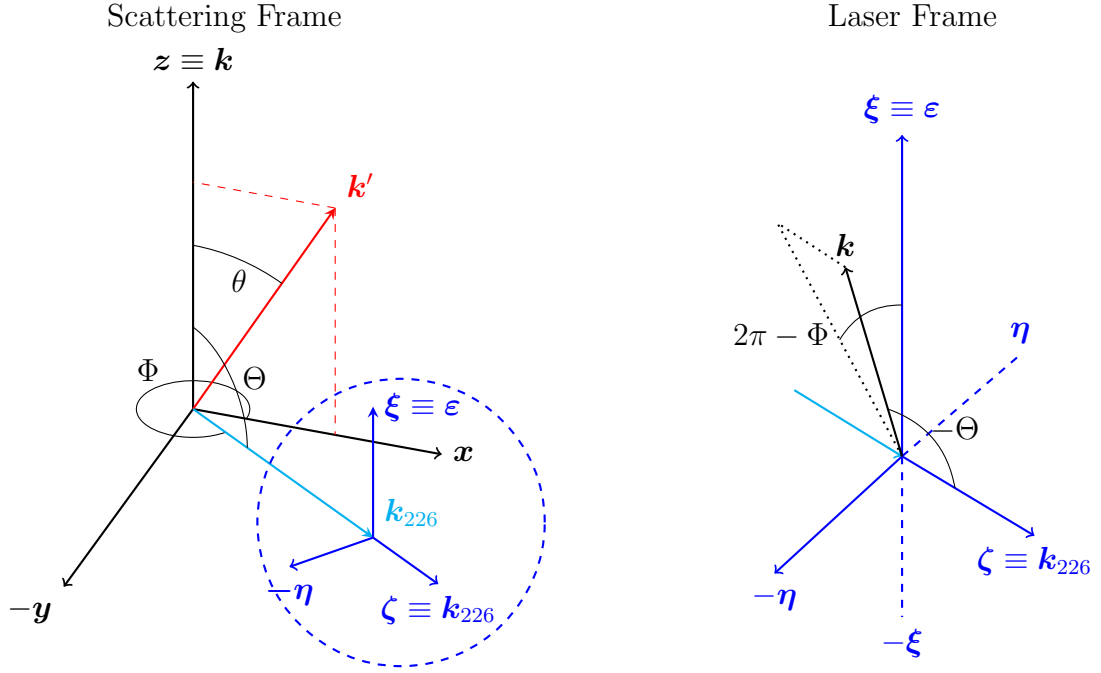


Figure 2.4: Left: a diagram of the scattering frame and its relationship to the laser frame (blue, circled). The ingoing wavevector $\mathbf{k}$ is defined as pointing along $\mathbf{z}$ and the outgoing wavevector, $\mathbf{k}'$ is shown in red and defines the xz plane with θ the scattering angle. The angle ϕ defines the degree of out-of-plane scattering and Θ the angle between $\mathbf{k}$ and the laser propagation direction $\mathbf{k}_{226}$. Right: The laser frame in which the alignment parameters are defined. The principal axis of the laser frame, ζ , is parallel to the laser propagation axis. The laser polarisation vector is ϵ , where its major component is always parallel to ζ , and the final axis, η , is chosen such that the frame is right handed.

[112, 118]

$$P(\theta, \theta_{j'}, \phi_{j'}) = \frac{1}{4\pi} \sum_{k=0}^{\infty} \sum_{q=-k}^k (2k+1) \left(\frac{2\pi}{\sigma} \frac{d\sigma_q^{(k)}}{d\omega}(\theta) \right) C_{kq}^*(\theta_{j'}, \phi_{j'}), \quad (2.36)$$

where σ is the ICS of the transition defined above in Eqn. (2.33) and $C_{kq}^*(\theta_{j'}, \phi_{j'})$ represents the complex conjugates of the modified spherical harmonics [8]. The expansion coefficients of the modified spherical harmonics are called the normalised PDDCSs, $n_{q\pm}^{(k)}$, such that they satisfy [8, 114, 119]

$$n_{q\pm}^{(k)}(\theta) = \frac{2\pi}{\sigma} \frac{d\sigma_{q\pm}^{(k)}}{d\omega}(\theta). \quad (2.37)$$

The values of the normalised PDDCSs are calculated from the expectation values of the modified spherical harmonics according to

$$n_{q\pm}^{(k)}(\theta) = \frac{1}{2} \sum_{k_2 \geq |q|} (2k_2 + 1) \langle C_{k_2-q}(\theta, 0) C_{kq}(\theta_{j'}, \phi_{j'}) \rangle C_{k_2-q}(\theta, 0). \quad (2.38)$$

The $k = 0, q = 0$ normalised PDDCS is representative of the $\mathbf{k}-\mathbf{k}'$ angular distribution function and $\langle \dots \rangle$ is the expectation value of the modified spherical harmonics. It is preferable to remove the effect of the angular scattering intensity from the directional preference of $\mathbf{j}$. This can be achieved by dividing the normalised PDDCSs by the angular distribution

$$\rho_{q\pm}^{(k)}(\theta) = \frac{n_{q\pm}^{(k)}(\theta)}{n_0^{(0)}(\theta)}. \quad (2.39)$$

In general, the polarisation moments encountered thus far are complex. In order to assign a directional significance to them, they must be renormalised to form real quantities. To undertake this operation correctly, the polarisation moments become the expectation values of real modified spherical harmonics [8]. The real polarisation moments will then contain the directional information as the spherical harmonics are functions of the orientation angles $(\theta_{j'}, \phi_{j'})$. Hertell and Stoll derived the normalisation functions for the Wigner rotation matrices which are applied to tensors in order to remove the imaginary part [8, 120]. The complex polarisation moments are denoted with (k) superscripts whereas the real polarisation moments have $\{k\}$ superscripts. The correct normalisation for the polarisation moments is given by

$$\rho_0^{\{k\}}(\theta) = \rho_0^{(k)}(\theta), \quad (2.40a)$$

$$\rho_{q+}^{\{k\}}(\theta) = \frac{\sqrt{2}}{2} \left[(-1)^q \rho_{+q}^{(k)}(\theta) + \rho_{-q}^{(k)}(\theta) \right], \quad 1 \leq q \leq k \quad (2.40b)$$

$$\rho_{q-}^{\{k\}}(\theta) = \frac{\sqrt{2}}{2i} \left[(-1)^q \rho_{+q}^{(k)}(\theta) - \rho_{-q}^{(k)}(\theta) \right], \quad 1 \leq q \leq k. \quad (2.40c)$$

The complex spherical harmonics and normalised PDDCSs can also be made into real quantities with similar expressions to those in Eqn. (2.40). The directional information in the polarisation moments is obtained through multipolar expansion of the modified

spherical harmonics

$$P(\theta_{j'}, \phi_{j'} | \theta) = \sum_{k=0}^{\infty} \frac{2k+1}{4\pi} \left[\rho_0^{\{k\}}(\theta) C_0^{\{k\}*}(\theta_{j'}, \phi_{j'}) \right] \quad (2.41)$$

$$+ \sum_{k=-j}^j \sum_{q=1}^k \left[\rho_{q+}^{\{k\}}(\theta) C_{q+}^{\{k\}*}(\theta_j, \phi_j) + \rho_{q-}^{\{k\}}(\theta) C_{q-}^{\{k\}*}(\theta_{j'}, \phi_{j'}) \right]. \quad (2.42)$$

Each term in the expansion carries directional information on the polarisation of $\mathbf{j}'$. The infinite summation over k ensures the angular momentum vector can be exactly specified, as is allowed classically.

If the terms in the expansion given in Eqn. (2.41) above $k = 0$ are zero, then the angular momentum distribution is isotropic. The odd k terms are called the orientation moments and describe orientation along the reference direction. The even k terms are referred to as the alignment moments. Positive values indicate parallel alignment whereas negative values indicate perpendicular alignment with respect to a reference axis, $\mathbf{k}$. The renormalised j' -PDDCSs will simply be referred to as renormalised PDDCSs throughout this thesis.

2.3.3 Quantum Mechanical PDDCSs

Quantum mechanically, the angular momentum vector is represented by a minimum uncertainty state, the direction around which the $\mathbf{j}$ vector is most likely to reside. As the x , y and z components of the angular momentum operator are non-commuting and are thus constrained by Heisenberg's uncertainty principle, the exact direction cannot be specified quantum mechanically. A quantum angular momentum vector is conveniently described by a mixture of different quantum states in m , the magnetic sublevels of j . The populations of each state and the coherences between them are contained in the density operator which is related to the classical probability distribution function [8, 112]. For a wavefunction that can be written as a linear combination of $|jm\rangle$ states as

$$|\Psi\rangle = \sum_{m=-j}^j c_m |jm\rangle, \quad (2.43)$$

the density operator that fully characterises the system is given by [102]

$$\hat{\rho} = \sum_{m_1, m_2} c_{m_1} c_{m_2}^* |jm_1\rangle \langle jm_2|. \quad (2.44)$$

The individual density matrix elements can be obtained *via* [8, 102, 119]

$$\langle jm | \hat{\rho} | jm' \rangle = \sum_{m_1, m_2} c_{m_1} c_{m_2}^* \langle jm | jm_1 \rangle \langle jm_2 | jm' \rangle \quad (2.45)$$

$$= c_m c_{m'}^*, \quad (2.46)$$

here m is the projection of $\mathbf{j}$ onto $\mathbf{k}$ and m' is the projection of $\mathbf{j}'$ onto $\mathbf{k}$. The diagonal elements of the density matrix, with $m = m'$, describe the state populations of each $|jm\rangle$ level, whilst the off diagonal elements give the coherence between different $|jm\rangle$ and $|jm'\rangle$ states. In the case of a pure, definite rotational state, the density matrix elements can be written in terms of Clebsch-Gordan coefficients by [102, 112]

$$\langle jm_1 | \hat{\rho}(\cos \theta) | jm_2 \rangle = \frac{1}{2j+1} \sum_{k=0}^{2j} \sum_{q=-k}^k (2k+1) (n_q^{(k)}(\theta)) \langle jm_1, kq | jm_2 \rangle, \quad (2.47)$$

where $\hat{\rho}(\cos \theta)$ is the scattering angle resolved density operator and $n_q^{\{k\}}(\theta)$ are the normalised PDDCSs. The trace of this density matrix gives the probability of finding the system in a particular rotational state at a particular scattering angle, θ , without regard to the polarisation of $\mathbf{j}$. The normalised PDDCSs themselves can be calculated from the scattering amplitudes defined in Eqn. (2.29), *via*

$$n_q^{(k)}(\theta) = \frac{2\pi}{\sigma} \frac{1}{4k^2} \frac{1}{2j+1} \sum_{m, m'_1, m'_2} f_{jm\Omega\epsilon \rightarrow j'm'_1\Omega'\epsilon'}(\theta) f_{jm\Omega\epsilon \rightarrow j'm'_2\Omega'\epsilon'}^*(\theta) \langle j'm'_1 kq | j'm'_2 \rangle. \quad (2.48)$$

The renormalised PDDCSs, $\rho_q^{(k)}(\theta)$, are then calculated according to

$$\rho_q^{(k)}(\theta) = \frac{n_q^{(k)}(\theta)}{n_0^{(0)}(\theta)}, \quad (2.49)$$

where $n_0^{(0)}(\theta) = (2\pi/\sigma)d\sigma/d\omega$ is the product angular distribution. Finally, the real renormalised PDDCSs, $\rho_{q\pm}^{\{k\}}(\theta)$, are obtained from the complex $\rho_{q\pm}^{(k)}(\theta)$ PDDCSs using the Hertel–Stoll scheme [120]

$$\rho_0^{\{k\}}(\theta) = \rho_0^{(k)}(\theta) \quad (2.50a)$$

$$\rho_{q+}^{\{k\}}(\theta) = \frac{\sqrt{2}}{2} \left[(-1)^q \rho_{+q}^{(k)}(\theta) + \rho_{-q}^{(k)}(\theta) \right], \quad 1 \leq q \leq k \quad (2.50b)$$

$$\rho_{q-}^{\{k\}}(\theta) = \frac{\sqrt{2}}{2i} \left[(-1)^q \rho_{+q}^{(k)}(\theta) - \rho_{-q}^{(k)}(\theta) \right], \quad 1 \leq q \leq k. \quad (2.50c)$$

The real, renormalised PDDCSs may be expanded in terms of a multipolar series in order to quantify the probability density function of the minimum uncertainty state which most localises the direction of $\mathbf{j}'$. The degree of orientation and alignment along the reference axis can then be determined. This can be achieved by making use of a scheme which is somewhat similar to that in the classical case (Eqn. (2.41)), however a coupling term is also included to ensure that as the rank, k , becomes larger than $2j + 1$, the multipoles disappear. This ensures that the direction of $\mathbf{j}'$ can not be as sharply defined as in classical mechanics, thereby satisfying the uncertainty principle. The expression for the probability distribution which quantifies the minimum uncertainty state is given by [8]

$$P(\theta_j, \phi_j) = \frac{1}{4\pi} \sum_{k=0}^{2j} \sum_{q=-k}^k (2k+1) \rho_q^{\{k\}}(\theta) \langle jj, k0 | jj \rangle C_{kq}^*(\theta_j, \phi_j). \quad (2.51)$$

A pictorial representation of the directional significance of the real renormalised PDDCSs is shown in Fig. 2.5 for the multipoles that are presented experimentally in this thesis.

2.4 Summary

In this chapter the theoretical methods that will be used throughout this thesis have been presented. The NO(X) rare gas system has been discussed in terms of the NO(X) electronic structure and the potential energy surfaces that govern the atom-diatom

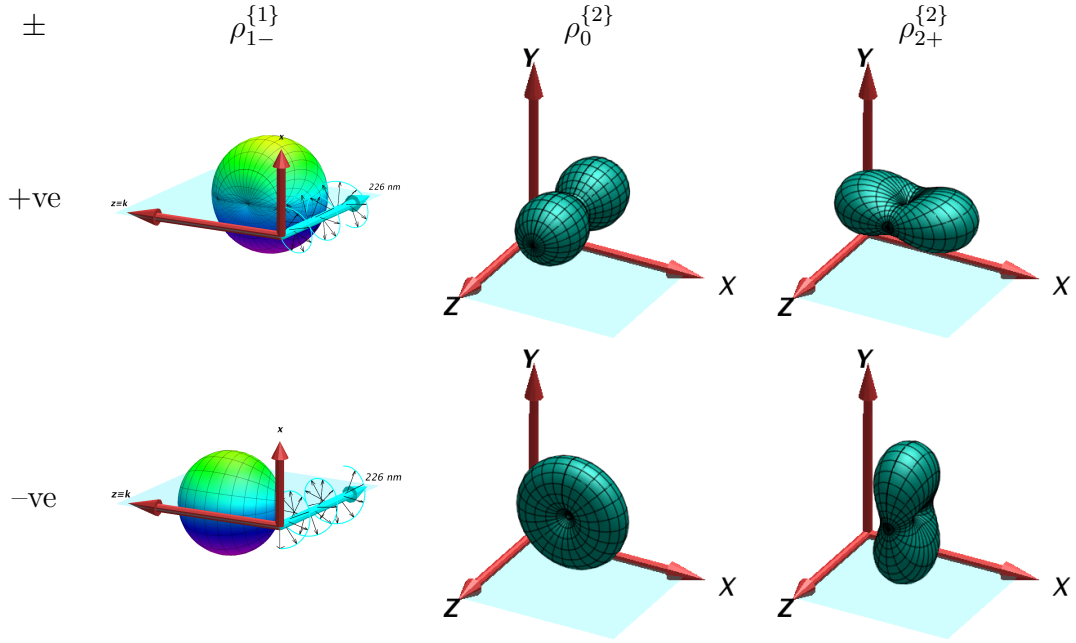


Figure 2.5: The directional meaning of the density matrix elements $\rho_q^{\{k\}}(\theta)$ when the value of the polarisation moments are the lowest possible and the highest possible [121].

collisions. The quantum mechanical and classical calculations enabling the analysis and comparison of DCSs and PDDCSs have been presented. Throughout the work the quantum mechanical and classical models outlined in this chapter will be employed in order to compare to the experimental observations. The angular momentum polarisation is a central aspect of this thesis and will be discussed in detail in Chapter 4 and Chapter 5.

Experimental Methods

In this chapter, the apparatus that allows the experimental determination of the two and three vector correlations presented in this thesis will be detailed. The characterisation of the various collision systems will also be described, as well as how the raw ion images are recorded and how the dynamical quantities are obtained from them.

3.1 Experimental Apparatus

The experimental apparatus has been described in detail previously [12, 19, 21, 25, 122] and is shown schematically in Fig. 3.1. In brief, the primary molecular beam [123] of 10% NO(X) in argon is expanded supersonically into a differentially pumped source chamber. The beam is cooled by supersonic expansion to the almost doubly degenerate ground rovibrational state. It is then skimmed (diameter 5 mm) and enters an electrostatic hexapole of length 1.65 m. The hexapole acts as a lens by focussing the low-field seeking f Λ -doublet into the interaction region whilst defocussing the e state. The beam of state-pure NO(X) is then collimated before entering the interaction region. In the interaction region, the beam is crossed by a second beam of pure rare gas atoms which enables rotational energy transfer to the NO(X) to take place. The scattered products

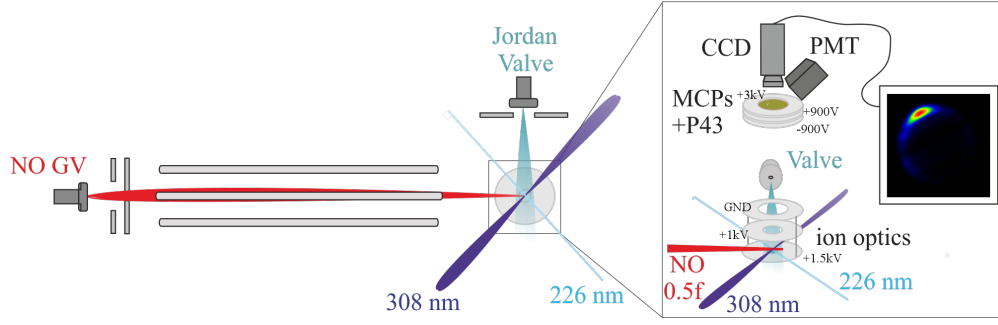


Figure 3.1: The experimental apparatus used to record the data in this thesis. The primary molecular beam of NO(X) passes through an electrostatic hexapole where the $j = 0.5f$ Λ -doublet is focussed into a molecular beam of atoms consisting of the collision partner rare gas. Ionisation and detection of the scattered products by $(1+1')$ REMPI coupled with velocity mapped ion imaging then occurs.

are probed by $(1+1')$ resonantly-enhanced multi-photon ionisation (REMPI) [124]. To perform the experiments, several different independent geometries of the interaction region are required in order to obtain the experimental data. The three primary geometries used in this thesis will be referred to as: 1) the alignment geometry, in which the plane of rotation and angular distributions of the scattered products can be probed, 2) the orientation geometry in which the sense of rotation of the scattered products can be measured, and 3) the steric geometry, in which the focussed NO(X) can be pre-oriented before collision. In each case, the scattered products are probed by $(1+1')$ REMPI and detected by velocity mapped [44] ion imaging [45] (VMI), after which the ion hits are collected and stored by a computer.

Each experimental geometry relies on subtle changes to the interaction region¹, which are detailed pictorially in Fig. 3.2. The bulk of the experiment, including molecular beams, remains unchanged for each experiment. The bulk apparatus is shown in Fig. 3.1. In the alignment geometry, the excitation laser at 226 nm is plane-polarised using a Rochon prism and the plane of the polarised light is then controlled on a shot-by-shot basis by a photo-elastic modulator (PEM). Both lasers are crossed in the plane of the molecular beam and therefore, with horizontal and vertical polarisation, are sensitive to the alignment moments $\rho_0^{\{2\}}(\theta)$, $\rho_{1+}^{\{2\}}(\theta)$ and $\rho_{2+}^{\{2\}}(\theta)$. In the orientation geometry, the excitation laser is directed up the time-of-flight (ToF) tube, perpendicular

¹The triggering setup is also affected by the geometry. Appendix 1 contains schematics of the triggering scheme for each experimental setup.

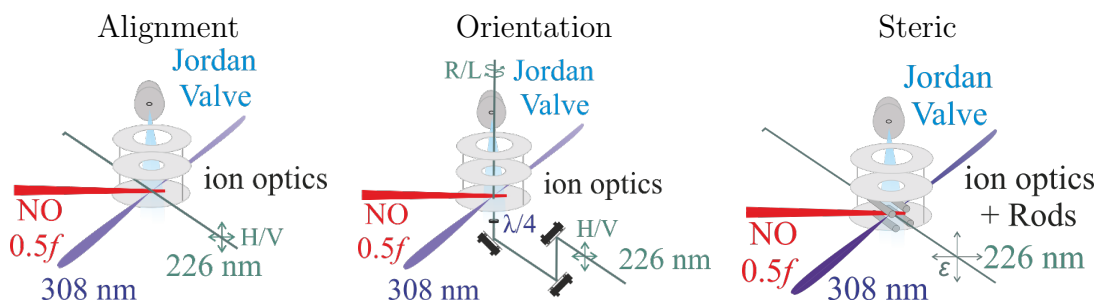


Figure 3.2: The experimental geometries used to perform different experiments. Left: the alignment geometry probes the collision-induced rotational alignment of the NO(X). Middle: the orientation geometry can probe the sense of rotation of the NO(X) ie the collision-induced orientation. Right: the steric geometry which is capable of orienting the NO(X) prior to collision. It can also measure the collision-induced alignment as in the alignment geometry.

to the plane of the molecular beams, and the scattered products are probed by right or left circularly polarised light. This allows the sense of rotation, characterised by the $\rho_{1-}^{\{1\}}(\theta)$ polarisation moment, to be recovered. In the steric geometry, the 226 nm excitation laser beam is again in the plane of the molecular beams. A new addition to the interaction region is the orientation rods which enable adiabatic orientation of the NO(X) prior to collision. Fast switching of the rod voltages allows VMI conditions to be achieved again after scattering [25].

In order to increase the resolution of the experiment and improve the signal-to-noise ratio, several other modifications are necessary to the detection and image processing scheme. These changes include using specialised molecular beam sources which allow for the production of very cold, very short pulses; modifying the detection scheme to access improved repetition rates; and installing a larger time-of-flight tube to increase the size of the ion image. The new apparatus must then be carefully characterised to obtain the beam speeds and collision energies in order to compare to state-of-the-art theory.

3.2 Characterisation of Molecular Beam Valves

In order to improve the experimental resolution and number densities, new molecular beam systems were deployed in the experiment. Careful calibration was necessary to ensure knowledge of the collision energies and beam profiles in order to simulate the

experiment as accurately as possible. Two different types of valves were tested: the standard Series 9 General Valve and a home-built Jordan [125] electromechanical valve.

When the internal energy of a gas is converted to kinetic energy *via* supersonic expansion from a pulsed molecular beam, the speed of the gas can be estimated thermodynamically [109, 123] by means of the heat capacities and an initial temperature, as follows:

$$|v| = \sqrt{\frac{2k_B}{m} \left(\frac{\gamma}{\gamma - 1} \right) (T_0 - T_{\text{beam}})}, \quad (3.1)$$

where $\gamma = C_p/C_v$, the ratio of the heat capacities at constant pressure and volume, m is the mass of the gas and T_0 is the stagnation temperature and T_{beam} is the beam temperature. At 300 K, the beam speed of 10% NO(X) in argon is predicted to be 620 m s^{-1} . We shall see that this theoretical speed proves accurate for a General Valve but somewhat underestimates the speeds of beams originating from a Jordan Valve due to the operation of the valve. The collision energy and the pixel-to-velocity ratio, needed for the image analysis, can also be obtained from the radius of the experimental images, as demonstrated by Eyles [109], and undertaken below.

3.2.1 Determination of The Beam Velocity

A microphone apparatus can be used to directly study the temporal profile of a molecular beam [126–128], as shown in Fig. 3.3. The gas packet hits the microphone and causes several vibrational modes of the microphone electret to become excited, which results in a measurable signal on an attached oscilloscope. The highest frequency mode of vibration defines the microphone’s ultimate temporal response to a gas pulse. In order to avoid interference from pump noises and other vibrations, a low pass filter was applied to remove low frequency vibrations from the microphone output. A gas pulse viewed by a microphone therefore looks like a Gaussian packet overlaid by the highly non-linear and oscillatory response of the microphone. Since the microphone is in a vacuum, there is little resistance to continued ringing after the gas pulse has ended. The ringing as the microphone electret oscillates only dies down after several milliseconds. The response to the pulse is several times larger than the ringing of the microphone so

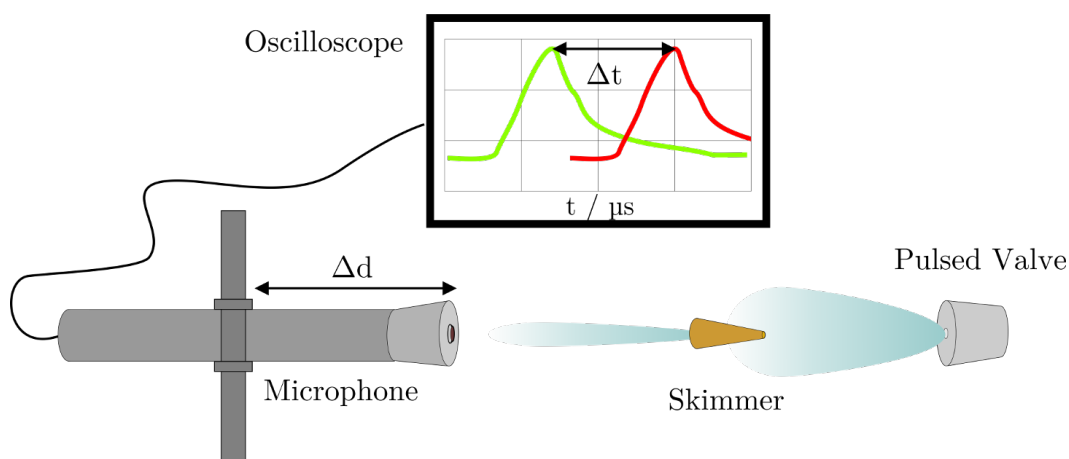


Figure 3.3: The experimental apparatus necessary to measure the profile and speeds of a molecular beam. The distance, Δd , is changed and the response Δt is observed a distance-time plot is then constructed to determine the speed with very high precision.

the pulse can still be easily resolved against the noise. A typical microphone response is shown in Fig. 3.4 where the intense arrival of the beam can be seen to approximate a Gaussian, and the ringing of the microphone can be seen to continue over the observed time range.

The microphone response to a General Valve is shown in Fig. 3.4. The microphone can only measure a change in pressure, and not the absolute flux-density. The microphone apparatus can be used to accurately determine the beam speeds. By translating the microphone a known small distance from the molecular beam Δd and monitoring the beam pulse as a function of time, the extra time taken for the pulse to reach the microphone gives an accurate measure of the speed. A distance-time plot can then be constructed using many different microphone extensions in order to obtain highly accurate measurements of the beam speed with real experimental gas pulses. By analysis of the beam speeds and the experimental geometry, the average collision energy can be calculated with high precision.

The speeds calculated by translating the microphone a known distance and measuring the time delay in order to construct a distance-time plot are shown in Fig. 3.3. By changing the gas in the molecular beam, speeds for each of the rare gases can be calculated from the observed microphone response. The speed-time plots used to determine the speeds of the NO(X) gas mix, neon, argon and krypton are shown in Fig. 3.5. The progression is as expected; the lightest neon molecules move considerably

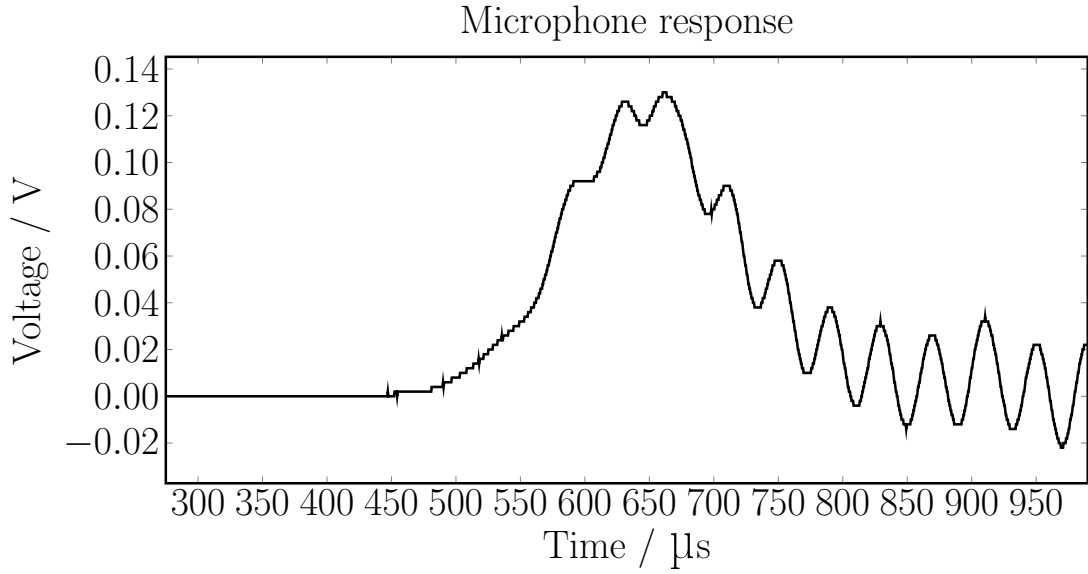


Figure 3.4: The voltage response of a microphone to a molecular beam pulse (highlighted) as a function of time from a fixed trigger. The microphone continues to ring for approximately 10 ms before returning to the baseline.

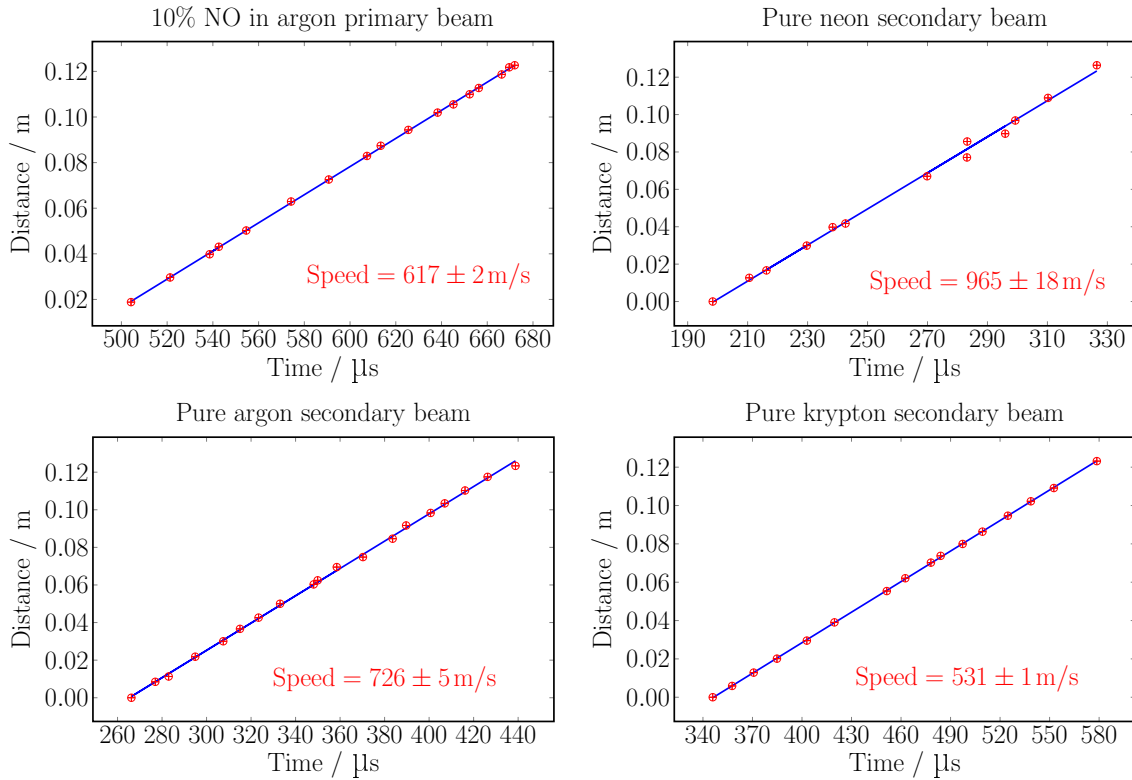


Figure 3.5: Distance–time plots for NO and rare gas beam expansions. The apparatus used to generate these plots is shown in Fig. 3.3. The 10% NO in Ar (top left) is expanded from a Series 9 General Valve, whereas the pure rare gases were expanded from a Jordan Valve. The standard error is given by the size of the point.

faster than the krypton, with argon an intermediate case. We find that the krypton and argon move faster than expected when emitted from a Jordan Valve. In a pure thermodynamic expansion, the speed of a molecular beam from a pulsed source is given by Eqn. (3.1). As shown in Fig. 3.5, we find that the krypton moves at 530 m s^{-1} , which corresponds to a stagnation temperature of 560 K. This is an unrealistic temperature for the beam valve. However, the mechanism of the valve may account for the discrepancy. The Jordan Valve uses a high current, high voltage discharge to open a mechanical barrier and allow the gas to escape into the vacuum chamber. The mechanism dissipates large amounts of thermal energy into the surrounding gas, which it is unable to efficiently radiate due to the thermal conductivity of the rare gases decreasing from helium ($141.84 \text{ mW m}^{-1} \text{ K}^{-1}$ [129]) to xenon ($5.06 \text{ mW m}^{-1} \text{ K}^{-1}$ [129]). The krypton is much less able to dissipate the thermal energy from the firing mechanism and therefore has a correspondingly high thermodynamic temperature from Eqn. (3.1).

3.2.2 Determination The Opening Time and Velocity Spread

The experimental apparatus used to observe the beam profiles and calculate the mean speed is shown in Fig. 3.3. The distance measurements were made with a pair of electronic Vernier scales which measured to an accuracy of $5 \mu\text{m}$. The microphone can also be used to observe the mean opening time of the molecular beam. By placing the microphone a very short distance away from the molecular beam valve, such that the velocity spreads will play a minimal role in the intensity profile viewed on the oscilloscope, the observed pulse profile will be primarily determined by the opening time of the valve. By fitting a Gaussian to the oscilloscope output, the FWHM opening time could be obtained.

To obtain the velocity spreads, the molecular beam was operated as normal and the laser was used to ionise unscattered NO(X) from the source. Ion yields were then obtained as a function of the laser delay, effectively scanning over the temporal profile of the molecular beam. The temporal profile of the molecular beam will be approximately that of a convoluted Gaussian, with contributions from the opening time and the beam velocity spreads. Since the beam velocity spreads have been calculated by means of

Monte-Carlo simulation with varying velocity spreads, a fit to the observed signal can be obtained by a Levenberg-Marquardt optimisation algorithm [130]. The simple model for the time profile of a molecular beam in the interaction region assuming no obstruction is given by

$$I = \frac{d}{v_i} + t_i, \quad (3.2)$$

where d is the distance from the valve to the interaction region, t_i is the time at which the i^{th} particle exited the beam valve with respect to the trigger pulse. t_i can be negative or positive and is sampled from a Gaussian distribution with mean zero and FWHM equal to the FWHM obtained from the microphone measurement of the opening time. v_i is the velocity of the i^{th} particle, sampled from a Gaussian distribution with the mean determined by microphone measurement and the FWHM is freely varied in order to minimise the χ -squared value between the simulated and experimental temporal profile. Approximately 1×10^6 trial trajectories with varying v_i and t_i were calculated. The resultant trajectories were histogram binned to the nearest 100 ns whence a kernel density estimation [131] was calculated from the histogram. The kernel density estimation represents the simulated ion yield as a function of time, which was then compared to the experimental ion yield as a function of time. The velocity spread was iterated using a Levenberg-Marquardt optimisation algorithm until convergence of the simulation to the experimental profile was achieved, a process taking much less than a minute with Maple 16 and an Intel i5-3550 CPU.

Series 9 General Valve

The General Valve is one of the most popular valves for molecular beam experiments in a wide range of fields [12, 132–136]. It is robust, reliable and easily repaired. The valve, however, does have weaknesses that make its use less attractive in high resolution experiments. When a voltage is applied to the coil, the current flowing in the coil produces a magnetic field in the iron armature which pulls the plunger up allowing gas to expand into the vacuum. The opening time is limited by the current in the solenoid. The relatively long opening time that results along with the comparatively poor velocity spreads are the beams key disadvantages. The analysis of the microphone

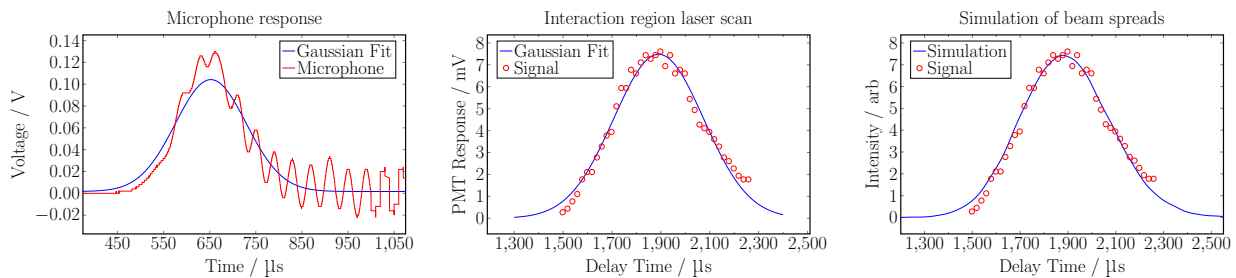


Figure 3.6: A progression of the method used to calculate the beam velocity spreads accurately. The valve was placed directly in front of the microphone and fired to ascertain the opening time (left). The beam is then placed in the interaction region 2.85 m away and the laser delay is altered to scan over the molecular beam (middle). Monte-Carlo simulation of the observed signal (right) taking into account velocity spreads in the beam.

data described above leads to a FWHM velocity spread of 49 m s^{-1} , and an opening time of $165 \mu\text{s}$ from the primary molecular beam of 10% NO seeded in Ar. The simulation reproduces the observed signal in the scattering chamber as a function of delay very well as shown in Fig. 3.6. The beam speed spread of 49 m s^{-1} corresponds to a velocity spread of approximately 8% of the speed of a 10% NO(X) in argon beam. This value, along with the spreads from the Jordan Valve, was used to calculate collision energy spreads for theoretical calculations and simulations used in this thesis. The value of 8% velocity spread agrees well with previous estimates of 10% velocity spread [109] and measurement of the measured radii of unscattered NO(X) ions velocity mapped onto the detector [84].

Jordan Valve

The Jordan Valve is a commercial valve sold by the R. M. Jordan company, described in detail in the original paper [125]. The valve has a FWHM opening time much shorter than the General Valve, as evidenced by the microphone profile in Fig. 3.7. The valve also has a conical nozzle compared to the free jet type nozzle of the General Valve. The conical nozzle aims to aid cooling by supersonic expansion and reduce the velocity spreads in the molecular beam. A similar analysis to that performed on the General Valve was performed on the Jordan Valve. The analysis yielded an opening time of $22 \mu\text{s}$, which is a marked improvement on the General Valve. The velocity spreads were calculated in a similar manner, however, due to the high number density delivered

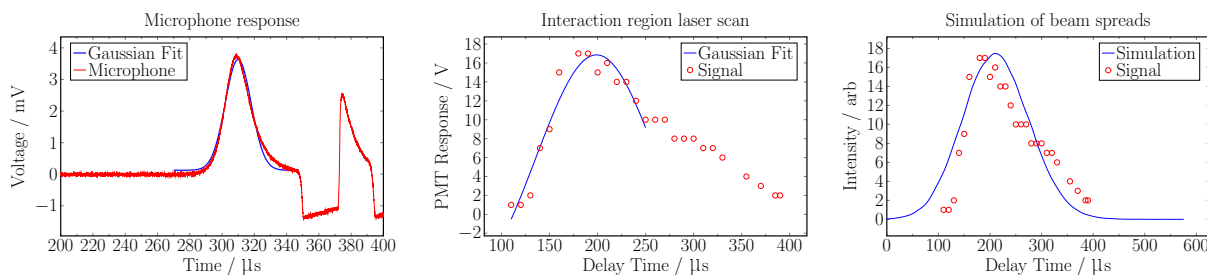


Figure 3.7: Left: microphone measurement of the Jordan Valve beam opening time with Gaussian fit to the beam profile yielding a FWHM opening time of $22\mu\text{s}$. The ringing features are much more extreme due to the higher peak power delivered by the gas pulse. Middle: fit of the observed signal in the interaction region from which the velocity spreads can be simulated. Right: observed signal compared to a best fit for the beam velocity spreads of 32 m s^{-1} . Discrepancies are likely caused by a build up of pressure behind the skimmer leading to the characteristic tail profile [123].

in such a narrow pulse, the form of the molecular beam in the interaction region is non-Gaussian, most likely due to unfavourable pressure build-up in the skimmer [123]. A sizeable tail towards high time is observed, which makes the fitting of the velocity spreads more prone to error; for this reason, the fit was truncated just after the peak in order to neglect the tail. Fitting of the velocity spread using the previously described Monte-Carlo technique leads to a velocity spread of 32 m s^{-1} at FWHM for a trace NO in Ar beam pulse. This corresponds to a velocity spread of approximately 5% of the total beam speed. The 5% beam speed spread was then used in calculations and simulations of experiments making use of the Jordan Valve.

3.2.3 Calibration of Collision Energy

One of the most important parameters in inelastic scattering is the collision energy, how much kinetic energy is available to be partitioned into other degrees of freedom throughout the course of the collision. This parameter is determined by the velocity and composition of the molecular beams. The beam speeds have been measured directly by the microphone and therefore provide a direct measure of the collision energy. An alternative method of calculating the collision energy is by analysis of the radius of the experimental ion images, and how the radius changes with increasing rotational excitation.

Table 3.1: Collision energies calculated from the beam speeds as measured by the microphone (Xe is obtained from radius measurement detailed below). The calculations in this thesis use collision energies with these values, unless otherwise indicated. The xenon data in Chapter 4 were recorded using a Series 9 pulsed valve as the secondary beam source and an image radius measurement was used to obtain the collision energy.

System	Collision energy (cm ⁻¹)	Energy Spread (cm ⁻¹)
NO(X)–He	514.0 [138]	–
NO(X)–Ne	661.8	59.9
NO(X)–Ar	650.1	55.9
NO(X)–Kr	612.0	61.4
NO(X)–Xe	519.0 [139]	58.2

Microphone Measurement

The microphone apparatus is able to provide a direct measure of the speeds of both the primary and secondary molecular beams. From these values, the collision energy can be calculated by [53, 109]

$$E_{\text{coll}} = \frac{1}{2} \mu \mathbf{v}_{\text{rel}}^2, \quad (3.3)$$

where the relative velocity (assuming a 90° geometry) is calculated from $|\mathbf{v}_{\text{rel}}| = \sqrt{|\mathbf{v}_{\text{NO}}|^2 + |\mathbf{v}_{\text{Rg}}|^2}$. The calculated collision energies of various different collision systems, along with corresponding error, are shown in Table 3.1. Of the collision systems presented in this work, the collision energy with neon is the highest as the kinetic energy increases with the square of the speed, and as neon is the lightest rare gas it moves the fastest. The helium measurement was made by Stolte and co-workers and is included for comparison [137]. The xenon experimental data was obtained before the installation of the microphone apparatus and the Jordan Valve, so the NO(X)–Xe collision energy was calculated from the image radius, as described below. The relative error in the collision energy increases with increasing rare gas mass, as the rare gas gets heavier, it moves more slowly and the energy spread remains consistent.

Image Radius Measurement

The radius of the images as a function of j' can also be used to determine the collision energy. This method requires high signal intensity for transitions to high rotational states in order to accurately determine the image radius. The Newton sphere radius is

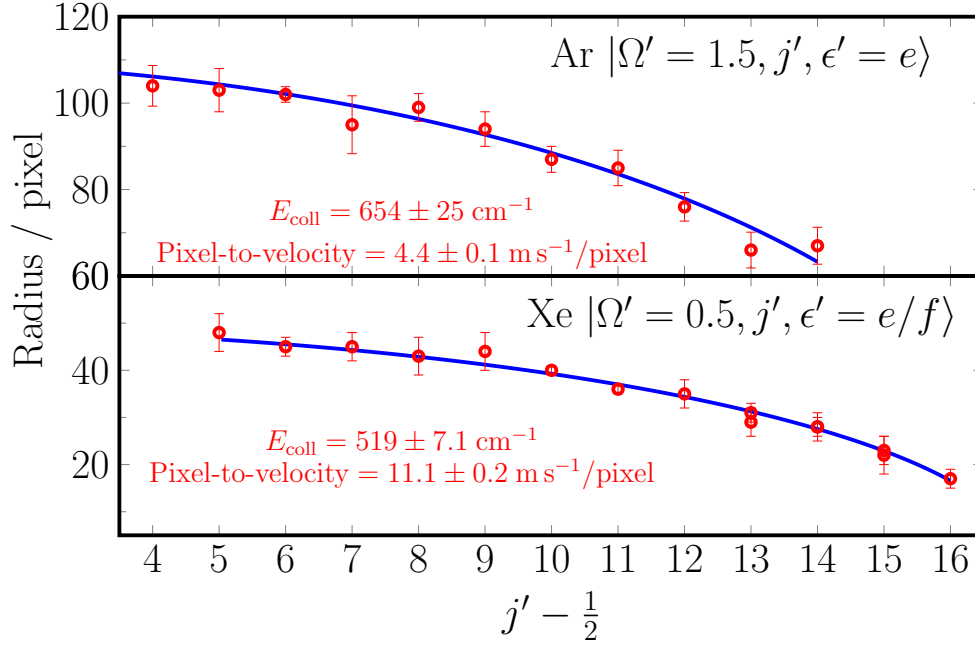


Figure 3.8: A plot of the radius of the velocity mapped NO(X)–Ar spin-orbit changing images as a function of $j' - \frac{1}{2}$ (top panel) and the NO(X)–Xe spin-orbit conserving images (bottom panel). The functional form of the plot (blue solid) is that of Eqn. (3.4), and can be fitted from the experimentally determined image radii (red circles) to obtain the pixel-to-velocity ratio and the collision energy. The pixel-to-velocity differs due to the flight tube extension.[']-

given in terms of the outgoing velocity by

$$r = |v'_{\text{NO}}| \times \text{PIXTOV} = \frac{m_{\text{Rg}}}{m_{\text{NO}} + m_{\text{Rg}}} \sqrt{\frac{2(E_{\text{Coll}} - \Delta E_{\text{rot}}(j' - j))}{\mu}} \times \text{PIXTOV}, \quad (3.4)$$

with PIXTOV the pixel-to-velocity ratio, a quantity which converts detector pixels into ms^{-1} . The quantity $\Delta E_{\text{rot}}(j' - j)$ is the change in rotational energy, calculated using Eqn. (2.4) in Chapter 2. The decrease in the image radius continues until all the available kinetic energy has been transferred to rotation and the image becomes as small as possible. By fitting the experimental image radii (Eqn. (3.4)) as a function of j' , the pixel-to-velocity ratio and the collision energy can be determined.

The image radii for the NO(X)–Ar spin-orbit changing states presented in Chapter 6 were used to corroborate the collision energy obtained from the microphone and obtain an accurate pixel-to-velocity ratio for use in image analysis. A plot of image radii and a fitted curve describing the radius as a function of $j' - \frac{1}{2}$ is shown in the top panel of Fig. 3.8. The radius measurement of the collision energy ($E_{\text{coll}} = 654 \pm 25 \text{ cm}^{-1}$)

agrees favourably with the beam speed measurement of the collision energy ($E_{\text{coll}} = 650 \pm 6 \text{ cm}^{-1}$) obtained from the microphone, lending confidence to the collision energy calibration.

The measurements of the xenon data presented in Chapter 4 took place before the installation of the microphone or Jordan Valve. Accordingly, the collision energy is obtained from the radii of the images, the radii as a function of j' for the xenon images (on the spin-orbit conserving manifold) are shown in the bottom panel of Fig. 3.8. The collision energy obtained from this fit and used for the xenon measurements is $519 \pm 7 \text{ cm}^{-1}$.

3.2.4 Rotational Temperature of The Beams

The rotational temperature of the molecular beam is an important parameter in the characterisation of the molecular beam. Ideally, the beam would be as close to zero Kelvin as possible, so that essentially the entire population of spin-orbit, rotational and parity states reside in the ground state. Supersonic expansion of the molecular beam into the vacuum leads to NO(X) rotational state distributions that approximate temperatures in the 10 K range, meaning that a number of rotational states are populated and the Λ -doublets, being almost doubly degenerate with an energy difference $\ll 1 \text{ cm}^{-1}$, are essentially evenly populated. As the rotational temperature of the beam increases, larger quantities of unscattered NO in a given rotational state will be present. In order to minimise background, and optimise the quality of forward scattered data, the rotational temperature of the beam should be minimised. The characterisation can be performed by using the REMPI system to perform a wavelength scan of the NO($A \leftarrow X$) transitions, the detection apparatus is then used to count the ion yield as a function of wavelength. In order to minimise the rotational temperature of the beam, the nozzle skimmer distance is optimised to ensure that the central, coldest part of the beam is selected [123] by the skimmer whilst maximising flux.

The REMPI spectrum of NO($A \leftarrow X$) can be simulated using the software package LIFBASE [140]. The experimental intensity, given by the ion count over 1000 laser shots for each rotational state, can then be fitted to the LIFBASE simulation at a given

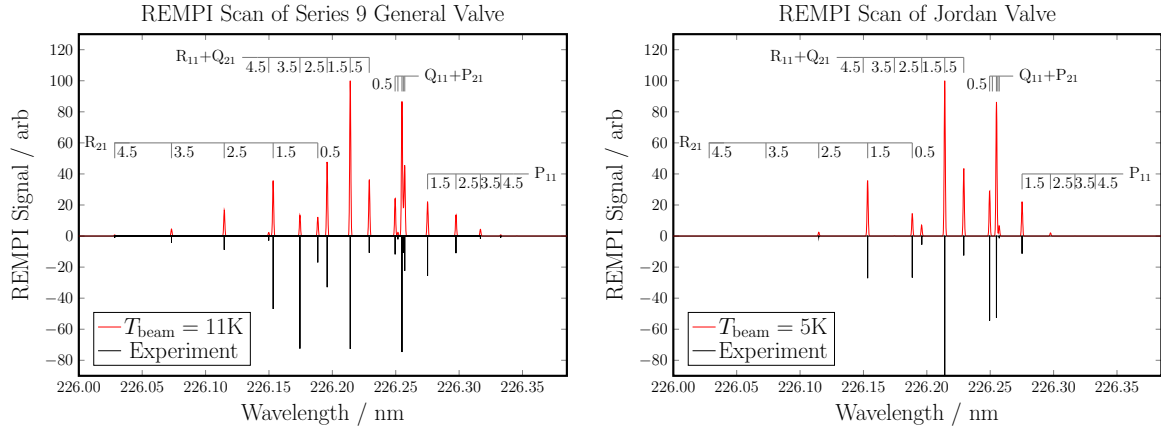


Figure 3.9: REMPI scans with 226 nm light on the $\text{NO}(A \leftarrow X)$ transitions described in Section 3.4. The gas is cooled by supersonic expansion from the valve leading to the spectrum shown in black. The simulated spectrum from LIFBASE is shown in red. All the accessible states were probed with both the pure P/R branch and mixed Q+P/R branch transitions in order to ensure an accurate beam temperature was obtained.

rotational temperature. Since the simulation is produced with a known temperature, fitting of the peaks to the simulation yields the rotational temperature of the beam. The REMPI scans across a range of wavelengths are shown in Fig. 3.9. The temperatures were obtained for both the General Valve (primary beam) and Jordan Valve (secondary beam). Their simulations reveal that the rotational temperature of the primary beam was 11 K and the rotational temperature of the secondary beam (when a 10% $\text{NO}(X)$ in Ar gas mix is discharged) was 6 K. The temperature of the secondary beam is important when considering scattering with other diatomics, as presented in Chapter 8.

3.3 Hexapole State Selection

As described in Chapter 2, each rotational level in $\text{NO}(X)$ is split into two Λ -doublet levels. These sublevels are symmetric and antisymmetric combinations of the $|j, m, +\Omega\rangle$ and $|j, m, -\Omega\rangle$ states. As the Λ -doublet levels are so close in energy (0.0119 cm^{-1} for $j = 0.5$ [141]) they will be essentially identically populated at the temperature of the molecular beam from supersonic expansion, approximately 11 K for a General Valve, as demonstrated in Section 3.2. If the two states remain unselected, as was the case with many experiments involving $\text{NO}(X)$ [13, 14, 142, 143], then the observed result will be summed and averaged over the two initial states, and it is therefore necessary to

de-convolute the observed signal.

An experimental apparatus which makes use of the Stark effect has been shown to be capable of selecting the initial state of symmetric top molecules or diatomic molecules with non-zero electronic angular momentum for example see [58, 144–146]. The NO(X) molecular beam is passed into an inhomogeneous hexapole electric field of length 1.65 m with alternating positive and negative voltages applied to each of the six rods (diameter 2.5 mm). The electric field interacts with the Λ -doublet levels *via* the Stark effect, the shifting of the molecular energy levels by an electric field. The Stark effect guides low-field-seeking states (in the case of NO(X), the $|j = 0.5, \Omega = 0.5, \epsilon = -1, f\rangle$ state) into the interaction region whilst expelling the high-field-seeking e state [58, 84, 109]. In the electric field, the NO(X) molecular Hamiltonian gains a term for the interaction energy of the molecule with the electric field $\mathbf{E}$ [147]

$$V_{\text{Stark}} = -|\boldsymbol{\mu}_{\text{el}}||\mathbf{E}| \cos \theta_{\mu\mathbf{E}}. \quad (3.5)$$

$\boldsymbol{\mu}_{\text{el}}$ is the electric dipole moment of the NO(X) molecule, approximately 0.16D, which necessitates the long hexapole, and $\theta_{\mu\mathbf{E}}$ is the angle between the $\boldsymbol{\mu}_{\text{el}}$ and $\mathbf{E}$ vectors. In the high field limit, the Stark interaction energy is written as

$$V_{\text{Stark}} = -\epsilon|\boldsymbol{\mu}_{\text{el}}||\mathbf{E}| \frac{|m\Omega|}{j(j+1)}, \quad (3.6)$$

where Ω denotes the spin-orbit manifold and ϵ is the spectroscopic index. If the rods are placed on the surface of a cylinder with radius given by r_0 with an applied voltage of V_0 , then the radial potential from the centre of the cylinder is approximated [148] by

$$V(r) = V_0 \left(\frac{r}{r_0} \right)^3 \cos 3\phi. \quad (3.7)$$

The magnitude of the electric field at a distance r from the centre of the hexapole is equal to

$$E = -\frac{dV}{dR} = -\frac{3r^2 V_0}{r_0^3}. \quad (3.8)$$

The molecules experience a radial force based on the parity of the state, obtained from

combining Equations. (3.6) and (3.8)

$$F(r) = \frac{6\mu_{\text{el}}V_0r}{r_0^3} \frac{\epsilon|m\Omega|}{j(j+1)}, \quad (3.9)$$

as they travel down the hexapole [148, 149]. It can be seen from Eqn. (3.9) that molecules in the $\epsilon = -1$ state will experience a restoring force to the centre of the hexapole whereas those with $\epsilon = +1$ will feel an ejecting force. This constant force down the length of the hexapole causes the low-field-seeking molecules to undergo harmonic motion about the centreline as they are restored, diverge and re-converge through the length. The frequency of the oscillation depends on the quantum numbers of the particular state, so each state will have its own characteristic frequency.

The hexapole voltage is simply tuned so that the ground rotational, low field seeking Λ -doublet level is focussed into the interaction region. Unfortunately, measurement of the high field seeking e Λ -doublet is not possible using hexapole techniques as it is defocussed by the inhomogeneous field. Many experimental issues prevent the measurement of the e Λ -doublet. However, by switching the hexapole on and off on a shot-by-shot basis, measuring the flux intensity with a microphone and monitoring the laser power, measurement of the e initial state may be possible in future experiments.

3.4 REMPI and Detection

In order to detect the scattered NO(X) whilst maintaining quantum state resolution, a suitable detection scheme is necessary. Resonantly enhanced multi-photon ionisation (REMPI) coupled with velocity-mapped ion imaging provides a suitable method for quantum-state-resolved detection. The laser systems, detection method and data acquisition will be outlined below.

3.4.1 Laser System

In order to perform REMPI on the scattered NO(X) [124], a XeCl excimer laser (Lambda-Physik EMG 202 MSC) was employed to generate approximately 150 mJ/pulse

of light at 308 nm. The pulse was passed through a beamsplitter where $\approx 90\%$ of the power was directed into a tuneable dye laser (Lambda-Physik FL3002) utilising Coumarin 2 in methanol as the lasing medium. A BBO crystal was then used to frequency double the 452 nm output light to ≈ 226 nm. The wavelength was tuned by the grating to particular rotational lines of the $\text{NO}(\text{A} \leftarrow \text{X})$ transition. The output of the dye laser was then passed through a Rochon polariser; and optionally, a photoelastic modulator, in order to control the polarisation of the laser on a shot-by-shot basis. Before entering the scattering chamber, the light was collimated with an iris of varying size. A typical pulse energy was 10 μJ with a diameter of the order 1 mm.

The geometry of the laser beams with respect to the molecular beams depends on the measurement being made, as described in Section 3.1. To measure the collision-induced alignment (CIA) of $\text{NO}(\text{X})$ after scattering with Xe (as discussed in Chapter 4), the alignment geometry, in which the 226 nm light is in the plane of the molecular beams and perpendicular to the relative velocity, was used. For the collision-induced orientation measurements of $\text{NO}(\text{X}) + \text{Kr}$, the geometry in which the 226 nm light propagates perpendicular to the plane of the molecular beams was used, as described in Chapter 5. The experiments in which the steric effect is probed require the addition of a homogeneous electric field applied to the interaction region, as described in Chapter 6.

After the 226 nm laser excites $\text{NO}(\text{X})$ to the $\text{NO}(\text{A})$ state, the remaining 10% of the excimer laser power is directed straight into the scattering chamber, which allows for near-threshold excitation of the $\text{NO}(\text{A})$ to the $\text{NO}^+(\text{X})$ ion. A schematic of the laser excitation is shown in Fig. 3.10. The direction of the 308 nm light is approximately parallel to the relative velocity vector. The excimer laser beam is slightly divergent, so a $f = 300$ mm lens is used to refocus the beam into the chamber. This leads to a detection volume of approximately $1 \text{ mm} \times 1 \text{ mm} \times 2.0 \text{ mm}$ in the centre of the scattering chamber for the co-planar geometry. For the perpendicular geometry, the interaction region is reduced in volume to approximately $1.5 \text{ mm} \times 1.5 \text{ mm} \times 1.5 \text{ mm}$, which leads to a slight drop in detected scattered signal.

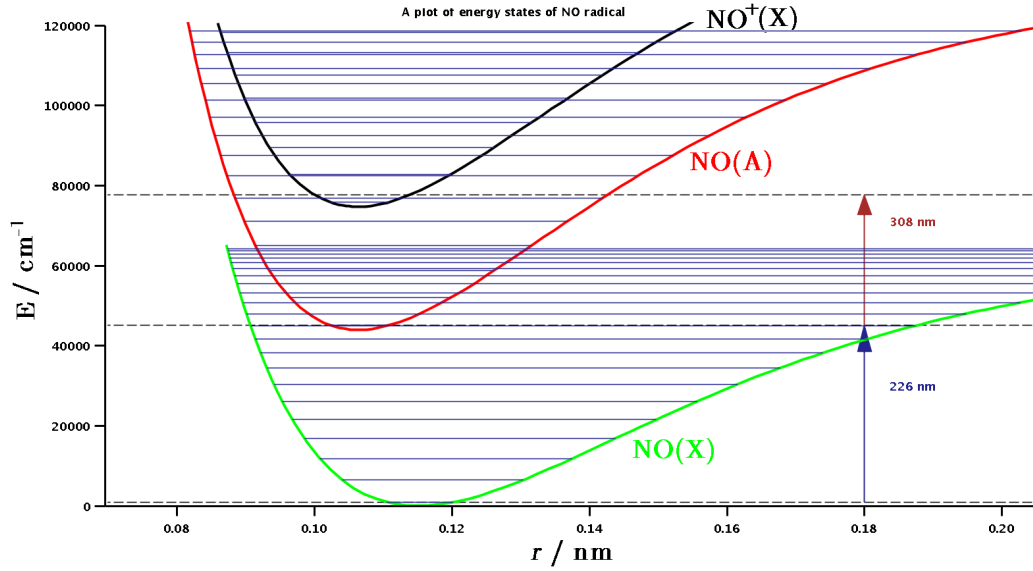


Figure 3.10: A plot of potential energy of the $\text{NO}(\text{X})$, $\text{NO}(\text{A})$ and $\text{NO}^+(\text{X})$ as a function of N–O bond distance. The 226 nm laser excites a particular rotational $\text{NO}(\text{A} \leftarrow \text{X})$ transition to the $\text{NO}(\text{A})$ state. The 308 nm laser then ionises the $\text{NO}(\text{A})$ to the NO^+ ion near to the threshold, ensuring ion recoil energy is low to minimise this source of blur. Spectroscopic data obtained from [150,151].

Excitation Branches

The branch used to excite the $\text{NO}(\text{X})$ to the $\text{NO}(\text{A})$ state must be considered. The Q branch is known to have larger cross sections for absorption of a photon, leading to higher levels of signal, however, it also complicates the analysis of images mapping the angular momentum of the $\text{NO}(\text{X})$. Classically for linearly polarised light, the probability of a molecule absorbing a photon is proportional to $\langle \cos^2 \theta_{\mu E} \rangle$, the average value of the cosine of the angle between the transition dipole moment of the NO, $\boldsymbol{\mu}$, and the electric vector of the excitation laser, $\hat{\mathcal{E}}$ [57]. For P or R branch transitions, the transition dipole moment, $\boldsymbol{\mu}$ will lie perpendicular to $\mathbf{j}$, while for a Q branch transition, $\boldsymbol{\mu}$ points parallel to $\mathbf{j}$ [152]. A Q branch transition typically overlaps with a transition on the P/R branch, and so these will be referred to as mixed branch transitions. The mixed branch transitions complicate image analysis as the P/R and Q branch transition dipole moments are at right angles to one another. For Q branch excitation, $\boldsymbol{\mu}$ is parallel to $\mathbf{j}$, but in P/R branch transitions it is perpendicular to $\mathbf{j}$, this will have important consequences in the determination of the $\rho_{q+}^{\{2\}}(\theta)$ renormalised polarisation dependent differential cross sections (PDDCSs) in Chapter 4 and the $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs

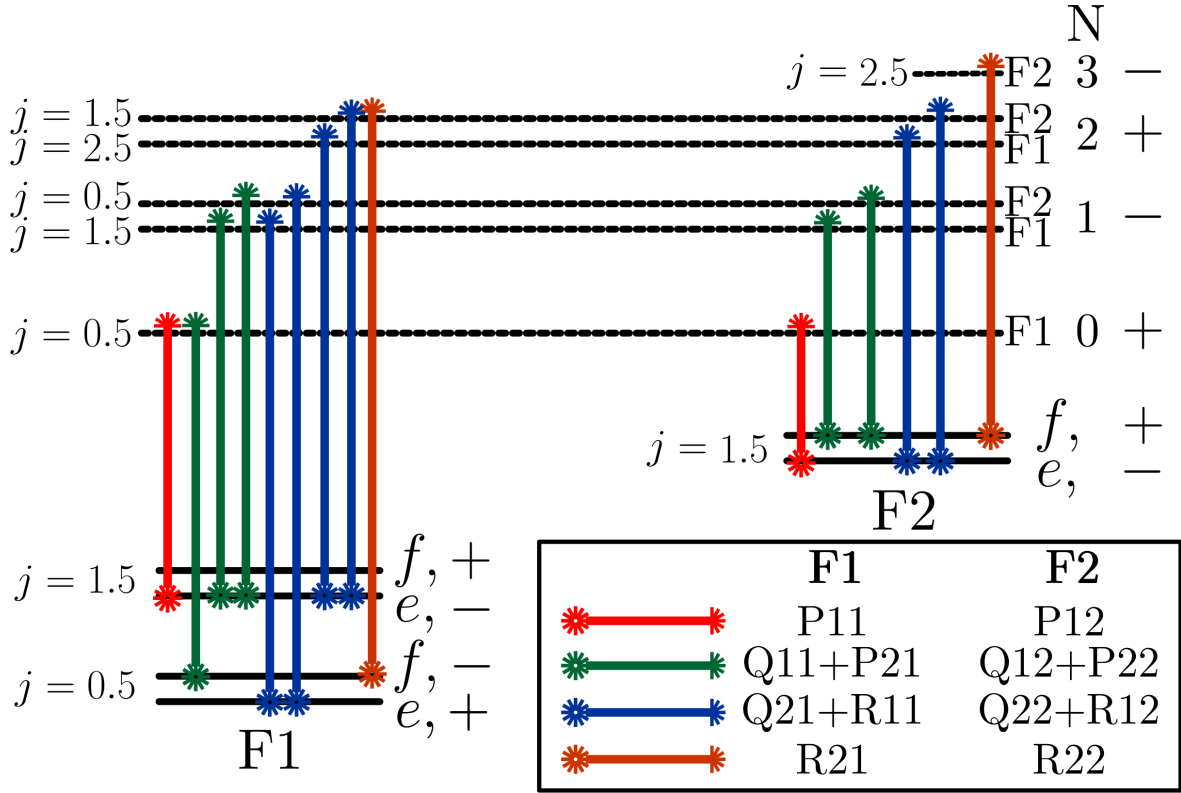


Figure 3.11: The 226 nm dye laser can be tuned to various lines in the NO($A \leftarrow X$) spectrum. The various lines can be used to probe both the ground spin-orbit states (F1) and the excited spin-orbit states (F2) with either spectroscopic index.

in Chapter 5.

Figure 3.11 shows the possible excitation branches for the first few excitation pathways for NO($A \leftarrow X$) transitions. Table 3.2 contains a summary of the information in Fig. 3.11 about which rotational lines can be used to probe the collisionally excited rotational states. The nomenclature used is Hund's case (a) with $\Delta j_{f_{\Sigma}f_{\Pi}}$ where the notation $\Delta j = P, Q, R$ corresponds to values of $\Delta j = -1, 0, +1$ respectively, $f_{\Sigma} = 1, 2$ represents $j = N \pm S$ and $f_{\Pi} = 1, 2$ corresponds to $\Omega = 0.5, 1.5$, respectively.

Since the direction of the transition dipole moment on the NO(X) is orthogonal

Table 3.2: The branches used to probe the rotational states given by the kets. The nomenclature used is Hund's case (a) with $\Delta j_{f_{\Sigma}f_{\Pi}}$ where $f_{\Sigma} = 1, 2$ represents $j = R \pm S$ and $f_{\Pi} = 1, 2$ corresponds to $\Omega = 0.5, 1.5$, respectively. The notation $\Delta j = P, Q, R$ corresponds to values of $\Delta j = -1, 0, +1$ respectively.

State	Pure	Mixed
$ \Omega' = 0.5, j', \epsilon' = f\rangle$	R_{21}	$Q_{11} + P_{21}$
$ \Omega' = 0.5, j', \epsilon' = e\rangle$	P_{11}	$Q_{21} + R_{11}$
$ \Omega' = 1.5, j', \epsilon' = f\rangle$	R_{22}	$Q_{12} + P_{22}$
$ \Omega' = 1.5, j', \epsilon' = e\rangle$	P_{12}	$Q_{22} + R_{12}$

to $\mathbf{j}$ in the P and R branches, and the Q branch (in which $\boldsymbol{\mu} \parallel \mathbf{j}$) dominates on the overlapping Q+P/R branch, ion images recorded using the mixed Q+P/R branch are inverted with respect to those recorded on the pure P or R branch transitions. This effect can be taken into account during the basis set generation.

3.4.2 Detection Scheme

The NO(X) beam molecules exit the hexapole and enter into the interaction volume where they collide with a pulsed beam of the collision partner, typically a rare gas. As the two beams collide, energy is transferred from the kinetic energy of the beams into rotational energy, and various rotational states of the NO(X) become populated. Each of the resultant rotational states is scattered into a shell of NO(X) molecules referred to as a Newton sphere. The radii of the spheres corresponding to the different rotational states depend on the outgoing relative velocity of the collision, $\mathbf{k}'$, as defined in Eqn. (3.4). The relative distribution of the NO(X) molecules on the surface of the sphere encodes the angular distribution of the collision, as well as its polarisation information.

The scattered NO(X) is then ionised by the laser system described in detail in Section 3.4.1: the 226 nm photon selects the rotational level of interest and the 308 nm photon ionises the NO(A). By using a (1+1') REMPI scheme, the dye laser power can be kept low to avoid saturation of the NO(A $\leftarrow$ X) transition, which would prevent accurate measurement of polarisation effects [124].

The sphere of NO⁺ ions corresponding to a specific $|\Omega', j', \epsilon'\rangle$ state is velocity mapped [44] onto a MCP chevron detector coupled to a P43 phosphor screen with a diameter of 40 mm.

The velocity mapping technique [44] uses an electric field to focus ions with the same LAB frame velocity onto the same point on the detector; this minimises the effect of blurring caused by the finite interaction volume. This electric field is generated with three charged plates; the repeller at 1500 V, the extractor at 650 V and the third plate at ground. The ratio of the extractor:repeller voltage allows focussing of the velocity mapped ions: alternatively, the ratio can be changed to allow spatial mapping of the

interaction volume, which aids with the determination of the laser widths.

The MCPs themselves are typically kept at ± 900 V and the MCP in the time of flight tube is pulsed from ground to minimise the effect of background ions formed by the laser system. The pore count of the MCP is around 100 000 000, each of diameter $10\text{ }\mu\text{m}$. As an ion hits the MCP pore, a shower of electrons is created which are accelerated towards another nearby MCP at $+900$ V, creating a further amplification in the number of electrons. The ejected electrons then hit the P43 phosphor screen where flashes of fluorescence are observed by a CCD camera.

Depending on the signal intensity, tens to hundreds of ions can be produced per laser shot, and (depending on the MCP and phosphor detection efficiencies) each is captured by the CCD camera. The intensity of the CCD response is sent to a computer for on-the-fly processing into flat datafiles for further analysis.

To integrate an image, hundreds of thousands of laser shots are required. To produce orientation and alignment resolved images, which contain twice the number of data channels, several hundred thousand additional laser shots are needed to ensure sufficient signal-to-noise ratio.

3.4.3 Centroiding Algorithm

Standard imaging methods [45] use direct sampling of the video stream of the CCD camera. This can lead to accumulation of noise as well as experimental ion signal and can threaten to overwhelm the image in low count conditions. Furthermore, each ion hit is non-uniform due to detector inhomogeneity, leading to a non-uniform blurring kernel [153] in the velocity space of the image. Since each ion hit is approximately 2-12 pixels wide, depending on MCP gain, it is advantageous to minimise the impact of the non-uniform ion hits on the final image. This can be achieved using a centroiding and event counting algorithm, modified to allow reconstruction of the raw ion image if so desired.

The algorithm chosen was implemented in real time using the NI LabView vision suite in a similar fashion to that described in [154]. The program analyses the image on-the-fly, filtering the camera noise by setting a user defined threshold chosen to remove

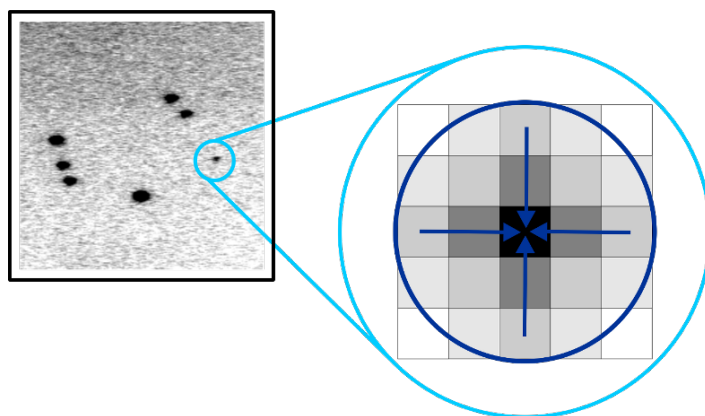


Figure 3.12: The raw image is thresholded and then for each ion hit, the computer calculates the weighted COM position based on the pixel intensities and positions. A circle is also fit to each ion hit and the radius of each along with a central position is also recorded.

the background while the intense ion hits are still observed. The algorithm then finds the centre of mass of each individual ion, which allows for the possibility of megapixel imaging from the non-integer pixel positions obtained from the center-of-mass (COM) binning algorithm. The algorithm then uses a copy of the thresholded image to fit circles to the raw ion hit pixels in order to include the possibility of restoring the non-centroided image (if desired) using the size and position of the raw ion hit. A schematic of the process is shown in Fig. 3.12.

It was found that due to the large number of pixels which comprise the images, convergence could not be satisfactorily achieved by centroiding alone. Two different methods were tested to reconstruct the experimental images from the centroided data. The first involved applying a Gaussian blurring kernel to the centroided points and the second expanding the radius of each of the ion hits to form a larger circle. By ensuring an equal weight of each ion hit, the effect of inhomogeneity in the MCP response and phosphor screen is minimised. To ensure convergence of the experimental image, it was found that a FWHM blur of three was necessary to produce good quality, converged ion images for analysis. A comparison of raw, centroided, 3 pixel FWHM Gaussian reconstruction and circle reconstruction data is shown in Fig. 3.13. The 3 pixel Gaussian reconstruction was used to produce the ion images in this thesis.

The algorithm has proven very effective in measuring the integral steric effect, as it was found that camera noise accumulation prevented accurate measurements.

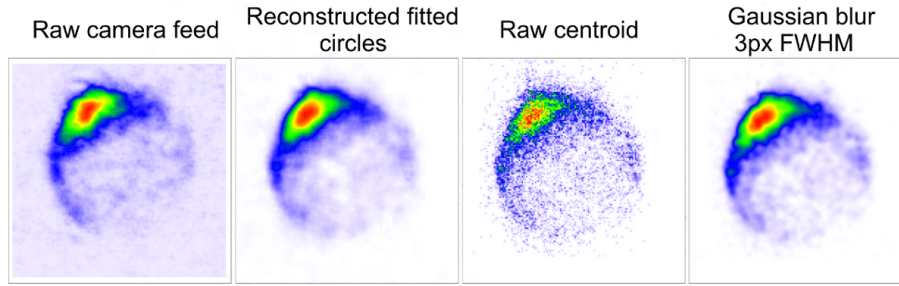


Figure 3.13: A comparison of an image reconstruction using a variety of methods. The raw camera image from the feed, the reconstructed image from the fitted circles to ion hits, the raw centroided and Gaussian blurred centroid images.

The implementation of the centroiding algorithm allows the counting of ions directly and hence integral steric effect measurements gained significantly more accuracy, as described in Chapter 6.

3.5 Data Analysis

The experimental images contain a wealth of dynamical information about the rotational energy transfer that occurred during the collision. The information density increases as more vector correlations are probed simultaneously. The most basic information obtained from the images is the differential cross section, which, as described previously, corresponds to the $\mathbf{k}-\mathbf{k}'$ correlation. These can be naïvely obtained by reading the intensity around the rim of the image and dividing through by the detection efficiency; which, in the limit of a point-sized interaction region, is exactly given by $1/v_{\text{LAB}}$ at each pixel, where v is the NO LAB-frame velocity. A more sophisticated algorithm is used which also takes into account the intensity in the interior of the image and minimises the influence of experimental artefacts and noise. This method is described in more detail below.

By controlling the polarisation of the 226 nm laser, the experiment is able to provide information about the plane and sense of rotation of the NO(X) after collision. These correspond to a $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ correlation and can be used to obtain the polarisation moments given formally by the renormalised PDDCSs, $\rho_{q\pm}^{\{k\}}(\theta)$ [8, 155].

Finally, by initial orientation of the NO(X) bond axis, N-end and O-end collisions can be achieved, giving steric resolution to the collision and providing either the $\mathbf{r}-\mathbf{k}$

correlation in the form of integral steric asymmetries, or the $\mathbf{r}\text{-}\mathbf{k}\text{-}\mathbf{k}'$ correlation in the form of oriented differential cross sections. The ultimate goal would be to combine the polarisation measurements which provide information on the scattered angular momentum vector with bond-axis orientation, allowing for multipoles of the full $\mathbf{r}\text{-}\mathbf{k}\text{-}\mathbf{k}'\text{-}\mathbf{j}'$ correlation to be measured. The four-vector correlation was described by Herschbach and Barnwell [2] in 1983 and resides atop the vector correlation hierarchy, as from it all other vector correlations can be calculated.

3.5.1 Fitting of Angular Distributions

The experimental velocity-mapped ion images obtained from the experiment are convoluted by differences in the detection efficiency of ions with different LAB frame velocities. Although, in principle, the angular distributions depend only on the COM frame differential cross section of the collision system, the detection efficiency must be taken into account in order to extract the experimentally determined angular distribution from the ion images. This flux-density correction is determined by understanding the experimental geometry and speeds of the molecular beams. These values are well known from the characterisation of the beams performed by the microphone and the analysis of the image radii described earlier.

Density-to-Flux Conversion

After the scattering event, molecules are ionised and detected using the (1+1') REMPI scheme covered above in section 3.4. A Newton sphere of ions is formed [156], the surface of which is comprised of ions with the same velocity relative to the centre of mass. The distribution of ions around its surface contains the angular distribution, the detection efficiency and also the information on the polarisation of $\mathbf{j}'$. A point on the Newton sphere is described by the angles θ and ϕ , where θ is parallel to the plane of the detector. In order for the image to be a true representation of the angular distribution of the collision, all of the products must spend an equal amount of time in the detection volume. However, due to the experimental geometry, the finite detection region and the spread of speeds in the molecular beam, molecules with a lower LAB frame velocity

spend longer in the detection volume. These molecules will have a higher detection efficiency which leads to the instrument function, a map of detection efficiency over the Newton sphere. This effect can be observed in the asymmetry of the detected images about the relative velocity vector, $\mathbf{k}$.

In the absence of polarisation effects, the instrument function quantifies the detection probability as a function of pixel and consists of several terms [12]

$$Z_{\text{exp}}(x, y) = \int \int \int \int \int \int \int n_{\text{NO}}(\mathbf{r}_{\text{NO}}, \mathbf{v}_{\text{NO}}, t_{\text{NO}}) n_{\text{Rg}}(\mathbf{r}_{\text{Rg}}, \mathbf{v}_{\text{Rg}}, t_{\text{Rg}}) P_{\text{det}}(\mathbf{r}_{\text{det}}) P_{\text{scatt}}(\theta) d\mathbf{r}_{\text{det}} d\mathbf{r}_{\text{coll}} dt_{\text{coll}} d\mathbf{r}_{\text{NO}} dt_{\text{NO}} d\mathbf{r}_{\text{Rg}} dt_{\text{Rg}} \quad (3.10)$$

The flux-density gives the detection efficiency of the ions on the detector, taking into account the number densities of the molecular beams, n_{NO} and n_{Rg} , which are given as a function of initial position, $\mathbf{r}_x$, velocity, $\mathbf{v}_x$, and starting ionisation time, t_x , where x indicates the identity of the collision partner. P_{det} is the probability of detection of NO, given as a function of $\mathbf{r}_{\text{det}}$ which quantifies how close the NO molecule is to the laser overlap region. P_{scatt} is the distribution of molecules on the surface of the Newton sphere and so is dependent on θ and ϕ . The distribution is independent of ϕ and so only depends on θ when the Newton sphere has been flattened into a 2D representation. This integration is performed numerically using Monte-Carlo techniques [12].

Basis set generation

The integral in Eqn. (3.10) gives the detection efficiency at a single point, (x, y) on the detector. The experimental flux can be separated into two parts: P_{scatt} , which gives the dependence of scattering on θ and the instrument function, $Z(x, y)$, which accounts for the variation in detection efficiency across the Newton sphere, defined in Eqn. (3.10). The experimentally determined angular distribution can be estimated from the ion image simply by dividing through by the instrument function. However, this method is only approximate as it does not include polarisation effects, and can introduce error into the differential cross section (DCS): modelling of the experiment must be perfect

as small inaccuracies can lead to a lack of symmetry in the corrected image. Instead, P_{scatt} can be expanded as a series of Legendre polynomials [12] and the polarisation correction can be included. The intensity at a particular point (x,y) on the detector is given by [20]

$$i_{V/H}(x_n, y_n) = Z(x_n, y_n) P_{\text{scat}}(\theta_n) A_{V/H}(\theta_n; \Gamma_{V/H}^n), \quad (3.11)$$

where $Z(x_n, y_n)$ is the experiment's instrument function, $P_{\text{scat}}(\theta_n)$ is the scattering distribution, which is used to obtain the DCS, and $A_{V/H}(\theta_n; \Gamma_{V/H}^n)$ is the polarisation dependent transition probability. In order to determine the experimental DCS, the contribution from the polarisation dependent transition probability must be taken into account. This is the rotational polarisation correction [122]. Previously, a simple kinematic apse model in which the angular momentum is assumed to be rigorously conserved along the direction defined by the apse vector has been used to perform the alignment correction [53, 84]. A comparison of fitted DCSs using the kinematic apse model alignment correction compared to the quantum alignment correction is presented in Chapter 4.

The equation necessary for performing the alignment correction and which relates the renormalised polarisation dependent differential cross sections (PDDCSs) to the polarisation transition probability is

$$A_{V/H}(\theta_n; \Gamma_{V/H}^n) = 1 + \sum_{kq} \rho_{q\pm}^{\{k\}}(\theta_n) F_{q\pm}^{\{k\}}(\Gamma_{V/H}^n), \quad (3.12)$$

where the $F_{q\pm}^{\{k\}}(\Gamma_{V/H}^n)$ functions represent the geometric information required to convert from the scattering to laser frame in order to calculate the contributions of each $\rho_{q\pm}^{\{k\}}(\theta)$ renormalised PDDCS. The precise values depend upon the polarisation of the excitation laser. By rewriting the renormalised PDDCSs as a series expansion and substituting Eqn. (3.12) into Eqn. (3.11), a key expression for the description of a single scattering event [20] is obtained

$$i_{V/H}(x_n, y_n, \Gamma_{V/H}^n) = P_{\text{scat}}(\theta) Z(x_n, y_n) \left[1 + \sum_{kq} \rho_{q\pm}^{\{k\}}(\theta_n) F_{q\pm}^{\{k\}}(\Gamma_{V/H}^n) \right]. \quad (3.13)$$

In order to obtain the angular distributions from Eqn. (3.13), the scattering probability is expanded as a series of Legendre polynomials

$$P_{\text{scatt}}(\theta) = \sum_l \frac{2l+1}{2} a_l P_l(\cos \theta), \quad (3.14)$$

with a_l representing expansion coefficients of the associated Legendre polynomial $P_l(\cos \theta)$. The experimental image is then fitted using a linear combination of basis functions

$$I(x_n, y_n, \Gamma_{V/H}^n) = \sum_l \frac{2l+1}{2} a_l B_l(x_n, y_n, \Gamma_{V/H}^n), \quad (3.15)$$

where the $B_l(x_n, y_n, \Gamma_{V/H}^n)$ basis functions contain the polarisation correction and instrument function weighted by the scattering probability from the l^{th} Legendre polynomial

$$B_l(x_n, y_n, \Gamma_{V/H}^n) = P_l(\cos \theta) Z(x_n, y_n) A(x_n, y_n, \Gamma_{V/H}^n). \quad (3.16)$$

The $A(x_n, y_n, \Gamma_{V/H}^n)$ terms contain the polarisation information and require knowledge of the $\rho_q^{\{k\}}(\theta)$ renormalised PDDCSs in order to calculate them. The $\rho_q^{\{k\}}(\theta)$ moments can be obtained from several different model calculations. The effect of different models on the extracted angular distributions is discussed in Chapter 4. Running a single trajectory per pixel is not sufficient to account for the fact that many initial conditions can lead to scattering to a particular pixel. In order to converge the basis sets, $n = 250\,000\,000$ individual trajectories were required. Their calculation takes approximately 45 minutes using an Intel i5-3550 CPU.

Fitting using basis sets

The fitting optimisation method employed to evaluate the proper a_l coefficients (see Eqn. (3.15)) that reproduce the experimental image is a genetic algorithm [109]. To decrease the computational load in the image optimisation, the experimental images and basis functions are converted to polar coordinates and written as a sum of their

Fourier moments [122, 157, 158]

$$I(r, \tau) = f_0(r) + 2 \left(\sum_{-m}^0 f_m(r\tau) \sin(m\tau) + \sum_0^m f_m(r\tau) \cos(m\tau) \right), \quad (3.17)$$

with r , the radius from the centre of the image and τ the angle from the centreline.

The Fourier moments themselves are given by [157, 158]

$$f_m^{\text{fit}}(r) = (2 - \delta_{m0}) \int_{r=0}^{2\pi} F(r, \tau) \cos(m\tau) d\tau \quad \text{if } m \geq 0 \quad (3.18)$$

$$f_m^{\text{expr}}(r) = \int_{r=0}^{2\pi} F(r, \tau) \sin(m\tau) d\tau \quad \text{if } m < 0. \quad (3.19)$$

The Fourier moments describe the anisotropy of the image as a function of radius. The larger the number of moments used in the fit, the greater the degree of experimental detail that can be recovered upon inverse transformation. The genetic algorithm optimises the overlap between the experimental and fitted Fourier moments by minimisation of the error function

$$\chi^2 = \frac{1}{2m_{\text{max}} + 1} \sum_{-m_{\text{max}}}^{+m_{\text{max}}} \int \frac{\left(f_m^{\text{expr}}(r, \tau) - \sum_0^l \frac{2l+1}{2} a_l f_m^{l, \text{fit}}(r, \tau) \right)^2}{f_{m=0}(r, \tau)} dr d\tau. \quad (3.20)$$

The genetic algorithm varies the values of a_l until several thousand iterations have been performed and χ^2 converges on a small value. The optimised coefficients are used to expand the basis set images with the weightings that produce the fitted image. The coefficients are then expanded in $P_l(\cos \theta)$ to obtain the fitted angular distribution.

Since the angular distribution is proportional to the DCS, in order to allow comparison with theory, the experimentally determined angular distribution is scaled to the quantum mechanical DCSs by setting the integral cross sections to be equal. This is performed by integration of the experimental angular distribution and multiplication by the QM cross section. In principle, it should be possible to obtain relative integral cross sections. However, this would be challenging due to the continuously changing beam flux, laser power, and other variables making images recorded at different times

have differing flux correction factors and thus would provide a poor measure of the relative cross sections. Other techniques such as LIF are better suited to record the integral cross sections.

3.5.2 Fitting of PDDCSs

The fitting procedure described above can be used to obtain angular distributions from the experimental data with horizontal (H) or vertical (V) polarisation². By taking a normalised difference, $\frac{i_V - i_H}{i_V + i_H}$, the PDDCSs can be obtained [21, 53]. A similar fitting procedure to that used for angular distributions is then undertaken. The PDDCSs are expanded in terms of Legendre polynomials as

$$\rho_{q\pm}^{\{k\}}(\theta) = \sum_0^l c_{q\pm,l}^{\{k\}} P_l(\cos \theta). \quad (3.21)$$

The k, q , dependent expansion coefficients, $c_{q\pm,l}^{\{k\}}$ will be optimised. If one was to rewrite the renormalised PDDCSs as a series expansion and substituting Eqn. (3.21) into Eqn. (3.11) one obtains a key expression for the description of a single scattering event [20]:

$$i_{V/H}(x_n, y_n) = \left[P_{\text{scat}}(\theta_n) Z(x_n, y_n) + \sum_{kq} \sum_{l=0}^{N_{q\pm}^{\{k\}}} c_{q\pm,l}^{\{k\}} a_l P_l(\cos \theta_n) \times F_{q\pm}^{\{k\}}(\Gamma_{V/H}^n, \beta) Z(x_n, y_n) P_{\text{scat}}(\theta_n) \right] \quad (3.22)$$

where a_l are a set of expansion coefficients for the $P_l(\cos \theta_n)$ Legendre functions. By performing n calculations based on a random sampling of many initial conditions, it is possible to obtain a set of basis images from which the experimental image can be

²With modifications discussed in Chapter 5, right or left circular polarised light can also be accounted for.

analysed

$$B_{q\pm}^{\{k\}}(x, y) = \frac{\sum_n g_{q\pm, l}^{\{k\}, V}(x_n, y_n, \Gamma_V^n) - \sum_n g_{q\pm, l}^{\{k\}, H}(x_n, y_n, \Gamma_H^n)}{2P_{\text{scat}}(\theta) \sum_n Z(x_n, y_n) + \sum_{kq} \sum_{l=0}^{N_{q\pm}^{\{k\}}} c_{q\pm, l}^{\{k\}} \left[\sum_n g_{q\pm, l}^{\{k\}, V}(x_n, y_n, \Gamma_H^n) + g_{q\pm, l}^{\{k\}, V}(x_n, y_n, \Gamma_H^n) \right]}. \quad (3.23)$$

The functions $g_{q\pm, l}^{\{k\}}(x_n, y_n)$ are a condensation of the scattering probability and instrument function:

$$g_{q\pm, l}^{\{k\}} = P_l(\cos \theta) F_{q\pm}^{\{k\}}(\Gamma_{H/V}^n) Z(x_n, y_n) P_{\text{scat}}(\theta). \quad (3.24)$$

The normalised difference image is generated from a set of basis function images as

$$\frac{i_V - i_H}{i_V + i_H}(x, y) = \frac{\sum_n i_V(x_n, y_n) - \sum_n i_H(x_n, y_n)}{\sum_n i_V(x_n, y_n) + \sum_n i_H(x_n, y_n)} = \sum_{kq} \sum_l^{N_{q\pm}^{\{k\}}} c_{q\pm, l}^{\{k\}} B_{q\pm, l}^{\{k\}}(x, y). \quad (3.25)$$

Using the coefficients $c_{q\pm, l}^{\{k\}}$ of Eqn. (3.25), a genetic algorithm can be utilised in order to recover the coefficients that accurately reproduce the experimental images. As with the angular distributions, the normalised difference images are fit in Fourier space with optimisation of the error function given in Eqn. (3.20). Once the optimised coefficients are recovered, the renormalised PDDCSs can be obtained by expansion of the coefficients according to Eqn. (3.21).

As was the case with the angular distribution basis set images, the normalised difference basis images were generated by using a Monte-Carlo method with n trajectories in order to sample the experimental conditions. Several hundred million trajectories are required in order to converge the basis images used in fitting, an operation taking approximately 45 minutes with an i5-3550 CPU.

3.5.3 Averaging DCSs and PDDCSs Over E_{coll}

Due to the finite time opening and velocity spreads in the molecular beams, the collision does not have a fixed collision energy, but is averaged over many different collision energies and weighted by the relative velocity. In order to accurately compare theory to experimental results, it is necessary to average over the collision energy spread of the

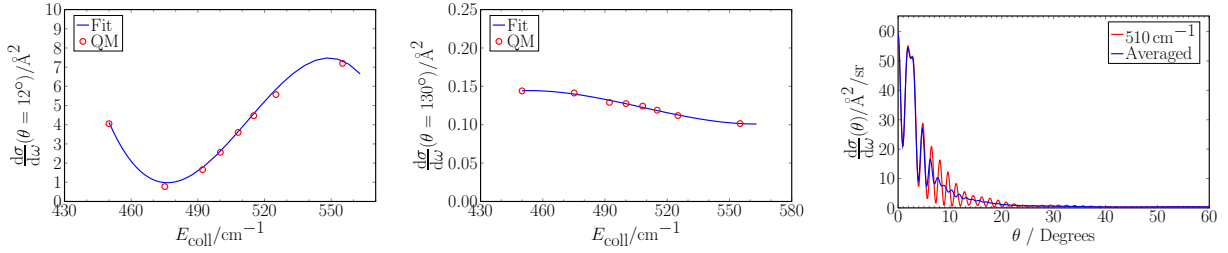


Figure 3.14: Left: the theoretical DCSs at low scattering angle ($\theta = 12^\circ$) are fitted with a polynomial. Middle: The theoretical DCSs at high scattering angle ($\theta = 130^\circ$) are fitted with a polynomial. Right: The DCS at the mean energy compared to the averaged DCS. All plots are for NO(X)–Xe ($\Omega' = 0.5, j' = 4.5e$) at a collision energy of 510 cm^{-1} , the averaged data use the Gaussian weighted energies between 440 cm^{-1} and 555 cm^{-1} .

experiment. The methods for applying this vary depending on the theoretical model. In the classical calculations, the initial collision energy is sampled from a Gaussian approximating the energy spread directly. In the quantum calculations, whose scattering matrix is correct at a single collision energy, it is necessary to run several calculations at differing collision energies and average over the DCSs and PDDCSs with a Gaussian weighting. Such a method can only sample a finite number of points on the curve describing the DCS as a function of collision energy, based on the number of individual scattering matrices calculated.

An improved algorithm was devised in order to interpolate between the calculated points with third order polynomials, allowing the coefficients of the fitted polynomials to give the value of the DCS as a function of collision energy. The procedure is as follows. A number of scattering matrices at different collision energies were calculated and the DCSs and PDDCSs were obtained from each in the manner described in Chapter 2. The DCSs at each scattering angle were then plotted as a function of collision energy as shown in Fig. 3.14 and a third order polynomial was fitted to the data points using SGESL of LAPACK [108] at each scattering angle. A third order polynomial was found to well approximate the form of the energy dependent curves at all scattering angles for the collision energies of the experiment, with a typical error of $R^2 > 0.99$ for the angle dependent fits.

The scattering angle dependent coefficients there obtained were then used to for-

mulate the average DCS by means of

$$\left\langle \frac{d\sigma^{\text{av}}}{d\omega}(\theta) \right\rangle = \sum_{E_{\text{coll}}=E_{\text{coll}}^{\text{min}}}^{E_{\text{coll}}^{\text{max}}} w_{E_{\text{coll}}} \left(c_0(\theta) + c_1(\theta)E_{\text{coll}} + c_2(\theta)E_{\text{coll}}^2 + c_3(\theta)E_{\text{coll}}^3 \right), \quad (3.26)$$

where $E_{\text{coll}}^{\text{min/max}}$ are the minimum and maximum energies of the calculated scattering matrices, E_{coll} is the collision energy of the sample, $c_n(\theta)$ are the cubic coefficients obtained from the fit, and $w_{E_{\text{coll}}}$ is the Gaussian weighting for that collision energy based on the spread of collision energies in the beams determined above. The averaged renormalised PDDCSs were obtained in a similar manner. The renormalised PDDCSs at each collision energy sampled from the quantum calculations were converted to the normalised PDDCSs by multiplying by the DCS. The normalised PDDCSs were then averaged over collision energy as follows

$$\langle n_{q\pm}^{\{k\},(\text{av})} \rangle = \sum_{E_{\text{coll}}=E_{\text{coll}}^{\text{min}}}^{E_{\text{coll}}^{\text{max}}} w_{E_{\text{coll}}} \left(c_0(\theta) + c_1(\theta)E_{\text{coll}} + c_2(\theta)E_{\text{coll}}^2 + c_3(\theta)E_{\text{coll}}^3 \right), \quad (3.27)$$

where the coefficients are this time obtained from a polynomial fit of the normalised PDDCS as a function of collision energy. The resulting normalised PDDCS was then renormalised with the averaged DCS to obtain the averaged renormalised PDDCSs

$$\langle \rho_{q\pm}^{\{k\},(\text{av})}(\theta) \rangle = \frac{\langle n_{q\pm}^{\{k\},(\text{av})}(\theta) \rangle}{\left\langle \frac{d\sigma^{\text{av}}}{d\omega}(\theta) \right\rangle}. \quad (3.28)$$

The resulting curves blur out the fast oscillations at low scattering angle. Unless otherwise stated, the theoretical calculations in this thesis, when compared to the experiment, are averaged in this manner over the spread of collision energies in the molecular beams.

3.5.4 Error Handling

Angular distributions

The error in the DCSs is primarily introduced while determining the flux-density correction. Whilst the experimental parameters that define the flux-density correction have been carefully determined, slight shifts in laser positions or other experimental parameters can have a comparatively large effect on the flux-density correction. To quantify this error, the experimental ion images were fitted using the angular distributions from the far and near side of the relative velocity vector separately to produce two distinct DCSs. The standard deviation of the measurements was then taken using the standard formula. If the instrument function is a perfect representation of the experimental geometry and kinematics, the fitting algorithm will have an exactly even intensity distribution on both sides of the image. The standard deviation of the fast and slow side therefore provides an estimate in the error of the fitting algorithm and the flux-density correction.

PDDCS

Unlike the angular distributions, batches of images are used to calculate the error in the PDDCSs due to the insensitivity to the flux-density correction of the normalised difference images. The PDDCS is reconstructed as described above for a sub-set of the total laser shots and the standard deviation between different images is used to reconstruct the error. The same method used for the angular distributions is no longer sufficient as the normalised difference causes the images to become symmetric about $\mathbf{k}$ so the fast side and slow side are nearly identical for fully converged ion images, barring depolarisation effects.

Integral steric asymmetry

As discussed in Chapter 6, the integral steric asymmetry is calculated from the equation

$$S\% = \frac{\sigma_{\text{NO}} - \sigma_{\text{ON}}}{\sigma_{\text{NO}} + \sigma_{\text{ON}}} \times 100. \quad (3.29)$$

The absolute cross sections of the experimental images could be found by integrating the intensity of the image and then multiplying by an unknown scaling factor. This scaling factor depends on a number of quantities, the flux-densities of the beams, the shot-to-shot laser power and the number of scattered molecules in the interaction region. Practically, these quantities are indeterminable. However, since the image is broken down into a very large number of pixels, the integral of the angular distribution of the image is well approximated by the sum of the intensity of each of its pixels. As the polarity of the orientation rods is changed very frequently during acquisition, the effect of long-term experimental instability should be negligible. Additionally, the N-end and O-end images are formed in the same interaction region and so have identical flux-density components, which implies the flux-density effects in the normalised difference of the images cancel (as does the unknown scaling factor). Equation (3.29) can then be replaced by

$$S\% = \frac{\sum_{xy} I(x, y)_{\text{NO}} - \sum_{xy} I(x, y)_{\text{ON}}}{\sum_{xy} I(x, y)_{\text{NO}} + \sum_{xy} I(x, y)_{\text{ON}}} \times 100, \quad (3.30)$$

which is easily computed by counting the centroided ion hits. The polarity of the rods is altered every 25 s in order to change the orientation of the NO(X) bond, and diminish the effects of experimental instability. Each individual image is made up of a batch of 20 000 individual laser shots, which is then concatenated to obtain the whole experimental dataset of around 300 000 laser shots. The steric asymmetry of each batch of images making up the total image is then calculated, and the mean and standard deviation obtained is reported as the value for the steric asymmetry and its error for a particular rotational state.

3.6 Summary

In this chapter, the experimental apparatus that was used to record the observations in this thesis has been described in detail, along with the data analysis methods used to create and analyse the images. Modifications to the apparatus were made to enhance resolution, and maximise scattered signal and reproducibility. The newly installed molecular beams and time-of-flight tube were characterised to obtain pixel-to-velocity

ratios and collision energies for all the systems probed in this thesis.

The apparatus itself consists of three distinct geometries, capable of recording different vector correlations in the NO(X)–Rg systems. The alignment geometry can probe the collision-induced alignment embodied in the $\rho_0^{\{2\}}$, $\rho_{1+}^{\{2\}}$ and $\rho_{2+}^{\{2\}}$ polarisation moments, and examples for the strongly attractive NO(X)–Xe system will be presented in Chapter 4. The orientation geometry allows probing of the collision-induced orientation and was used to probe the $\rho_{1-}^{\{1\}}$ polarisation moment in the NO(X)–Kr collision system, as described in Chapter 5. The steric geometry allows probing of the steric effect. The integral steric asymmetry was recorded for a number of collision systems and is presented in Chapter 6.

Scattering of NO(X) with Xe

In this chapter, the scattering of NO(X) with Xe is investigated, and the differential cross sections (DCSs) and polarisation dependent differential cross sections (PDDCSs) obtained from both experiment and theory are presented. The scattering of NO(X) with Xe has received comparatively little attention compared to the other rare gases. The DCSs for certain rotationally excited states were calculated by Klos *et al.* although these had not yet been confirmed by experiment [62], a differential cross section in the forward scattered region has also been presented by Onvlee *et al.* [82] The NO(X)–Xe potential is characterised by a relatively deep attractive well of around 141.7 cm^{-1} facilitated by the polarisability of the xenon atom ($27a_0^3$). The extent of the attractive lobe of the potential energy surface of xenon (141.7 cm^{-1}) is also larger than that of krypton (139.3 cm^{-1}) or argon (115.98 cm^{-1}), as a result of the increased polarisability.

Analysis of the experimental ion images recorded with the hexapole apparatus in the alignment geometry described in Chapter 3 allow the two-vector $\mathbf{k}-\mathbf{k}'$ and three vector $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ correlations to be probed. Since the transition dipole moment, $\boldsymbol{\mu}$, of the NO(X) lies in a well defined direction with respect to the angular momentum vector of the diatomic NO(X), the polarisation of the laser light used to ionise the NO(X) is important and must be accounted for in analysing the data. The laser polarisation can

also be actively controlled, allowing it to be used as a probe of the collision-induced alignment of the scattered NO(X), a multipole of the $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ correlation. When the two-vector $\mathbf{k}-\mathbf{k}'$ correlation is measured, it is necessary to correct the observed ion image for the polarisation of the laser. Often, a classical kinematic apse model [64, 159] is used to correct the experimental ion images for the polarisation of the laser. In order to obtain the best fit to the data, it can be shown that in circumstances where the kinematic apse model appears to be inadequate, it is desirable to use the more rigorous close-coupled quantum mechanical (CC QM) calculations to correct for the laser polarisation.

By virtue of changing the laser polarisation on a shot-by-shot basis, not only can the DCSs be obtained, but PDDCS measurements can also be made. The data presented in this chapter represent the first experimental measurements of the $\rho_0^{\{2\}}(\theta)$ and $\rho_{2+}^{\{2\}}(\theta)$ renormalised PDDCSs which describe the alignment of the angular momentum vector of NO(X) after interaction with a large polarisable xenon atom. The measurements taken span the entire energy accessible range of product rotational states at a collision energy of 519 cm^{-1} (63 meV). Collision-induced alignment (CIA) effects have been probed for a select number of states, and renormalised PDDCSs were obtained by means of a Fourier fitting routine described in Chapter 3. Previous studies of the lighter rare gas collision systems have uncovered the classical and quantum mechanical hard-shell origins of the collision-induced alignment [19, 20, 84, 103, 143], a theme that will be continued in this chapter.

Many of the approximations used in the modelling of the collision-induced alignment make use of impulsive models [19, 64, 160], in which there is no attractive potential present at all. By using the alignment experimental geometry, described in Chapter 3, the experiment is able to probe CIA effects in a regime where these simple impulsive models may no longer be adequate. By making use of a newly developed quantum mechanical hard shell (QMHS) model [63], quassi-classical trajectory (QCT) calculations, and exact CC QM calculations, the effects caused solely by impulsive collisions and those caused by long range interactions that primarily sample only the attractive part of the intermolecular surface are able to be identified. The effect of the attractive forces,

which are most pronounced in the $NO(X)$ – Xe collision system, can not be reproduced by impulsive models.

4.1 Kinematic Apse Model

For an excitation from an initial state $|i\rangle$ to a final state $|f\rangle$ using linearly polarised light, the absorption probability of the photon depends on the cosine of the angle between the electric vector of the light, ϵ , and the molecular transition dipole moment, μ . Since the angular momentum vector $\mathbf{j}$ lies in a well defined direction with respect to μ , if the molecule undergoes collision-induced alignment, the angular momentum vector and hence transition dipole moment will have a non uniform distribution with scattering angle. Thus, the transition probability of absorption will be scattering angle dependent. In order to correct for the modified absorption probability, a kinematic apse model, or a fully CC QM model can be used to obtain PDDCSs which describe the scattering angle dependent rotational alignment. The PDDCSs can therefore be used to correct the ion images for the collision-induced polarisation effect, allowing DCSs to be obtained. An additional important experimental consideration is the spectroscopic branch used to excite the $NO(X)$ to $NO(A)$, as the branch determines the direction which μ lies with respect to $\mathbf{j}'$. For the Q branch, the direction of $\mathbf{j}'$ is parallel to μ , and for the P or R branches, it is perpendicular. Figure 4.14 shows the interaction of the light with the dipole moment, a table of the possible excitation branches for each of the spectroscopic transitions is shown in table 3.2 in Chapter 3. The pure branch transitions were preferred for the images recorded in this chapter, in order to simplify the image analysis.

Classically, the projection of the angular momentum, m_j , onto the kinematic apse direction can be shown to be rigorously conserved during an impulsive collision [64,161]. As the $NO(X)$ molecule is initially in its lowest rotational state, $j = 0.5$, the projection of $\mathbf{j}$ onto $\mathbf{a}$ will equal 0.5 throughout the collision, and so the magnetic quantum numbers will be given by $m_j^a = m_{j'}^a = \pm 0.5$ with the kinematic apse as the quantisation axis. Therefore, if $j' > 0.5$ after the collision, $\mathbf{j}'$ must lie perpendicular to the kinematic apse.

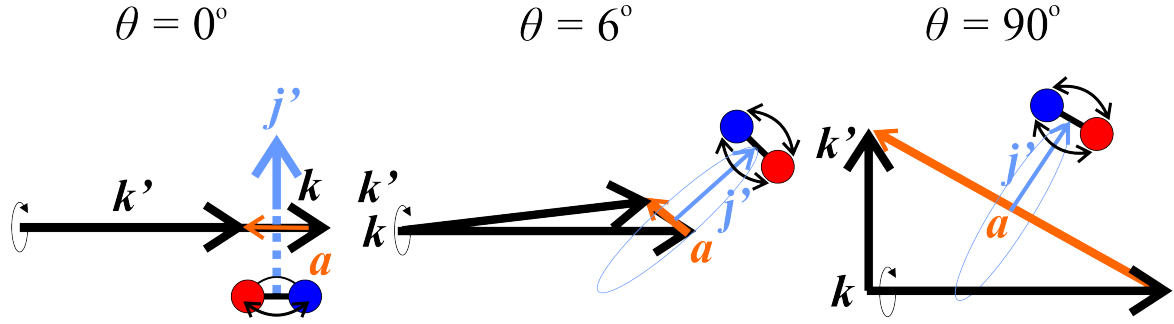


Figure 4.1: Cartoon of the direction of the angular momentum vector as a function of scattering angle in the kinematic apse model. The cartoon is cylindrically symmetric about the vector $\mathbf{k}$. The NO(X) molecule at zero scattering angle is constrained to rotate as a frisbee (left). As the scattering angle increases slightly, the apse angle, $\beta(\theta)$ between $\mathbf{a}$ and $\mathbf{k}$, rapidly changes and the NO(X) rotates in an approximately propeller type motion (middle). At higher scattering angles, the NO(X) rotates as a frisbee again (right). The degree of in plane rotation is largely defined by the difference in magnitude between $\mathbf{k}$ and $\mathbf{k}'$ which is governed by the collision energy and the degree of rotational excitation, j' .

The kinematic apse model has been successful at producing an alignment correction to the experimental ion images of NO(X) scattering with small rare gases such as He and Ne, and it has also been applied to Ar. In the kinematic apse model (described pictorially in Fig. 4.1), the kinematic apse, usually denoted $\hat{\mathbf{a}}$, lies in the scattering plane and is defined by

$$\hat{\mathbf{a}} = \frac{\mathbf{k} - \mathbf{k}'}{|\mathbf{k} - \mathbf{k}'|}. \quad (4.1)$$

The core assumption of the kinematic apse model is that the projection, m_a , of $\mathbf{j}$ onto the apse direction, $\hat{\mathbf{a}}$, is conserved during the collision, leading to the projections as shown in Fig. 4.1. Although collisions of NO(X) with Xe are not strictly hard-shell as prescribed by the kinematic apse model, the model is surprisingly good at predicting the collision-induced rotational alignment of the NO(X) when compared to rigorous CC QM calculations, as shown in Fig. 4.19 and Fig. 4.20. The reason for this is that the plane of rotation is primarily governed by the repulsive interactions and is only mildly perturbed by the attractive part of the potential.

The renormalised PDDCSs determined from the kinematic apse model can be obtained from considering the geometry of the scattering system, as described by Hornung [103]. The kinematic apse model renormalised PDDCSs for a molecule initially in the $j = 0.5$ rotational state are given in terms of the reduced rotation matrices [57]

as [20, 162, 163]

$$\rho_{q\pm}^{\{k\}}(\theta) = \begin{cases} \frac{1}{2}[1 + (-1)^k]d_{0q}^k(-\beta(\theta))\langle j'\frac{1}{2}, k0 | j'\frac{1}{2} \rangle & \text{if } q = 0 \\ (-1)^q \frac{\sqrt{2}}{2}[1 + (-1)^k]d_{0q}^k(-\beta(\theta))\langle j'\frac{1}{2}, k0 | j'\frac{1}{2} \rangle & \text{if } q > 0 \end{cases} \quad (4.2)$$

where $\langle j'\frac{1}{2}, k0 | j'\frac{1}{2} \rangle$ is a Clebsch–Gordan coefficient and $d_{0q}^k(\beta(\theta))$ is the reduced rotation matrix [57]. The apse angle, $\beta(\theta)$, between $\mathbf{k}$ and $\hat{\mathbf{a}}$ in the reduced rotation matrix is determined from a set of geometric transforms as shown in Fig. 5.2 of [103]

$$\cos \beta(\theta) = \frac{D - \cos \theta}{\sqrt{D^2 + 1 - 2D \cos \theta}}, \quad (4.3)$$

with $D = (E_{\text{coll}} - \Delta E_{\text{rot}}(j' - j))/E_{\text{coll}}$.

As can be seen from Fig. 4.1, the kinematic apse model predicts frisbee like rotation at very low scattering angle ($\theta \lesssim 5^\circ$) where $\mathbf{k}$ and $\mathbf{k}'$ are almost parallel. If the collision results in scattering of only a few degrees ($5^\circ \lesssim \theta \lesssim 10^\circ$), the apse direction is almost perpendicular to $\mathbf{k}$ and the NO(X) rotates in a propeller like motion (middle panel Fig. 4.1) which, after averaging over the azimuthal angle, results in $\mathbf{j}'$ polarisation in the plane of the molecular beams. This accounts for the rapid rise of $\rho_0^{\{2\}}(\theta)$ in the low scattering angle region. In the sideways to backwards direction, the apse vector $\hat{\mathbf{a}}$ begins to be more parallel to $\mathbf{k}$ again, resulting in more frisbee like rotation.

Given the limitations of the apse model, such as the classical impulsive formulation, one might expect more rigorous models to provide better predictions of the $\rho_0^{\{2\}}(\theta)$ and $\rho_{2+}^{\{2\}}(\theta)$ renormalised PDDCSs and hence that of the alignment correction. The close-coupled quantum mechanical (CC QM) DCSs have been very successful in describing the angular distributions obtained experimentally, and one might expect that the quantum mechanical PDDCSs would describe the polarisation correction of the velocity mapped ion images more precisely. Quantum mechanically, the angular momentum along the apse is not rigorously conserved, but has a propensity to be conserved. This is especially true at low scattering angle where the assumptions that underpin the kinematic apse model – that the interaction is sudden and point-like, are less valid.

The pixel dependent alignment correction to the obtained ion images depends on the value of the renormalised PDDCSs, which can be obtained from the kinematic apse model as described earlier by means of geometric transformations. They can also be obtained from exact CC QM calculations by methods also described in Chapter 2. For horizontally and vertically polarised light, the state dependent transition probability is given in terms of the $\rho_{q+}^{\{2\}}(\theta)$ real renormalised PDDCSs

$$A(x, y, \Gamma_{H/V}, \beta) = 1 + \sum_q F_q^{\{2\}}(\Gamma_{V/H}, \beta) \rho_q^{\{2\}}(\theta), \quad (4.4)$$

where $\Gamma_{V/H}$ is a quantity depending on the angles relating the scattering frame to the detector frame and β is the laser polarisation angle, 0 or 90° for horizontal and vertically polarised light respectively. The factors $F_q^{\{2\}}(\Gamma_{V/H})$ depend on the geometry of the experiment and the linestrength factors and are given by [20, 84, 103]

$$F_0^{\{2\}}(\Gamma_{H/V}, \beta) = \frac{1}{4} h^{(2)}(j, j') c_2(j) [3 \sin^2 \Theta \cos 2\chi \cos 2\beta - (3 \cos^2 \Theta - 1)] \quad (4.5a)$$

$$F_{1+}^{\{2\}}(\Gamma_{H/V}, \beta) = \frac{\sqrt{3}}{4} h^{(2)}(j, j') c_2(j) [2 \sin \Theta \cos \Phi \sin 2\chi + 2(\sin \Theta \cos \Theta \sin \Phi \cos 2\chi - \sin 2\Theta \cos \Phi) \cos 2\beta] \quad (4.5b)$$

$$F_{2+}^{\{2\}}(\Gamma_{H/V}, \beta) = \frac{\sqrt{3}}{4} h^{(2)}(j, j') c_2(j) \{[(1 + \cos^2 \Theta) \cos 2\Phi \cos 2\chi - 2 \cos \Theta \sin 2\Phi \sin 2\chi] \cos 2\beta - \sin^2 \Theta \cos 2\Phi\}, \quad (4.5c)$$

where the linestrength factor is given by $h^{(2)}(j, j')$ obtained from [117] and the $c_2(j)$ factors are conversion factors between polarisation parameters and renormalised PDDCSs¹. The Θ and Φ angles are identical, as the geometry of the laser propagation axis do not change, however the angle χ depends on the polarisation of the laser. The angle β is effectively constant.

By substituting the calculated values of the renormalised PDDCSs from the CC QM and kinematic apse models into Eqn. (4.1), the correction factor as a function of scattering angle (θ) and polar angle (ϕ) was calculated and applied to the basis sets used to fit the ion images (as described in Chapter 3).

¹The explicit value of the conversion factor is $c_2(j') = \{(2j' + 3)(2j' - 1)/[j'(j' + 1)]\}^{0.5}$

4.2 Differential Cross Sections

Experimental ion images have been recorded for almost the entire energetically accessible range of $|j', \Omega', \varepsilon'\rangle$ states. The experimental images recorded span from $j' = 2.5$ to $j' = 15.5$ for spin-orbit conserving collisions and from $j' = 1.5$ to $j' = 11.5$ for spin-orbit changing collisions. The experimentally determined ion images were then fitted in the manner described in Chapter 3. The complete set of velocity mapped ion images were fit using the alignment correction calculated using the renormalised PDDCSs from the kinematic apse model. The fitting was then repeated using the CC QM renormalised PDDCSs for the alignment correction.

Due to the non-strict constraint on the angular momentum quantum mechanically, subtle differences in the fitted DCSs appear in the fits. The relative differences in the obtained DCSs are small, however, at low scattering angle the difference can be somewhat more apparent. Since the extent of the xenon potential is large and the attractive well is deep compared to argon, and slightly deeper than krypton, it is desirable that the forward scattered section of the image is fitted correctly and not unduly influenced by the perturbations resulting from deficiencies in the kinematic apse model alignment correction in the forward scattered direction.

The experimental ion images contain distinct features such as ℓ -type rainbows and parity dependent oscillations. The CC QM performed with the HIBRIDON suite of codes [97] are shown to be in good agreement across the full range of final rotational states.

4.2.1 Spin-Orbit Conserving Collisions

The experimental ion images obtained from the hexapole apparatus (described in detail in Chapter 3) when the excitation laser is tuned to excite rotational states with $\Omega = 0.5$ are shown in Fig. 4.2 and Fig. 4.4. The white arrow in the top right image shows the direction of the relative velocity vector, $\mathbf{k}$. The images shown were recorded with either horizontal or vertical polarisation and integrated over approximately 200 000 laser shots to ensure convergence to allow the relative intensity with horizontal and

vertical polarisation to be determined. The images show the characteristic features of the inelastic scattering process. The images decrease in radius with increasing rotational excitation resulting in lower COM frame recoil velocities. The images then become more backward scattered as the energetic limit of rotational excitation is approached. The radius of the Newton sphere in pixels is given by the outgoing NO velocity multiplied by an instrument specific pixel-to-velocity ratio, determined as in Chapter 3 such

$$r_{\text{img}} = |v_{\text{NO}}| \times \text{PIXTOV} = \frac{m_{\text{Rg}}}{m_{\text{NO}}m_{\text{Rg}}} \sqrt{\frac{2(E_{\text{coll}} - \Delta E_{\text{rot}}(j' - j))}{\mu}} \times \text{PIXTOV}. \quad (4.6)$$

$\Delta E_{\text{rot}}(j' - j)$ is the change in rotation energy due to the collision, which is calculated by applying Eqn. (2.4) from Chapter 2.

The images are also clearly asymmetric about the relative velocity vector. This is due to the flux-density effects introduced in Chapter 3. Because the xenon is comparatively polarisable, the attractive limb of the potential energy surface is quite large, extending to approximately 7 Å. This leads to a large degree of forward scattering in the observed images [62], which persists to high rotational excitation. Forward scattering is so prevalent as glancing blow collisions can impart significantly more torque at long range due to the spatial extent and well depth of the attractive part of the potential being much larger in $\text{NO}(X)\text{--Xe}$ than for smaller rare gases, such as neon [84].

The observed DCSs obtained from fitting the experimental horizontally and vertically polarised ion images with the algorithm described in Chapter 3, broadly agree with the CC QM DCSs obtained from the RCCSD(T) *ab initio* PESs. The QM calculations were performed with the HIBRIDON [97] suite of codes with $J_{\text{max}} = 310.5$ and all rotational states up to and including $j' = 21.5$ included in the basis set. The CC QM DCSs were calculated over a grid of collision energies and weighted by using a Gaussian weighting function in order to approximate the collision energy spread in the beams, as described in Chapter 3. The mean collision energy used was 519 cm^{-1} with a collision energy spread at FWHM of 50 cm^{-1} sampled at 1 cm^{-1} . After weighting and averaging over the collision energy, the diffraction oscillations at low scattering angles are diminished, but still visible in the resultant DCSs. They are typically dominated

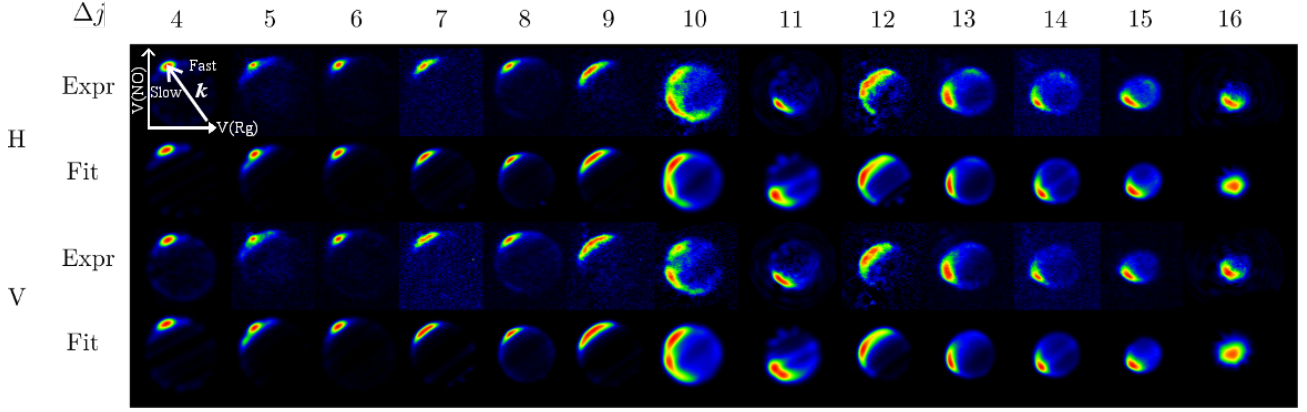


Figure 4.2: Experimental and fitted ion images recorded on the spin-orbit conserving manifold of the $NO(X)+Xe$ collision system. The images shown are those in a final $\epsilon' = f$ state on the spin-orbit conserving manifold, fitted for horizontal and vertically polarised light using the quantum mechanical polarisation correction.

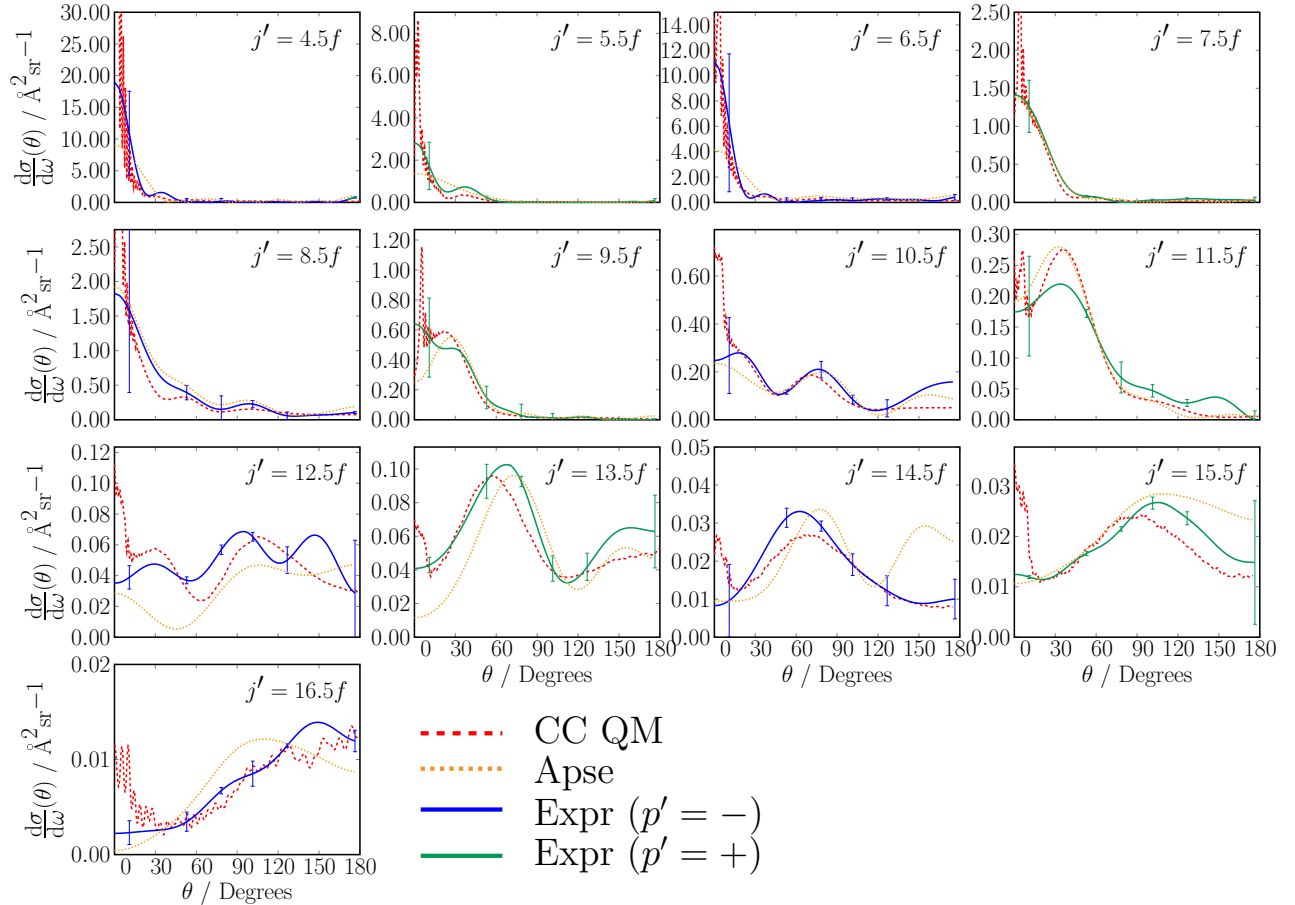


Figure 4.3: DCSs obtained from fitting the ion images in Fig. 4.2. The DCSs shown are those satisfying $|j = 0.5, \Omega = 0.5, \epsilon = f\rangle \rightarrow |j', \Omega' = 0.5, \epsilon = f\rangle$. The CC QM predicted DCS (red dashed) is compared to the experimental parity conserving (blue solid) or parity changing (green solid) DCS obtained by using a quantum mechanical polarisation correction. The DCSs were also fitted with the classical impulsive polarisation correction (orange dotted) for comparison.

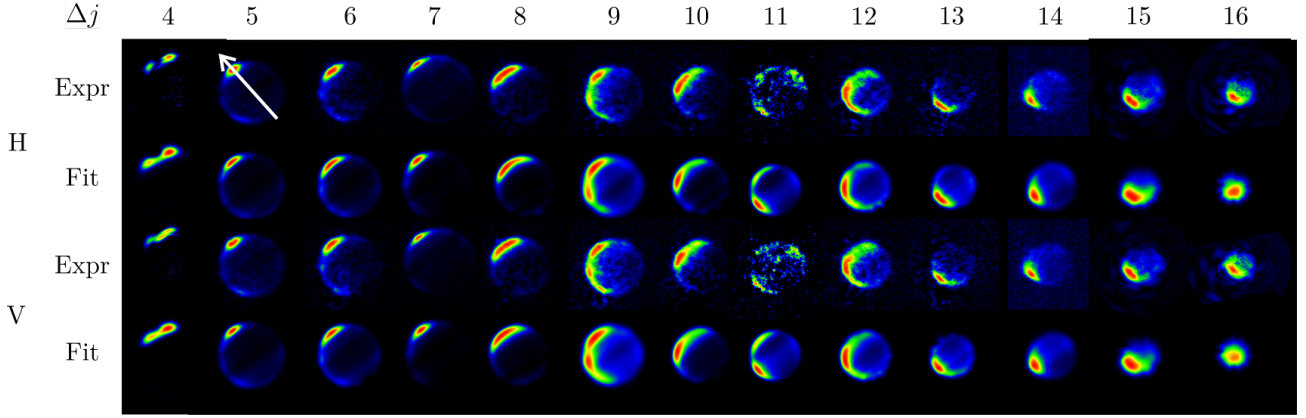


Figure 4.4: Experimental and fitted ion images recorded on the spin-orbit conserving manifold of the $NO(X)+Xe$ collision system. The images shown are those in a final $\epsilon' = e$ state on the on the spin-orbit conserving manifold, fitted for horizontal and vertically polarised light using the quantum mechanical polarisation correction.

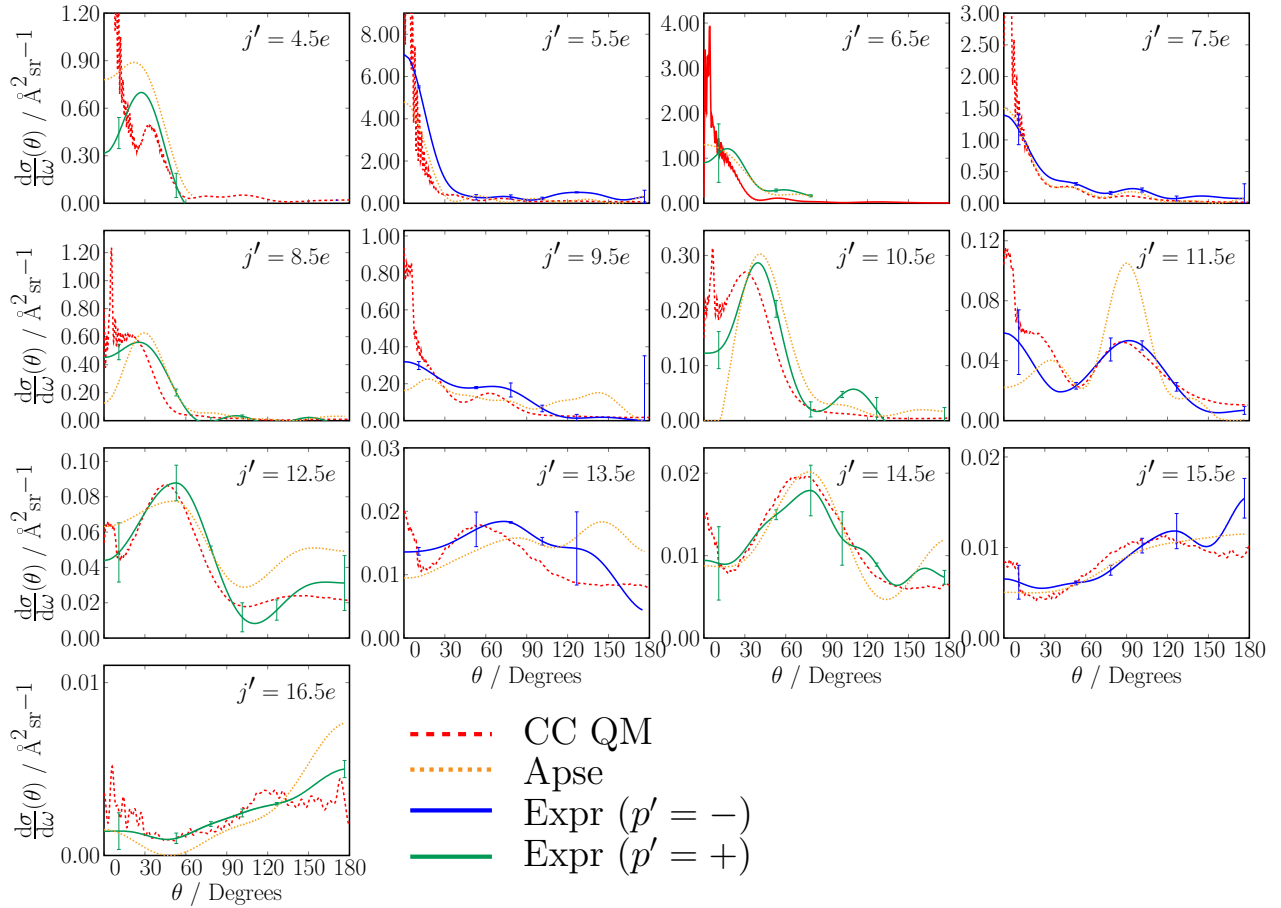


Figure 4.5: DCSs obtained from fitting the ion images in Fig. 4.4. The DCSs shown are those satisfying $|j = 0.5, \Omega = 0.5, \epsilon = f\rangle \rightarrow |j', \Omega' = 0.5, \epsilon = e\rangle$. The DCSs predicted by CC QM calculations (red dashed) are compared to the experimentally determined parity conserving (blue solid) or parity changing (green solid) DCS obtained by a quantum polarisation correction. A classical impulsive polarisation correction (orange dotted) is also shown for comparison.

by one peak, which will be described further in Chapter 7. The angular resolution of the experiment is not high enough to observe this feature in the experimental DCSs.

ℓ -Type Rainbow

One striking feature in the images shown in Fig. 4.2 and Fig. 4.4 are the pronounced peaks referred to as ℓ -type rainbows [19, 62, 82, 86, 164, 165]. These peaks are visible in the parity changing low j' states, for example at $\theta = 30^\circ$ for $j' = 5.5f$ in Fig. 4.3 or at $\theta = 30^\circ$ for the $j' = 4.5e$ state in Fig. 4.5. Here, ℓ is the magnitude of the orbital angular momentum of the NO-Xe pair. Low- ℓ collisions are head-on, while high- ℓ collisions are glancing encounters [19, 84]. An ℓ -type rainbow arises from attractive forces between the NO and Xe and, as in atom-atom scattering [164], can be attributed to the focussing of trajectories at scattering angles at the minimum of the classical deflection function. As Xe has a larger attractive limb than the $\text{NO}(\text{X})\text{-Kr}$ potential, higher rotational states display an ℓ -type rainbow, allowing it to be seen up to $j' = 5.5f$ [62]. As was the case with Kr , the rainbow in $\text{NO}(\text{X})\text{-Xe}$ scattering arises from trajectories scattering at $\approx 5 \text{ \AA}$, a distance corresponding to the outermost attractive limb of the $\text{NO}(\text{X})\text{-Xe}$ potential. This classical picture does not contain parity and results in the prediction of an ℓ -type rainbow for all low Δj ($= j' - j$) states. As the experimental data shows, the rainbow can only be observed in parity changing collisions.

The classical deflection functions shown in Fig. 4.6 show that for the xenon system, the glory impact parameter, at which the attractive and repulsive forces acting balance and result in scattering at 0° , is at approximately $4.6 \text{ \AA}$. Above this, the deflection angle is negative leading to far-side scattering. At impact parameters bigger than the glory impact parameter, trajectories primarily sample the outermost attractive limb of the potential. The rainbow angle and the form of the rainbows in xenon and krypton have been noted to be quite similar [62], a reflection of the similar well depths and the importance of the attractive part of the potential in both systems.

As can be seen from the deflection functions, the rainbow diminishes as Δj increases, the main reason for this is that the potential anisotropy becomes increasingly averaged as Δj increases [62] and the effect of the attractive well is diminished until no such

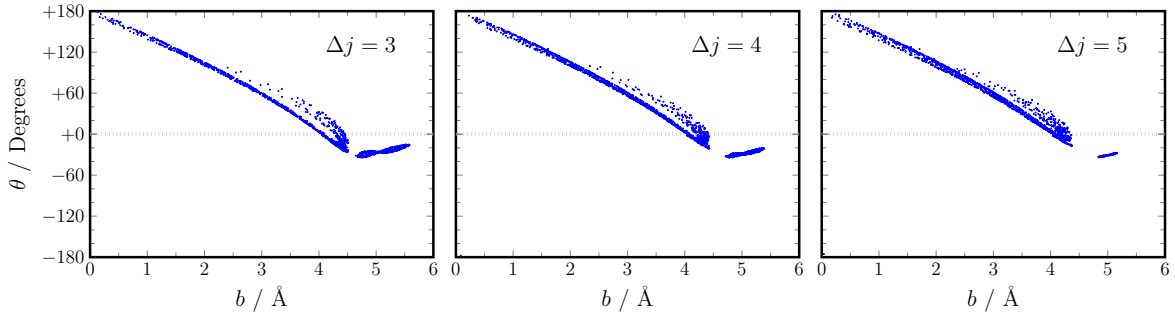


Figure 4.6: Classical deflection functions calculated on the V_{sum} potential surface. The ℓ -type rainbow feature is clearly shown as the minimum in the deflection function corresponding to far-side scattering at or around the rainbow angle, $\theta_r \approx 28^\circ$.

features are obvious. The other contrasting effect is that as rotational state increases, low scattering angle collisions can no longer classically deliver enough torque to reach high rotational states, causing the classically forbidden region to reduce to lower impact parameter.

It has previously been observed for krypton scattering with $\text{NO}(X)$ that parity also plays a significant role in the appearance of the ℓ -type rainbow. As in krypton scattering with $\text{NO}(X)$, the ℓ -type rainbow appears predominantly in parity changing collisions in the full QM calculations, an effect not reflected in the QCT calculations due to its closed shell and classical formulation.

Parity Effects

Due to the quantum mechanical nature of the collision, the classical picture of a trajectory sampling the potential is no longer appropriate. Individual partial waves can interfere with one another leading to constructive or destructive interference as a function of the scattering angle. Interference from scattering from the N-end and O-end can influence the observed differential, and hence integral cross sections [109]. Previous work has shown that a simple four-path model can qualitatively reproduce the interference pattern observed from scattering from four limiting Jacobi angles corresponding to head on or side on collisions [12, 84]. Within the model, the parity

conserving and the parity changing scattering amplitudes are given as,

$$f_{i \leftarrow f}^{\text{cons}}(\theta) = 2 + \exp(-i\Delta\phi_N) + \exp(-i\Delta\phi_O), \quad (4.7)$$

$$f_{i \leftarrow f}^{\text{chan}}(\theta) = \exp(-i(\Delta\phi_N - \pi)) + \exp(-i\Delta\phi_O), \quad (4.8)$$

with the phase shifts of the N-end and O-end of the molecules, $\Delta\phi_{N/O}$ given in logarithmic form² by

$$\Delta\phi_{N/O} = \sqrt{\Delta j_{\theta,N/O}^2 - j'^2} - j' \left[\frac{\pi}{2} + i \ln \left(\sqrt{1 - \frac{j'^2}{\Delta j_{\theta,N/O}^2}} + \frac{ij'^2}{\Delta j_{\theta,N/O}} \right) \right]. \quad (4.9)$$

Here, the values of $\Delta j_{\theta,N/O}$ are the scattering angle dependent functions³

$$\Delta j_{\theta,N/O} = -\frac{i}{2} \Delta j_{\text{max},N/O} \left[\exp\left(+\frac{i}{2}\theta\right) - \exp\left(-\frac{i}{2}\theta\right) \right]. \quad (4.10)$$

The maximum allowed change of the angular momentum, $\Delta j_{\text{max},N/O}$ is related to the wavevector by $\Delta j_{\text{max},N/O} = 2k(A_{N/O} - B_{N/O})$ where $A_{N/O}$ and $B_{N/O}$ are the semi-axes obtained from the hard-shell contour of the V_{sum} potential surface. The values of A and B for xenon are 4.3×10^{-11} m and 5.7×10^{-11} m respectively. The use of the logarithmic and exponential forms of the trigonometric functions above allows the evaluation of the equations across the full angular range, including the classically forbidden region.

Inspection of Fig. 4.7 shows that the 4-path model can qualitatively match the number of oscillations in the DCS and the approximate positions. The parity-conserving transition (Fig. 4.7, top panel) are characterised by multiple peaks, caused by interference between the different sides and the ends of the NO(X), whereas the parity changing transitions have a single peak caused by interference between the two ends of the NO(X) and not the sides [12]. The four possible paths are shown in Fig. 4.8.

The frequency and number of oscillations is governed by two factors, the anisotropy of the potential encoded in the difference of the A and B semi-axes and the de Broglie wavelength of the system. The Xe system has the smallest de Broglie wavelength of

²The identity $\arccos \theta = -i \ln(\theta + \sqrt{\theta^2 - 1})$ is made use of.

³The $\sin$ function was converted to exponential form using the identity $\sin \theta = \frac{i}{2} (\exp(i\theta) - \exp(-i\theta))$.

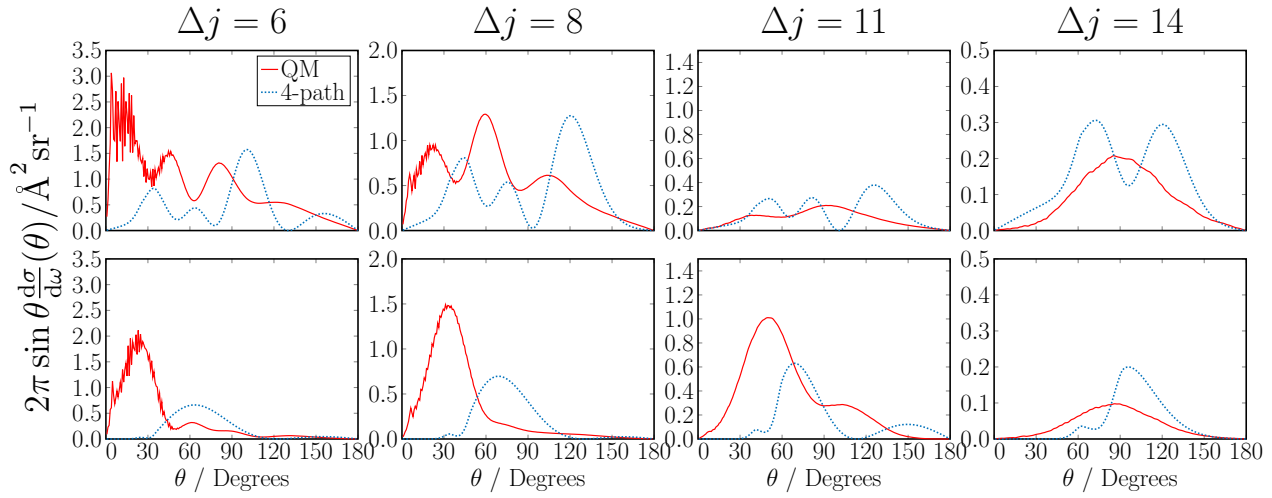


Figure 4.7: 4-Path (light blue) and QM (red) calculations for the $NO(X)$ – Xe collision system at 63 meV. The top panel shows parity conserving transitions and the bottom panel parity changing transitions.

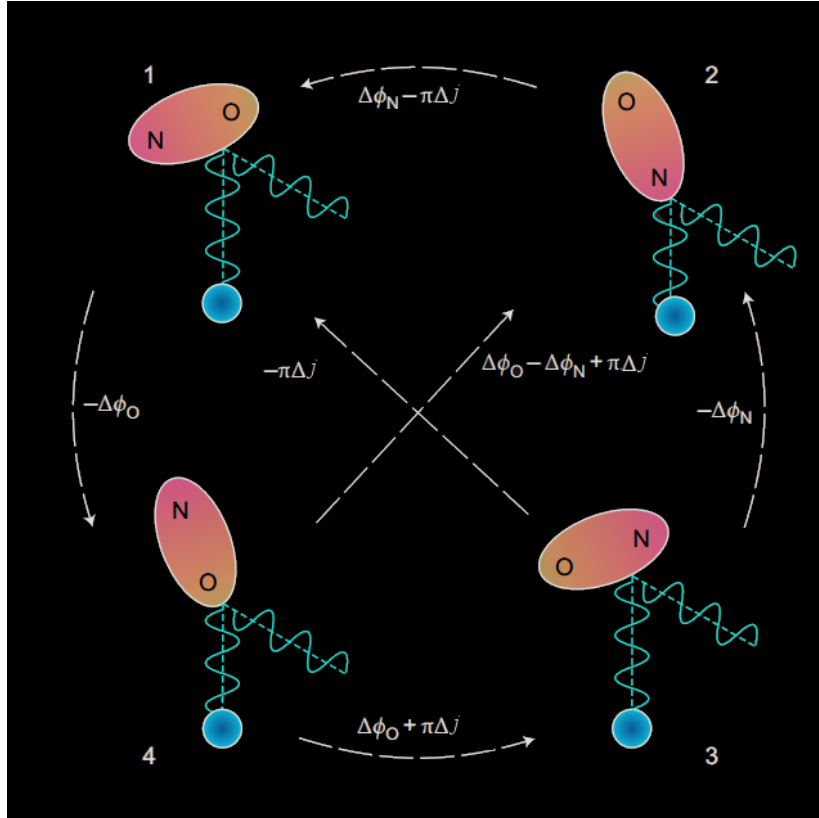


Figure 4.8: Figure showing the four limiting paths leading to parity-dependent interference. The four paths are the two sides and the N-end and O-end. Interference between collisions sampling these paths leads to the interference. Image adapted from reference [12].

any of the rare gases for a given collision energy, leading to multiple peaks in the DCSs from the 4-path model. The simple 4-path model is a good indicator of which peaks are due to parity-dependent oscillations. The 4-path model also shows that they arise from interference between trajectories sampling multiple bond axes orientations of the NO(X).

Another parity related phenomenon is the so-called parity pair effect [91, 109, 137], where the DCS for a $j' = n + 0.5f$ state is similar to the DCS of a $j' = n - 0.5e$ state (with n an integer), but with a slightly different magnitude. This effect can be seen across the experimental images in Fig. 4.2 and Fig. 4.4. Parity pairs can be rationalised by direct scattering [12], where the potential matrix elements coupling the initial and final states are given by

$$\langle V_{l0} \rangle \propto \frac{1}{2} [1\epsilon\epsilon'(-1)^{\Delta j+l}] \begin{pmatrix} j' & l & j \\ -\Omega & 0 & \Omega \end{pmatrix} \begin{pmatrix} \ell' & l & \ell \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} j & \ell & J \\ \ell' & j' & \ell \end{matrix} \right\}. \quad (4.11)$$

Here, the $(\dots)$ are the 3- j symbols [57], and $\{\dots\}$ are the 6- j symbols [57]. The equation above holds in the limit of Hund's case (a) and so works best for low rotational states. Higher states are best described as being accessed by tiers of virtual transitions [75], as there is a mixing between Hund's case (a) and Hund's case (b). Since the parity pairs are coupled by the same matrix elements, the resulting DCSs will be quite similar. In the case of parity changing collisions, both odd and even matrix elements are required to effect the transition so if the odd terms in the potential are zero, these transitions disappear. In a homonuclear molecule, as the odd terms in the potential are zero, parity changing collisions do not exist.

Compared to inelastic scattering of NO(X) by the lighter rare gases, the parity pair behaviour is somewhat less apparent in the case of Xe. In collisions resulting in higher j' , there is some evidence of parity pairs but the effect is diminished compared to that in Ar and Ne scattering [84]. As the extent of the xenon surface is larger than that of the lighter rare gases, and as the scattering takes place over a greater period of time and samples more parts of the potential, there is less direct scattering. Since the effect of direct scattering is reduced, the collision takes place *via* tiers of virtual states [91].

More terms in the interaction potential are involved in coupling between each initial and final state resulting in Eqn. (4.11) becoming less valid. The similarity of the DCSs within a given parity pair is therefore diminished, but still evident. Other parity effects also still remain evident. The parity conserving transitions (those states with even/odd Δj and f/e spectroscopic index) show markedly larger DCSs than the parity changing transitions (those with odd/even Δj and f/e spectroscopic index), as evidenced by the integral cross sections for the spin-orbit conserving and spin-orbit changing transitions in Fig. 4.9.

4.2.2 Spin-Orbit Changing Collisions

The spin-orbit-changing collisions predominantly take place on the V_{diff} surface in the limit of Hund's case (a). The V_{diff} surface is more attractive than the V_{sum} surface and does not have the usual 'stadium' appearance of the V_{sum} potential surfaces. The unusual form of the potential, as well as the fact that V_{diff} is the half difference between the A' and A'' PESs, makes the spin-orbit changing transitions sensitive to small differences between the two *ab initio* surfaces (even though they have received comparatively little attention). The images were recorded over almost the full range of energetically accessible states. The higher states near the energetic threshold with $j' > 11.5$ were not collected due to unacceptably low signal-to-noise. In general, the signal-to-noise is lower when probing rotational states on the spin-orbit changing manifold, due to the comparatively small cross sections of collisions leading to these states when compared to those leading to rotational states on the spin-orbit conserving manifold (see Fig. 4.9). All of the states probed displayed non-zero scattering across the full angular range of the image, in contrast to the spin-orbit conserving images.

For any given final rotational state on the spin-orbit changing manifold, the images themselves are smaller than their spin-orbit-conserving counterpart images as they are about 123 cm^{-1} higher in internal energy than the the ground state $\Omega = 0.5$ spin-orbit manifold. Since the spin-orbit changing collisions require an extra 123 cm^{-1} of energy to access due to the spin-orbit energy, the images tend to be more sideways and backward scattered for a given rotational state. This somewhat counterbalances the

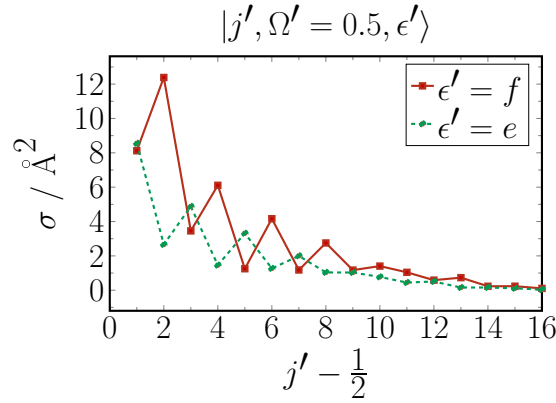


Figure 4.9: The quantum mechanical integral cross sections of the $\text{NO}(X)$ – Xe collision system at a collision energy of 510 cm^{-1} on the spin-orbit conserving (left) and spin-orbit changing (right) manifolds. The red lines represent ϵ -conserving collisions and the green ϵ -changing collisions.

more attractive nature of the V_{diff} potential which would otherwise lead to more forward scattering. Parity pair effects are also less prevalent than in the spin-orbit conserving images.

The extracted DCS obtained with the kinematic apse and CC QM alignment corrections are shown in Fig. 4.11 and Fig. 4.13. The agreement between the two corrections is good, with most states displaying only small differences between the two extracted angular distributions.

The experimental ion images display many of the same trends as the images recorded on the spin-orbit conserving manifold. For a given rotational state however, an extra $A \approx 123 \text{ cm}^{-1}$ of energy is required to reach the $\Omega' = 1.5$ spin-orbit manifold, resulting in fewer accessible states and smaller images in general. The spin-orbit changing images tend to have intensity around the entire image, with some states, such as $j' = 11.5e$, having almost isotropic DCSs. This makes fitting the spin-orbit changing images particularly challenging as any small difference in the instrument function or alignment correction will cause large divergence in the extracted DCSs for these images, resulting in larger errors. The parity pair effect, although diminished by the factors mentioned in the spin-orbit conserving section, are still evident in the spin-orbit changing images.

Scattering into spin-orbit changing states requires overcoming the spin-orbit changing energy of 123 cm^{-1} , making the collisions more endoergic. The ion images show a

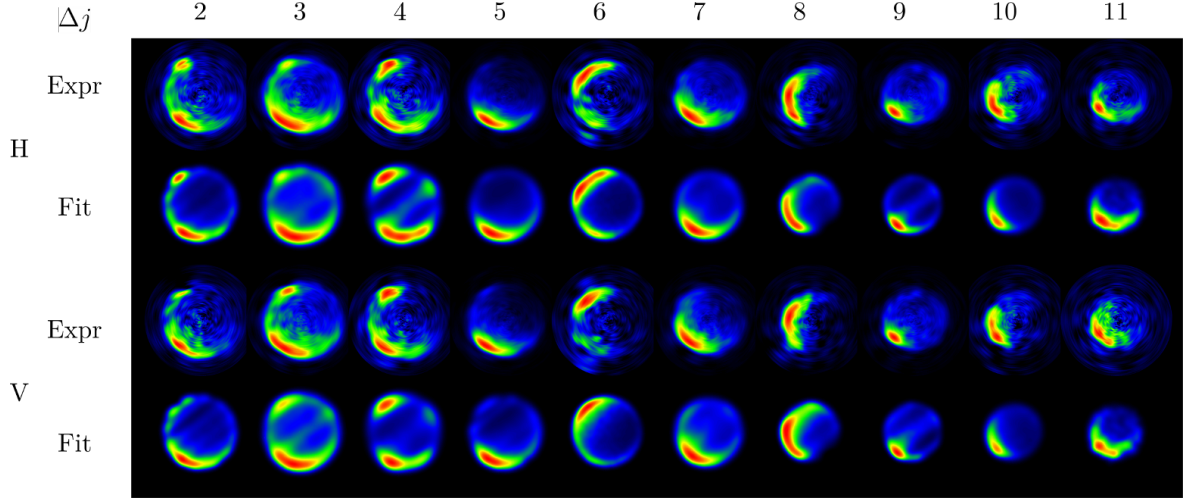


Figure 4.10: Experimental and fitted ion images recorded for the $\text{NO}(X)+\text{Xe}$ collision system. The images shown are those satisfying $|j = 0.5, \Omega = 0.5, \varepsilon = f\rangle \rightarrow |j', \Omega' = 1.5, \varepsilon = e\rangle$. The images were fitted using a quantum mechanical polarisation correction.

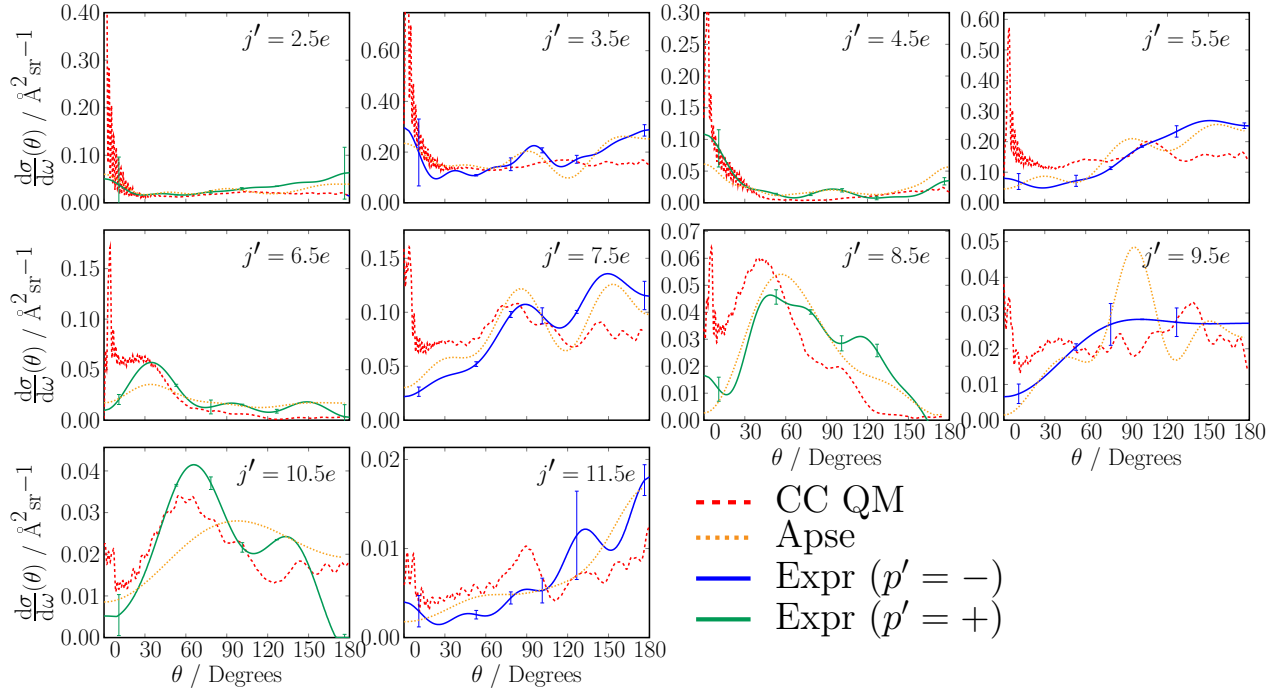


Figure 4.11: DCSs recorded for the $\text{NO}(X)+\text{Xe}$ collision system. The DCSs shown are those satisfying $|j = 0.5, \Omega = 0.5, \varepsilon = f\rangle \rightarrow |j', \Omega' = 1.5, \varepsilon = e\rangle$. The CC QM DCSs (red dashed) are compared to the experimental parity conserving (blue solid) or parity changing (green solid) DCSs determined with a quantum mechanical polarisation correction. Fitting performed with a classical impulsive polarisation correction (orange dotted) is also shown for comparison.

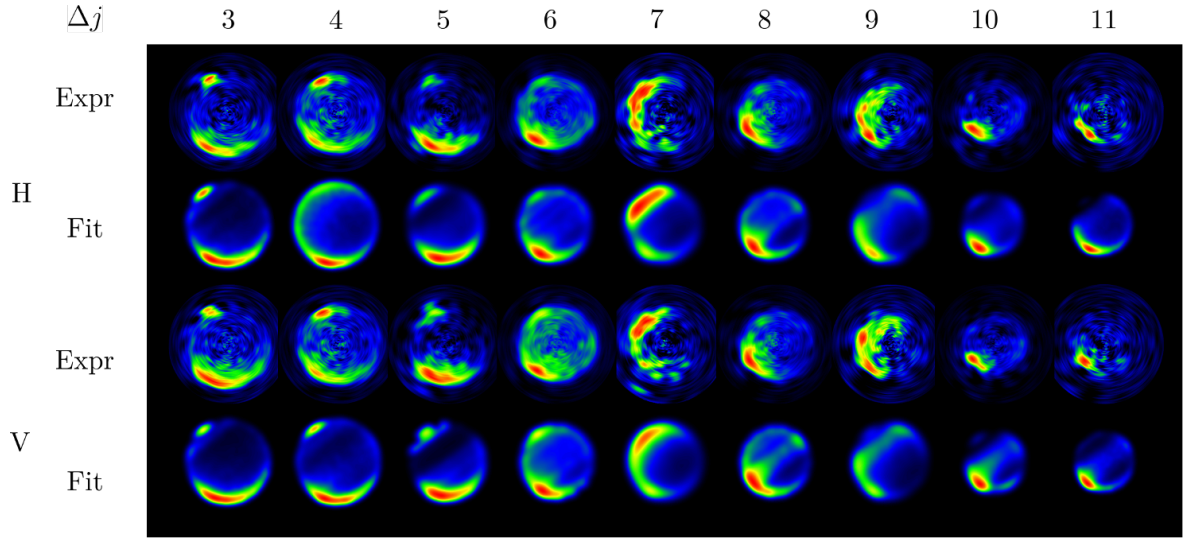


Figure 4.12: Experimental and fitted ion images recorded for the $NO(X)+Xe$ collision system. The images shown are those satisfying $|j = 0.5, \Omega = 0.5, \varepsilon = f\rangle \rightarrow |j', \Omega' = 1.5, \varepsilon = f\rangle$. The images were fitted using a quantum mechanical polarisation correction.

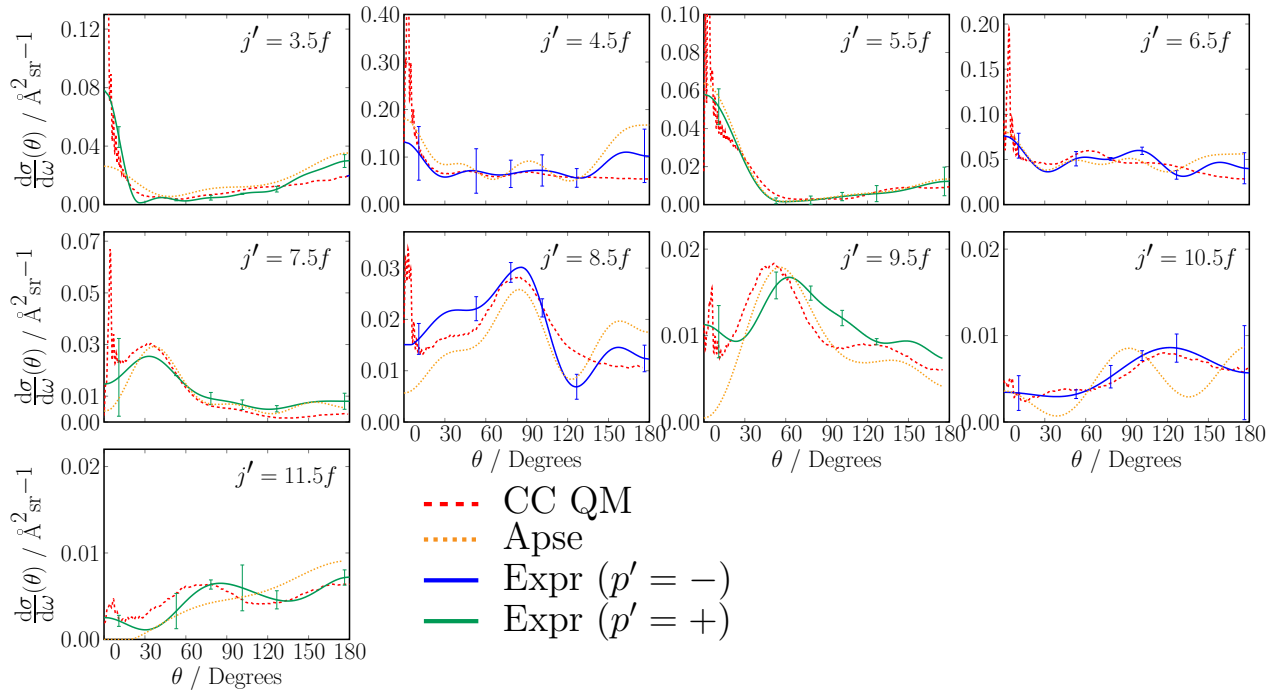


Figure 4.13: DCSs recorded for the $NO(X)+Xe$ collision system. The DCSs shown are those satisfying $|j = 0.5, \Omega = 0.5, \varepsilon = f\rangle \rightarrow |j', \Omega' = 1.5, \varepsilon = f\rangle$. The CC QM DCSs (red dashed) are compared to the experimental parity conserving (blue solid) and parity changing (green solid) DCSs determined with a quantum mechanical polarisation correction and a kinematic apse polarisation correction (orange dotted).

small forward scattered peak and strong sideways and backwards scattering. Unlike the spin-orbit conserving collisions leading to low rotational states, there is no evidence of secondary maximum associated with an ℓ -type rainbow in the ion images or fitted DCSs. In the low rotational states, there is evidence of parity dependent oscillations, as was the case for the spin-orbit conserving collisions. In the higher rotational states, the parity dependent oscillations are diminished and the images are single peaked in nature. Also in the higher rotational states, Hund's case (a) is no longer valid so coupling between the V_{sum} and V_{diff} potentials is expected. The breakdown in Hund's case (a) will be further explored in Chapter 6.

Since, in the limit of Hund's case (a), the spin-orbit changing collisions take place primarily on the V_{diff} potential, which is the difference between the A' and A'' potentials, any significant discrepancies between theory and experiment may hint at errors in one or the other PES. Since no significant differences between the fitted and experimental ion images are evident, the agreement indicates that the A' and A'' surfaces of Kłos [62] have been theoretically determined to very high precision. Other work published for Xe [82] also demonstrates near quantitative agreement with the theoretical PESs, however, such work was so far limited to probing low rotational states on the spin-orbit conserving manifold where ℓ -type rainbows are present.

Classical calculations cannot be run on the spin-orbit changing surface, since classical mechanics treats the $\text{NO}(X)$ as a closed shell species resulting in no spin-orbit coupling. A rigorous comparison between the classical and CC QM spin-orbit changing DCSs is therefore not possible⁴.

⁴Trajectory surface hopping [166] could allow trajectories to sample V_{diff} in future studies.

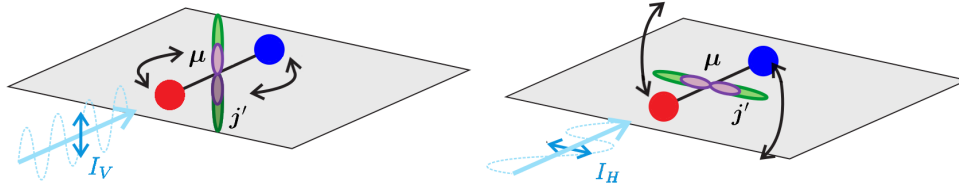


Figure 4.14: The direction of the transition dipole moment, μ with respect to the angular momentum vector, j' for a pure Q branch transition. The grey rectangle is the plane of the molecular beams. Detection of frisbee like rotation is shown in the left panel and propeller like rotation in the right panel. The absolute sense of rotation can not be probed with H or V polarised light.

4.3 Collision Induced Alignment

The experimental ion images recorded with horizontal and vertical polarisations were combined to form normalised difference images which encode the collision-induced alignment information. The collision-induced alignment measured by the hexapole apparatus is a multipole of the three-vector $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ correlation. Quantum mechanically, the $\mathbf{j}'$ vector cannot be localised to a specific direction with respect to a reference frame. Instead, the angular momentum is described by a minimum uncertainty state, localised as closely as possible about the direction specified [119]. The renormalised PDDCSs, when expanded in the multipolar series given in Eqn. (2.51) of Chapter 2, give the relative probability that $\mathbf{j}'$ is to be found in the minimum uncertainty state centred around the direction (θ, ϕ) with respect to the relative velocity vector, $\mathbf{k}$. The exact spatial significance of the real renormalised PDDCSs is determined by the rank and order. The $\rho_0^{\{2\}}(\theta)$ renormalised PDDCSs quantify alignment along $\mathbf{k}$ when positive and perpendicular to $\mathbf{k}$ when negative. The $\rho_{2+}^{\{2\}}(\theta)$ renormalised PDDCSs describe alignment along $\mathbf{k}$ when positive and alignment along $\mathbf{y}$ when negative, pictorial representations of the distributions are shown in Fig. 2.5 of Chapter 2. As discussed earlier regarding the alignment correction used in fitting horizontal and vertically polarised ion images to obtain angular distributions, the probability of absorbing a photon is dependent on the square of the cosine of the angle between the electric vector, ϵ , of the light and the molecular transition dipole moment, μ . When the electric vector of the light is parallel to the transition dipole, the transition probability is maximal.

For a Q branch transition, when $I_V(x, y) > I_H(x, y)$, $\mathbf{j}'$ must lie perpendicular to the plane of the molecular beams, with a bond axes motion corresponding to ‘frisbee’ like rotation. Similarly when $I_H(x, y) > I_V(x, y)$, $\mathbf{j}'$ lies parallel to the beam plane, and rotate like a ‘propeller’.

For the $\epsilon' = f$ states recorded using pure (R21) branch excitation (shown in Fig. 4.15), the positive intensity that can be seen in the forward scattered direction corresponds to propeller like rotation. As the scattering angle increases, the intensity becomes less positive, and then negative indicating the transition to ‘frisbee’ like rotation in the very backward scattered direction. The extent of the propeller like rotation in the forward direction decreases with increasing rotational excitation. For high rotational states ($j' \geq 10$), ϵ -changing collisions, and the $j' = 9.5, \Omega = 1.5$ state, the mixed (Q+P/R) branch was used due to the low signal intensity. Since the intensity of the Q branch is approximately twice as sensitive to alignment as the P or R branch, the contribution from the Q branch will be dominant. Consequently, the intensity of the images is inverted with respect to the experimental images recorded with pure branch excitation. The extent of ‘propeller’ like rotation is very small for the highest Δj states, effectively, only ‘frisbee’ like rotation is observed in the higher states.

For the spin-orbit conserving and changing transitions, good agreement is to be seen between the experimental and fitted ion images, resulting in good agreement between the CC QM renormalised PDDCSs and the experimentally determined renormalised PDDCSs shown in Fig. 4.16. Although the experiment is partially sensitive to $\rho_{1+}^{\{2\}}(\theta)$, the contribution to the observed ion image is very small, approximately only 5% of the total, so although this moment was included in the fit, no meaningful interpretation of these fits could be made due as the signal-to-noise ratio was too low. The images tend to be slightly asymmetric about $\mathbf{k}$, with greater positive intensity on the fast side. Since the normalised difference images should be symmetric about $\mathbf{k}$ due to the removal of the flux-density effects, the enhanced intensity is thought to be due to collisional and/or magnetic depolarisation. Molecules scattered to the slow side of the image spend longer in the interaction region as the LAB frame velocities are lower, giving an opportunity for collisional or magnetic depolarisation to occur before ionisation

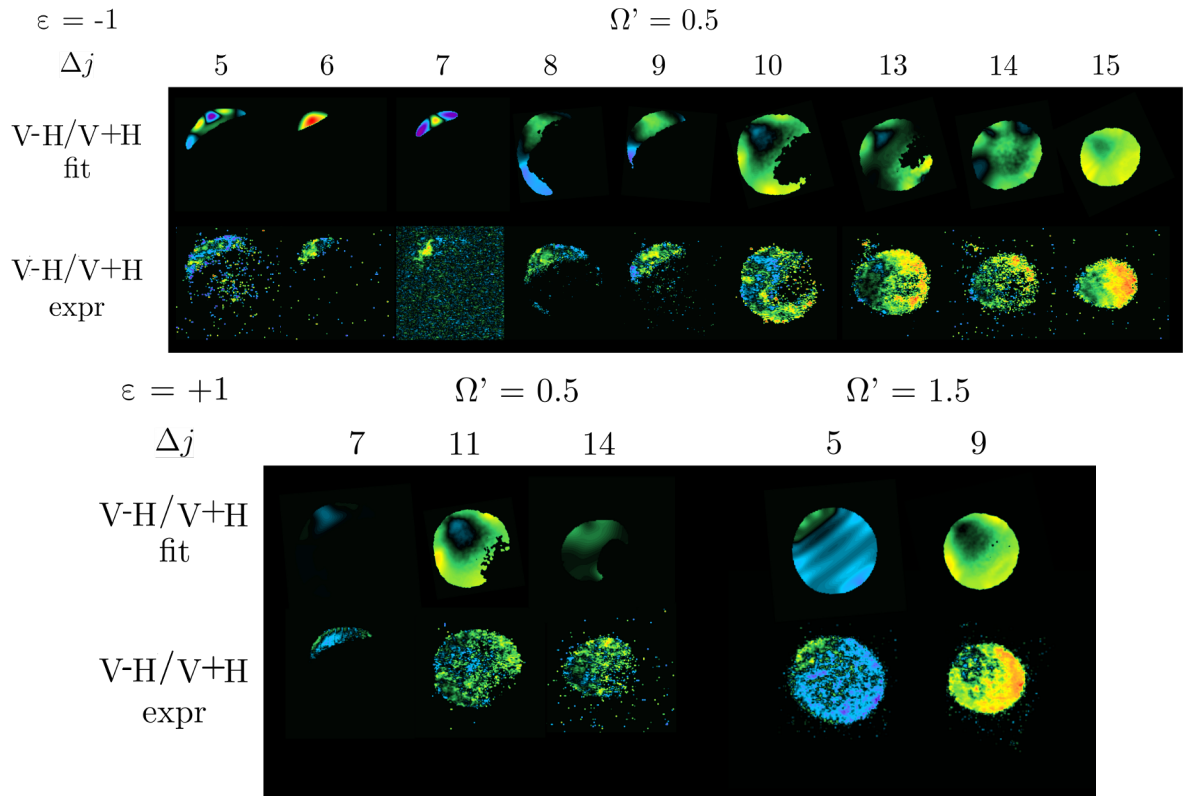


Figure 4.15: Normalised difference images using horizontal and vertically polarised light for the scattering of $NO(X)$ by Xe . The top rows of each panel contain the fitted images using the algorithm described in Chapter 3. The bottom rows contains experimental images recorded using the hexapole apparatus. The top panel shows ϵ conserving collisions, and the bottom ϵ changing collisions. The color scale spans from red/orange being positive to blue/purple being negative.

takes place. If significant depolarisation is taking place, the experimental images will slightly underestimate the magnitude of the alignment of $\rho_0^{\{2\}}(\theta)$ and $\rho_{2+}^{\{2\}}(\theta)$. The effect of magnetic depolarisation was minimised by placing a block of μ -metal shielding around the interaction region to block the Earth's magnetic field. Sensitivity studies have previously shown that the effect of magnetic depolarisation is negligible at the μT strength of Earth's field [109].

The $\rho_{2+}^{\{2\}}(\theta)$ renormalised PDDCSs, shown in the bottom panel of Fig. 4.16, are less well reproduced experimentally than the $\rho_0^{\{2\}}(\theta)$ renormalised PDDCSs. This is to be expected due to the sensitivity to $\rho_{2+}^{\{2\}}(\theta)$ of the experiment, see Fig. 2.5 in Chapter 2. The main discrepancies are in the lowest lying states where the rapid changes of the magnitude and lack of intensity around the image make fitting more sensitive to errors. The forward scattered region tends to be the least well reproduced in all the fits. However, in general the agreement between the QM and the experimental data is

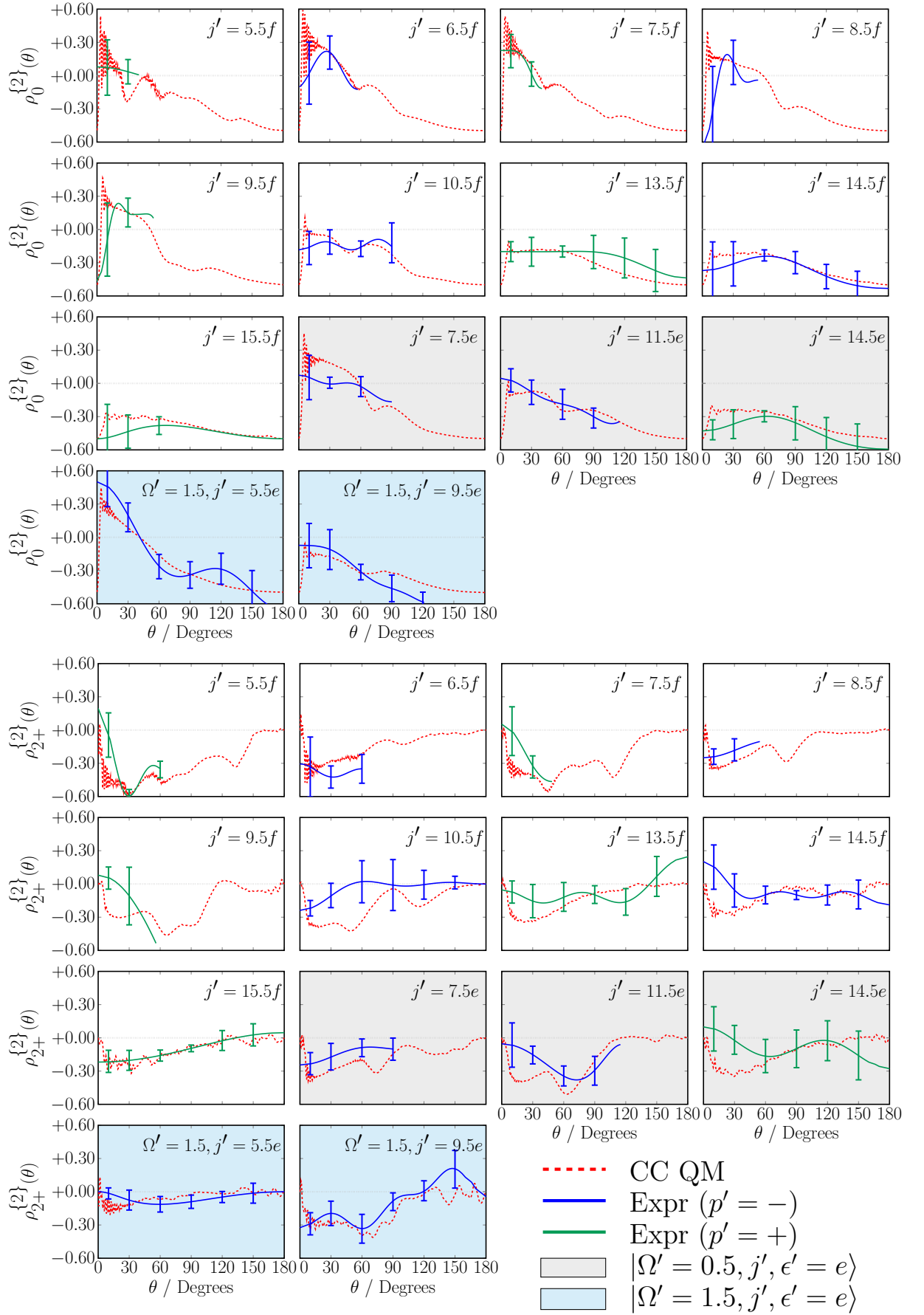


Figure 4.16: The experimentally determined $\rho_0^{\{2\}}(\theta)$ (top panel) and $\rho_{2+}^{\{2\}}(\theta)$ (bottom panel) renormalised PDDCSs for the NO(X)-Xe collision system recorded at a collision energy of 64 meV (519 cm⁻¹). CC QM calculations (red dashed) are compared to the experimentally recorded data (blue or green).

good. The $\rho_{2+}^{\{2\}}(\theta)$ renormalised PDDCS, like the $\rho_0^{\{2\}}(\theta)$ renormalised PDDCS, is also governed primarily by impulsive forces and is only slightly augmented by the attractive forces.

4.4 Theoretical Analysis of DCSs and PDDCSs

The collision-induced alignment can be studied using a number of theoretical techniques outlined in Chapter 2. The relative differences between the theoretical and experimental results provide insight into the mechanistic origins of the collision-induced alignment which have been demonstrated to be strongly repulsive in character [19–21]. The large attractive potential of the NO(X)–Xe collision system is an extreme test case. For collision systems in which the attractive potential is strongest, the collisions are expected to be least impulsive in nature of any of the rare gas systems, especially at low j' . The efficacy of various models in reproducing the observed experimental alignment will prove a stringent test of the understanding of the origins of the collision-induced alignment.

4.4.1 Classical and Close-Coupled Quantum Calculations

Classical trajectories provide an intuitive way of unpicking quantum mechanical and classical effects in observable properties. The classical renormalised PDDCSs can be obtained as described in Chapter 2 allowing for comparison to exact quantum mechanics. In order to facilitate this comparison, the open shell CC QM normalised PDDCSs must be summed and averaged over the spin-orbit and Λ -doublet states by means of

$$n_{q\pm}^{\{k\},\text{QCT}}(\theta) = \frac{1}{2} \sum_{\Omega'} \sum_{\epsilon, \epsilon'} n_q^{\{k\},\text{QM}}(\theta, j, \epsilon, \Omega \rightarrow j', \epsilon', \Omega'). \quad (4.12)$$

The normalised PDDCSs can then be renormalised by dividing the normalised PDDCS by the summed and averaged DCSs

$$\rho_{q\pm}^{\{k\},\text{QCT}}(\theta) = \frac{n_q^{\{k\},\text{QCT}}(\theta)}{\frac{1}{2} \sum_{\Omega'} \sum_{\epsilon, \epsilon'} \frac{d\sigma^{\text{QM}}}{d\omega}(\theta, j, \epsilon, \Omega \rightarrow j', \epsilon', \Omega')}. \quad (4.13)$$

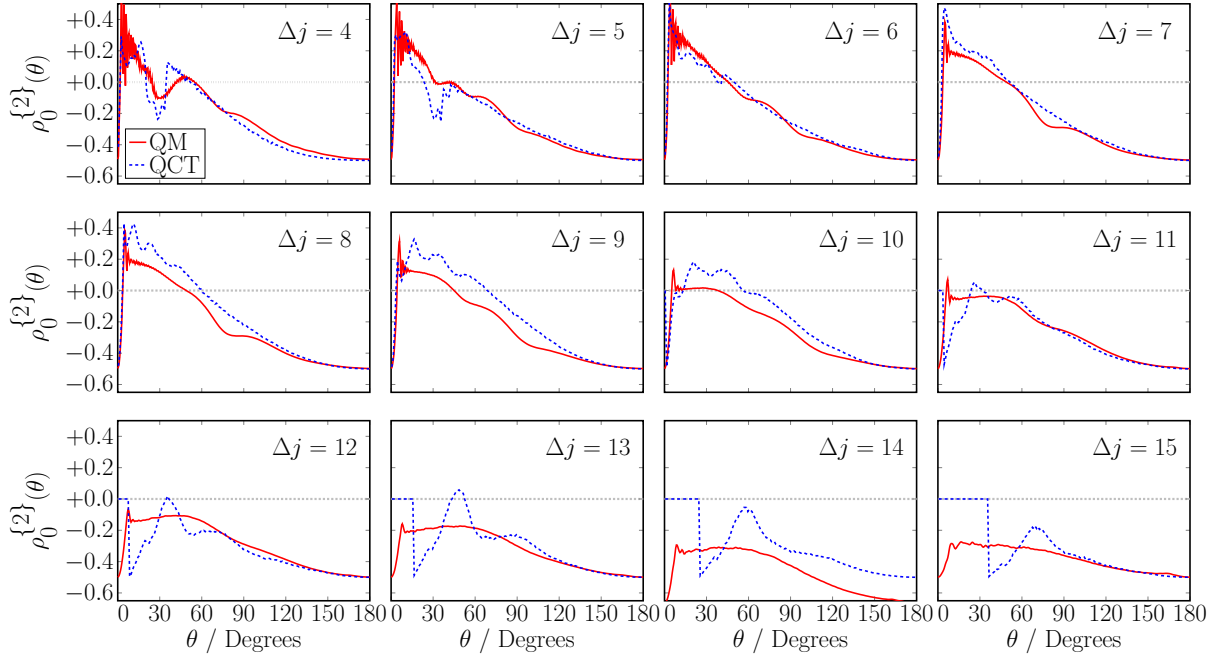


Figure 4.17: Quantum (red) and classical (blue) renormalised PDDCSs for the $NO(X)$ – Xe collision system. The classical and CC QM renormalised PDDCSs agree well over the angular range with small discrepancies at $\Delta j = 4, 5$ at low θ and at high Δj where secondary maxima in the renormalised PDDCSs are observed in the classical calculations that are not present in the CC QM calculations. To facilitate comparison between the closed shell classical calculation and the quantum, the CC QM renormalised PDDCSs have been summed and averaged over Λ -doublets according to Eqn. (4.12).

The parity effect is thereby washed out by the averaging allowing direct comparison to the open shell QM data [62].

The averaged $\rho_0^{\{2\}}(\theta)$ renormalised PDDCSs are shown in Fig. 4.17. The agreement between the classical and CC QM calculations is generally good. There are, however, some significant discrepancies. The most obvious of these are at low $\Delta j (= j' - j)$, particularly $\Delta j = 5$. The classical calculations predict an ℓ -type rainbow in these states at approximately 30° . As has been demonstrated previously for Kr [19, 84], the classical mechanics balances the attractive and repulsive parts of the potential incorrectly, and predicts an ℓ -type rainbow in all low Δj states. Quantum mechanically, the ℓ -type rainbow is only observed in low j' parity changing collisions, else it is masked by glory scattering [19]. The change in the total parity dictates which terms in the potential are most important, as has been discussed with reference to the four path model. The rainbow peak is characterised by a large dip in the $\rho_0^{\{2\}}(\theta)$ renormalised PDDCS, indicating an enhanced preference for ‘frisbee’ like rotation

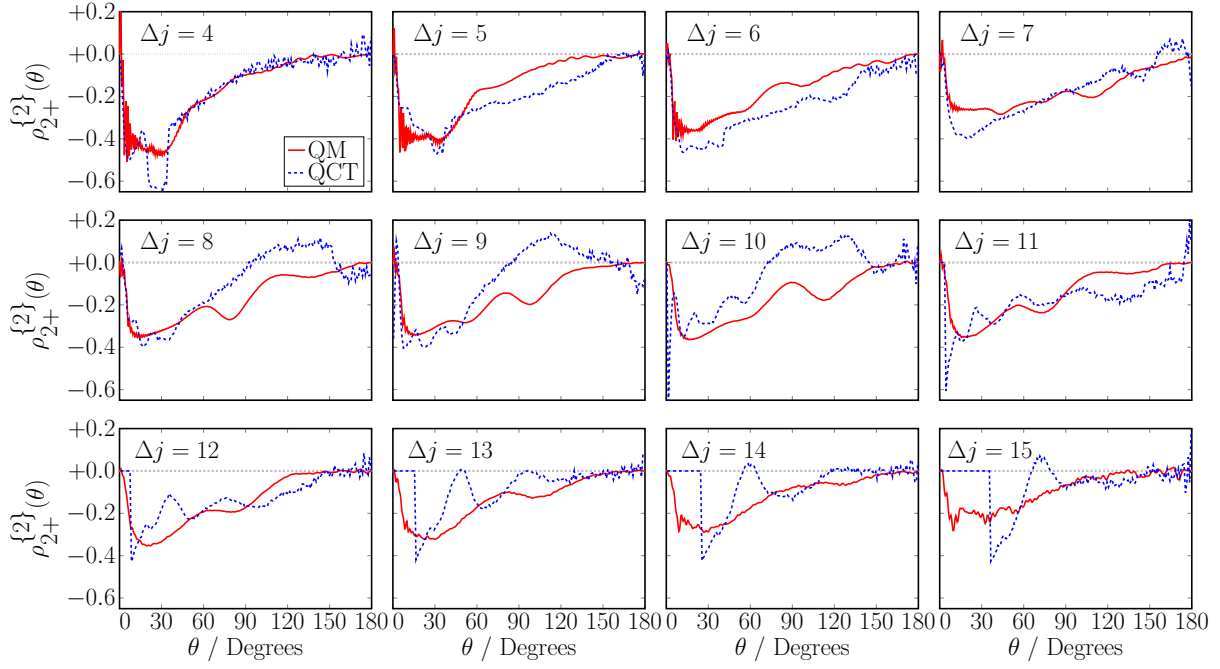


Figure 4.18: CC QM (red) and classical (blue) $\rho_{2+}^{\{2\}}(\theta)$ renormalised PDDCSs for the NO(X)–Xe collision system. The classical and CC QM renormalised PDDCSs agree relatively well, however a dip at around the rainbow angle is observed in the classical renormalised PDDCSs that is absent in the QM. To facilitate comparison between the closed shell classical calculation and the quantum, the CC QM renormalised PDDCSs have been summed and averaged over Λ -doublets according to Eqn. (4.12).

caused by trajectories sampling the attractive region and leading to far-side scattering. At intermediate rotational excitation, the agreement is excellent between classical and CC QM calculations, however the agreement diverges at higher Δj . The classically forbidden region, where low scattering angles classically can not transfer enough torque to excite the molecule to high Δj are clearly evident above $\Delta j = 9$ and lead to the square features in Fig. 4.17 and Fig. 4.18. Classical mechanics tends to over-estimate the magnitude of the $\rho_0^{\{2\}}(\theta)$ renormalised PDDCS at high Δj , whereas the quantum mechanical model predicts frisbee like rotation across the angular range, reflected in the lower values.

At low Δj , the $\rho_{2+}^{\{2\}}(\theta)$ polarisation moments obtained from classical calculations compare well with the CC QM renormalised PDDCSs. The dip in the $\rho_{2+}^{\{2\}}(\theta)$ PDDCS associated with the scattering angle of the ℓ -type rainbow is clearly visible at low Δj (for instance in $\Delta j = 4$ at $\approx 30^\circ$) and diminishes at Δj increases. The classical renormalised PDDCSs obtained from QCT calculations tend to slightly overestimate the degree of alignment in the scattering plane at low scattering angles and at low

Δj . This is due to the role of parity being ignored in the QCT calculations, leading to incorrect balancing of attraction and repulsion. This effect cannot be seen at high Δj due to the onset of the classically forbidden region, where low scattering angles cannot generate enough torque to reach high rotational states. At middle Δj , the $\rho_{2+}^{\{2\}}(\theta)$ moment is overestimated, but balances out at higher Δj . Slight oscillations in the classical $\rho_{2+}^{\{2\}}(\theta)$ renormalised PDDCS are also noticeable at higher Δj that are not reproduced in the CC QM calculations.

The insight from classical calculations is that the role of attractive part of the potential is overstated because of the absence of parity used in describing the rotational energy transfer. The averaged CC QM calculations do not display such a large dip. This is the case as only the parity changing transition contains a rainbow which is washed out by the averaging over parity conserving and parity changing states in order to compare with the classical mechanics calculations. In general however, the classical calculations are good at reproducing the observed alignment, apart from in the forward scattered direction where the balance between attraction and repulsion is most important in the determination of the $\rho_{q+}^{\{2\}}(\theta)$ renormalised PDDCSs.

4.4.2 Kinematic Apse Model and Close-Coupled Quantum Calculations

The alignment renormalised PDDCSs based on classical and CC QM calculations using the full potential energy surface have so far been presented. As we have seen from the kinematic apse model, simple models can also adequately describe the collision-induced alignment. The simplest, and most commonly used method for calculating the direction of the angular momentum vector after collision is the kinematic apse model described in Section 4.1. As has been discussed, the kinematic apse model is based on the assumption that the projection of the angular momentum vector is conserved along the apse direction during a collision, an assumption that proves rigorous if the collision takes place instantaneously and at a defined point in space.

Although the kinematic apse model has a simple formulation, the main characteristics of the renormalised PDDCSs probed experimentally are accurately reproduced, and

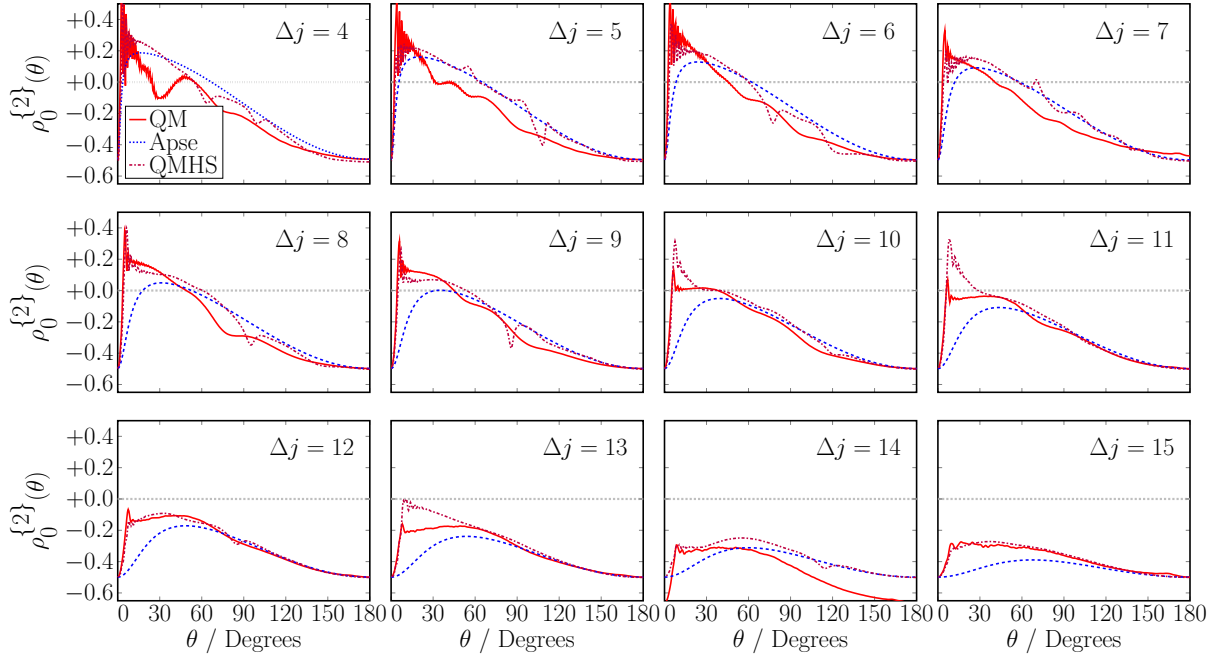


Figure 4.19: CC QM (red), kinematic apse (blue) and QMHS (purple) $\rho_0^{\{2\}}(\theta)$ renormalised PDDCSs for the $NO(X)$ – Xe collision system. The classical and CC QM renormalised PDDCSs agree relatively well, however a dip at around the rainbow angle is observed in the classical renormalised PDDCSs that is absent in the QM. To facilitate comparison between the closed shell classical calculation and the quantum, the CC QM renormalised PDDCSs have been summed and averaged over Λ -doublets according to Eqn. (4.12).

the failures in the kinematic apse model relate to particular dynamical phenomenon mainly associated with the attractive part of the potential for the low Δj transitions, at high Δj the nonlocality of the collision becomes important. As can be seen in Fig. 4.19 and Fig. 4.20, when a quantum hard shell model (QMHS) is used [103] to produce the alignment moments, a quite similar overall structure to that produced by the kinematic apse model is observed. The agreement with the CC QM and QMHS is better at low Δj as the QMHS contains the diffraction contribution and takes into account the QM temporal and spatial nonlocality. What is clear is that the kinematic apse accounts for the broad trends in the alignment moments and that, quantum mechanically, the attractive forces augment the alignment from the simple picture of conservation of angular momentum projection onto the apse direction, $\hat{\mathbf{a}}$. These augmentations are largely due to the long range nature of the potential energy surface as demonstrated by comparing to the results of QMHS calculations.

The CC QM, QMHS and kinematic apse models, in general, predict the alignment

at low Δj very accurately. The CC QM, averaged over initial and final Λ -doublet levels and spin-orbit states, broadly follow the simple kinematic apse model for the $\rho_0^{\{2\}}(\theta)$ renormalised PDDCS. The QMHS model, which does not have strict projection conservation onto the kinematic apse, agrees with the CC QM renormalised PDDCSs very well. Given the QMHS model completely neglects attractive forces yet agrees well with the full CC QM PDDCSs, the interaction resulting in alignment perpendicular or parallel to $\mathbf{k}$, quantified by the $\rho_0^{\{2\}}(\theta)$ renormalised PDDCS is shown to be mainly due to the dominance of the repulsive part of the potential. The broad agreement between the kinematic apse model and the full CC QM models also demonstrates that the projection preserving propensity along $\hat{\mathbf{a}}$ is also present in collisions with the large polarisable xenon atom, even though the attractive part of the potential is quite strong. The largest discrepancies exist at low scattering angles where collisions sample the attractive part of the potential more predominantly; and in these cases the magnitude of $\rho_0^{\{2\}}(\theta)$ is reduced, an effect not observed in the QMHS or kinematic apse models which neglect attraction entirely.

The largely impulsive origin of the $\rho_{2+}^{\{2\}}(\theta)$ moment is also evident, as shown in Fig. 4.20. The apse model consistently underestimates the degree of alignment of $\rho_{2+}^{\{2\}}(\theta)$. Strong oscillations are evident in the $\rho_{2+}^{\{2\}}(\theta)$ renormalised PDDCSs from the QMHS model which are not present in the CC QM. These oscillations tend to occur at high scattering angles in the low Δj states, where the hard shell model performs least reliably. The CC QM and kinematic apse models show a similar trend across the angular and Δj range. At low scattering angle where the attractive region of the potential is dominant, the kinematic apse model and CC QM do not show very close agreement.

To understand the deviations in the QMHS and kinematic apse model calculations when compared to the QM, it is necessary to consider the physical encounter in detail. The main assumption of the kinematic apse model, that the projection of $\mathbf{j}$ on the apse direction, $\hat{\mathbf{a}}$, is conserved throughout the course of collision, will be true only in the case when its underlying approximations are exactly met [64, 103]. In the limit of a sudden collision at a well defined point of contact, the molecule rotates slowly

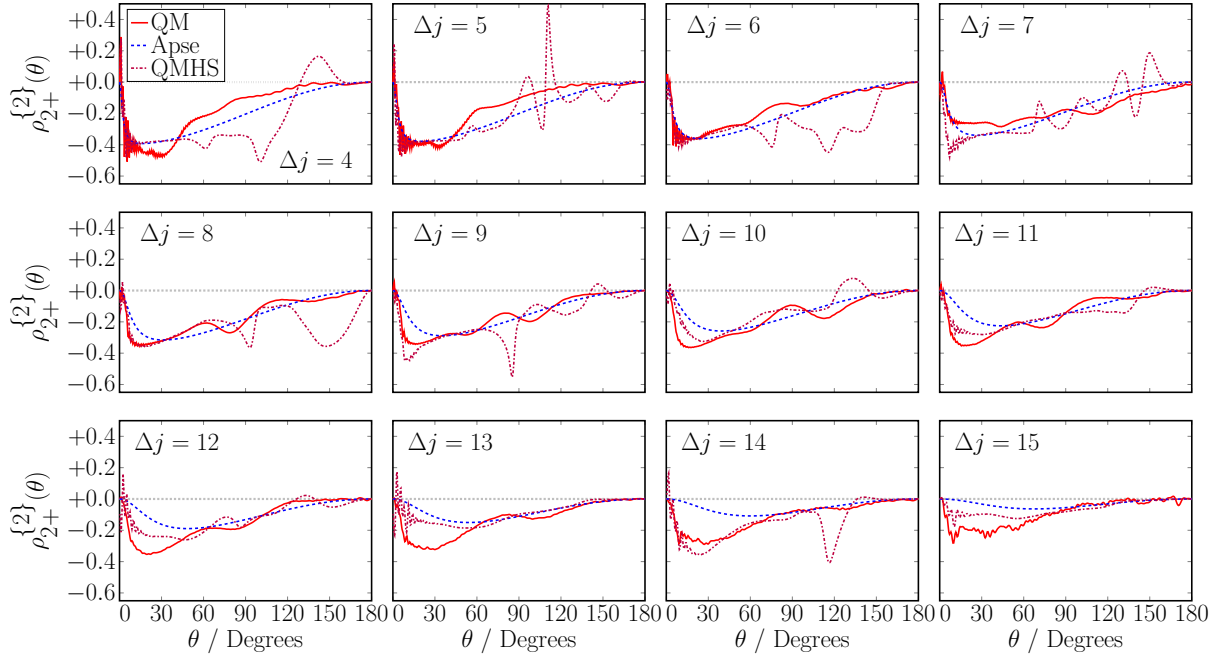


Figure 4.20: CC QM (red), kinematic apse (blue) and QMHS (purple) $\rho_{2+}^{\{2\}}(\theta)$ renormalised PDDCSs for the NO(X)–Xe collision system. The classical PDDCSs have been smoothed with Bezier curves to remove noise. The classical and CC QM renormalised PDDCSs agree relatively well, however a dip at around the rainbow angle is observed in the classical renormalised PDDCSs that is absent in the QM. To facilitate comparison between the closed shell classical calculation and the quantum, the CC QM renormalised PDDCSs have been summed and averaged over Λ -doublets according to Eqn. (4.12).

enough to be considered stationary during the interaction time. For low Δj states, the NO(X) molecule will be rotating slowly, and as the atom is moving very fast, it will depart as quickly from the encounter region as it entered. As more rotational energy is transferred to the molecule, the NO(X) will be rotating faster and less kinetic energy will be available to the departing moiety. This will result in an increasingly long interaction time, diminishing the validity of the models assumption of an instantaneous and point like collision. In the real encounter, the atom will sample a large range of bond axis orientations over an extended period of time, and the collision can no longer be assumed to have occurred at a specific point on the molecule or at a specific moment in time [63]. This is related to multiple impact scattering, previously it has been shown by Hornung that $\approx 10\%$ of trajectories resulting in high rotational excitation are caused by double impact collisions [103].

As discussed previously, in a forward scattered collision, an atom will stay within the attractive part of the potential for longer than during a backward scattered collision.

This is because the low scattering angle collisions are primarily caused by long range forces associated with large impact parameters, which causes the radial velocity to be relatively low. The projection of $\mathbf{j}$ onto $\hat{\mathbf{a}}$ in the QM encounter is not strictly conserved during collisions, and the deviations from the kinematic apse model are thus more pronounced for low scattering angles and at high Δj where the approximation breaks down. The QMHS and QM calculations remain in better agreement in these regions as the QMHS allows nonlocality of interaction even if the energy transfer is strictly sudden. The CC QM, having no such limitations, is therefore considered to provide the most accurate prediction of the collision-induced alignment over the full angular range.

4.5 Comparison With Other Rare Gases

The DCSs [12,14,59,86,91,122,167–169] and collision-induced alignment [20,21,170–172] of rare gases scattering with $NO(X)$ have been extensively studied in the past. More recently, the DCSs and collision-induced alignment of krypton has been studied [19, 84, 173]. In comparison to the argon and krypton collision systems, the PES of the $NO(X)$ – Xe system is more attractive, with a well depth of 142 cm^{-1} compared to krypton’s 139 cm^{-1} , as seen from Table 2.1 in Chapter 2, also notable is the increased extent of the attractive potential. There are also differences in the range and anisotropy of the surfaces, most notably at long range [82, 84]. This has a significant influence on the scattered images and hence on the obtained angular distributions and renormalised PDDCSs. The collision energy of the systems changes very little, as although the Xe is heavier and travels more slowly from the molecular beam, the difference is partially offset by the increase in mass. The crucial difference is the decrease in de Broglie wavelength, which is reduced by approximately 25% in the xenon system compared to the krypton system.

The effect of the slightly increased well depth and the longer range potential in the xenon system causes the scattering to all rotational states to be more forward. This effect is quite large at low j' as the extent of the $NO(X)$ – Xe potential is slightly greater than that of the krypton potential surface. This allows a greater degree of

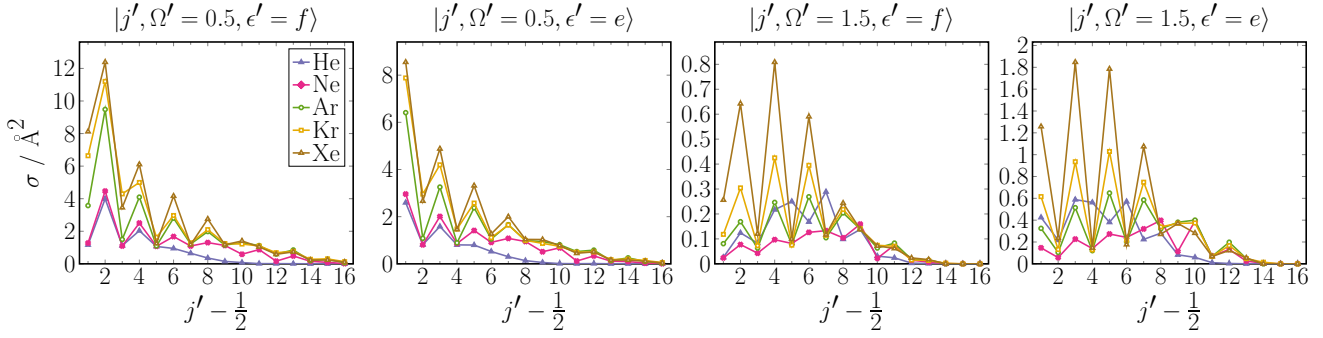


Figure 4.21: Comparison of the integral cross sections of scattering of the $|j = 0.5, \Omega = 0.5, \epsilon = -1\rangle$ state into particular $|j'\Omega'\epsilon'\rangle$ states for the $\text{NO}(X)$ –Rg collision systems at a collision energy of 510 cm^{-1} . A clear progression in integral cross section is seen corresponding to the increased size of the atom, and hence the extent of the potential surface.

forward scattering at long range and increasing the torque able to be applied by long range collisions. The decreased de Broglie wavelength causes a shift in the position of oscillations in the angular distribution. This shift has previously been shown to be dependent on interference from trajectories sampling different regions of the potential, as discussed in Section 4.2.1. The frequency of the oscillations is dependent on the de Broglie wavelength of the system, and on the range and anisotropy of the interaction between $\text{NO}(X)$ and the rare gas [63, 84, 103].

4.5.1 Comparison of Integral Cross Sections

The increased extent of the xenon potential energy surface causes the resultant integral cross sections to be larger for xenon than in any of the other rare gas collision partners. The increase in cross section corresponds to the increasing size and polarisability of the rare gas atom, helium being the smallest rare gas with the most impulsive potential surface displays only small cross sections. The integral cross sections for the rare gases at a collision energy of 510 cm^{-1} are shown in Fig. 4.21.

Parity effects are clearly visible in the integral cross sections for all of the systems. The integral cross sections oscillate from high to low depending on whether the collision is parity conserving or parity changing. This is evident at low j' in both the spin-orbit conserving and spin-orbit changing collisions. All the rotational transitions shown in Fig. 4.21 start in an initial $\epsilon = f$ state.

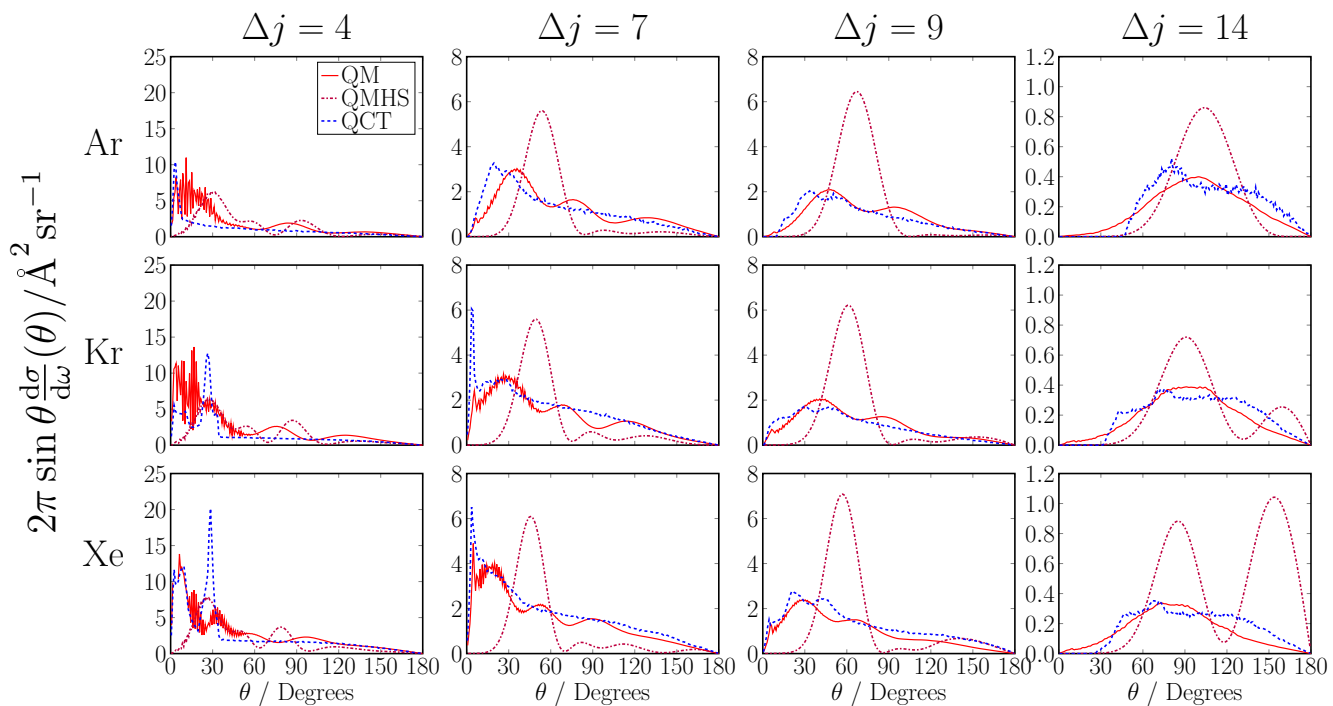


Figure 4.22: Comparison of the CC QM (red), QCT (blue dotted) and QMHS (purple dotted) DCSs at a collision energy of 500 cm^{-1} for scattering of NO(X) with argon (top panel), krypton (middle panel) and xenon (bottom panel). The red lines are the Λ -doublet summed and averaged DCSs obtained from CC QM calculations with the HIBRIDON suite of codes [97], and the blue dashed plots are classical calculations performed on the V_{sum} PES, the purple dash-dotted lines represent scattering calculations that were performed using the QMHS code of Hornung [103].

The spin-orbit changing states show the same trends as the spin-orbit conserving states, but have much smaller integral cross sections.

4.5.2 Comparison of Differential Cross Sections

The integral cross sections for xenon are somewhat larger than those for argon and krypton in general, as can be seen from the progression in Fig. 4.21. As was discussed this is due to the extent and polarisability of the intermolecular potential. The effect of this on the $\sin \theta$ weighted DCSs of each of the rare gas collision systems is shown in Fig. 4.22. The magnitude of the DCSs becomes larger as the rare gas atom becomes larger and more polarisable, however many of the same general features remain. The CC QM data display obvious oscillations at high scattering angles in the DCSs. The position of the oscillations depends on the de Broglie wavelength [63, 103], which is shorter for the NO(X)–Xe collision system than for the Ar or Kr systems for the same

collision energy. These features are absent from the classical calculations, however, good agreement between the classical and CC QM calculations is observed across the angular range for each of the collision systems.

In the lower states, the cross section is dominated by intense forward scattering (diminished by the $\sin \theta$ weighting). This is true for argon, krypton and xenon. The xenon potential shows the greatest degree of forward scattering, along with intense diffraction oscillations (which will be explained in more detail in Chapter 7). In contrast, the QMHS calculations, which do not include any attraction, show a double peaked structure at high scattering angles. This structure shifts to lower scattering angles as the size of the potential increases. This is a reflection of the reduced de Broglie wavelength. The QM hard shell does not reproduce ℓ -type rainbow features, since it does not have an attractive potential. The balance between attractive and repulsive forces necessary to give rise to an ℓ -type rainbow is not included. For this reason, it also lacks glory scattering as there is no point where attraction and repulsion perfectly balanced and these features are therefore absent. However, the full QM calculations which completely take into account the open-shell character, show significant forward scattering, and these features become more prominent as the potential becomes more attractive. The classical calculations reproduce the intense forward scattering, and also include the appearance of the ℓ -type rainbow. The angular position of the rainbow is reproduced, but the intensity is slightly overestimated. At higher Δj , the xenon remains the most forward scattered and a broad peak is also observed in each of the collision systems. As this peak moves to lower scattering angles the range of the potential increases and the de Broglie wavelength increases. At high Δj when the de Broglie wavelength is the longest, significant backward scattering is required to excite xenon to $\Delta j = 14$ compared to the lighter rare gases.

4.5.3 Comparison of $\rho_0^{\{2\}}(\theta)$ Renormalised PDDCSs

The $\rho_0^{\{2\}}(\theta)$ renormalised PDDCSs for the argon, krypton and xenon systems are shown in Fig. 4.23. As discussed previously, the alignment renormalised PDDCSs are dominated by repulsive forces during the collision. The QMHS and CC QM tend to be

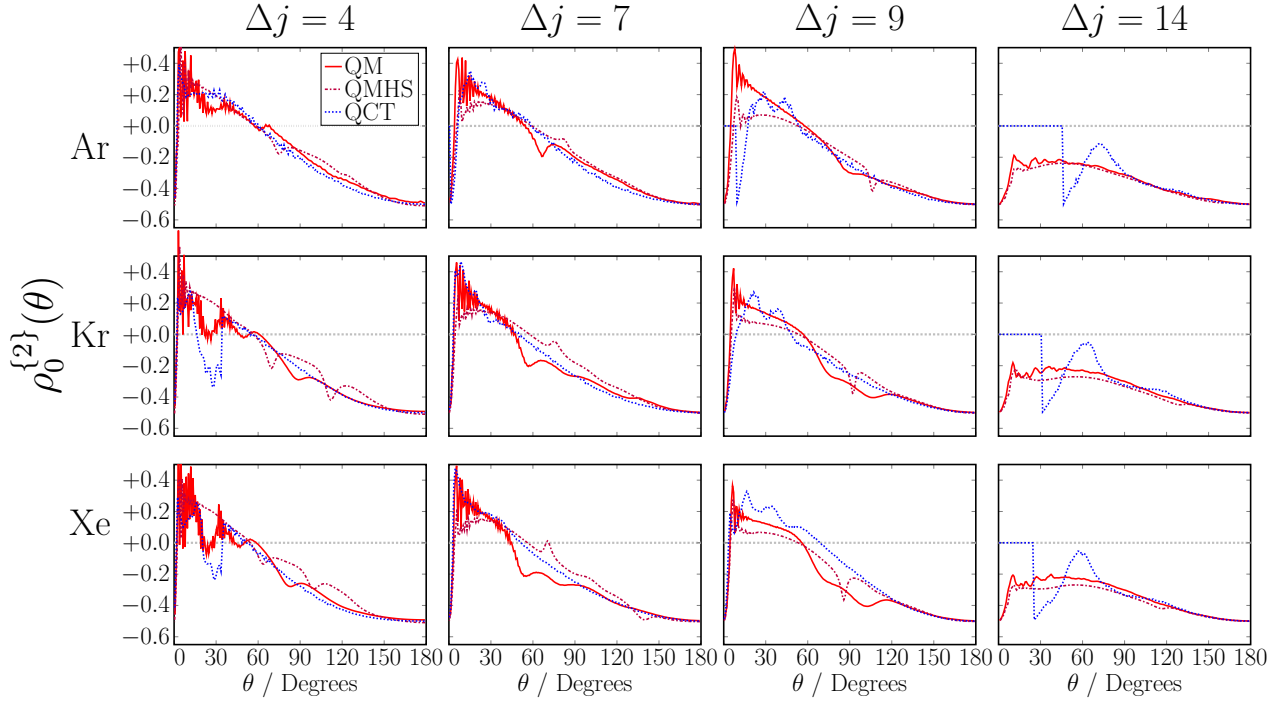


Figure 4.23: Comparison of the $\rho_0^{\{2\}}(\theta)$ renormalised PDDCSs at a collision energy of 510 cm^{-1} for scattering of NO(X) with argon (top panel), krypton (middle panel) and xenon (bottom panel). The red lines are the PDDCSs obtained from CC QM calculations of the ϵ and spin-orbit conserving transitions with the HIBRIDON suite of codes [97], the blue dotted plots are the classical $\rho_0^{\{2\}}(\theta)$ renormalised PDDCSs and the purple dash-dotted plots are PDDCSs from a QMHS code developed by Hornung [103].

in good agreement. In the lighter rare gases, the agreement between the QMHS $\rho_0^{\{2\}}(\theta)$ renormalised PDDCS and the CC QM renormalised PDDCS is better than in xenon. The attractive part of the potential, especially at low scattering angle augments the renormalised PDDCS and reduces the magnitude of the alignment, moving it to prefer in plane rotation as opposed to out of plane rotation.

At middle Δj , the agreement begins to converge for all the systems. In the sideways scattering region, there is a significant difference between the QMHS and CC QM calculations. This is likely a mixture of two effects, that of parity and that of the attractive part of the potential. At larger Δj , the agreement becomes better until at high Δj , where the collision is most impulsive and the attractive part of the potential has the least influence, the agreement is nearly quantitative.

It has previously been shown by Hornung that the QMHS and kinematic apse models are not identical [103]. The QM temporal and spatial nonlocality of the interaction, implicitly included in the hard shell but absent from the kinematic apse model which

assumes the interaction is instantaneous at a specific point, cause deviations from the strict projection conservation behaviour prescribed by the kinematic apse model. This is most pronounced at low scattering angle where diffractive and attractive contributions to the renormalised PDDCSs are evident. The full CC QM rotational alignment closely resembles that of a quantum mechanical hard shell collision, apart from the effects of its open shell nature and the attractive features of its potential. The rotational alignment is still dominated by the impulsive nature of the collision, and quantum mechanical effects induce only small deviations from the simple kinematic apse frame transform mechanism.

4.6 Summary

In this chapter, collision-induced rotational alignment of fully Λ -doublet state selected $NO(X)$ collisions with Xe have been recorded experimentally and investigated theoretically using a variety of methods. The experimental renormalised PDDCSs, $\rho_0^{\{2\}}(\theta)$ and $\rho_{2+}^{\{2\}}(\theta)$, have been compared to classical mechanical, quantum mechanical and impulsive calculations for a variety of spin-orbit conserving and spin-orbit changing states. The alignment has been shown to be in good agreement with that predicted by quantum mechanics and the overall impulsive characteristic of the alignment has been described.

The classical kinematic apse model can explain the form of the experimental images but fails to correctly predict the alignment at low scattering angle as the attractive nature of the potential reduces the validity of the underlying assumptions of the kinematic apse model. Classically, the effect of the attractive part of the potential is easily seen in the prediction of an ℓ -type rainbow for low Δj states such as $\Delta j = 5$. Quantum mechanically, and classically, there is a large effect on the alignment for this state. The effect is diminished for parity-conserving and collisions leading to high j' due to masking by glory scattering as demonstrated for the Kr system [19]. The alignment itself is broadly well reproduced classically, although the importance of the attractive part is over-stated in some low Δj states.

A comparison to argon and krypton has been made, highlighting the different characteristics of the potential that are responsible for the increase in forward scattering and the diminished role of parity dependent oscillations in the DCSs. This chapter has focussed on the determination of the DCSs and renormalised PDDCSs which relate the plane of the angular momentum vector $\mathbf{j}'$ to the initial relative velocity $\mathbf{k}$ and the outgoing velocity $\mathbf{k}'$. Such information has provided a measurement of the $k = 2$ multipole of the $\mathbf{k}\text{--}\mathbf{k}'\text{--}\mathbf{j}'$ correlation which quantifies the rotational alignment as a function of scattering angle. In the subsequent chapter, another multipole of the $\mathbf{k}\text{--}\mathbf{k}'\text{--}\mathbf{j}'$ correlation will be explored, this time by focussing on the rotational orientation effects in krypton.

Scattering of NO(X) with Kr

In this chapter, collisions of fully Λ -doublet state selected NO(X) scattering with Kr will be investigated. The differential cross sections (DCSs), recorded with right (R) and left (L) circularly polarised light in the orientation geometry from Chapter 3 will be presented and contrasted with previous measurements. By making use of the circular polarisation, $\rho_{1-}^{\{1\}}(\theta)$ renormalised polarisation dependent differential cross sections (PDDCSs) can be obtained from the $\frac{L-R}{L+R}(\theta)$ experimental normalised difference images, in an analogous manner to those in the previous chapter. The $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs represent a measurement of a multipole of the $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ vector correlation and describes the orientation of $\mathbf{j}'$ with respect to the scattering frame $\mathbf{y}$ -axis. By integrating over the scattering angle, the $a_{1-}^{\{1\}}$ polarisation moments can be obtained from the experimental data.

Theoretical investigations of the collision-induced orientation (CIO) have been conducted by a multitude of research groups [63, 67, 106, 112, 143, 174]. It is now established that in classical single collision encounters of a rigid ellipse with a point-like atom, no orientation is possible due to the system symmetry [63, 103, 169]. Previous investigations have found two limiting classical mechanisms associated with the attractive and repulsive regions of the potential, which are responsible for the breakdown of this

symmetry [63, 103, 175]. Investigation of a quantum mechanical hard shell (QMHS) model by Hornung [63] have revealed that quantum mechanically, the temporal and spatial nonlocality of the collision gives rise to a third, quantum mechanical mechanism responsible for the collision-induced rotational orientation.

Miranda *et al.* have recently re-framed the collision-induced orientation in terms of canonical mechanism theory [176, 177]. In this treatment, there are $2 \min(j, j') + 1$ mechanisms responsible for transformation of the initial states to the final states. For $\text{NO}(\text{X})$ scattering from $j = 0.5$, there are two possible canonical mechanisms and the observed collision-induced orientation is determined by the angular dependence of the weighting factor between them [176].

Previous experiments investigating the sense of rotation in collisions with argon have been conducted. Experiments with Λ -doublet averaged $\text{NO}(\text{X})$ were undertaken by Lorenz *et al.* [22] and Λ -doublet state selected measurements were later reported by Brouard *et al.* [68]. In addition to describing the orientation effects in the $\text{NO}(\text{X})$ – Kr system, comparisons to the collision-induced orientation effect in Ar will also be made.

5.1 Classical Collision-Induced Orientation Mechanisms

In classical mechanics, the formalism which describes the $\rho_{q\pm}^{\{k\}}(\theta)$ renormalised PDDCSs allows an infinite summation over k (see Chapter 2), allowing for the exact direction of the angular momentum vector to be specified. Through QCT calculations, it is possible to propagate a trajectory across the V_{sum} surface and calculate the classical DCSs and PDDCSs that result. The collision itself can lead to a preferred sense of rotation of the $\text{NO}(\text{X})$ molecule which is scattering angle dependent. A convenient way to analyse the collision-induced orientation is through the polarisation moment, the integrated scattering probability weighted renormalised PDDCS, $a_{1-}^{\{1\}}$. $a_{1-}^{\{1\}}$ quantifies the preferred

sense of rotation for a given final rotational state as [8]

$$a_{1-}^{\{1\}} = \frac{2\pi}{\sigma} \int_0^\pi \frac{d\sigma}{d\omega}(\theta) \rho_{1-}^{\{1\}}(\theta) \sin \theta d\theta. \quad (5.1)$$

The classical polarisation moments for scattering of $\text{NO}(\text{X})$ with Kr show a strong positive orientation (clockwise rotation) in the low Δj ($= j' - j$) states (as shown in Fig. 5.1) but decrease monotonically for middle Δj until negative orientation is observed at high Δj (anti-clockwise rotation). Analysis of the deflection functions and trajectories reveals two limiting mechanisms, one relating to the attractive part of the potential and the other to the repulsive part of the potential.

5.1.1 Attractive Mechanism

The attractive mechanism, as can be seen from the left hand panel of Fig. 5.1 results in strong positive orientation. This mechanism involves scattering from high impact parameters. At impact parameters lower than the glory impact parameter, b_g (where $\theta = 0$), there are typically two types of trajectory associated with every scattering angle (as can be seen by close inspection of the deflection function in Fig. 5.1), one that results in positive (red) and another that results in negative (blue) rotational orientation, leading to net zero collision-induced orientation. At impact parameters higher than the glory impact parameter, trajectories sample primarily the attractive part of the potential, and there is a strong preference for positive orientation. The $\text{NO}(\text{X})$ molecule starts to rotate in the direction of the departing rare gas atom due to the strong attractive interactions between them, as can be seen from the deflection functions in the middle panel of Fig. 5.1 at high b . As there is no negative orientation to cancel the positive orientation, the classical mechanics predicts strong positive orientation in the region of the ℓ -type rainbow and hence strong positive orientation overall, leading to the peak in the polarisation moments.

The attractive mechanism can only operate on trajectories which sample the outermost attractive part of the potential. The high impact parameter collisions cannot generate enough torque to promote a high Δj transition, therefore, the attractive mech-

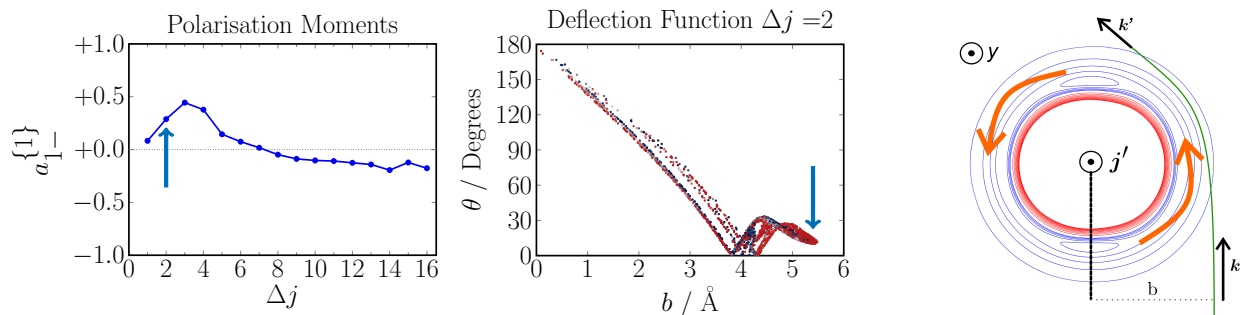


Figure 5.1: The limiting attractive mechanism of the CIO. Left: the classical polarisation moments are shown with $\Delta j = 2$ indicated. Middle: classical deflection function showing positive (red) and negative (blue) rotational orientation for $\Delta j = 2$. A sample trajectory (a single point in the deflection function) is indicated by the arrow. Right: cartoon of the trajectory indicated in the middle panel traversing the $NO(X)$ - Kr PES leading to strong positive rotational orientation.

anism becomes less important as Δj increases and the degree of rotational orientation is diminished.

5.1.2 Repulsive Mechanism

At high Δj ($\Delta j > 3$), the polarisation moments in the left hand panel of Fig. 5.2 display a decreasing trend. The polarisation moments are in general negative after $\Delta j = 7$, representing overall negative orientation. The deflection function in the middle panel of Fig. 5.2 shows that at very low scattering angles, the trajectories leading to positive (red) and negative (blue) orientation cancel out, however, above a certain point ($b \approx 1.8 \text{ \AA}$ for $\Delta j = 16$), the trajectories leading to negative orientation are almost exclusively present. These relatively low scattering angle collisions sample the repulsive wall of the potential and scatter off in the forward and sideways direction, a typical cartoon of such a trajectory is shown in the right hand panel of Fig. 5.2. The finite range of the repulsive potential repels the atom from the molecule at small impact parameters. The equivalent trajectories that would result in positive orientation are therefore not possible and the net result is negative orientation.

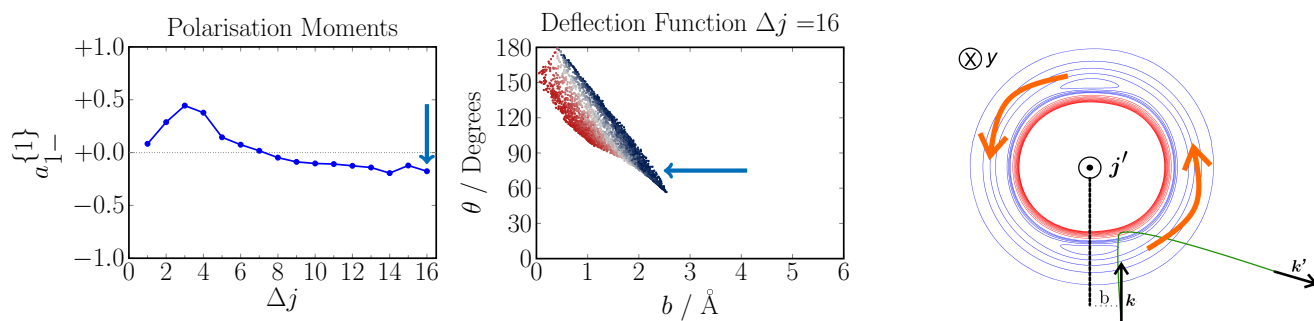


Figure 5.2: The limiting repulsive mechanism of the CIO. Left: the classical polarisation moments are shown with $\Delta j = 16$ indicated. Middle: classical deflection function showing positive (red) and negative (blue) rotational orientation for $\Delta j = 16$. A sample trajectory is indicated by the arrow. Right: cartoon of the trajectory indicated in the middle panel traversing the $\text{NO}(\text{X})$ – Kr PES leading to negative rotational orientation.

5.2 Quantum Mechanical Collision-Induced Orientation

The QMHS model was used in Chapter 4 to accurately predict the collision-induced alignment of the $\text{NO}(\text{X})$ – Xe collision system. It may be expected that, due to the lack of an attractive region and the infinitely steep potential, the QMHS will not display collision-induced orientation due to the similarity with a classical hard shell. For scattering of a classical rigid ellipse with a point like atom, the collision takes place at an infinitely small point-of-contact, causing the symmetry of the system to always have an equal and opposite trajectory resulting in the opposite orientation, so no net orientation is observed. However, QMHS collision-induced orientation is observed, as was theoretically predicted by Hornung as part of an investigation into the origins of the collision-induced orientation [63]. During the quantum mechanical collision, the plane wave of the atom will interact with the molecule over a finite region of the molecular surface, largely determined by the de Broglie wavelength of the system. The symmetry of the trajectories is thereby removed, preventing the trajectories leading to positive orientation, enhancing those leading to negative – or vice versa. The rotation of the molecule during the interaction also removes the temporal aspect of the symmetry, causing the collision to sample a range of bond axes orientations. The

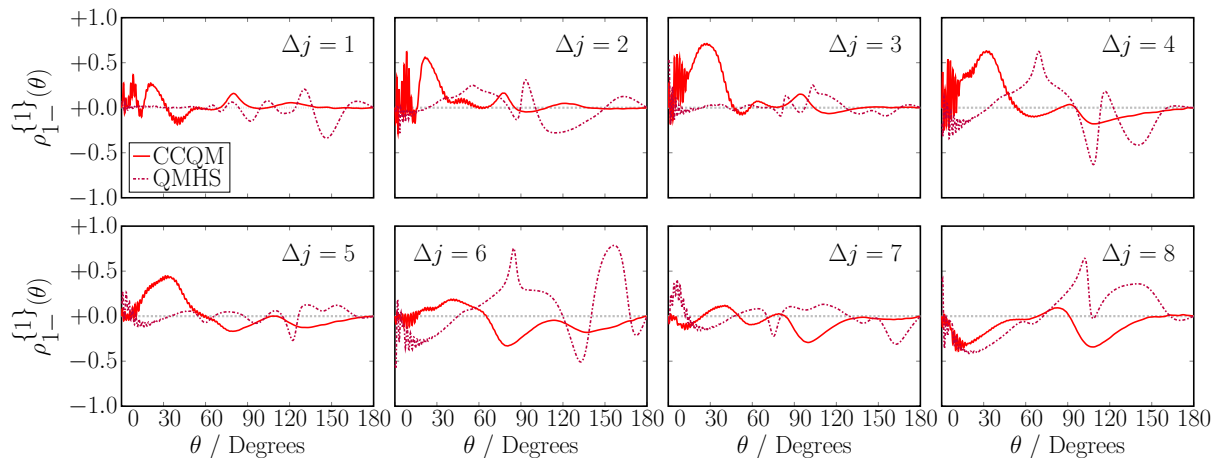


Figure 5.3: In order to determine the effect of the attractive part of the potential, a QMHS model (purple dash-dotted) which has no attraction and an infinitely repulsive at the molecular contour was utilised and compared to the full CC QM (red), averaged over initial Λ -doublets at a collision energy of 520 cm^{-1} .

temporal and spatial non-locality of the QMHS model breaks the symmetry of the collision and allows collision-induced orientation effects to be observed. A comparison of the collision-induced orientation in the $\text{NO}(X)\text{--Kr}$ system obtained from CC-QM calculations and a QMHS model is shown in Fig. 5.3.

The QMHS calculations do not accurately reflect the experimentally observed rotational orientation as it does not take into account the attractive part of the potential. In the forward scattered region (for example $\Delta j = 3$ of Fig. 5.3), where the attraction is most dominant, there is very poor reproduction of the observed orientation. At higher Δj , the agreement becomes slightly better as the collisions become more impulsive and central. From these data, it is possible to conclude that the collision-induced orientation is strongly affected by the attractive part of the potential and is influenced by the quantum mechanical mechanism. This contrasts with the mainly impulsive nature of the collision-induced alignment probed in Chapter 4.

The polarisation moments predicted by open shell CC QM calculations (left panel Fig. 5.4) show a trend similar to the classical polarisation moments (middle panel Fig. 5.4), an indication that the classical limiting mechanisms described above are also important quantum mechanically. The QMHS calculation shows considerably less orientation than the classical or CC QM calculations confirming that although the $a_{1-}^{\{1\}}$ polarisation moment is non-zero, treatment of both the attractive and repulsive region is necessary to reproduce the observed orientation.

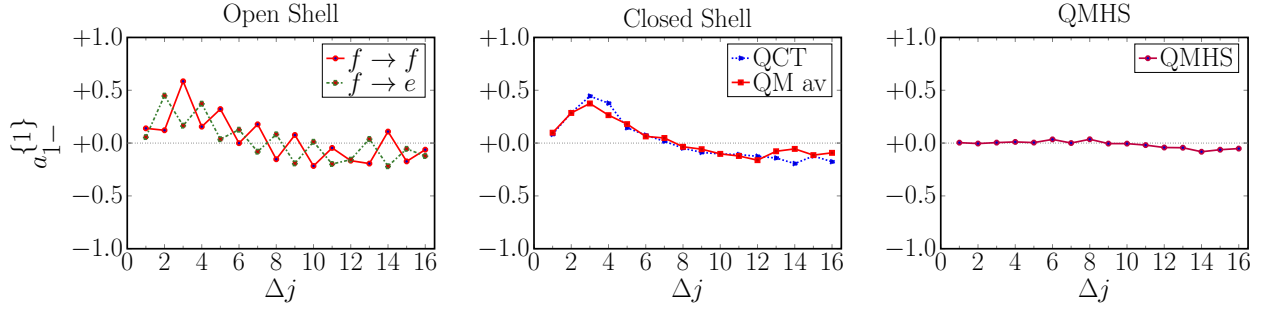


Figure 5.4: Comparison of the $a_{1-}^{\{1\}}$ polarisation moments. The left panel shows the open shell ϵ -conserving (red) and ϵ -changing (green dotted) polarisation moments. The middle panel shows the Λ -doublet averaged QM (red) compared to classical (blue dotted) calculations. The right hand panel shows the $a_{1-}^{\{1\}}$ polarisation moment obtained from QMHS.

5.3 Experimental Results

The scattering of NO(X) with Kr in the orientation geometry described in Chapter 3, was performed for a number of rotational states of interest spanning from $j' = 1.5$ to $j' = 8.5$. In a manner somewhat similar to the horizontal and vertical images obtained in the previous chapter, DCSs were obtained from the angular distributions of the right circularly polarised (R) and left circularly polarised (L) laser images. By utilising the normalised difference of the L and R intensities, the preferred sense of rotation can be obtained. Starting from Eqn. (3.13), in Chapter 3, we must use the $F_{q\pm}^{\{k\}}(\Gamma_{V/H}, \beta)$ factors for the orientation geometry. The orientation geometry directs the excitation laser perpendicular to the plane of the molecular beams (Fig. 3.2 Chapter 3). In this geometry the experiment is primarily sensitive to the $F_{1-}^{\{1\}}(\Gamma_{R/L}, \beta)$ coefficients. These coefficients are given by¹

$$F_{1-}^{\{1\}}(\Gamma_{R/L}, \beta) = \frac{3}{2} h^{(1)}(j, j') c_1(j) \sin \Theta \sin \Phi \sin(2\beta), \quad (5.2)$$

where the angles Θ and Φ obtained from the direction of the laser frame relative to the scattering frame (see Fig. 2.4 in Chapter 2) and $h^{(1)}(j, j')$ is obtained from reference [117]. The direction of the primary axes of the laser frame is given by $\xi = \frac{\sqrt{2}}{2}(0, \pm i, 1)$ for circularly polarised light when the angle $\beta = \pm\pi/4$ [21]. By

¹The $c_1(j)$ coefficients are given as $c_1(j) = [j(j+1)]^{-0.5}$.

making use of Eqn. (3.13) and Eqn. (3.25), we can write the normalised difference in terms of the basis functions generated with the quantum $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs

$$\frac{i_L - i_R}{i_L + i_R}(x, y) = \frac{\sum_n i_L(x, y) - \sum_n i_R(x, y)}{\sum_n i_L(x, y) + \sum_n i_R(x, y)} = \sum_{l=1}^{N_{1-}^{\{1\}}} c_{1-,l}^{\{1\}} B_{1-,l}^{\{k\}}(x, y). \quad (5.3)$$

In the experimental and fitted normalised difference images, black indicates no preferred orientation (an isotropic $\mathbf{j}'$ distribution about the scattering plane), whilst red or green indicates that $I_L > I_R$ and blue or purple indicates that $I_L < I_R$ (the intensity of L is smaller than that of R). Correspondingly then, positive regions of intensity (red to green) indicate preferred clockwise (CW) rotation of the NO as if looked upon from the detector, and negative (purple to blue) indicates that counter-clockwise (CCW) rotational orientation is preferred.

Due to the strongly forward scattered nature of the images from the low states, the fit was truncated to only include the low scattering angle region of the image, where signal intensity is present. In higher states, the whole ion image was included in the fit. Areas of no intensity can therefore have one of two meanings, that there is no preferred sense of rotation or that the scattered intensity in the region is low. To ensure good S/N, a 5% threshold was applied to the raw experimental ion images.

5.3.1 Differential Cross Sections

Differential cross sections for the scattering of NO(X) with Kr, probed with horizontally and vertically polarised light in order to determine the collision-induced rotational alignment have previously been reported by Nichols *et al.* [84] for a wide range of final rotational states in both the spin-orbit conserving and spin-orbit changing manifolds. Images recorded with R and L polarised light also allow determination of the DCSs, the experimentally determined ion images are shown in Fig. 5.5. The images were recorded using the centroiding method outlined in Chapter 3 which allowed for the lowest rotational states of the NO(X)–Kr collision to be probed, and DCSs obtained. The centroiding algorithm allows the blurring associated with the ion ‘splat’ on the phosphor

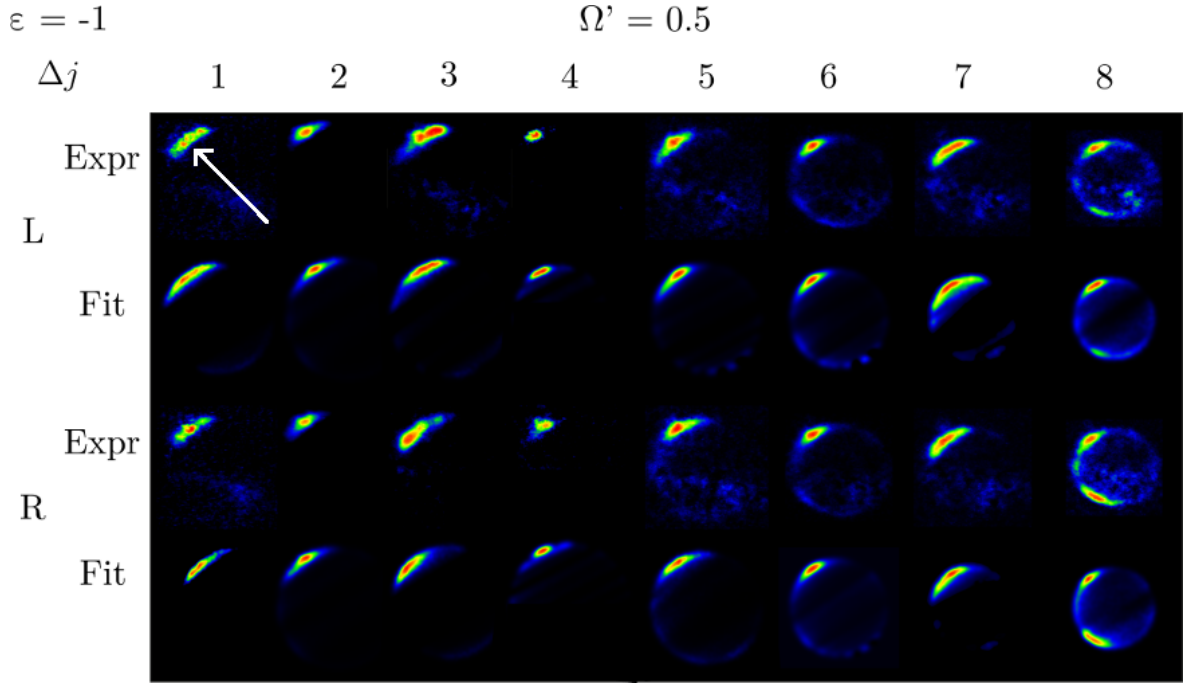


Figure 5.5: Experimental and fitted ion images recorded with R and L polarisation for the $\text{NO}(X)$ – Kr collision system. The images shown pertain to ϵ -conserving -ns on the $\Omega' = 0.5$ spin-orbit manifold.

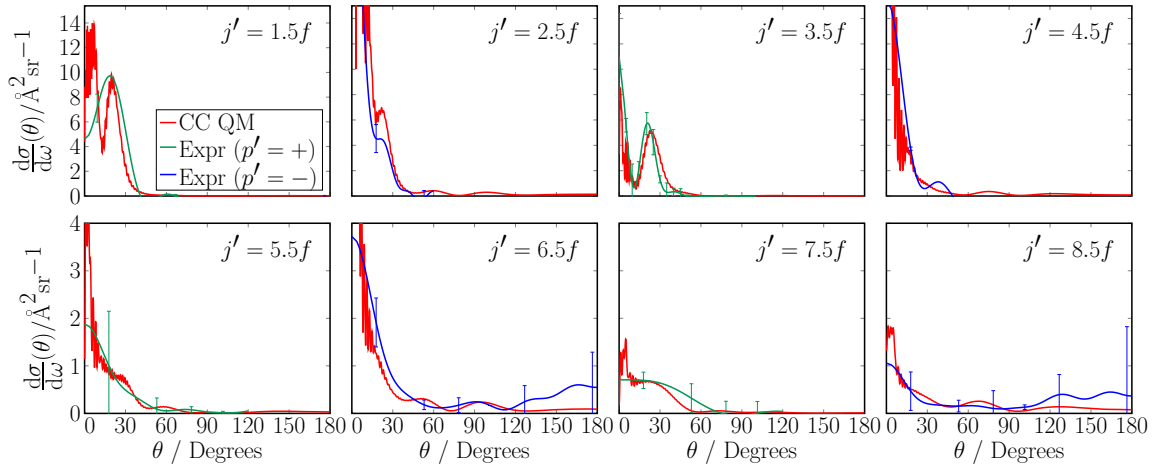


Figure 5.6: The experimental (blue) and CC QM (red) DCSs for the $\text{NO}(X)$ – Kr collisions. The data shown corresponds to the spin-orbit conserving manifold into the final $\epsilon = -1, f$ states and are probed with circularly polarised light the fits are performed for R and L polarisation separately and then summed and averaged.

screen to be minimised and hence allows for efficient background subtraction. The intense forward scattered images could then be separated efficiently from the unscattered background $\text{NO}(X)$ in the beam to obtain a well converged set of experimental images.

The general trends of ion images outlined in Chapter 4 are also followed in the $\text{NO}(X)$ – Kr collision system. The R and L images seen in Fig. 5.5 get smaller as the rotational energy is increased and, like scattering of the $\text{NO}(X)$ – Xe system, the images show a strong degree of forward scattering due to the large polarisable nature of the Kr atom (see Table 2.1 in Chapter 2). The DCSs, extracted by means of the routine described in Chapter 2, are compared with the predictions of CC QM calculations performed with the HIBRIDON [97] suite of codes. The PES of Wen *et al.* [77] was used to propagate the wavefunction from 2 Å to 30 Å. The rotational basis set consisted of j' from 0.5 to 20.5 with partial waves up to and including $J = 300.5$ in order to ensure convergence. The calculations were performed over a grid of collision energies from 400 cm^{-1} to 600 cm^{-1} and the interpolation algorithm described in Chapter 2 was employed in order to average and interpolate the observables to the collision energy of the experiment.

The extracted DCSs are shown in Fig. 5.6, where excellent agreement between the scaled experimental angular distributions and CC QM calculations is demonstrated. The good agreement between the CC QM calculations and experimental DCSs has been noted in the past by Nichols [84] for DCSs recorded on the spin-orbit conserving manifold for both ϵ -conserving and ϵ -changing collisions with a H/V polarised excitation laser. Near quantitative agreement has also been found by Onvlee *et al.* in the forward scattered region and the region of the ℓ -type rainbow for scattering of krypton on the spin-orbit conserving manifold [82]. These measurements of the DCS also show good agreement with the potential surfaces of Wen *et al.* [77].

ℓ -type Rainbow

As was shown for the low j' scattering in xenon (see Chapter 4), the experimental images of krypton display evidence of ℓ -type rainbows in the forward scattered region

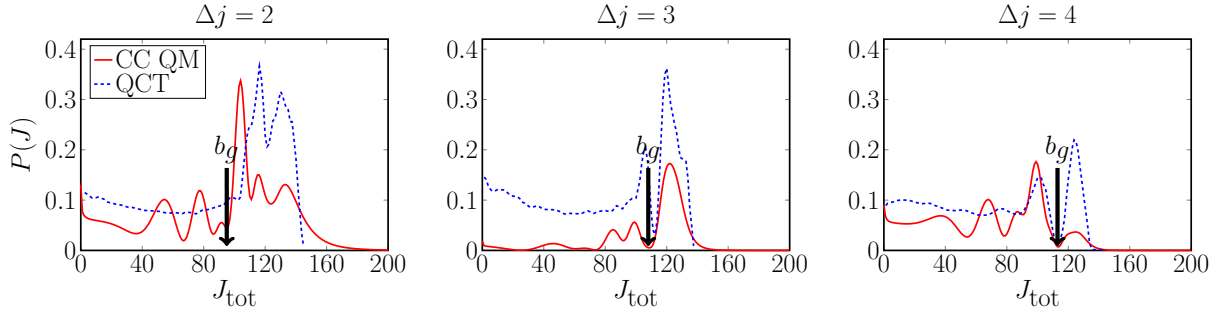


Figure 5.7: Classical QCT (blue dashed) and CC QM (red) opacity functions for the low Δj transitions where the attractive part of the potential leads to the appearance of an ℓ -type rainbow. The classical impact parameter is given in terms of $|\ell| = \mu v_{\text{rel}} b$, which at low Δj approximates the total angular momentum, J_{tot} . The glory impact parameter at which $\theta = 0$ is highlighted by the black arrow.

of the low $j' \in (1, 3)$ images. As was the case as scattering with Xe, the ℓ -type rainbow has been shown to be a result of trajectories above the glory impact parameter being deflected by the attractive part of the potential, as shown in Fig. 5.1. Comparison of the classical and quantum opacity functions in Fig. 5.7 highlights this point, with the classical glory impact parameter marked by the arrow.

The orientation in the area of the ℓ -type rainbow is of particular interest, as it is here that the limiting classical mechanism leading to positive orientation is most intense. As has been shown in the classical deflection functions in Fig. 5.1, the region of the rainbow past the glory impact parameter leads almost exclusively to positive orientation, so a strong orientation effect is expected to be observed experimentally. Inspection of $j' = 3.5f$ in Fig. 5.5 shows a strong orientation effect. As the scattering frame y -axis changes sign along $\mathbf{k}$, the R polarised light preferentially detects molecules rotating in an anti-clockwise direction in the plane of the molecular beams (if looked at from above) [22] and the L polarised light preferentially detects molecules rotating clockwise. Although these molecules have the opposite sense of rotation in the plane defined by the molecular beams, the scattering frame has inverted along $\mathbf{k}$ leading to the same orientation preference on the fast side and the slow side of the image. In $j' = 3.5f$, there is a very clear difference in the R and L polarised images, showing near total asymmetry about $\mathbf{k}$ indicating a very strong orientation effect is present. These parity effects will be explored further in the next section.

Parity Effects

As in the scattering of NO(X) with Xe investigated in Chapter 4, the experimental images for NO(X) scattering with Kr display strong parity effects, illustrated by Fig. 5.5. For the parity conserving (Δj even in the experimental images presented here) transitions, the images are very forward scattered with little intensity beyond that region. In the parity-changing transitions, there is significant intensity to higher angular range. As was demonstrated in Chapter 4, these parity dependent oscillations can be explained qualitatively by a simple 4-path model that accounts for interference between trajectories scattering off the ends and sides of the NO(X). The model has been shown to successfully explain the parity dependent behaviour in the scattering of NO(X) with Ar by Eyles *et al.* [12] and in the scattering of Kr by Nichols *et al* [84,173].

5.3.2 Collision Induced Orientation

The R and L images can be used in an analogous way to the H and V images in Chapter 4 to retrieve the degree of collision-induced orientation. As the laser light used in this experiment is left or right circularly polarised and directed perpendicular to the plane of the molecular beams, the experiment is primarily sensitive to the $\rho_{1-}^{\{1\}}(\theta)$ orientation renormalised PDDCSs [68]. The experiment therefore gives a measure of the sense of rotation of the NO(X) after collision with the rare gas, the collision-induced orientation. The CIO is a multipole of the three vector $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ correlation, and provides information on whether the NO(X) is rotating clockwise or counter-clockwise as a function of scattering angle. The CIO has been shown previously to be highly sensitive to attractive and repulsive forces that govern the collision [68], and is strongly affected by the temporal and spatial non-locality of the collision [63]. The mechanism giving rise to the CIO has been demonstrated to be a result of quantum interference, which leads to highly oscillatory and asymmetric intensity distributions in the R and L images [63,103]. The effect of the attractive region is most clearly seen in $j' = 3.5f$ (see Fig. 5.8), where at the rainbow angle, there is maximum orientation of the $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCS. This strong positive orientation occurs at the angular range in

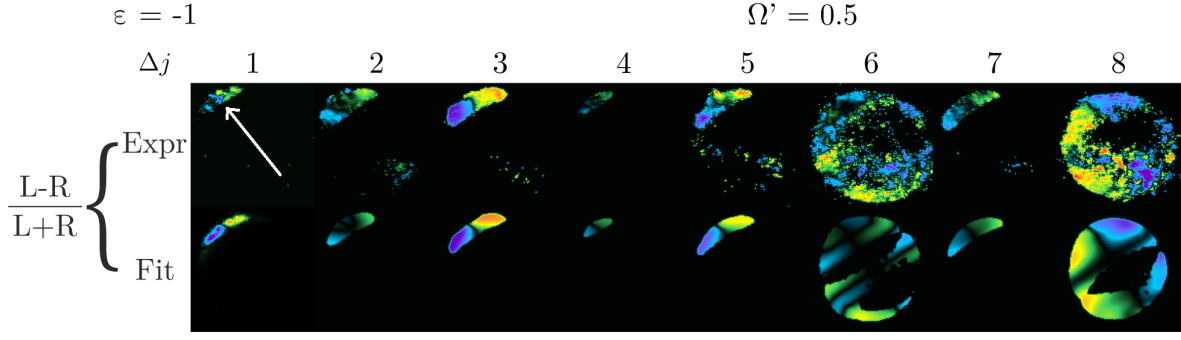


Figure 5.8: $\frac{L-R}{L+R}$ normalised difference images obtained from the raw R and L images shown in Fig. 5.5. Blue indicates areas of negative intensity and red of positive intensity. The experimental images are shown in the top panel and fits to the data are shown in the bottom panel. All transitions shown pertain to ϵ -conserving transitions on the spin-orbit conserving manifold. The directional significance of the positive and negative regions is described at the end of Section 5.3.

which the ℓ -type rainbow is observed in the angular distribution.

The experimental and fitted normalised difference $\left(\frac{L-R}{L+R}(x, y)\right)$ images obtained from the right and left circularly polarised light are shown in Fig. 5.8. The normalised difference images show the sign inversion when rotated around the relative velocity vector, $\mathbf{k}$. This is understood by considering the sign of the scattering frame $\mathbf{y}$ -axis for the different parts of the image, as discussed in section 5.3.1. Towards the centre of the image, where the out-of-plane scattering contributions are maximal, the scattered intensity is low and therefore the sense of rotation cannot be easily probed.

The experimentally determined $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs are shown in Fig. 5.9. There is generally good agreement between the fitted and experimental $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs. There are some differences: for instance, in $j' = 8.5f$ where the magnitude of the change in orientation is not completely captured, and in $j' = 5.5f$ where the orientation appears to be underestimated. This may not be an issue with depolarisation as the positive and negative orientation would become equally depolarised. The magnitude of the orientation in the forward scattered region is very sensitive to the attractive part of the potential at low rotational excitation, highlighting the importance of the attractive mechanism. For the parity-changing transitions, the ℓ -type rainbow can be seen in the DCSs and the sense of orientation is almost at the quantum mechanical maximum [19, 121]. For the parity-conserving states, no ℓ -type rainbow is observed in the experimental DCS images as it is masked by glory scattering. The

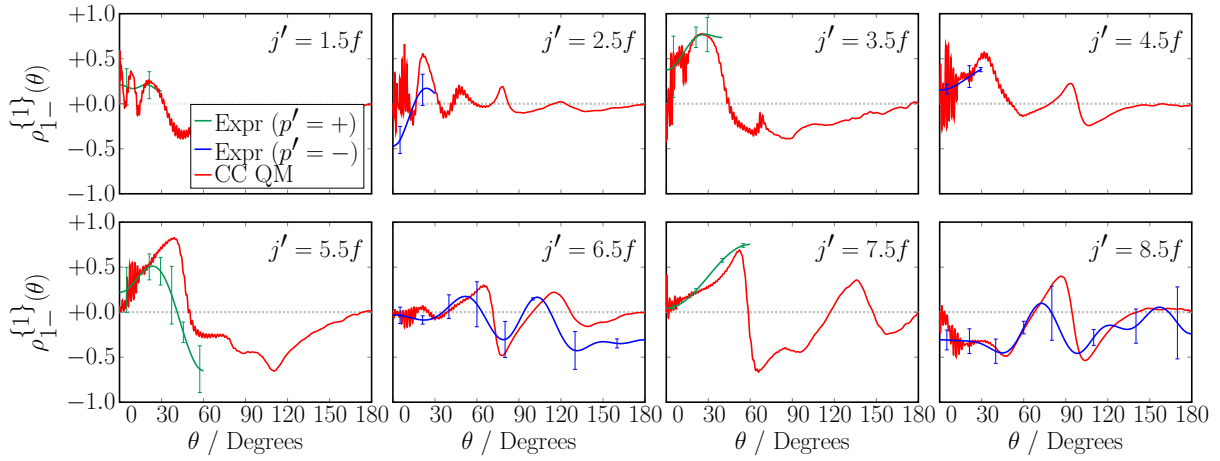


Figure 5.9: The CC QM (red) versus experimental (blue, $p' = -$ and green, $p' = +$) $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs are compared. The experimental PDDCSs are obtained from the fitting algorithm described in Chapter 2. There is generally excellent agreement between the CC QM and experimental data highlighting the accuracy of the PES of Wen *et al.* [77]

limiting attractive orientation mechanism still leads to strong positive orientations as trajectories above the glory impact parameter are deflected by the potential in a similar manner to the parity-conserving transitions. The limiting mechanism leading to the intense rainbow scattering is illustrated by Fig. 5.10, showing how far-side scattering results in the same positive orientation. Deflection of the molecule to the far side of the Kr atom results in anticlockwise rotation of the NO molecule and therefore preferential detection by R polarised light and consequently negative intensity in the normalised difference ion image. In the situation shown in Fig. 5.10, the rotational angular momentum $\mathbf{j}'$ lies parallel to the $\mathbf{y}$ -axis, and is therefore positively oriented. The path of an equivalent trajectory, rotated about the dashed grey line representing V_{Kr} , is shown by blue arrows in Fig. 5.10. In this situation, although the molecule is rotating clockwise in the lab frame after the collision (and thus the normalised difference experimental ion image is positive), the scattering frame is inverted due to the different direction of $\mathbf{k}'$, and so $\mathbf{j}'$ is still parallel to the y -axis.

As j' increases, the frequency of the oscillations in the $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs can be seen to decrease, and the magnitude of the integrated $a_{1-}^{\{1\}}$ polarisation parameter also decreases, as has been shown previously [103]. The decrease in the magnitude of the $a_{1-}^{\{1\}}$ polarisation parameter is caused by the classical repulsive mechanism becoming

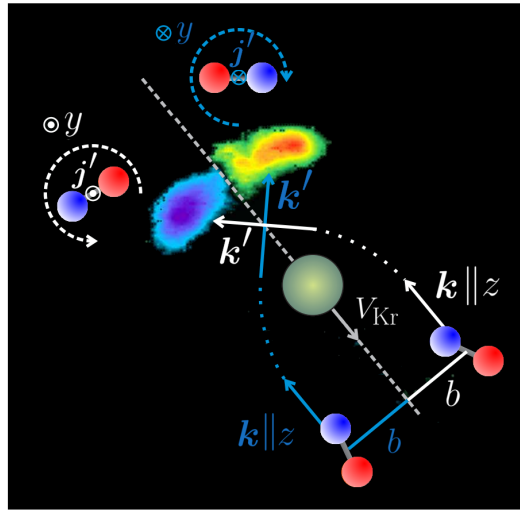


Figure 5.10: Cartoon of the classical attractive collision interaction with scattering leading to strong positive orientation. The attractive forces result in strong polarisation along $+y$, the y -axis lies parallel to $\mathbf{k} \times \mathbf{k}'$.

dominant, as discussed earlier in the chapter. At low j' , the sign change in $\rho_{1-}^{\{1\}}(\theta)$ occurs over the entire angular range at high frequency, but is especially evident in the low scattering angle range. At higher j' , the fast sign changes disappear and a few broad nodes appear in $\rho_{1-}^{\{1\}}(\theta)$. As has been discussed, at higher j' the limiting repulsive mechanism begins to play a role and the $a_{1-}^{\{1\}}$ moments become more negative. The decreased frequency of the oscillations observed in the $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs can be explained in terms of the outgoing de Broglie wavelength of the system, as has been described in the $\text{NO}(\text{X})$ –Ar system previously [84, 103]. The final relative velocity, $\mathbf{k}'$, of the system decreases in magnitude as more energy is transferred into rotation, resulting in a corresponding increase in the outgoing de Broglie wavelength. If the de Broglie wavelength is large in comparison to the phase shift that results in the parity dependent oscillations (see Chapter 4), then the interference will cause a slow rise or drop in the $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCS with scattering angle.

Comparison to classical renormalised PDDCSs

Classical trajectories run over the V_{sum} surface of $\text{NO}(\text{X})$ –Kr can be used to compare the quantum to the classical effects. After running several million classical trajectories, the results reveal the sense of rotation and the classical angular distributions of the $\text{NO}(\text{X})$ –Kr collision. The QCT and QM angular distributions are shown in Fig. 5.11.

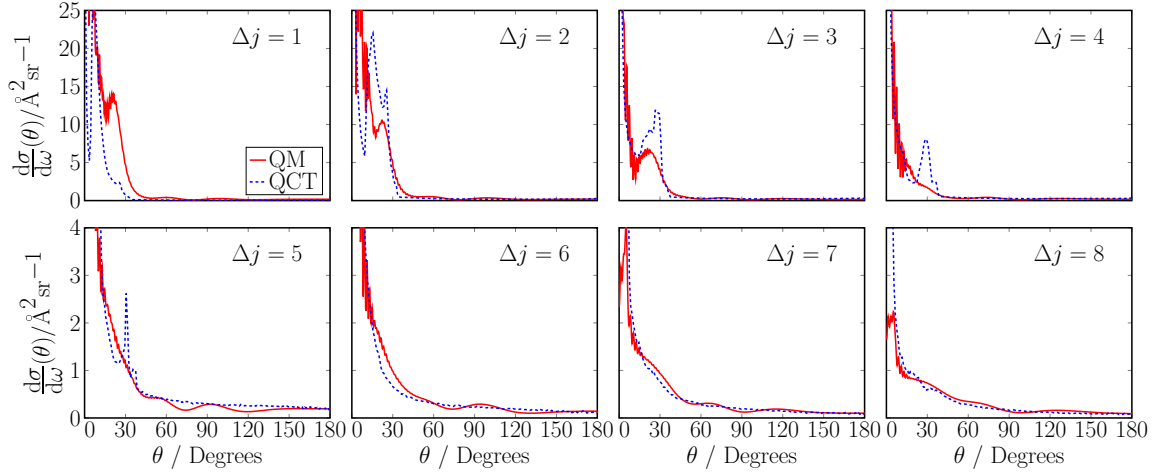


Figure 5.11: A comparison between the Λ -doublet averaged CC QM (red solid) and classical QCT calculations (blue dotted) at a collision energy of 515 cm^{-1} . CC QM calculations have been summed and averaged over initial and final Λ -doublet and spin-orbit levels to facilitate comparison with the closed-shell classical calculations.

The angular distributions themselves highlight the classical nature of the forward ‘glory’ type scattering, but also that a secondary ℓ -type rainbow peak appears in many Δj states in the QCT that is not present in the CC QM calculations.

The key differences in the CC QM and QCT DCSs are that in the forward scattered direction, where the QCT results displays evidence of an ℓ -type rainbow phenomenon at all low Δj states [19, 84], whereas the QM calculations do not. More informative is the $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCS calculated from the classical trajectories across V_{sum} , shown in Fig. 5.12. The classical $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs from QCT calculations shows marked differences from the CC QM $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs. In the forward direction, where the attractive part of the potential is probed, the classical QCT calculations display strong orientation across the ℓ -type rainbow (between $\theta = 20^\circ$ and $\theta = 40^\circ$) and it is predicted for all low Δj states. In the CC QM treatment, there is no such strong preference unless the rainbow is correctly predicted, as for $\Delta j = 3$. The oscillations at higher Δj are not observed in the classical treatment at all; instead, the polarisation of $\rho_{1-}^{\{1\}}(\theta)$ decreases towards zero at higher scattering angle. The QCT $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs give further evidence for two limiting mechanisms for the orientation, one involving the attractive and the other involving the repulsive part of the potential [68].

A qualitative description of the rotational alignment of the angular momentum

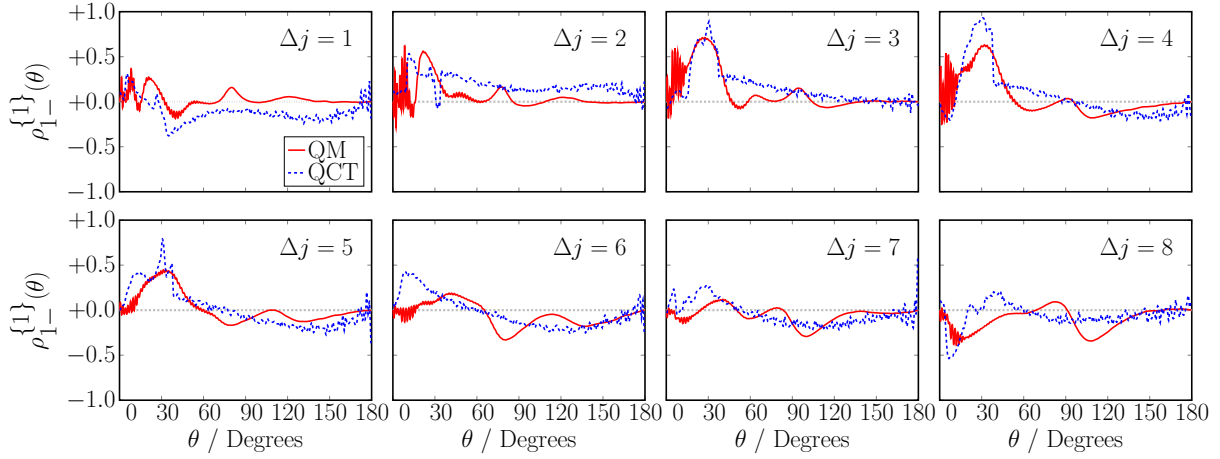


Figure 5.12: A comparison of the summed and averaged CC QM (red) and classical QCT (blue dashed) $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs. The effect of the attractive part is clearly visible in the classical calculations at low θ where an ℓ -type rainbow is consistently predicted, this feature is significantly diminished in the CC QM calculations, highlighting the importance of the correct treatment of the attractive part of the potential.

vector, $\mathbf{j}'$, can be given by the kinematic apse model. Quantitative information about the angular momentum vector that agrees with experiment can only be obtained from a fully quantum mechanical model of the collision, as has been shown by the study of the NO(X)–Xe system in Chapter 4. In order to visualise the differences between the CC QM and classical collision-induced polarisation, angular momentum portraits [116], introduced in Chapter 2, can be formulated from the $\rho_{q\pm}^{\{k\}}(\theta)$ renormalised PDDCSs.

The angular momentum portraits quantitatively display the direction about which the polarisation of $\mathbf{j}'$ is as localised as possible [119]. Differences between the collision-induced polarisation as a function of scattering angle between the CC QM and classical models can then be visualised by expanding the renormalised PDDCSs from the CC QM and classical mechanics calculations. The angular momentum portraits over the region of the ℓ -type rainbow in $\Delta j = 3$ are shown in Fig. 5.13.

The angular distributions in the background, obtained from simulation with the classical and CC QM DCSs, also show how the QCT model wrongly predicts a rainbow in all low Δj transitions as it does not account for the parity dependent effects. The CC QM calculations however, predict a strong ℓ -type rainbow resonance only for $j' = 3.5f$. The collision-induced polarisation, consisting of the $\rho_0^{\{2\}}(\theta)$, $\rho_{1+}^{\{2\}}(\theta)$ and $\rho_{2+}^{\{2\}}(\theta)$ alignment renormalised PDDCSs and the $\rho_{1-}^{\{1\}}(\theta)$ orientation renormalised

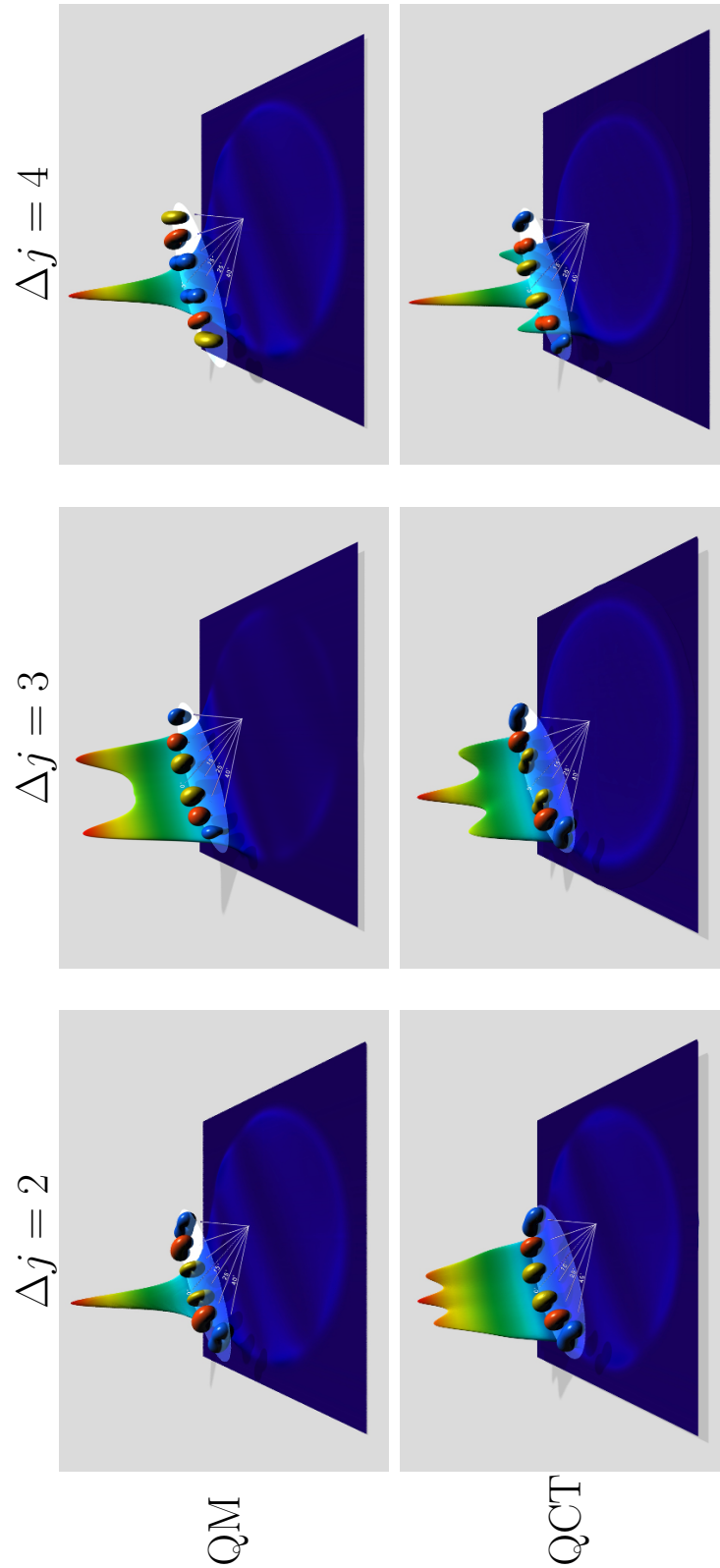


Figure 5.13: Simulated angular distributions using the CC QM (top panel) and classical (bottom panel) DCS. The angular momentum portraits created with the $\rho_{1-}^{\{1\}}(\theta)$, $\rho_0^{\{2\}}(\theta)$, $\rho_{1+}^{\{2\}}(\theta)$ and $\rho_{2+}^{\{2\}}(\theta)$ renormalised PDDCSs are drawn at the corresponding angles on the angular distributions. The yellow probability density function is at 15° , the red at 25° and the blue is drawn at 45° . Each portrait represents the direction of the angular momentum vector with respect to $\mathbf{k}$.

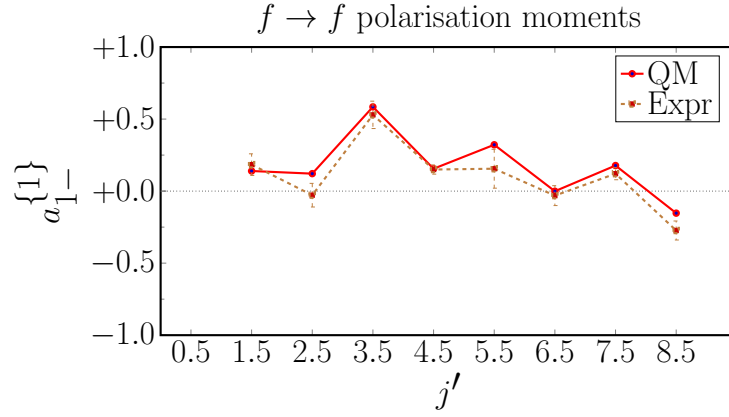


Figure 5.14: The experimentally determined and CC QM $a_{1-}^{\{1\}}$ polarisation moments for the spin-orbit and ϵ -conserving transitions of $\text{NO}(X)$ after scattering with Kr at 514 cm^{-1} .

PDDCSs, also show substantial differences. These differences highlight the importance of quantum effects in the collision and reinforce the results presented in Chapter 4 regarding the importance of the correct treatment of the attractive part of the potential, especially in the forward scattered direction.

5.3.3 Polarisation Moments

The $a_{1-}^{\{1\}}$ polarisation moments were calculated from the experimental angular distributions and renormalised PDDCSs. The $a_{1-}^{\{1\}}$ polarisation moments are a measure of the $\mathbf{k}-\mathbf{j}'$ correlation and quantify the degree of rotational orientation expected to be observed upon scattering to a particular final state. The experimental polarisation moments are obtained from the experimental angular distribution and renormalised $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs *via*

$$a_{1-}^{\{1\},\text{expr}} = \frac{2\pi}{\sigma^{\text{QM}}} \int_0^\pi \frac{d\sigma^{\text{expr}}}{d\omega}(\theta) \rho_{1-}^{\{1\},\text{expr}}(\theta) \sin \theta d\theta \quad (5.4)$$

The CC QM integral cross section, σ^{QM} , is used in place of an experimentally determined integral cross section as the experiment does not provide a direct measure of the state-to-state integral cross section. The values of the experimentally determined polarisation moments compared to CC QM calculations are shown in Fig. 5.14.

The QM polarisation moments tend to be larger than those determined experimen-

tally, as demonstrated in Fig. 5.14. This is likely due to the truncation in the DCS and PDDCS measurements when there is very low scattering intensity. The QM integral cross section is not truncated, so using it in the denominator causes the experimental $n_{1-}^{\{1\}}$ normalised PDDCSs to be slightly reduced in magnitude. None of the $a_q^{\{k\}}$ polarisation moments have been previously measured for the $\text{NO}(\text{X})$ – Kr system, although the data could be obtained from the $\rho_{q+}^{\{2\}}(\theta)$ moments presented by Nichols [84]. The close agreement demonstrates that the *ab initio* surfaces of Wen *et al.* [77] correctly model the attractive and repulsive regions of the potential, as well as the parity dependent interference evident in the oscillatory character of Fig. 5.14.

5.4 Orientation on Modified Potential Energy Surfaces

To further explore the influence of the attractive part of the potential, and the potential anisotropy, the surfaces can be modified to remove the attractive part of the V_{sum} surface and then used in subsequent CC QM calculations with the HIBRIDON suite of scattering codes.

5.4.1 Effect of The Attractive Part

As has been shown, the attractive part of the potential strongly influences the sense of rotation and the degree of preference for a particular sense as a function of scattering angle. This effect is most apparent in collisions resulting in low rotational excitation. The QMHS model demonstrates the origins of the collision-induced orientation as being a manifestation of temporal and spatial nonlocality of the collision interaction, as has been demonstrated by Hornung in the $\text{NO}(\text{X})$ – Ar system [63]. The CC QM calculations can also be modified to remove most of the attractive region. This quantum soft-shell, created by truncating the $\text{NO}(\text{X})$ – Kr potential in order to remove the attractive part,

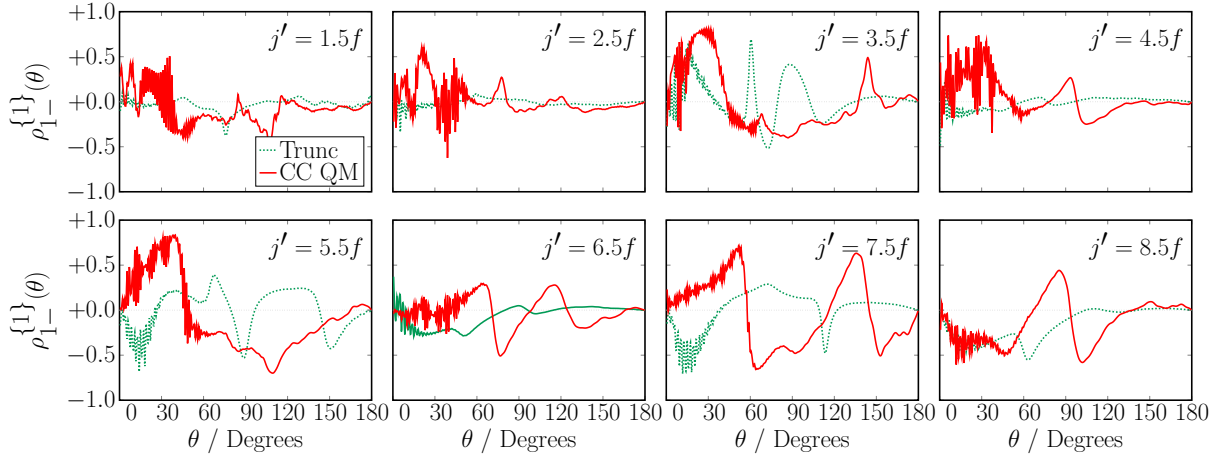


Figure 5.15: Figure comparing the full potential (red) with the soft-shell potential (green, dashed) for the NO(X)–Kr system. The open-shell CC QM calculations shown are for the ϵ and spin-orbit conserving transitions at a collision energy of 520 cm^{-1} .

can be constructed by applying [68, 103]

$$V_{\text{sum}}(R, \gamma) = V_{\text{sum}}(R, \gamma) f(R, R_0, R_{\text{shift}}, \alpha) \quad (5.5)$$

$$V_{\text{diff}}(R, \gamma) = V_{\text{diff}}(R, \gamma) f(R, R_0, R_{\text{shift}}, \alpha) \quad (5.6)$$

where the truncation function $f(R, R_0, R_{\text{shift}}, \alpha)$ is given in terms of the Jacobi distance, R , by

$$f(R, R_0, R_{\text{shift}}, \alpha) = 1 - \frac{1}{1 + \exp(-\alpha(R - R_0 + R_{\text{shift}}))}. \quad (5.7)$$

Here, α is a parameter that determines the steepness of the scaling as a function of R and R_0 is the size of the potential contour at a collision energy of 0 cm^{-1} . The critical parameter R_{shift} ensures the potential drops below 1% of the collision energy at a value of R_0 by shifting the inflection point of the function. The function varies asymptotically between 0 and 1, which ensures smooth scaling of the PESs and that propagation will not fail due to discontinuities in the potential. The soft-shell quantum mechanical PES can then have the usual scattering calculations performed on it using the HIBRIDON suite of codes [97]. Analysis of the $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs shown in Fig. 5.15 show quite a marked difference between the full potential and the QM soft-shell potential. The orientation is strongly diminished at low scattering angle and in the cases of the parity-changing, high j' states, inverted. The attractive part of the potential, being dominant in collisions leading to low rotational excitation, results to

the sense of rotation at these angles being nearly zero due to the removal of paths that would otherwise lead to positive orientation through the limiting classical attractive mechanism described earlier in the chapter. For the highest rotational excitation, the soft-shell CC QM and full potentials show more similar behaviour, showing in general negative orientation. The oscillation in the $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCS observed at middle θ for most states is not as prevalent in the soft-shell CC QM model.

5.4.2 Effect of The Homonuclear Terms

The potential can also be modified to remove contributions from the odd V_κ terms. Since the odd terms define the potential anisotropy, their removal makes the $\text{NO}(\text{X})$ potential homonuclear in nature. The anisotropy of the potential has a very clear influence on the collision-induced orientation. As has been discussed, the origins of the CIO lie in the spatial and temporal non-locality of the collision and the plane wave of the $\text{NO}(\text{X})$ interacting with the rare gas causes the collision to sample many different bond axis orientations [84]. If each end of the $\text{NO}(\text{X})$ is the same, *i.e.* homonuclear, then the CIO is heavily influenced as interference resulting from scattering off the nearly similar ends will no longer occur. The general trends in the even Δj transitions remain, although at higher j' multiple oscillations are predicted and the phase and angular positions of the oscillations in $\rho_{1-}^{\{1\}}(\theta)$ are often incorrect. The form of the $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCS gives information about the anisotropy of the potential and the good agreement between the experimental and theoretical $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs is further evidence of the accuracy of the potentials of Wen *et al.*

The difference in magnitudes for the QCT and QM DCSs shown in the previous section reflect the limitations in the closed shell QCT calculations. For a given impact parameter, rotational excitation can result from trajectories striking either the N-end or the O-end of the molecule. Quantum mechanically, these paths will interfere. For a homonuclear molecule such as N_2 , the interference will result in the cross sections for parity changing collisions going to zero. If $\text{NO}(\text{X})$ is treated as a homonuclear molecule, the total interference makes the parity changing (odd) transitions disappear, as can be seen in Fig. 5.16. The added symmetry of the potential surface on the N-end and

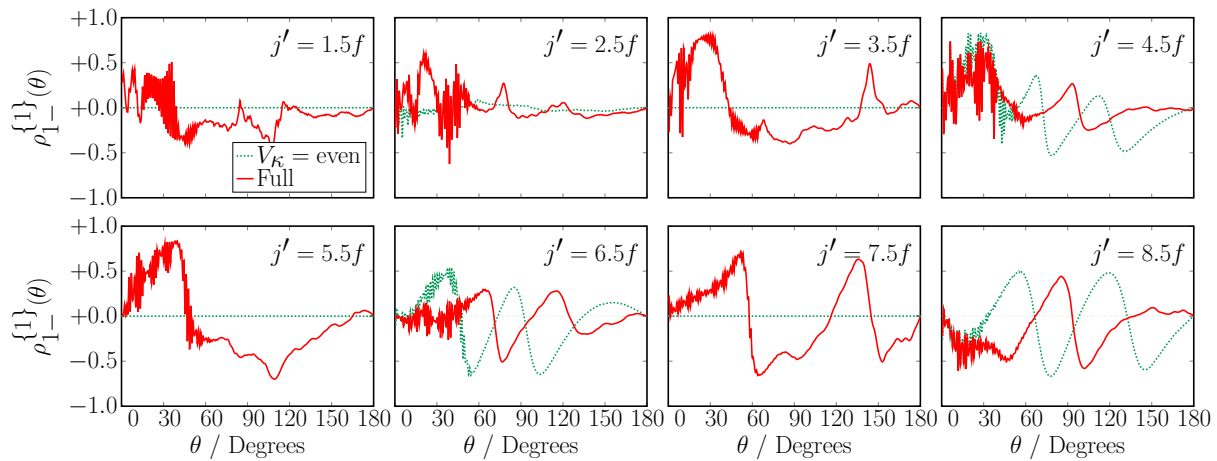


Figure 5.16: The $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs are shown on a model potential in which the odd terms have been set to zero (green dotted), compared to the PDDCSs obtained from the full CC QM potential (red). The anisotropy of the molecular potential plays a critical role in the determination of the collision-induced orientation.

O-end of the molecule radically affects the observed $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs.

5.5 Comparison to Argon

Studies of the collision-induced orientation with argon have been extensively reported, both without initial state selection [22] and with state selection [63, 68]. Compared to argon, krypton has a larger, more extensive attractive potential and has a considerably larger mass. The attractive part of the potential has a large effect on the degree of orientation, which is clearly seen in the plot of the polarisation moments of Ar and Kr shown in Fig. 5.17. The effect of the attractive part is clear at low rotational excitation, where, since Ar has a much smaller attractive region, the classical attractive mechanism is less effective and therefore leads to a lower degree of orientation in the calculated (and experimental [84]) $a_{1-}^{\{1\}}$ polarisation moments. Since the $\text{NO}(X)$ –Ar potential is less attractive and better approximated by a hard shell, the classical repulsive mechanism leads to a greater degree of negative orientation at high rotational excitation compared to Kr. The parity dependent oscillations are still clearly visible in both systems.

The differences between the polarisation moments of the Ar and Kr collision systems warrants closer inspection of the renormalised PDDCSs. The comparison between the $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs obtained from CC QM calculations for the Ar and Kr

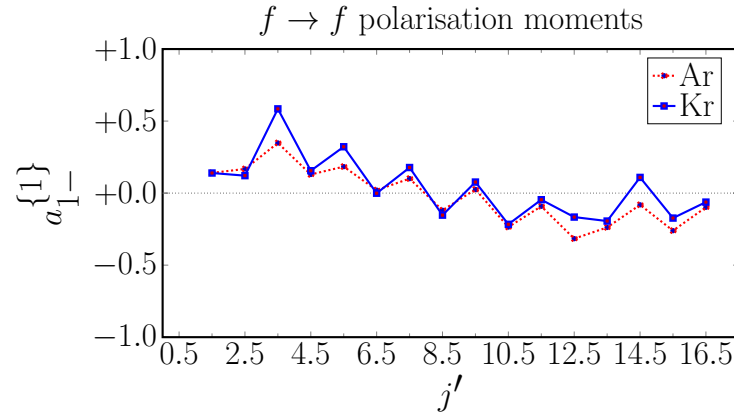


Figure 5.17: $a_{1-}^{\{1\}}$ polarisation moments calculated for Kr (blue) and Ar (red dotted). The data shown are ϵ and spin-orbit conserving at a collision energy of 520 cm^{-1} .

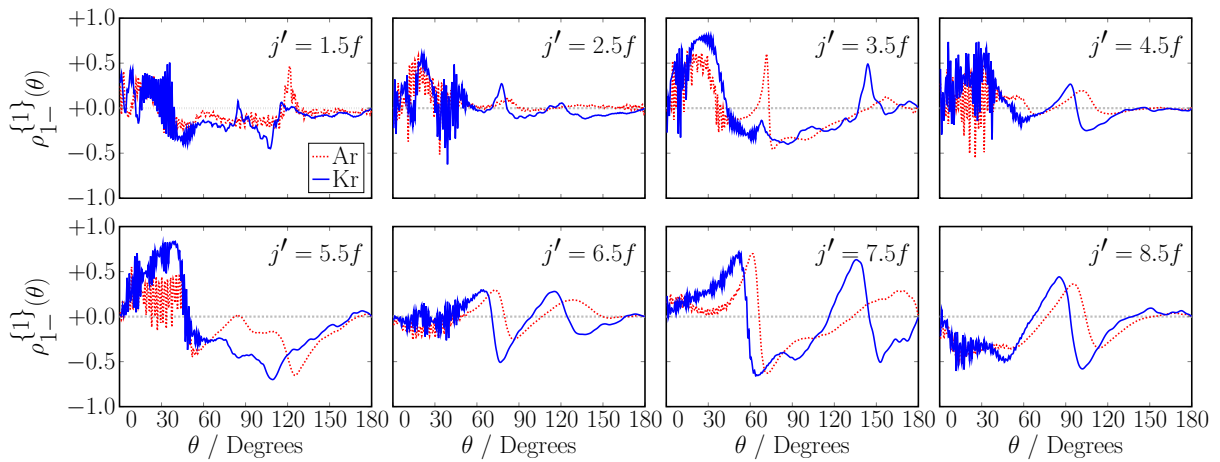


Figure 5.18: $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs obtained from CC QM scattering calculations are compared between krypton (blue) and argon (red dotted) at a collision energy of 520 cm^{-1} . The transitions shown are ϵ -conserving on the spin-orbit conserving manifold.

collision systems are shown in Fig. 5.18. The most obvious difference between the $\text{NO}(X)\text{--Ar}$ and $\text{NO}(X)\text{--Kr}$ $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs is the degree of orientation. The $\text{NO}(X)\text{--Kr}$ potential gives rise to a stronger sense of orientation than that of the $\text{NO}(X)\text{--Ar}$ potential for all states. This is mainly due to the attractive part of the potential which strongly affects the degree of CIO in the low rotational transitions. It is expected that the decreased de Broglie wavelength of the $\text{NO}(X)\text{--Kr}$ collision system ($\lambda = 2.47 \times 10^{-11} \text{ m}$ for Kr and $\lambda = 2.75 \times 10^{-11} \text{ m}$ for Ar) will also have an effect in diminishing the degree of negative orientation at higher rotational excitation, as has been discussed previously [103]. At low scattering angle, argon also displays a build up in orientation preference near the rainbow angle, as in krypton. The ℓ -type rainbow in

the low j' states of $\text{NO}(\text{X})$ –Ar collisions is much smaller than in $\text{NO}(\text{X})$ –Kr collisions due to the reduced well depth. It is also largely hidden by glory type scattering in the DCS. Consequently, the degree of orientation at the rainbow angle is also lower in the $\text{NO}(\text{X})$ –Ar collision system.

The classical repulsive mechanism is more effective at producing negative orientation in Ar than in Kr. The wavevector and de Broglie wavelengths of the systems are also different which will effect the parity dependent oscillations – this affect is balanced by the modest decrease in the de Broglie wavelength of the $\text{NO}(\text{X})$ –Kr system compared to the $\text{NO}(\text{X})$ –Ar system ($\lambda = 2.47 \times 10^{-11}\text{m}$ and $\lambda = 2.75 \times 10^{-11}\text{m}$ respectively).

5.6 Summary

The collision-induced orientation of collisions of $\text{NO}(\text{X})$ with Kr has been probed. The collision-induced orientation provides an example of a $\mathbf{k}$ – $\mathbf{k}'$ – $\mathbf{j}'$ correlation and can be used to localise the direction of the angular momentum vector to a minimum uncertainty probability distribution. By using previously determined experimental results on the collision-induced alignment, combined with experimental values of the $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCS, the minimum uncertainty direction of the angular momentum vector after collision with Kr can be determined. The CIO has been shown to be highly sensitive to both the attractive and repulsive parts of the molecular potential. The polarisation moments, obtained from integrating the intensity weighted normalised PDDCSs, reveal two mechanisms that lead to CIO, one that relies upon the long range attractive part of the potential and the other which relies on short range repulsive interactions. Λ -doublet averaged CC QM calculations show good agreement with the classical calculations, however, the full CC QM polarisation moments and renormalised PDDCSs show oscillations as a function of parity, indicating that parity dependent interference effects influence the CIO. A hard shell model and soft-shell QM potentials were used to demonstrate that the classical mechanisms apply to the quantum calculations and that the parity dependent interference is qualitatively explained by the extent of the PESs and de Broglie wavelengths of the system. A fully QMHS model

was shown to display CIO, hinting that quantum mechanically, the CIO arises from temporal and spatial non-locality [63]. The data presented in this chapter support the conclusions of Chapter—4, however, the CIO is more sensitive to the attractive part of the potential across the angular range than the collision-induced alignment or the angular distributions.

Future experiments will allow the determination of the $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCS with steric resolution, a multipole of the $\mathbf{r}-\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ 4-vector correlation which is predicted to show high sensitivity to the end of the molecule upon which the collision is focussed. Such an experiment would highlight the importance of interference between the N-end and O-end of the molecule and the relative balance between attractive and repulsive forces that govern the $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCS.

Integral Steric Effects

The steric preference for excitation to a particular rotational state is quantified by the steric asymmetry, which represents a multipole of the $\mathbf{r}\text{-}\mathbf{k}$ vector correlation. Measurement of the steric effect corresponds to a vector correlation which defines how the inelastic cross section varies with the polarisation of the initial bond axis, $\mathbf{r}$ of the NO(X) with respect to some initial axis. The initial relative velocity $\mathbf{k}$ was chosen as the initial axis as it is well known from the direction and speeds of the molecular beams. The experimental apparatus also allows the determination of the final relative velocity $\mathbf{k}'$ by analysis of the velocity mapped [44] ion images [45]. The scattering intensity weighted integral of the orientation resolved ion images over all scattering angle θ , yields the preference for N-end or O-end collisions, and is quantified by the equation

$$\%SA = \frac{\sigma_{NO} - \sigma_{ON}}{\sigma_{NO} + \sigma_{ON}} \times 100, \quad (6.1)$$

where σ_{NO} quantifies the cross section for the N-end collision and σ_{ON} quantifies the cross section for the O-end collision. A positive value indicates a preference for an N-end collision and a negative value the preference for an O-end collision.

Many systems have had the steric preference quantified [34, 178–185]. Early work by Bernstein focussed on the asymmetry of CH_3I reacting with alkali metal atoms,

this showed the existence of a cone of acceptance in the scattering from the methyl group. Here, the focus will be on the integral steric asymmetries of NO(X) scattering with rare gases. NO(X)–Ar integral steric asymmetries on the spin-orbit conserving manifold have previously been reported by Nichols *et al.* [25], as have the NO(X)–He steric asymmetries been reported by Stolte *et al.* [24]. They will be presented here for completeness and to facilitate comparison to the other rare gas systems.

Experimentally determined integral steric asymmetries for a number of NO(X)-Rg systems will be presented here, pertaining to collisions upon the spin-orbit conserving (NO(X)–Kr) and spin-orbit changing (NO(X)–Ar) manifolds to the $\epsilon' = e$ Λ -doublet state. The theoretical steric asymmetry from QCT and QM scattering theory is also presented along with calculations performed on modified potential energy surfaces, in order to better understand the dynamics that give rise to the steric effect in NO(X) rare gas collisions.

6.1 Adiabatic Orientation of NO(X)

When hexapole state selection is used to achieve an initial NO(X) $|j = 0.5, \epsilon = -1, f\rangle$ state, the direction of the bond axis does not have a sharply defined polarisation in the scattering frame. To achieve an oriented distribution of $\mathbf{r}$ in the scattering frame, a number of methods could be employed, from optical techniques [34, 179, 180, 186–188], (that orient $\mathbf{j}$), brute force orientation [181, 182, 189–191] (that orients $\mathbf{r}$) or, as is the case in this work, adiabatic orientation of $\mathbf{r}$ using the Stark effect [23, 25, 192–194].

By orienting the NO(X) bond axis prior to collision, measurements of both the integral and differential steric asymmetries for each energetically accessible rotational state is possible. In order to achieve adiabatic orientation, a four rod electrode setup is used, as shown in Fig. 6.1. The direction of the electric field is set so that the field vector is pointing parallel or anti-parallel to $\mathbf{k}$. The angle, θ_{rods} , of the rods relative to $\mathbf{k}$ is calculated from the arctangent of the beam speeds so the field is acting parallel to $\mathbf{k}$

$$\theta_{\text{rods}} = \arctan \left(\frac{v_{\text{NO}}}{v_{\text{Rg}}} \right). \quad (6.2)$$

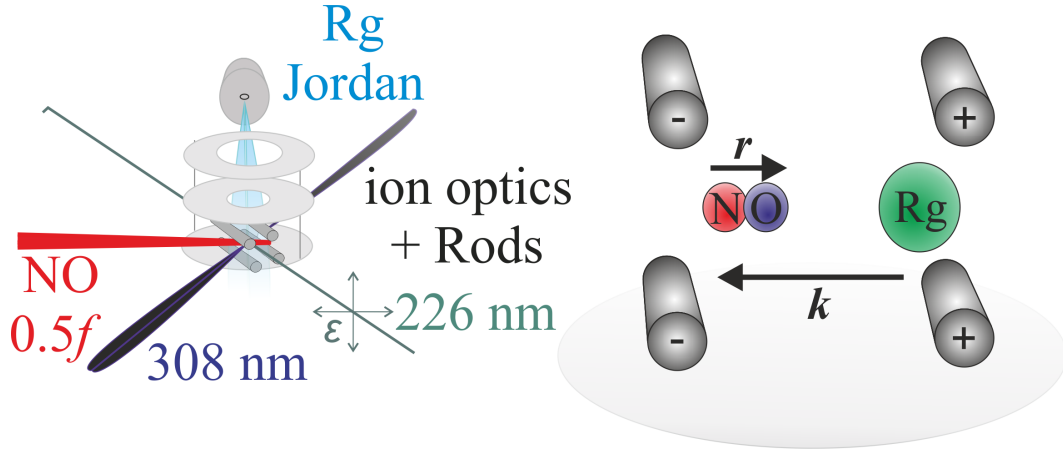


Figure 6.1: Left: The modified experimental apparatus used to adiabatically orient the NO(X) molecule. Note the guiding rods in the interaction region. Right: A representation of the NO(X) becoming oriented by the static guiding field just prior to collision with the rare gas moiety, overlaid are the directions of the bond axis vector, $\mathbf{r}$ and the relative velocity, $\mathbf{k}$.

The rods were spaced 10 mm apart from one another requiring a voltage of ± 8 kV on each rod to achieve the desired field strength of 9.6 kV cm^{-1} . Since the NO(X) entering into the interaction region from the hexapole field is a low-field-seeking state in the $\varepsilon = -1$ Λ -doublet level, application of the electric field causes the N-end of the NO(X) to orient essentially adiabatically towards the negative electrode [25].

The presence of a static electric field in the interaction region induces a Stark effect, resulting in a linear combination of field free e and f states, as described further in Chapter 2. The wavefunction of the NO(X) molecule in the field is then given by [149, 194]

$$|jm\Omega\mathcal{E}\rangle = \frac{1}{\sqrt{2}}[\alpha|jm\Omega e\rangle + \beta|jm\Omega f\rangle], \quad (6.3)$$

where $\mathcal{E}$ is the strength of the electric field and α and β are the electric field mixing coefficients given by [194]

$$|\alpha| = +\sqrt{1 - \frac{1}{\sqrt{1 + E_{\text{red}}^2}}} \quad |\beta| = +\sqrt{1 + \frac{1}{\sqrt{1 + E_{\text{red}}^2}}}. \quad (6.4)$$

Here, E_{red} is the reduced electric field strength which is given by

$$E_{\text{red}} = \frac{2W_{\text{Stark}}}{W_{\Lambda}}. \quad (6.5)$$

W_Λ is the spacing between the Λ doublet levels and W_{Stark} is the Stark energy, given by the expectation value of Eqn. (3.5). Combining with Eqn. (6.4) gives

$$W_{\text{Stark}} = \mu \mathcal{E} \frac{|\Omega m|}{j(j+1)}. \quad (6.6)$$

The degree of orientation of the NO(X) molecule in a field is dependent on the values of α and β and is given by the probability distribution [25, 194]:

$$P(\theta_{\mu\mathcal{E}}) = \frac{1}{2}[1 + \alpha\beta \cos \theta_{\mu\mathcal{E}}], \quad (6.7)$$

where $\theta_{\mu\mathcal{E}}$ is the angle between the dipole moment of NO(X) and the electric field vector. A plot of this function is shown in Fig. 6.2, it describes the degree of orientation in the experimental field and theoretical infinite field. The expectation value of $\cos \theta_{\mu E}$ is given by

$$\begin{aligned} \langle \cos \theta_{\mu E} \rangle &= \alpha\beta \langle \cos \theta_{\mu E} \rangle_{\text{max}} \\ &= \alpha\beta \frac{m\Omega}{j(j+1)}. \end{aligned} \quad (6.8)$$

Once the orientation specified by Eqn. (6.7) has been achieved, scattering with the partner atom takes place and the detection scheme described in Chapter 3 section 3.4 is used to infer the collision outcome. The scattering chamber setup used is that of the Steric geometry, described in Chapter 3. The polarity of the rods can be switched so the N-end and O-end collisions can be measured in an alternating cycle to minimise the effects of experimental instability. With moderate field strengths of around 8 kV (9.6 kV cm⁻¹), a relatively high degree of orientation of the NO(X) bond axis is possible. Using these oriented NO(X) molecules, combined with fast switching electronics to allow velocity mapping conditions to be achieved, allows the sterically resolved $\mathbf{r-k-k'}$ vector correlation, corresponding to the differential steric asymmetry, to be probed. Appropriate integration of the bond oriented differential cross section (DCS) images allows recovery of the integral steric asymmetry corresponding to an $\mathbf{r-k}$ correlation to be obtained.

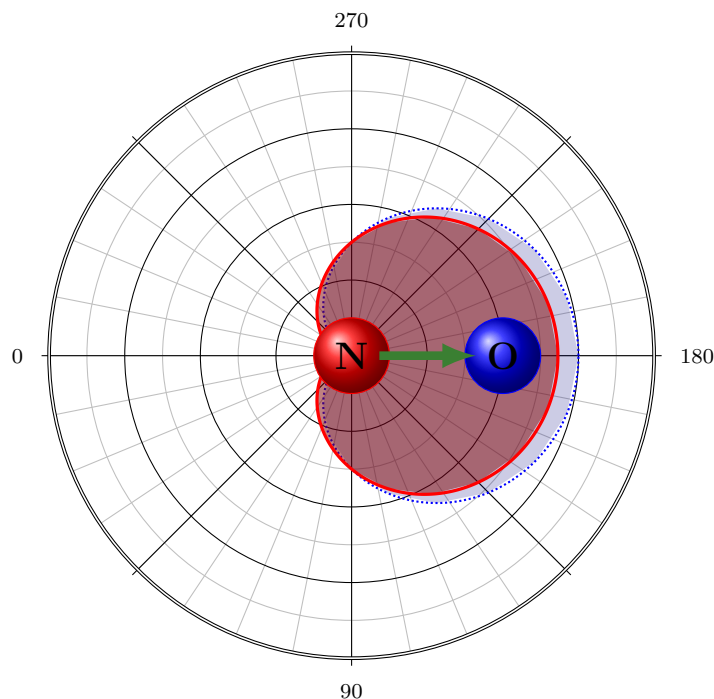


Figure 6.2: A diagram of the cardioid probability distributions associated with orienting a NO(X) molecule using an electric field strength of 9.6 kV cm^{-1} (red) and a hypothetical infinite field (blue). The plots are in polar co-ordinates using Eqn. (6.7), with the green arrow representing the direction of the dipole moment, μ which is parallel to the bond axis, $\mathbf{r}$, and points anti-parallel to the electric field, $\mathbf{E}$.

In order to maintain the velocity mapping conditions with the distorting effects of the static electric field in the interaction region, fast switching was applied to change the rods from the orientation voltages of $\pm 8 \text{ kV}$ to the velocity mapping voltages of approximately 1 kV . This switch occurred on a nanosecond timescale, before the laser ionised the scattered products, in order to ensure that the orientation of the NO(X) was preserved as scattering and took place. It has been found previously that the delay time can be as long as $1 \mu\text{s}$ before any significant loss of orientation is observed [84]. In practice, the delay time is usually set between 300 ns and 500 ns which ensures the rod voltages are uniform at the exact time the laser fires and that the experiment is not affected significantly by electrical noise in the switch to VMI conditions. The extraction field is not strong enough to cause orientation of the NO(X) in the VMI conditions used in these experiments.

The direction of the electric field gradient must be parallel to $\mathbf{k}$ as it is currently unknown how the mixing function Eqn. (6.3) changes as a function of angle between $\mathbf{k}$ and $\mathbf{E}$. To obtain the correct angle of rotation of the rods, the arctangent of the NO(X)

and collision partner speed was taken and the rods rotated by means of a mechanical feed through to the correct orientation. The angle is typically between 40° and 50° for the systems studied in this thesis.

6.2 Theoretical Calculations

In order to compare the experimentally determined steric asymmetry to theory, equations for the determination of the oriented ICSs must be obtained both classically and quantum mechanically. These quantities require the introduction of some general theory specifically relating to the polarisation of the bond axis before collision.

6.2.1 Classical Mechanics

r-PDDCSs

As was the case with the polarisation of the angular momentum vector presented in Chapter 2, the polarisation dependence of the inelastic scattering is conveniently represented by a j' -PDDCS. The bond axis polarisation can also be expressed in terms of PDDCSs, however instead of describing the distribution of $\mathbf{j}'$ with respect to $\mathbf{k}$ and $\mathbf{k}'$, they represent the distribution of $\mathbf{r}$ with respect to $\mathbf{k}$ and $\mathbf{k}'$. To differentiate between the two different PDDCSs, the PDDCS that refers to the $\mathbf{r}\text{--}\mathbf{k}\text{--}\mathbf{k}'$ correlation will be referred to as an r-PDDCS, $R_{q\pm}^{(k)}(\theta)$. Classically, the distribution of the bond axis can be written as [67, 84, 116, 183]

$$P(\omega_{k'}, \omega_r) = \frac{1}{4\pi} \sum_{k_2} \sum_{q=-k_2}^{q=k_2} (2k_2 + 1) R_{q\pm}^{(k_2)}(\theta) C_{k_2 q}(\theta_r, \phi_r)^*. \quad (6.9)$$

The r-PDDCSs, $R_{q\pm}^{(k)}(\theta)$ are expressed in terms of modified spherical harmonics [8] by

$$R_{k_2 q}(\theta) = \frac{1}{2} \sum_{k_1 \geq |q|} (2k + 1) r_{k_2 q}^{k_1} C_{k_1 - q}(\theta, 0), \quad (6.10)$$

with the $r_{k_2q}^{k_1}$ coefficients expressed in terms of Wigner 3- j symbols by [84]

$$r_{k_2q}^{k_1} = \sum_k (-1)^K (2K+1)^{1/2} \begin{pmatrix} k_1 & K & k_2 \\ -q & 0 & q \end{pmatrix} h_0^K(k_1 k_2), \quad (6.11)$$

with $k_{1/2} = 2n + 1$, $n = j = 0.5$ and the values of $h_0^K(k_1 k_2)$ are obtained from reference [117]. The $r_{k_2q}^{k_1}$ coefficients are obtained from the expectation values of the bond axis orientation [67, 84, 116, 183]

$$r_{k_2q}^{k_1} = \langle C_{k_1-q}(\theta, 0) C_{k_2q}(\theta_r, \phi_r) \rangle. \quad (6.12)$$

Since the $h_0^K(k_1 k_2)$ values are real for all values of k_1 and k_2 , it follows that the $r_{k_2q}^{k_1}$ coefficients are also real [84].

In this chapter, the effect of the bond axis orientation will be probed by determining the two vector $\mathbf{r}$ - $\mathbf{k}$ correlation. The pertinent r-PDDCS has order $k = 1$ as $j = 0.5$. The $R_0^{\{1\}}(\theta)$ r-PDDCS quantifies the orientation of $\mathbf{r}$ with respect to $\mathbf{k}$ [112], whereas the $R_{1+}^{\{1\}}(\theta)$ moment describes the orientation with respect to the $\mathbf{x}$ -axis (see Fig. 2.4 in Chapter 2). For $R_0^{\{1\}}(\theta)$, the limiting values of $+1$ and -1 correspond to orientation parallel and anti-parallel to $\mathbf{k}$.

Observable Calculations

Classically¹, the oriented differential cross section can be written in terms of ‘intrinsic’ and ‘extrinsic’ polarisation moments [116, 196]. The extrinsic polarisation moments describe the reagent polarisation which results from the experimental preparation of the system. The moments are a consequence of the external circumstances such as the geometry of the experiment chosen – they do not depend on the sterics of the collision. The intrinsic polarisation moments describe these steric preferences. These intrinsic moments depend only on the dynamics and are not affected by the external preparation of the system. This allows the separation of the external preparation from the underlying dynamics. In the quasi-classical trajectory (QCT) treatment, the

¹These formulae are likely correct quantum mechanically [195], however, the formalism is complicated by the mixing of the Λ -doublet levels, and further clarification is required.

oriented differential cross sections are given by [116, 196]

$$\frac{d\sigma_{N/O}}{d\omega}(\theta) = \frac{\sigma_{\text{iso}}}{2\pi} \sum_{kq} (2k+1) [R_q^{(k)}(\theta)]^* a_q^{(k)}, \quad (6.13)$$

with σ_{iso} the integral cross section (ICS) of the unpolarised collision. $R_q^{(k)}(\theta)$ are the intrinsic r-PDDCSs, defined in the previous section, and $a_q^{(k)}$ are the polarisation moments that describe the bond axis polarisation in the scattering frame. Since the bond axis distribution is prepared in the laboratory frame, a rotation is required to determine the values of the scattering frame moments [116, 196] from those in the lab frame

$$a_q^{(k)} = \sum_{Q=-k}^k D_{q0}^{k*}(\theta_{Zz}, \phi_{Xx}, \chi) A_Q^{(k)} = C_{kq}(\theta_{Zz}, \phi_{Xx}) A_0^{(k)}, \quad (6.14)$$

where $D_{q0}^k(\theta_{Zz}, \phi_{Xx}, \chi)$ is a Wigner rotation matrix, $A_Q^{(k)}$ are the polarisation moments and θ_{Zz} , ϕ_{Xx} and χ are the angles associated with the rotation from the scattering frame into the laboratory frame. The Wigner rotation matrix is equal to the corresponding modified spherical harmonic, $C_{kq}(\theta_{Zz}, \phi_{Xx})$. The DC guiding electric field is parallel to the laboratory frame z axis which is directed parallel or anti-parallel to $\mathbf{k}$, so $\theta_{Zz} = 0^\circ$ for N-end collisions and $\theta_{Zz} = 180^\circ$ for O-end collisions, with the azimuthal angle, $\phi_{Xx} = 0^\circ$ in both cases.

The laboratory frame bond axis distribution given in Eqn. (6.9) can be written as a normalised distribution such that

$$P(\theta_{\mu E}) = \frac{1}{4\pi} \left[1 + \frac{2\alpha\beta}{\alpha^2 + \beta^2} P_1(\cos \theta_{\mu E}) \right], \quad (6.15)$$

where $P_1(\cos \theta_{\mu E})$ is an associated Legendre polynomial, $P_1(\cos \theta_{\mu E}) = C_{10}(\theta_{\mu E}, 0)$. The $A_0^{(1)}$ moment is obtained from taking the expectation value $A_0^{(1)} = \langle P_1(\cos \theta) \rangle$ [6], calculated from the mixing coefficients α and β by

$$\begin{aligned} \langle P_1(\cos \theta_{\mu E}) \rangle &= \int_0^{2\pi} \int_{-1}^1 P_1(\cos \theta_{\mu E}) P(\theta_{\mu E}) d \cos \theta_{\mu E} d\phi \\ &= \frac{1}{3} \frac{2\alpha\beta}{\alpha^2 + \beta^2}. \end{aligned} \quad (6.16)$$

As the distribution is normalised, $A_0^{(0)} = 1$. Equation (6.13) is written in terms of the laboratory frame polarisation moments as

$$\begin{aligned} \frac{d\sigma}{d\omega}(\theta) &= \frac{\sigma_{\text{iso}}}{2\pi} \sum_{kq} (2k+1) [R_q^{(k)}(\theta)] C_{kq}(\theta_{Zz}, \phi_{Xx}) A_q^{(k)} \\ &= \frac{\sigma_{\text{iso}}}{2\pi} [1 + 3R_0^{(1)}(\theta)^* C_{10}(\theta_{Zz}, \phi_{Xx}) A_0^{(1)} \\ &\quad + 3R_{+1}^{(1)}(\theta)^* C_{1+1}(\theta_{Zz}, \phi_{Xx}) A_0^{(1)} + 3R_{-1}^{(1)}(\theta)^* C_{1-1}(\theta_{Zz}, \phi_{Xx}) A_0^{(1)}], \end{aligned} \quad (6.17)$$

In this case, as $\phi_{Xx} = 0$ and $\theta_{Zz} = 0^\circ$ or 180° , $C_{1-1}(\theta_{Zz}, \phi_{Xx}) = 0$ and $C_{1+1}(\theta_{Zz}, \phi_{Xx}) = 0$, only the first two terms of equation Eqn. (6.17) can contribute to the oriented DCS. The observed DCS is then determined by

$$\frac{d\sigma}{d\omega}(\theta) = \frac{\sigma_{\text{iso}}}{2\pi} \left[1 + 3R_0^{\{1\}}(\theta) C_{10}(\theta_{Zz}, 0) \frac{1}{3} \frac{2\alpha\beta}{\alpha^2 + \beta^2} \right]. \quad (6.18)$$

The classical ICS is then integrated over scattering angle in order to determine the classical oriented ICS and Eqn. (6.1) is used to determine the steric asymmetry.

6.2.2 Quantum Calculations

In order to calculate the oriented ICSs quantum mechanically, the bond axis oriented differential cross sections are determined and then integrated over scattering angle by means of

$$\sigma_{\text{N/O}} = 2\pi \int_0^\pi \frac{d\sigma_{\text{N/O}}}{d\omega} \sin \theta d\theta. \quad (6.19)$$

The oriented differential cross sections can be obtained from the oriented scattering amplitudes. The scattering amplitudes are related to the α and β coefficients defined in Eqn. (6.4) by [197]

$$f_{j m E \rightarrow j' m' \epsilon'}(\theta) = \frac{\sqrt{2}}{2} [\alpha f_{j m E \rightarrow j' m' \epsilon'}(\theta) + \beta f_{j m f \rightarrow j' m' \epsilon'}(\theta)]. \quad (6.20)$$

The differential cross section is determined by taking the square modulus of mixed the scattering amplitudes

$$\frac{d\sigma_{N/O}}{d\omega}(\theta) = \frac{1}{k^2(2j+1)} \sum_{mm'} |f_{jm|E| \rightarrow j'm'\epsilon'}(\theta)|^2. \quad (6.21)$$

After integration over scattering angle, the steric asymmetry can be obtained by taking the normalised difference of the two ends, as in Eqn. (6.1).

6.3 Integral Cross Sections

In order to understand the steric preference of molecular collisions, it is also instructive to look at the trends and relationships in the ICSs of the systems. ICSs were calculated for each of the NO(X) rare gas systems using quantum and classical scattering calculations at the collision energy specified in Table 3.1 for each system. The REMPI scheme employed experimentally does not allow for the exact ICSs to be obtained, however previous experiments employing laser induced fluorescence do allow the ICSs to be obtained with high accuracy [142]. These values have been shown to be in close agreement with the calculated close-coupled quantum mechanical (CC QM) ICSs obtained from the HIBRIDON suite of codes as described in Chapter 2.

In order to provide a meaningful comparison with the QCT calculations, the CC QM calculations are summed over initial and averaged over the final Λ -doublet levels

$$\sigma_{\text{QCT}}(j \rightarrow j') \approx \frac{1}{2} \sum_{\epsilon, \epsilon', \Omega'} \sigma_{\text{QM}}(j, \epsilon, \Omega = 0.5 \rightarrow j' \epsilon', \Omega'). \quad (6.22)$$

As shown in Fig. 6.3, as j' is increased, the ICSs decrease. This can be rationalised classically by considering that higher Δj ($= j' - j$) states have a more restricted range of impact parameters which can supply enough torque to effect rotational energy transfer to these states. As has been discussed in Chapter 4 and 5, more backwards scattering is observed at high Δj , due to the importance of low impact parameter collisions which lead to efficient rotational energy transfer.

ICSs drop off faster for the lighter rare gases than the heavier ones as the collision

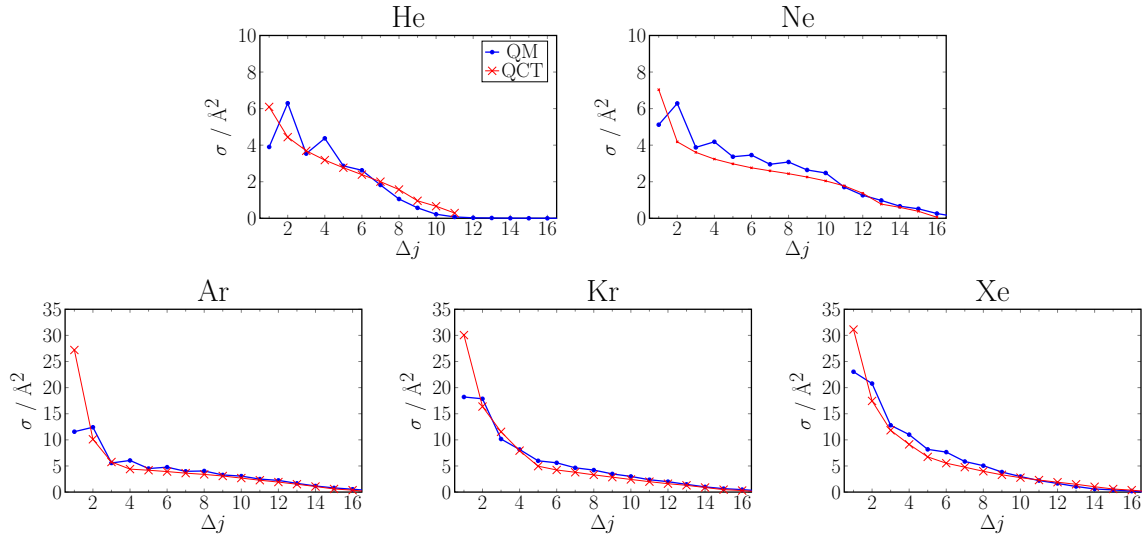


Figure 6.3: The CC QM (blue circles) and classical QCT (red crosses) ICSs calculated for the NO(X)–Rg collision systems. The ICSs are obtained from the CC QM calculations by application of Eqn. (6.22). The oscillations seen previously in the CC QM ICSs have been diminished by the averaging over spin-orbit and Λ -doublet levels to facilitate comparison to the QCT, as in Eqn. (6.22). The agreement between the QCT calculations and CC QM is good for all collision systems. The QCT calculations tend to underestimate the cross sections as they have no intensity in the classically forbidden region.

energy for the lighter rare gas systems is insufficient to cause excitation into high rotational states due to the smaller radial extent of the potentials, hampering rotational energy transfer. The agreement between QCT and CC QM calculations is in general good; however, at low values of Δj , there are oscillations in the CC QM ICSs which are not reproduced in the QCT calculations. These oscillations are discussed in detail by McCurdy and Miller [198]. They are caused by the near homonuclearity of the NO(X) molecule, which results in destructive interference for collisions resulting in odd Δj values, reducing the magnitude of the ICSs for these states, as discussed in Section 6.3. This near homonuclearity, as will be shown, also manifests itself in the characteristic oscillations in the sign of the integral steric asymmetry as a function of Δj .

6.3.1 Λ -Doublet Resolved Cross Sections

The parity averaging of the QM ICSs when comparing to the QCT masks the parity dependent oscillations in the ICSs. In the full CC QM ICSs, the parity-conserving collisions show markedly larger cross sections than those of parity-changing transitions,

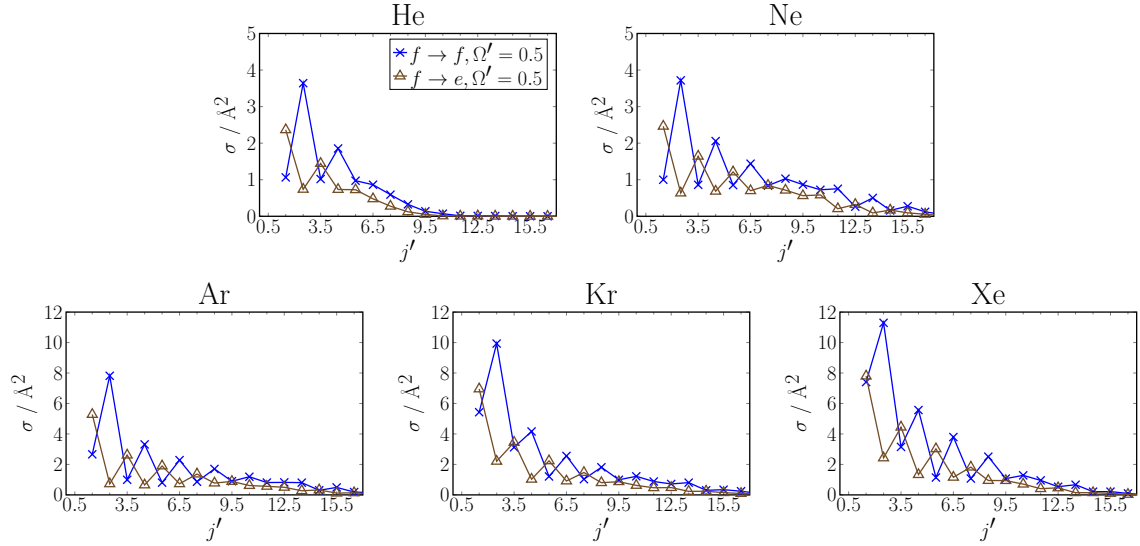


Figure 6.4: ICSs for the spin-orbit conserving manifold for the ϵ conserving and ϵ -changing collisions from an initial $j = 0.5, \epsilon = -1, f$ state. The ϵ -changing collisions are shown by brown triangles and the ϵ -conserving collisions with blue crosses. The cross sections are strongly parity dependent and so change in intensity with Δj .

as can be seen in Fig. 6.4.

The oscillations are most apparent at low j' and lose intensity with increasing j' as the mixing of Hund's case (a) and Hund's case (b) becomes more important. The large oscillations in the ICSs diminish to almost zero in He and Ne by $j' = 5.5$ but persist until $j' = 8.5$ in the heavier rare gas potentials. The magnitude of the oscillations in the ICSs increases with increasing mass of collision partner, this is due to the longer range and more polarisable nature of the heavier rare gases.

The oscillations in the unoriented ICSs has been investigated extensively [138, 167, 199]. The parity dependent oscillations are primarily caused by the nearly homonuclear character of the NO(X) molecule. This results in either constructive or destructive interference, dependent on the initial and final parities of the collision. For collisions between an atom and a Hund's case (a) molecule in a $^2\Pi$ electronic state, the coupling between j and j' states is given by [192]

$$\epsilon\epsilon'(-1)^{j+j'+\kappa} = \epsilon\epsilon'(-1)^{\Delta j+\kappa+1} = -1, \quad (6.23)$$

with $|j' - j| \geq \kappa \geq j + j'$ and κ defining the PES expansion term. As NO(X) is nearly homonuclear, the even (homonuclear) terms in the potential are considerably larger

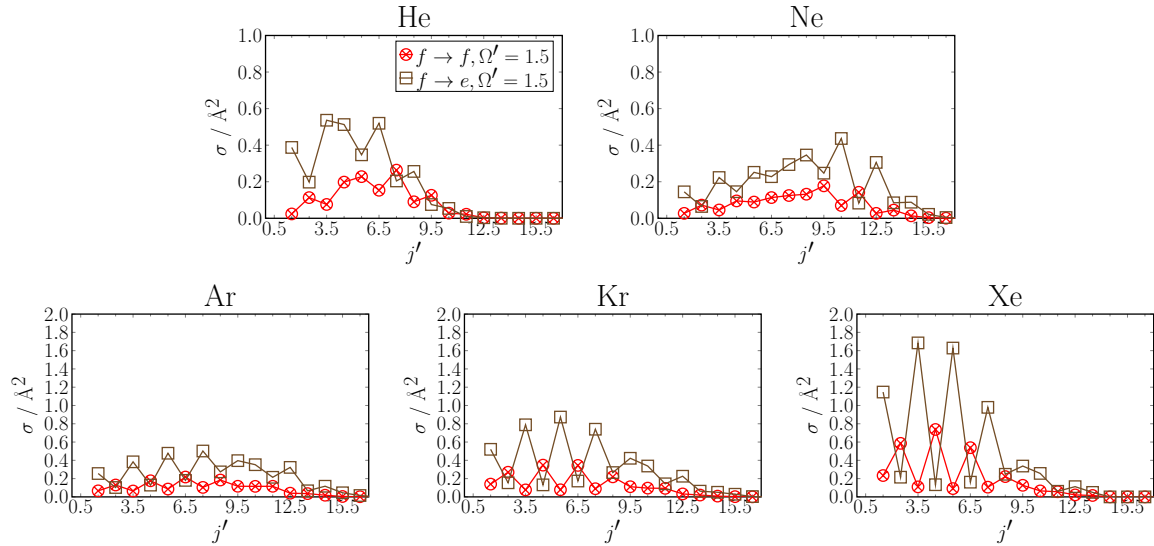


Figure 6.5: ICSs for the spin-orbit changing manifold showing ϵ -conserving and ϵ -changing collisions from an initial $j = 0.5, \epsilon = -1, f$ state. The red crosses show the ϵ -conserving collisions and the brown squares show the ϵ -changing collisions. The cross sections are much lower and more variable than the spin-orbit conserving collisions due to the complexity of the V_{diff} surface.

than the odd terms in the potential expansion. As parity conserving collisions are more strongly coupled for even values of Δj , whilst parity-changing collisions are more strongly coupled for odd Δj , the relative magnitudes can be rationalised. The origins of these effects have been explained using a semi-classical interference model by McCurdy and Miller [198], which was later expanded by Eyles [109] and were reformulated in exponential form in Chapter 4.

As discussed in the previous sections, orienting the NO(X) bond results in a linear combination of field free e and f initial states, so the initial parity becomes ill defined. Oscillations are however observed in the bond orientation resolved ICSs as presented in Fig. 6.6, these are most obvious in the lighter rare gas systems and diminish in intensity as the rare gases become heavier and more polarisable. These oscillations are caused by a different interference mechanism to those seen previously in the parity resolved ICSs observed in Figs. 6.4 & 6.5. At low j' the cross sections for each end of the molecule are similar, with oscillations becoming apparent at higher values of j' . Oscillations begin at lower j' for He and Ne than for the heavier rare gases, in a similar pattern to that in the spin-orbit conserving ICSs in Fig. 6.4. For all of the rare gases, apart from He, the ICS is much higher for the N-end at large Δj values. Although, given the very low

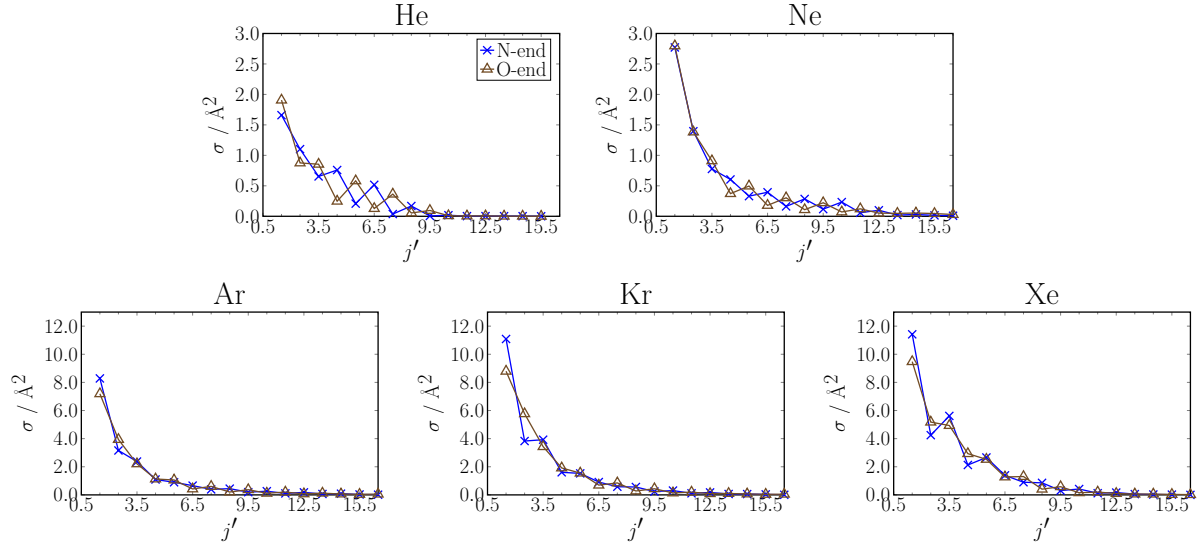


Figure 6.6: ICSs for the spin-orbit conserving manifold for collisions into the $|j', \epsilon' = e, \Omega' = 0.5\rangle$ state. N-end (blue crosses) and O-end (brown triangles) j' dependent oscillations are clearly visible with odd Δj preferred by the N-end and even Δj by the O-end. This is related to the ingoing wavefunction being a linear combination of e and f states leading to interference effects in the observed cross sections.

cross sections of the high j' He collisions, it may well prove difficult to observe these collisions at all [138, 200].

The magnitude of the ICS is closely related to the value of the integral steric asymmetry, and as the integral steric asymmetry is defined as a normalised difference, it is very sensitive to the relative magnitude of the oriented ICSs. Understanding the oscillations in ICSs facilitates an understanding of the variation in steric asymmetry, which is discussed in detail in the subsequent sections. Due to the linear combination of e and f states in the initial scattering wavefunction, the oriented cross sections demonstrate constructive and destructive interference due to scattering out of the initial e and f Λ -doublet states. The oscillations in the oriented ICSs are therefore diminished compared to the unoriented ICSs. In order to achieve a high value of steric asymmetry, the difference between the oriented N-end and O-end cross sections will be largest when the ICS of each Λ -doublet is maximised [115]. As observed in Fig. 6.4, at low values of Δj , the difference between collisions to the same final Λ -doublet state from different initial Λ -doublet states will be large due to the preference for parity conservation which is manifested by the coupling of j, j' shown in Eqn. (6.23). In the heavier rare gases, the scattering is less direct, so the oscillations as a function of Δj

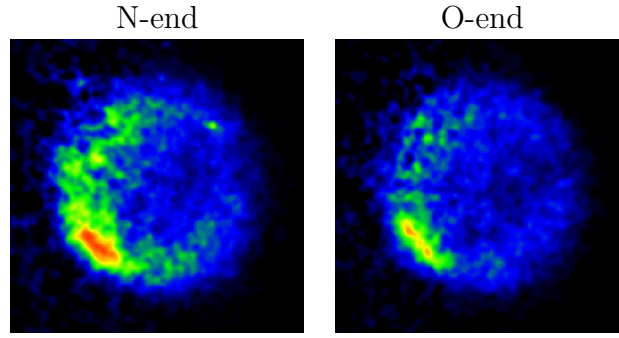


Figure 6.7: Raw ion images for the N-end and O-end collisions leading to the $|\Omega' = 1.5, j' = 7.5, \epsilon = e\rangle$ state when scattered with Ar. These ion images are used as described in the text to obtain the integral steric asymmetry.

Channel	Primary Beam	Secondary Beam	Orientation rod polarity
NO _{BG}	ACTIVE	OFF	N-end
ON _{BG}	ACTIVE	OFF	O-end
NO _{sig}	ACTIVE	ACTIVE	N-end
ON _{sig}	ACTIVE	ACTIVE	O-end

Table 6.1: The state of the primary beam, secondary beam and orientation rods for each of the four experimental acquisition channels needed to record the integral steric asymmetry. The background channels allow the subtraction of unscattered NO(X) from the signal channels for both rod polarities.

are less prominent.

6.4 Experimental Integral Steric Asymmetry

The experimental apparatus was configured in the steric geometry described in Chapter 3 which allows almost adiabatic orientation of the NO(X) bond axis, $\mathbf{r}$, as described in Section 6.1 above. In order to obtain the integral steric asymmetry from the experimental ion images, the acquisition program was used to report the ion yield per experimental channel. For the measurement of the integral steric asymmetry, four acquisition channels are required: NO_{BG}, ON_{BG}, NO_{sig} and ON_{sig}. These channels are explained further in Table 6.1. The background channels ensure that unscattered NO(X) in high rotational states is discounted and that sources of random noise are correctly subtracted.

In order to obtain an ion image for the N-end and the O-end, the background channels are subtracted from the signal channels to yield the raw experimental ion

image, a raw ion image for the $|\Omega' = 1.5, j' = 7.5, \epsilon = e\rangle$ state of NO(X) after scattering with Ar is shown in Fig. 6.7. From these images, the steric asymmetry can be obtained by summing the total ion yield of each pixel to obtain a quantity proportional to the integral cross section

$$\sigma_{\text{NO}} \propto \sum_{xy} \text{NO}_{\text{sig}}(x, y) - \text{NO}_{\text{BG}}(x, y) \quad (6.24a)$$

$$\sigma_{\text{ON}} \propto \sum_{xy} \text{ON}_{\text{sig}}(x, y) - \text{ON}_{\text{BG}}(x, y). \quad (6.24b)$$

Since the interaction volume does not change between collisions of the N-end and O-end, and the polarity of the rods is changed so frequently, the flux-density effects should be almost identical for both the N-end and O-end collisions. The unknown scaling quantity that relates the ion yield to the ICS will cancel on taking the normalised difference, allowing the integral steric asymmetry to be calculated from the ion yields by applying Eqn. (6.1). The error in the integral steric asymmetry is determined by calculating the steric asymmetry of small batches of laser shots (typically 2000) and taking the standard deviation using the usual formulae.

This technique will be used to obtain the integral steric asymmetry for the NO(X)–Ar spin-orbit changing collisions and the NO(X)–Kr spin-orbit conserving collisions. These new measurements will be compared to those performed previously on the NO(X)–He system by Stolte *et al.* [138] and the NO(X)–Ar system by Nichols *et al.* [25]. All the collisions presented are those which end in the $\epsilon' = e$ final Λ -doublet state. The $\epsilon' = f$ state has been noted to be almost identical to the $\epsilon' = e$ state, so was not recorded.

6.4.1 Spin-Orbit Conserving Manifold

It has been shown by Alexander that collisions which take place on the spin-orbit conserving manifold primarily sample V_{sum} [61]. At high j' this breaks down as Hund's case (a) stops being a good description of the NO(X). Hund's case (b) begins to be a better representation of the NO(X) molecule and a significant contribution from V_{diff} becomes identifiable in the steric asymmetries.

A comparison of experimental and theoretical integral steric asymmetries for the

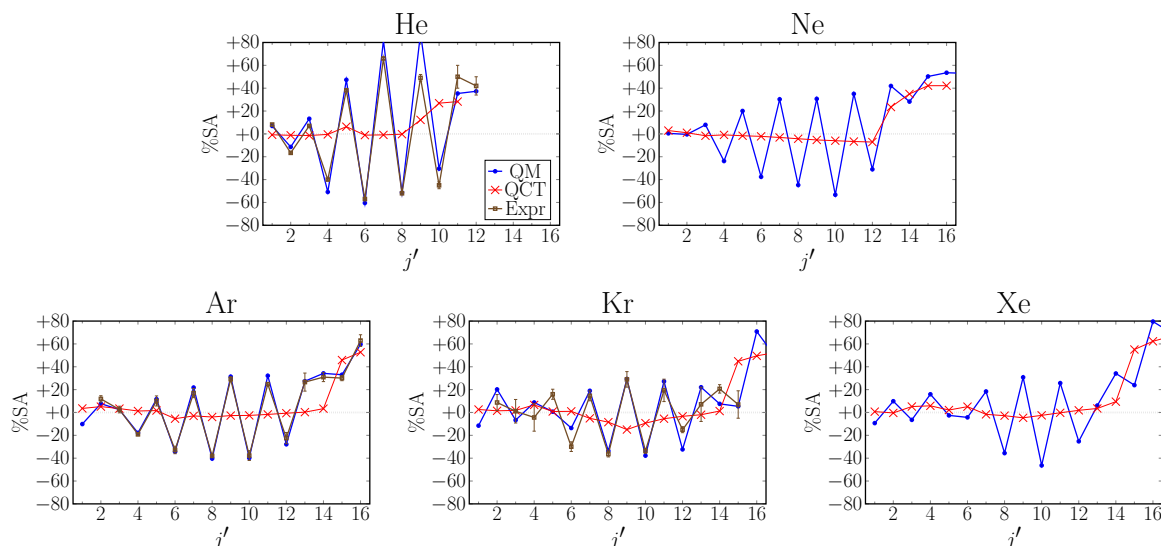


Figure 6.8: Plots of the integral steric asymmetry for spin-orbit conserving collisions as a function of Δj for all the NO(X)–Rg systems. Experimentally determined results (brown squares) are presented where appropriate and are compared to CC QM calculations (blue circles) and classical QCT calculations (red crosses). The NO(X)–Ar experimental results were previously recorded by Nichols *et al.* [25] and the NO(X)–He results were previously recorded by Stolte *et al.* [138] and are included here for completeness.

NO(X)–Rg systems on the spin-orbit conserving manifolds is presented in Fig. 6.8. An excellent agreement between the experimentally determined integral steric asymmetry and that obtained from CC QM calculations for the NO(X)–Ar system is observed. Good agreement is also achieved for the other systems, highlighting the accuracy of the *ab initio* V_{sum} potential surfaces.

Of immediate interest in the experimental data is the rotational state dependent oscillations, which are not reproduced in the QCT calculations. The absence of the oscillations in the QCT calculations strongly indicates the quantum mechanical origin of these oscillations. The oscillations have been interpreted in terms of a quantum interference effect [25, 115]. Further insight was obtained by Stolte and co-workers using a quasi-quantum treatment [137], from which it is found that the alternation in sign is due to quantum interference from trajectories scattering off the two ends of the NO(X) molecule, this effect is described further in the next subsection.

All the systems show an N-end preference when scattered into a high Δj rotational state. The agreement of classical and quantum theories at high Δj suggests a classical mechanism for the scattering into these states. The most succinct explanation for this

is scattering from a ball and stick, where the high Δj states are near the energetic limit for the rotational energy transfer. In order to transfer enough energy, a high torque blow on the N-end of the molecule, which is further from the centre of mass, allows the efficient transfer of kinetic energy to rotation. This is a classical rather than quantum effect, and the interference oscillations become less noticeable as they are dampened by the classical mechanism, hence the classical ball and stick mechanism dominates. At high Δj , Similar arguments have been discussed for the steric asymmetry in the OH system [201]. This effect will be discussed further by analysis of theoretical calculations at varying collision energy presented in section 6.5.2

At low values of Δj , the attractive part of the potential dominates the scattering and the steric asymmetries are smaller. When comparing the oriented ICSs at low Δj , we see that the differences in cross section from scattering from the N-end and O-end are less dramatic than at middle and high Δj , especially for the lighter rare gases where the attractive part of the potential is much weaker.

6.4.2 Origin of The Interference

The most obvious features in the experimental and theoretical integral steric asymmetry presented in Fig. 6.8 is the rotational state dependent oscillations. The oscillations in %SA are diminished at higher Δj by the classical torque effect. The oriented DCS itself is obtained from the square modulus of the scattering amplitude, which is defined in terms of the field-free scattering amplitudes for the e and f states mixed by the α and β field dependent mixing coefficients. Therefore, the steric asymmetry is intimately related to the $f_{e \rightarrow e'}$ and $f_{f \rightarrow e'}$ scattering amplitudes of Eqn. (2.32).

Whilst the oscillations in %SA qualitatively reflect the parity dependent oscillations in the unoriented ICSs, they can be understood more quantitatively in a terms of interfering trajectories from the N-end and the O-end of the NO(X). This was first recognised by Stolte and co-workers [137] who formulated a quasi-quantum treatment (QQT) method in order to account for semi-classical interference between trajectories in a rigorous manner [122, 137]. The QQT method for inelastic scattering models the diatom as a rigid ellipse. The trajectories are propagated at all angles, in a similar

manner to the QCT calculations, in order to provide DCSs and ICSs. The phase shift allows the interference between the N-end and O-end to be rationalised; it is defined as the difference between a virtual trajectory that hits the centre-of-mass and a trajectory that hits the rigid ellipse. The phase shift in the QQT model is given by [137]

$$\Delta\phi = \Delta\phi_k + \Delta\phi_{k'} = -(k'_\perp + k_\perp)b(\gamma)\cos(\Gamma - \gamma), \quad (6.25)$$

with $b(\gamma)$, the classical impact parameter, Γ the angle of the contour of the ellipse, which is collision energy dependent and γ the angle between the kinematic apse, $\hat{\mathbf{a}}$, and the bond-axis, $\mathbf{r}$. In the apse frame, the oriented scattering amplitude may be written [137]

$$f_{jm\Omega|\mathbf{E}|\rightarrow j'm'\Omega'\epsilon'} = \alpha \tilde{f}_{j'+\frac{\epsilon'}{2}} \pm \beta \tilde{f}_{j'-\frac{\epsilon'}{2}}, \quad (6.26)$$

where the tilde ($\tilde{f}_{j'\pm\epsilon'/2}$) denotes that the scattering amplitude is in the kinematic apse frame. Assuming that Γ remains constant during the collision, the apse frame scattering amplitude is given by [137]

$$\tilde{f}_{j'\pm\epsilon'/2}(\Gamma, \Theta) = \int_{-1}^1 \tilde{f}^{\text{geom}} e^{i\Delta\phi} P_{j'\pm\epsilon'/2}(\cos \Gamma) \, d\cos \Gamma. \quad (6.27)$$

Here, Θ is the angle between the apse and the incoming wave vector, $\tilde{f}^{\text{geom}}$ is the geometric scattering amplitude and $P_n(\cos \Gamma)$ is an associated Legendre polynomial of $j' \pm \epsilon'/2^{\text{th}}$ order. The differential cross section may be recovered from the apse-frame scattering amplitude by including the symmetry of the rotational wavefunction [137]. Within the QQT framework, the origin of the Δj dependent oscillations in the integral steric asymmetry can be rationalised by considering the $j' - \frac{1}{2}$ and $j' + \frac{1}{2}$ orientation resolved scattering amplitudes of Eqn.(6.26). Using the definition of the bond-axis orientation in the apse frame from reference [137] we have

$$f_{\text{N/O}} = \begin{cases} \alpha f_{j'-\frac{1}{2}} + \beta f_{j'+\frac{1}{2}} & \text{N-end,} \\ \alpha f_{j'-\frac{1}{2}} - \beta f_{j'+\frac{1}{2}} & \text{O-end.} \end{cases} \quad (6.28)$$

From these oriented scattering amplitudes, the differential cross section is obtained

via [137]

$$\frac{d\sigma}{d\omega} = \frac{(2j' + 1)}{8k^2} \frac{\sin \theta}{\sin \gamma} \left| \frac{d\theta}{d\gamma} \right| |f_{N/O}|^2. \quad (6.29)$$

The magnitude of the differential cross section will be dominated by the value of the associated Legendre polynomial around the phase shift maximum. By integration to recover the oriented ICSs, the integral steric asymmetry can be obtained from the QQT calculation. Such a treatment is sufficient to show that there will be an oscillation in the sign of the steric asymmetry upon each successive increase in j' and that the magnitude will increase as a function of Δj .

6.4.3 Spin-orbit Changing Manifold

Spin-orbit changing collisions have received comparatively little attention compared to spin-orbit conserving collisions in radical-atom scattering. They have comparatively lower cross sections and are therefore harder to record experimentally. The steric asymmetry for the NO(X)-Rg systems on the spin-orbit changing manifold is presented in Fig. 6.9. As discussed previously, the spin-orbit changing collisions have been shown in the Hund's case (a) limit to take place on V_{diff} . The V_{diff} potential is the half difference between the A' and A'' potentials and as such has a different form to the V_{sum} surface.

The experimentally determined argon integral steric asymmetry is well reproduced by the CC QM calculations performed with the HIBRIDON suite of codes. The steric asymmetry is seen to be very different to that of the spin-orbit conserving steric asymmetry. The most obvious feature is that the oscillations in sign are less pronounced for the heavier rare gas systems, and are also strong at low j' , this could be due to the spin-orbit changing collisions being 123 cm^{-1} more endoergic due to the spin-orbit energy. For scattering with He, the oscillations in %SA look remarkably similar to the oscillations on the spin-orbit conserving manifold, indicating that for He the V_{sum} surface is playing an important role in the scattering.

For the heavier rare gas systems, there is a preference for scattering off the N-end and the interference mechanism is not as pronounced. At high j' , there is evidence of a ball and stick type mechanism operating as the collisions resulting in high rotational

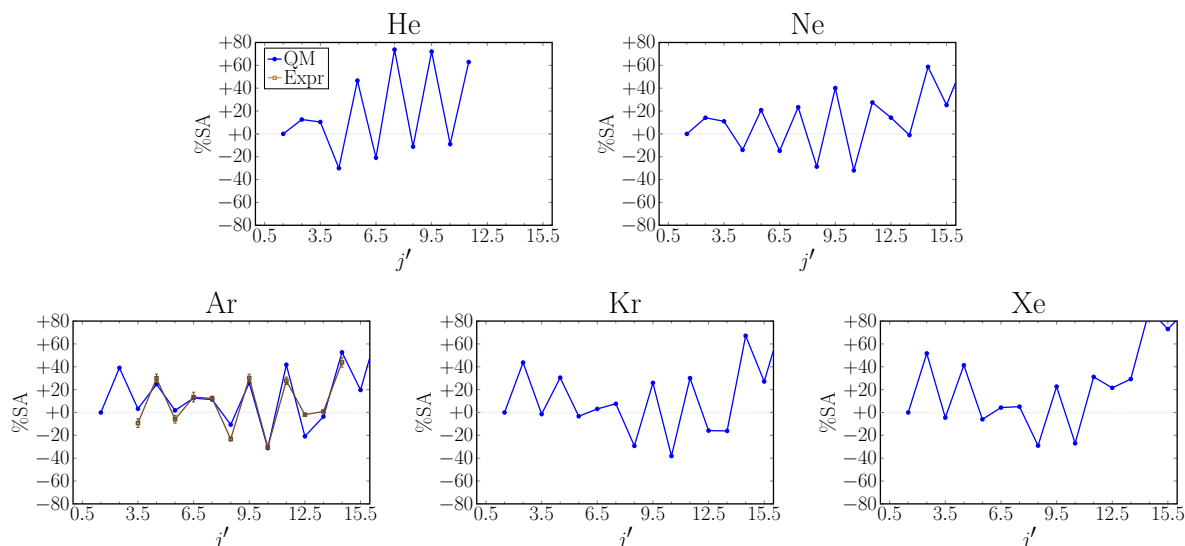


Figure 6.9: The spin-orbit changing steric asymmetry for the NO(X)–Rg systems in the $\epsilon' = e$ final state. The QM data as calculated by HIBRIDON are shown in blue and experimental values, where available are shown in brown. The error is calculated as the standard deviation of batches of 20 000 laser shots. The lightest He system shows a clear N-end preference compared to the heavier more attractive rare gas collision partners.

excitation appear to favor N-end collisions, this is most noticeable for the NO(X)–Xe system in Fig. 6.9. The QCT calculations cannot proceed on V_{diff} , so it is not possible to compare classical steric asymmetry to the calculated QM steric asymmetry or to the experimental data on the spin-orbit changing manifold. Some interesting features are observable in the spin-orbit changing steric asymmetries, for example in Fig. 6.9, there is a phase change of the steric asymmetry at $j' = 6.5$ for the heavier rare gases. This phase change is also seen in the spin-orbit conserving manifold for the heavier rare gases, but at slightly lower rotational excitation.

6.5 Theoretical Integral Steric Asymmetry

6.5.1 Steric Effect as a Function of Collision Partner

In the previous section, the experimentally determined variations of the steric asymmetry with the rare gases was presented for the spin-orbit conserving and changing manifolds, the comparison of the spin-orbit conserving steric asymmetries are shown in Fig. 6.8 and those pertaining to the spin-orbit changing manifold in Fig. 6.9. Observa-

tion of the theoretical and experimental steric asymmetries shows a clear divide between the lighter and heavier rare gases. The steric effect for He and Ne is considerably larger in magnitude, and the oscillations are therefore more pronounced than for those in the heavier rare gases. In comparison, the QCT remains broadly similar between the rare gas systems. Some differences are observed at low Δj , where the attractive part of the potential is dominant in determining the magnitude of the steric asymmetry, especially in the heavier rare gases where the attractive part of the potential results in ℓ -type rainbow scattering (see Chapter 4 and Chapter 5). For the NO(X)–He potential, calculated cross sections up to $\Delta j = 12$ are shown, above $\Delta j = 12$ the cross sections become very small, a consequence of rotational energy disposal [87, 198]. Rotational states higher than this are accessible at the collision energy employed, however the very low cross sections make observation difficult [24, 202].

The QCT calculations on the V_{sum} surface shows that it is necessary to impact as far from the centre of mass as possible in order to efficiently transfer kinetic energy into rotational energy and reach the highest possible rotational excitation. This classical high-torque effect was observed by Nichols *et al.* [84] and described in terms of a ball and stick model, in which the high rotational states are only accessible by impacts at the N-end of the molecule far from the centre of mass. In the collisions resulting in low rotational excitation, the integral steric asymmetry depends strongly on the attractive part of the potential and comparison between the rare gases shows that for Xe, the mechanism leading to the oscillations is weakened at low Δj by the attractive part of the potential. As the collision system becomes more attractive (from He to Xe), the oscillations at higher Δj also diminish in intensity. He, which is very well approximated by a hard shell [137], shows very large magnitude oscillations in the integral steric asymmetry compared to the larger more attractive Ar, Kr and Xe collision systems.

6.5.2 Steric Effect as a Function of Collision Energy

In order to investigate the classical effect demonstrated by the QCT calculations and rationalised by the ball and stick model, a number of CC QM calculations on the full potential energy surfaces were undertaken at numerous different collision energies

for each of the NO(X)–Rg systems. These calculations will show if the interference mechanism extends to higher Δj as collision energy is increased, and as new rotational states become energetically accessible, the highest accessible levels should display a strong N-end preference.

The variation of steric asymmetry at high Δj demonstrates the quantum interference effect responsible for the middle Δj oscillations becoming diminished as more collision energy is available to the system. As shown in Fig. 6.10, as additional collision energy becomes available, more inelastic scattering channels open, allowing for populations of higher rotational states (dark red lines in Fig. 6.10 and 6.11 reach higher $\Delta j_{\max}$, most obvious in the heavier rare gases). Greater total energy is also available for partitioning into k' and j' . Classically, this allows for collisions nearer the centre of mass to excite the NO(X) to the higher rotational states on energetic grounds. At lower collision energies, these states would only be accessible with efficient rotational energy transfer from a low impact parameter, N-end collision. As the energy becomes high enough that a new Δj transition is only just energetically allowed, the steric asymmetry initially shows a very strong N-end preference and is slowly reduced as the available energy increases, this is shown best by the $\Delta j = 14$ collisions for Ar, Kr and Xe. The N-end and O-end interference mechanism outlined in the previous section begins to become more important than the classical torque effect, giving rise to the characteristic oscillations as a function of Δj .

The middle and low Δj states on the spin-orbit conserving manifold are little affected by the increasing collision energy. This is due to these states being more energetically accessible, which prevents any change in the steric effect as the interference mechanism is dominant. In contrast, a number of states across the entire range of accessible rotational states are affected by changing the collision energy, as shown in Fig. 6.11. This is possibly due to the more complex and attractive nature of the V_{diff} potential upon which spin-orbit changing collisions primarily take place (in the Hund's case (a) limit). Some of the same effects that are seen in the spin-orbit conserving data are still present in the spin-orbit changing data. For instance, the even Δj collisions at high Δj show the same rapid decrease in integral steric asymmetry as the collision

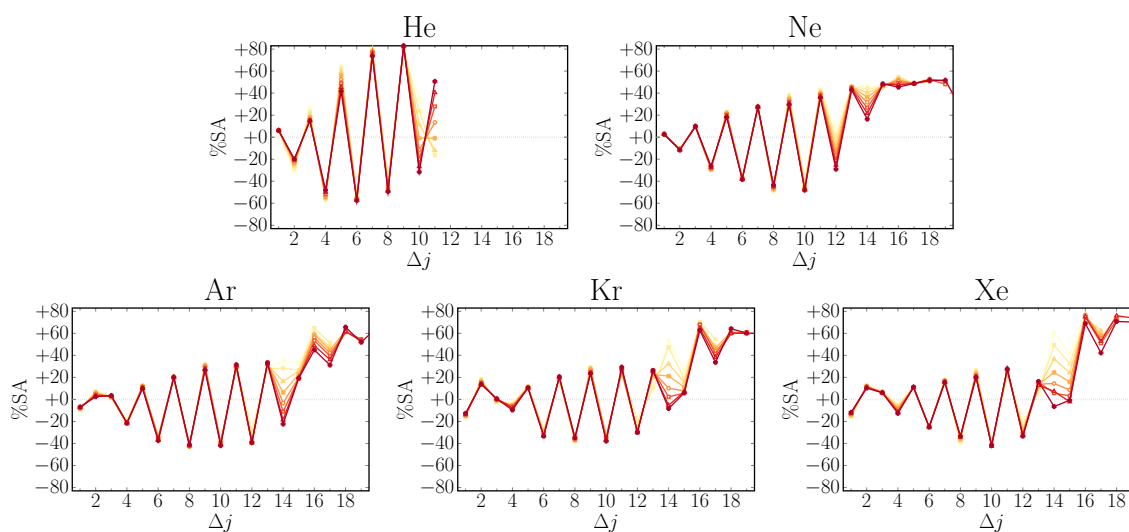


Figure 6.10: The integral steric asymmetry for the NO(X) rare gas systems as a function of collision energy for scattering to the spin-orbit conserving manifold $\epsilon' = e$ states. Dark red represents highest collision energy calculated, 720 cm^{-1} for each system and yellow represents lowest collision energy calculated, 430 cm^{-1} for each system. The collision energy is incremented in 30 cm^{-1} steps. The effect of the increasing collision energy is seen in the rapid reduction of steric asymmetry in some of the high Δj states, most notably $\Delta j = 14$ as more collision energy becomes available.

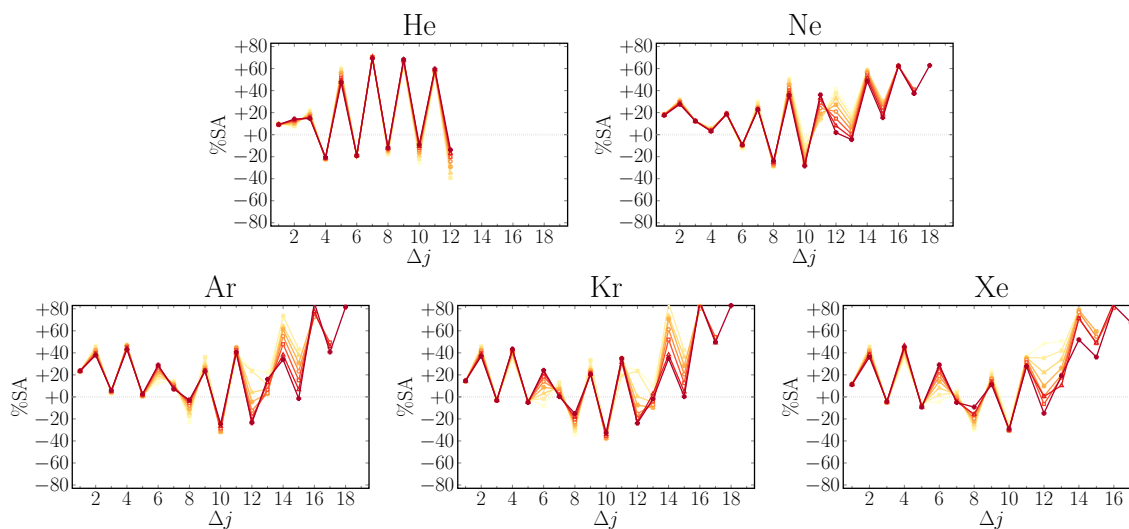


Figure 6.11: The integral steric asymmetry for the NO(X) rare gas systems as a function of collision energy for scattering into the spin-orbit changing manifold $\epsilon' = e$ states. Dark red represents the highest collision energy calculated, approximately 720 cm^{-1} for each system and yellow represents lowest collision energy calculated around 430 cm^{-1} for each system. The collision energy is incremented in 30 cm^{-1} steps. In contrast to the spin-orbit conserving manifold, more Δj states are affected by the changing collision energy on the spin-orbit changing manifold reflecting its more attractive nature.

energy is increased. The low and middle Δj collisions are also affected. This is likely due to the attractive part of the potential as the helium spin-orbit changing values are little changed due to the small and less attractive nature of the He V_{diff} potential when compared to Xe, which has an anisotropic and attractive V_{diff} potential.

6.5.3 Modification of The Potential Energy Surfaces

The experimental and theoretical integral steric asymmetries clearly show trends as a function of collision energy and collision partner. These trends have broadly been separated into three parts: (i) Trends that have been attributed to the attractive part of the potential, most significant at low Δj (ii) Trends that have been attributed to semiclassical interference by a QQT model (iii) Trends that have been attributed to classical ‘ball and stick’ model at high Δj . The regions of the PES that govern a system’s scattering dynamics can be investigated by systematic modification of the surface. To investigate the effects outlined above in relation to features of the PES, recall from Eqn. (2.12) and Eqn. (2.13) that the intermolecular potential can be expanded in terms of reduced Wigner d_{00}^{κ} or d_{20}^{κ} matrices for the V_{sum} and V_{diff} surfaces respectively. The potential expansion coefficients can be modified to change and augment the repulsive or attractive contributions to the potential surfaces.

Even κ terms in the potential contribute symmetrically to both the N-end and O-end and are called the homonuclear terms. The odd κ terms contribute asymmetrically to the anisotropy and are called the heteronuclear terms. Homonuclear molecules are only allowed to undergo parity conserving collisions, which puts constraints on the Δj and Λ -doublet levels allowed to be populated. Consequently, the potential of homonuclear molecules only contain even κ in the potential expansion. At low Δj , direct scattering is dominant, as has been discussed in Chapter 4 with reference to the parity pairs. The direct scattering model describes a transition such that a single potential matrix element couples the initial state to the final state. At higher Δj the direct scattering model becomes a less good approximation as tiers of virtual transitions, based on combinations of the matrix elements, couple states to one another [91] (as has been discussed in Chapter 4).

Alexander has shown that the collisions resulting in low rotational excitation can be thought of as sampling well defined terms in the potential whilst higher rotational excitation requires the sampling of a wider range of potential terms [61]. The coupling in the direct scattering model is complicated by the fact that the initial Λ -doublet levels in the potential are mixed by the α and β coefficients. This means that at least two terms will always couple the initial to the final state in the oriented transition as there is initial e and f character in the transition, and as shown by Eqn. (6.23), the initial and final parities govern the potential matrix element which will couple the initial to the final state. This has important consequences for the form of the steric asymmetry.

Another insightful manipulation that can be performed on the intermolecular potential is to truncate the attractive part whilst preserving the shape of the repulsive part. This can be achieved by using certain functions that preserve the half sum/difference nature of the V_{sum} and V_{diff} potentials [103]. A home-made truncation function developed by Hornung [68] was used to perform the potential truncations of the rare gas systems. The modified potentials are given in terms of a scaling function by [68, 103]

$$V_{\text{sum}}(R, \gamma) = V_{\text{sum}}(R, \gamma) f(R, R_0, R_{\text{shift}}, \alpha) \quad (6.30)$$

$$V_{\text{diff}}(R, \gamma) = V_{\text{diff}}(R, \gamma) f(R, R_0, R_{\text{shift}}, \alpha) \quad (6.31)$$

where the truncation function $f(R, R_0, R_{\text{shift}}, \alpha)$ is given in terms of R by

$$f(R, R_0, R_{\text{shift}}, \alpha) = 1 - \frac{1}{1 + \exp(-\alpha(R - R_0 + R_{\text{shift}}))} \quad (6.32)$$

where α is a scaling factor which determines the function steepness as a function of R , R_0 is the potential contour at a collision energy of 0 cm^{-1} . The critical parameter R_{shift} ensures the potential drops below 1% of the collision energy at a value of R_0 by shifting the inflection point of the function. The function varies asymptotically between 0 and 1 which ensures smooth scaling of the PESs and that propagation will not fail due to discontinuities in the potential. An added advantage is that V_{diff} is not turned off, allowing the spin-orbit changing collisions to be probed. A comparison of the full and truncated potential contours in Cartesian co-ordinates is shown in Fig. 6.12. In

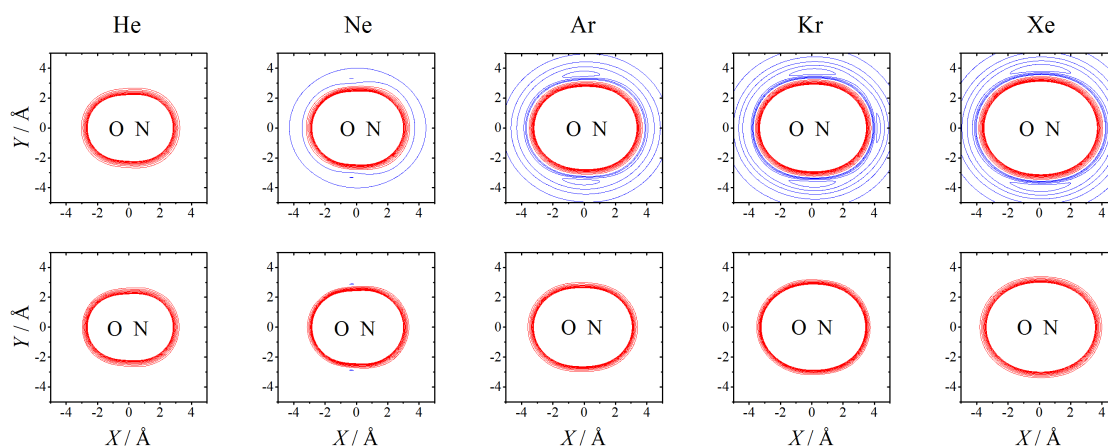


Figure 6.12: A figure showing the full (top) and truncated (bottom) V_{sum} potential energy surfaces for the NO(X)-Rg systems shown. The attractive parts (blue, contour spacing 10 cm^{-1}) are removed while maintaining the repulsive wall (red, contour spacing 100 cm^{-1}).

general, there is good agreement between the steric asymmetry calculated on the full and truncated potential surfaces as shown by Fig. 6.13. The regions where there is significant difference tend to be at high and low Δj . For NO(X)-He there is almost quantitative agreement between the two potentials as the attractive part has a very small well depth (see table 2.1 in Chapter 2), so truncation minimally effects the potential. For the heavier, more attractive potential energy surfaces, more pronounced differences at low Δj are observed.

Analysis of the stereodynamics of ℓ -type rainbow scattering by Nichols *et al.* [19,84], has demonstrated that classically, the N-end plays an important role in the ℓ -type rainbow scattering. The rainbow scattering has also been observed with enhanced resolution for a number of systems by the group of Van de Meerakker [82]. The interactions leading to ℓ -type rainbow scattering sample the attractive part of the potential and lead to strong, parity dependent resonances at relatively high scattering angles in low Δj , parity changing collisions. The ℓ -type rainbows observed in the NO(X)-Xe system were detailed in Chapter 4, and the strong effect that the ℓ -type rainbow has on the collision-induced orientation was described in Chapter 5.

At middle Δj , where the agreement between the truncated and full potential is best, the truncation demonstrates that the steric asymmetry is primarily defined by the repulsive part of the intermolecular potential. This agrees with the analysis of Stolte

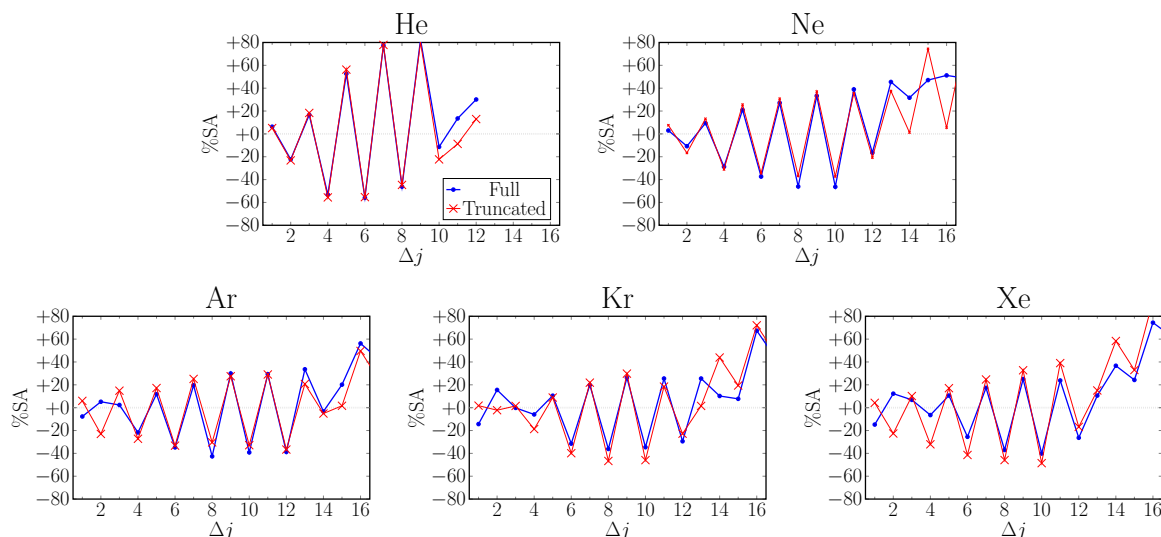


Figure 6.13: Comparison of integral steric asymmetries calculated on the full (blue circles) and truncated (red crosses) potential energy surfaces. The truncated potential and full potentials agree very well for all collision systems at middle Δj , however agreement is less good at low Δj where attractive forces are important and at high Δj where Hund's case (a) is a less good representation of the angular momentum coupling in NO(X).

et al. [137] in his QQT approach which treats the potential as a hard shell and uses the phase shifts (Eqn. (6.25)) to recover the steric asymmetry almost quantitatively for collisions resulting in intermediate rotational excitation.

At high rotational excitation, the agreement between calculations performed on the truncated and full potential surfaces becomes poor for all of the collision systems. This is likely due to the influence of V_{diff} on collisions resulting in high rotational excitations. In these high Δj collisions, Hund's case (a) is a less good description of the angular momentum coupling in NO(X), therefore the coupling is better described as being mixed Hund's case (a) and Hund's case (b). In this case, the interaction occurs on both V_{sum} and V_{diff} , and since V_{diff} is removed from the truncated potential, the lack of agreement at high Δj is expected. V_{diff} has a large attractive part and upon truncation the surface becomes distorted, to prevent this distortion affecting the results, the V_{diff} potential is set to zero in order to prevent discontinuities. Another possibility is that the high rotational collisions are sensitive to the precise contour of the repulsive part of the potential which is modified slightly upon truncation. As the integral steric asymmetry is normalised by the sum of the oriented integral cross sections, small changes in the already small integral cross sections can have a large effect on the magnitude of the

steric asymmetry. To investigate the effect of V_{diff} on the steric asymmetry, a modified potential energy surface with V_{diff} removed was constructed for each system, whilst the attractive part was retained.

Effect of V_{diff}

By including all the potential expansion terms in V_{sum} , but setting the terms of V_{diff} to zero, the difference potential is removed and the effect of scattering on the V_{sum} surface only is observed. As mentioned in Chapter 2, the V_{sum} surface dominates scattering of the spin-orbit conserving states at low Δj , as in the limit of pure Hund's case (a), scattering solely takes place upon V_{sum} . In the limit of Hund's case (a) being a good approximation of the angular momentum coupling in NO(X), little difference should be observed between the full potential and one in which V_{diff} is removed (for the spin-orbit conserving collisions). Differences manifest themselves at high Δj when the Hund's case (a) coupling approximation starts to break down and NO(X) is better described as a mixed Hund's case (a) and (b) molecule. Figure 6.14 shows the effect of the removal of V_{diff} . It can now be concluded that the high states are effected by the V_{diff} potential. This will prove important later in the chapter when the expansion terms in the potential are modified.

To highlight the effect of removing V_{diff} , we can also look at the steric effect in the spin-orbit changing collisions as shown in Fig. 6.15. In the Hund's case (a) limit, these collisions are dominated by the V_{diff} potential. The removal of V_{diff} has a substantial effect and causes the steric asymmetry to diverge strongly from those predicted by the full potential and look more reminiscent of the V_{sum} potential steric asymmetry. It can be seen from Fig. 6.15 that the steric asymmetry in the spin-orbit changing collisions is influenced by V_{sum} , this contrasts with the steric asymmetry on the spin-orbit conserving manifold where the steric effect is dominated only by V_{sum} . If the V_{diff} potential is removed, the spin-orbit conserving collisions are well approximated, but the coupling between V_{sum} and V_{diff} means we can no longer approximate the spin-orbit changing collisions with only V_{sum} terms included.

V_{diff} has a large effect on the high Δj spin-orbit conserving, and all of the spin-orbit

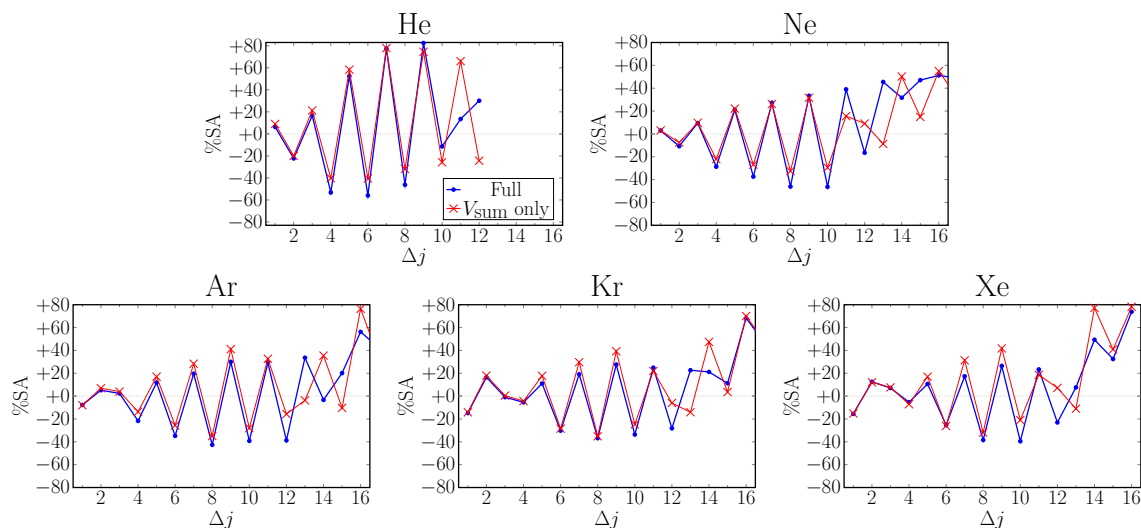


Figure 6.14: A figure showing the effect of removing V_{diff} on the spin-orbit conserving collisions steric asymmetry. The blue circles show the full potential, and the steric asymmetry on the V_{sum} only potential is shown by the red crosses. The full and V_{sum} only potentials show excellent agreement for the spin-orbit conserving collisions apart from at higher Δj where Hund's case (a) begins to break down.

changing collisions. The steric asymmetry can be investigated further by making further modifications to the potential energy surfaces, as will be undertaken in section 6.5.3

Dampening the high order terms

The previous calculations show that the V_{sum} potential is important in the determination of the steric asymmetry. By means of Eqn. 2.12 we can remove different terms of the potential to test how the shape of the surfaces affect the steric asymmetry. In doing so, the sensitivity to the high order terms in the potential can also be investigated. Modified potentials were produced with varying $V_{0\kappa}$ in Eqn. (2.12) set to zero, V_{diff} was set to zero in all cases — effectively disabling the spin-orbit changing collisions and reducing the cross sections of the high Δj collisions. For this reason, the dampened potentials will be compared to a potential with all V_{diff} $V_{2\kappa}$ terms set to zero. As has already been shown in Fig. 6.14 the removal of V_{diff} has a strong effect on the high Δj collisions where Hund's case (a) is no longer a good description of the coupling in the NO(X) molecule.

By removing the terms in the V_{sum} potential with $\kappa > 1$ the effect of the extent of the potential given by the zeroth order term and the first order term can be investigated. The potential contours are shown in Fig. 6.16. It is immediately clear that the potential

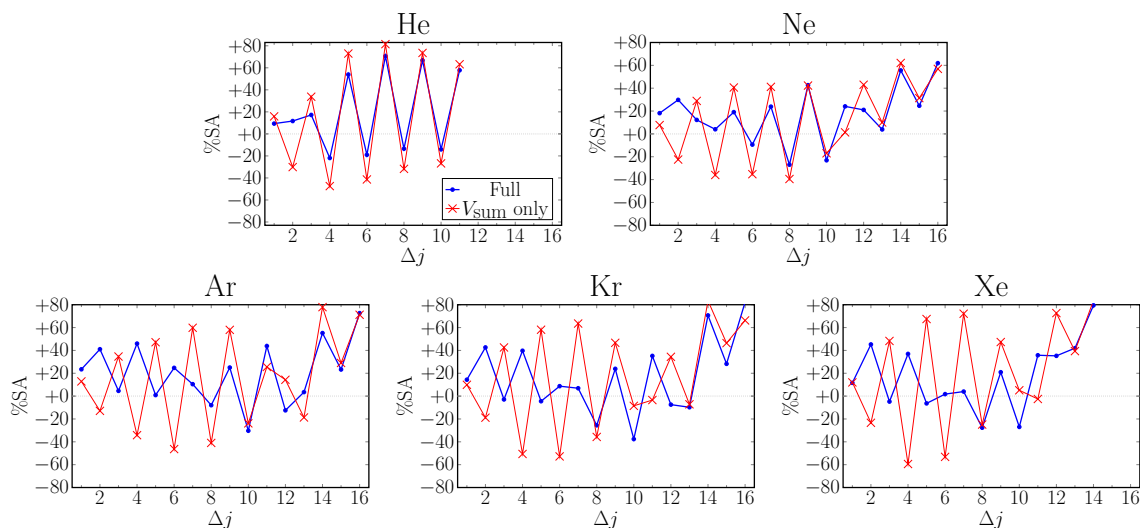


Figure 6.15: A figure showing the effect of removing V_{diff} on the spin-orbit changing collisions steric asymmetry. The blue circles show the full potential, and the steric asymmetry on the V_{sum} only potential is shown by the red crosses. The full and V_{sum} only potentials show poor agreement highlighting the importance of the V_{diff} potential on governing the spin-orbit changing collisions.

is malformed compared to the full potential and the extent of the attractive part is strongly localised on the O-end of the potential. The results of CC QM and classical calculations performed on this dampened potential are shown in Fig. 6.17.

The potential demonstrates a very strong O-end preference at all Δj and the characteristic oscillations seen in each of the integral steric asymmetry plots so far have disappeared. The first heteronuclear term with $\kappa = 1$ defines the magnitude of the steric effect. Since there are no homonuclear terms in the potential, we have a purely heteronuclear molecule with a strong O-end attractive well which naturally shows a strong preference for the O-end as the extent of the potential is much greater at the O-end, as is seen in Fig. 6.16. Since there are no homonuclear (even κ) terms in the potential, the interference between the N-end and the O-end is absent and the sign change as a function of Δj vanishes.

Adding in the first homonuclear term with $\kappa = 2$ has an enormous effect on the integral steric asymmetry, as shown by Fig. 6.18. The interference between the N-end and O-end turns on as the ends have become much more similar, and the oscillations as a function of Δj reappear. The phase matching of the oscillations breaks down at intermediate Δj where the collision interaction is no longer dominated by direct scattering and proceeds *via* tiers of virtual transitions. The shape of the potential is

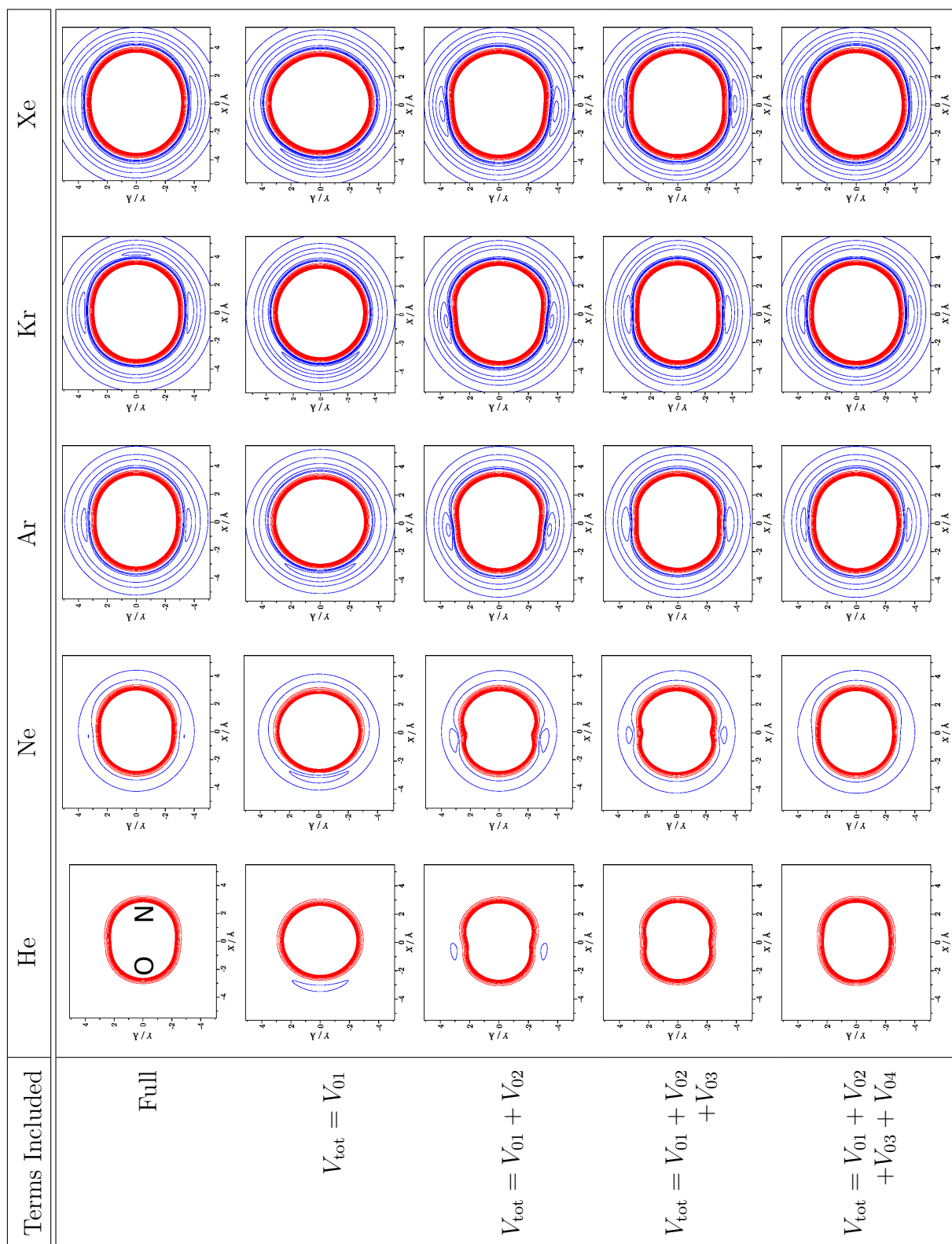


Figure 6.16: The full and modified V_{sum} potential energy surfaces for the NO(X)-Rg systems. The Potential contours show the strong repulsive wall (red, 100 cm^{-1} spacing) and the attractive part of the potential (blue, 25 cm^{-1} contour spacing) for each of the collision systems of interest.

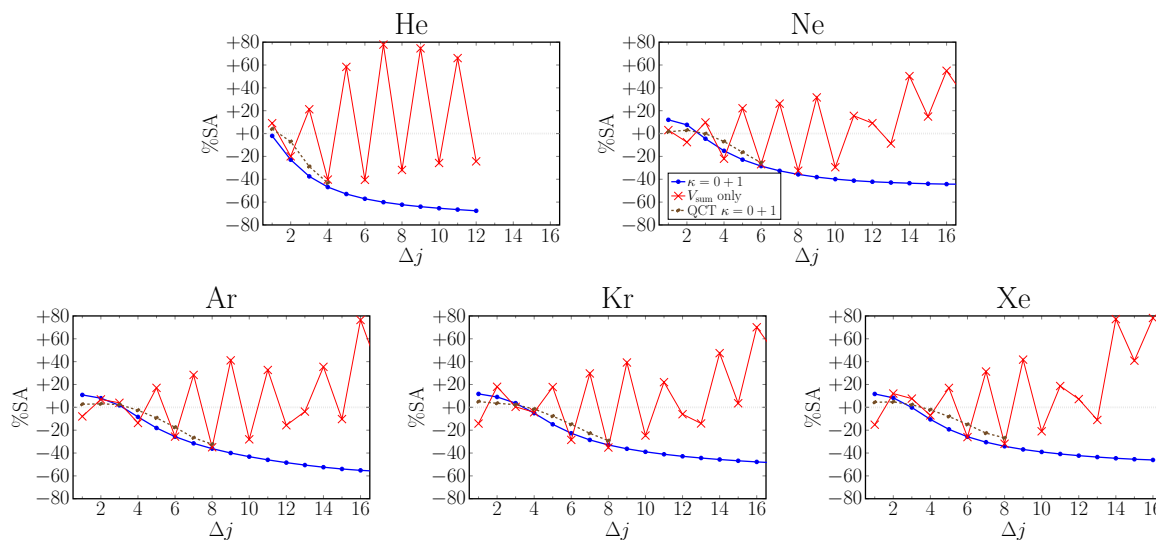


Figure 6.17: By removing all expansion terms in V_{sum} except for the $\kappa = 0$ and $\kappa = 1$ terms (blue circles), the steric asymmetry shows a very strong O-end preference and loses its oscillations. This is due to the completely heteronuclear nature of the potential where the N-end and O-end are distinctly different. The absolute magnitude of the steric asymmetry is well approximated by the $\kappa = 1$ term in the potential. The full V_{sum} potential surfaces steric asymmetry (red crosses) is also shown for comparison. The classical steric effect (brown dashed) closely matches the QM on this surface as all interference has been disabled by turning off the high order expansion terms.

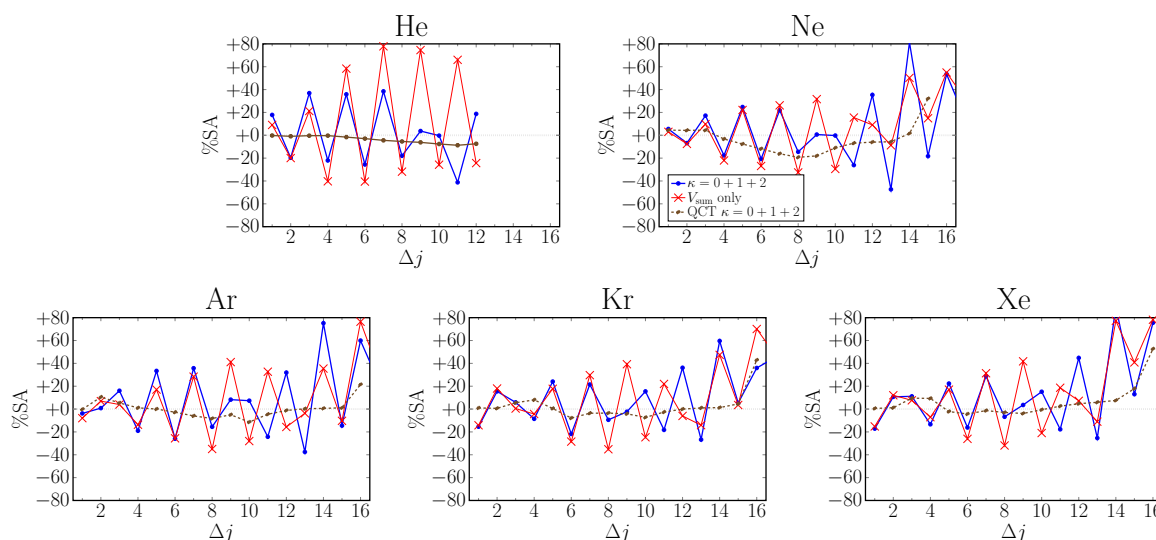


Figure 6.18: Removal of the expansion terms in V_{sum} above the $\kappa = 2$ term (blue circles) reintroduces interference between the near homonuclear N-end and O-end. The steric asymmetry then begin to match the V_{sum} steric asymmetry (red crosses) apart from a phase shift at mid Δj . The classical steric effect on this surface is shown for comparison (brown dashed).

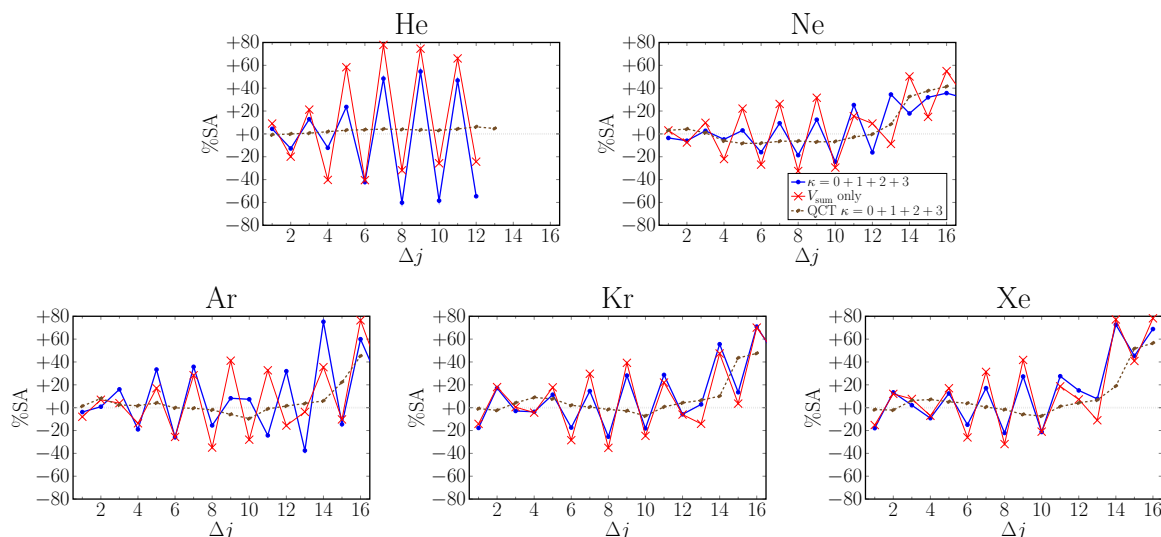


Figure 6.19: Addition of the expansion term $\kappa = 3$ (blue circles) reintroduces interference between the near homonuclear N-end and O-end. The steric asymmetry then begin to match the V_{sum} steric asymmetry (red crosses) apart from a phase shift at mid Δj . The classical steric effect on this surface is shown for comparison (brown dashed).

no longer dominated by the O-end as can be seen in Fig. 6.16.

By adding in the $\kappa = 3$ term, the steric asymmetry begins to have a matching phase across the whole Δj range for most of the NO(X)-Rg systems shown. The NO(X)-Ar system behaves slightly differently and displays poor phase matching at middle Δj , as shown by Fig. 6.19. This is probably due to the higher order $\kappa_{\text{max}} = 8$ expansion used in the potential energy surface of NO(X)-Ar compared to the other systems which have $\kappa_{\text{max}} = 6$. The magnitude of the steric asymmetry is slightly dampened by having the extra heteronuclear term, as the interference which causes the sign changing oscillations is not fully matched, and the attractive limb of the O-end has a greater extent than the N-end again. This effect is most easily seen by the attenuation of the steric effect in the NO(X)-Ne system at low to middle Δj shown in Fig. 6.19. The effect on the NO(X)-He system is also of interest as the steric preference is shifted towards the O-end, this is due to weak attractive forces localised primarily on the O-end of the potential.

Addition of the second homonuclear $\kappa = 4$ term into the expansion allows recovery of the steric asymmetry for each of the systems. The interference is now well matched and the phase change at middle Δj is well reproduced, as shown in Fig. 6.20. The good matching of the full CC QM steric asymmetry to the steric asymmetry obtained from

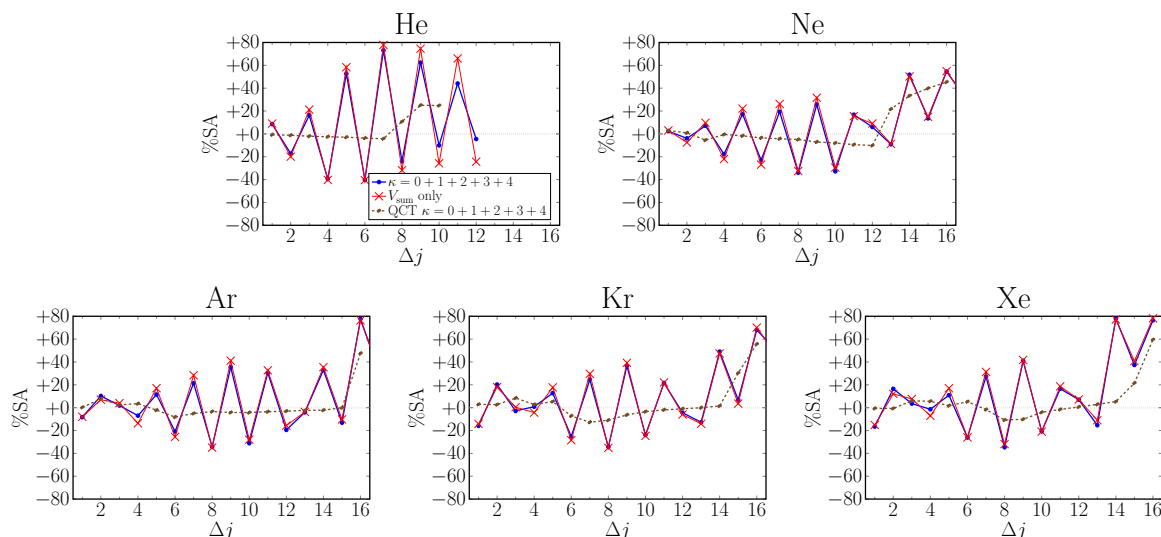


Figure 6.20: Removal of the expansion terms in V_{sum} above the $\kappa = 4$ term (blue circles) causes the phase shift at mid Δj to disappear as the interference between the two homonuclear and two heteronuclear terms balances to reproduce the full potential (red crosses) well. The steric effect is well matched in all systems highlighting the importance of the interference between the terms. The classical (brown dashed) steric effect on this surface is shown for comparison.

calculations performed on the V_{sum} potential when terms up to $\kappa = 4$ are included highlight the importance of interference between the even and odd terms. This interference plays an important role in the determination of the magnitude and sign of the integral steric asymmetry. The contour plots in Fig. 6.16 are now almost indistinguishable from the full potential contour plots in Fig. 6.20.

The steric asymmetry is characterised by its large sign changes as a function of Δj . The magnitude of the sign change is primarily bounded by the $\kappa = 1$ term in the potential which defines the heteronuclearity of the NO. The first homonuclear term $\kappa = 2$ turns on the interference between the N-end and O-end and the sign changing oscillations appear. The phase matching and magnitudes are reproduced by the third and fourth order terms which tune the interference and all but reproduce the full V_{sum} steric asymmetry.

6.6 Summary

This chapter details an investigation into the effect of the potential surfaces and collision energies on the integral steric asymmetry in NO(X)–Rg collisions. The behaviour at

low Δj is sensitive to the attractive part of the potential as evidenced by truncating the potential in order to remove the attractive part, whilst maintaining the contour at the collision energy. The light rare gases are shown to have a steric asymmetry almost identical to those of the truncated potentials for all the final rotational states, whereas the heavier, more polarisable rare gases have had the low Δj steric asymmetry significantly distorted by the loss of the attractive part of the potential. We have also seen that after $\Delta j = 8$, the spin-orbit conserving collisions become influenced by V_{diff} due to the increasing degree of mixing between Hund's case (a) and Hund's case (b).

The effect of the collision energy on the system's steric asymmetry was also investigated, revealing that the high Δj steric asymmetry is sensitive to the collision energy, and as more energy becomes available, the quantum interference responsible for the oscillation in the steric asymmetry as a function of Δj results in large %SA changes at increasingly higher Δj as more energy is left in translation after the rotational energy transfer. The lower states are little affected by the changing collision energy on the spin-orbit conserving manifold, a result of the contour at the collision energy changing very little over the range due to the steepness of the repulsive wall in the NO(X)–Rg systems. The spin-orbit changing steric asymmetry is, however, much more affected by the changing collision energy. This is due to the unusual shape and highly attractive nature of the V_{diff} potential upon which spin-orbit changing collisions primarily take place. As a function of collision energy, the spin-orbit changing states change significantly more than the spin-orbit conserving collisions, providing a sensitive test of the shape of the V_{diff} potential and therefore subtle differences of the A and A' potential surfaces which make up V_{sum} and V_{diff} . The experimentally determined spin-orbit changing and spin-orbit conserving steric asymmetries agree well with collision energy averaged theory giving confidence that the relative magnitude difference between the oriented ICSs is well reproduced by the *ab initio* potential energy surfaces employed.

Finally the influence of the potential expansion $V_{0\kappa}$ terms on the V_{sum} potential was investigated. The $\kappa = 1$ term was shown to define the magnitude of the oscillations in the steric asymmetry at least until the V_{diff} potential also influences the cross sections of the collisions with intermediate to high Δj . The $\kappa = 1$ homonuclear term has a

strong O-end preference which is rationalised by the large attractive limb on the O-end of the potential, as shown by plots of the potential contour. Adding in the $\kappa = 2$ heteronuclear term turns on the N-end O-end interference and makes the attractive part of the potential more isotropic around the NO. The characteristic oscillations as a function of Δj then turn on, a result of the now near-homonuclearity of the NO(X) thanks to the addition of the first even term in the potential expansion. Although the magnitude does not match perfectly, and indeed the phase matching at middle and high Δj is poor, it is clear that the steric asymmetry on V_{sum} can be thought of as being defined in magnitude by $\kappa = 0$ and $\kappa = 1$ and the interference is controlled by the even terms in the potential.

This effect is highlighted by turning on the $\kappa = 3$ and $\kappa = 4$ terms in the potential and recovering the complete steric asymmetry as given by the full potential with V_{diff} removed. This shows that compared to the three vector $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ correlation explored in Chapter 5, the steric asymmetry is not as sensitive to the high order terms in the potential, and instead accurately samples the molecular contour which is well described by a hard shell interaction. Extension of the closed-shell quantum hard shell model of Hornung [103] with open-shell wavefunctions should provide a further tool to investigate the shape of the contour, this could prove a fruitful direction for future investigations not only into the integral steric asymmetry, but also the differential steric asymmetry given by the $\mathbf{r}-\mathbf{k}-\mathbf{k}'$ correlation.

7

Fraunhofer Oscillations In Inelastic Scattering

This chapter details investigations into the diffraction peaks in the first 40° of scattering angle, and the origin of one particularly prominent low-angle peak. In order to investigate this irregular peak, a collaboration with the van de Meerakker group in Nijmegen was started, and several fruitful exchanges between the Oxford and the Nijmegen groups lead to a concise explanation of the irregular peak and its importance. Work performed in Nijmegen will be clearly stated where appropriate.

As has been shown in the previous chapters, different techniques for controlling the bond orientation and measuring various quantities pertaining to vector correlations can be employed. Each of these quantities gives information on the dynamics which occur during a molecular collision. Due to the finite velocity spread in the molecular beams, and other effects such as the electron recoil from the resonant ionisation, it is currently not possible to exactly specify all the parameters that govern the molecular collisions in this thesis. Instead, as has been shown in each chapter previously, we must measure and take into account the blurring factors associated with the molecular beams and electric fields. Progress towards high resolution experiments has however been made, with the installation of new advanced beam valves with short opening times and narrow velocity spreads in the longitudinal and transverse velocities. However, it remains possible to improve the molecular beams with novel new valves, such as the Nijmegen valve [203].

Additional technical progress has been made in recent years by further exploitation of the Stark effect. The use of a Stark decelerator in inelastic scattering experiments allows fine control over the collision parameters. The Stark decelerator is capable of selecting velocities from a molecular beam by utilising pulsed electric fields that interact strongly with the dipole of the molecule, resulting in a typical FWHM velocity spread of 3 m s^{-1} for the selected molecules. Such devices have been utilised to study inelastic scattering in unprecedented detail [204–206] and have opened up the possibility of so called collisional spectroscopy, in which the individual collisions are well-defined and therefore allow vector properties to be investigated systematically as a function of collision energy [205].

Given the recent advances, it is desirable to compare the hexapole experimental resolution with that of highly controllable experiments, in order to obtain a quantitative understanding of the angular resolution and the effects which limit it. The obvious choice for such an investigation is to look into the very forward scattered region of a rotationally inelastic DCS, where high frequency, narrow scattering angle peaks are observed [204]. These peaks, separated by only a few degrees in θ , are a general consequence of the quantum mechanical nature of the scattering process [207, 208] and

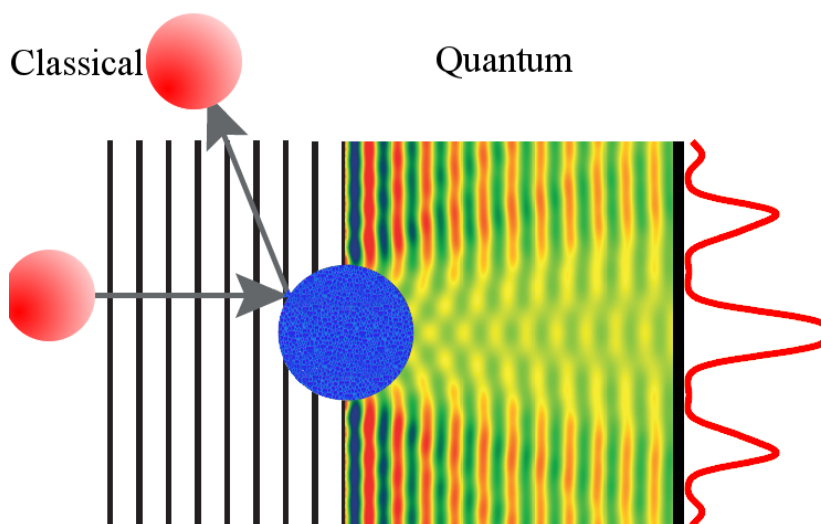


Figure 7.1: Cartoon of classical and quantum scattering. Classically, scattering can not occur into the shadow of the object. However, quantum mechanically, diffraction into the shadow can occur leading to interference fringes in the angular distribution. Image adapted from reference [207].

are caused by molecular diffraction as shown in the cartoon Fig 7.1. The peaks in the forward scattered direction are present with varying magnitude for all inelastic scattering cross sections, regardless of spin-orbit or parity state, most noticeably at middle j' . These peaks display an entirely different form of dynamics, one that has no classical analogue and is purely quantum mechanical in nature. As the incoming colliders are wave-like in nature, they can undergo reflection and refraction in an analogous manner to other types of wave. These narrow angle oscillations not only allow a benchmarking of the angular resolution, but also give detailed information about the shape of the NO(X) potential. The resulting oscillations can be almost quantitatively modelled by the simple and analytical Fraunhofer model. The model was first developed by Faubel [209] and later extended by Leshchko and Friedrich [208,210]. In this chapter, the angular resolution of the experiment will be benchmarked and compared to the current highest resolution imaging experiments. The data obtained will be used to reveal the characteristics of a surprisingly intense peak (called the irregular peak), present in all¹ inelastic scattering differential cross sections (DCSs). This Fraunhofer diffraction peak yields significant information about the state-to-state dynamics of the system and can be used to probe the shape of the potential energy surface.

¹The intensity of the peak varies considerably at high rotational excitation where there is little forward scattering.

7.1 Observing Diffraction Peaks

There are many features in the first 30° of the DCSs and polarisation dependent differential cross sections (PDDCSs) that would be desirable to be resolvable in the experimental images. Upon averaging and interpolation over the collision energy of the experiment, narrow angular features in the very forward scattered direction are diminished, but not eliminated. This would indicate that barring any other blurring effects, it should be possible to image the diffraction peaks in the DCS — even after consideration of the collision energy spread. The collision energy spread is not the only source of blurring in the experiment, numerous other sources are present, including blurring from the near-threshold ionisation with 308 nm light (threshold is at 322 nm [206]), imperfect velocity mapping, large size of the interaction region and timing jitter introduced by the thyatron of the excimer laser.

7.1.1 High Resolution Imaging in The Alignment Geometry

The hexapole, in the alignment geometry described in Chapter 3, can be modified to allow high resolution images to be obtained. These changes result in low throughput of ions as the modifications are often a trade off between signal intensity and angular resolution. The laser interaction volumes were minimised by focussing the excitation laser to the focal point and iris-ing the excitation laser to < 1 mm. Power levels were set by attenuating the excitation laser to allow only a few ions per shot to be registered on the detector in order to limit any possible Coulomb repulsion. Further, the molecular beam widths were optimised to the lowest possible voltages and opening times whilst flux was still observed and routinely optimised with the microphone apparatus to ensure the narrowest time and velocity spreads. In addition, the detector gating system (which usually selects the NO(X) mass peak) was set to open only after the top half of the Newton sphere had arrived, allowing a limited form of Newton sphere slice imaging [211] to be performed. The resultant ion images, for several different systems, are predicted to show particularly strong scattering in the forward direction from QM theory. They were recorded over some 400 000 laser shots in order to ensure good

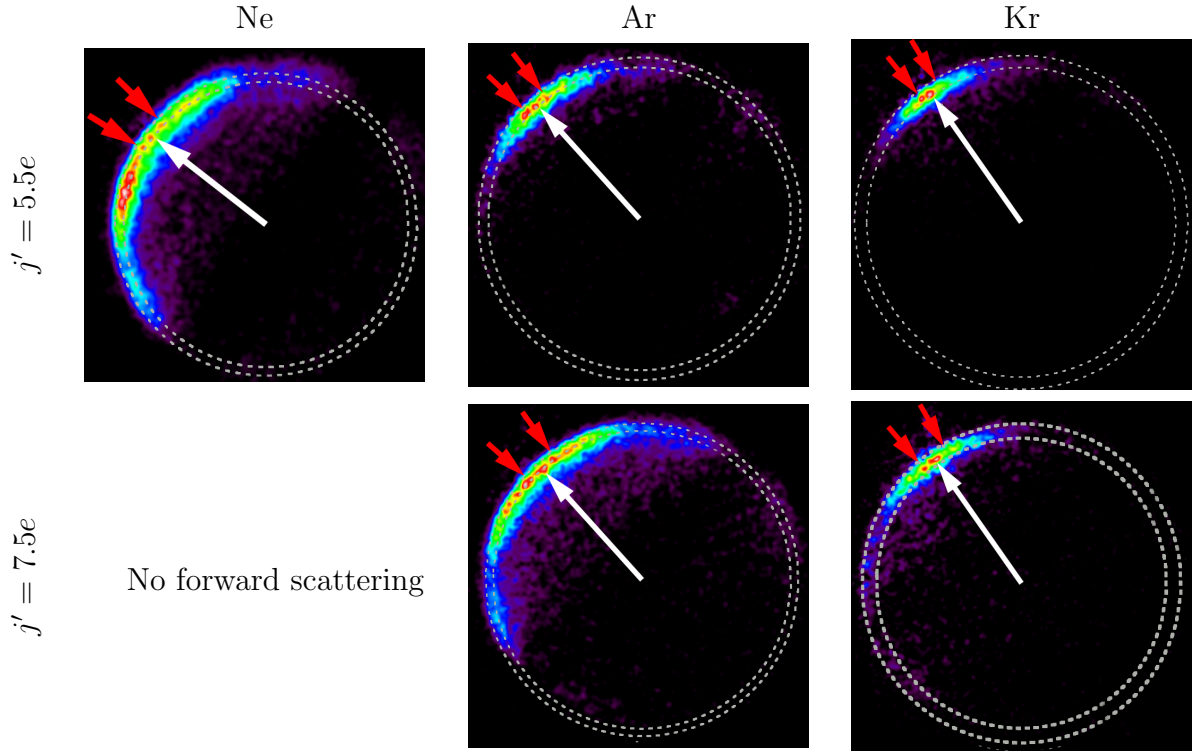


Figure 7.2: High resolution images obtained from the hexapole with possible fingerprints of diffraction oscillations in the forward scattered region. The red arrows indicate the most intense irregular feature in the forward scattered direction at a scattering angle of $\approx 6^\circ$. The images pertain to ϵ -changing collisions on the spin-orbit conserving manifold.

S/N. The resultant experimental images are shown in Fig. 7.2. The experimental images presented in Fig. 7.2 show hints of fast oscillations in the forward scattered direction. The superimposed red arrows give the position of the most intense peak at approximately 6° of scattering angle, whilst the white arrow gives the direction of the relative velocity vector $\mathbf{k}$. Careful inspection of the images shows slight dips and peaks in intensity which could indicate the presence of diffraction oscillations, or alternatively artefacts in the images. In order to determine if the oscillations can be observed conclusively in the hexapole apparatus, comparison with theory may be performed to ensure the oscillations match the expected angular positions and phases, as has been observed previously [204].

7.1.2 Analysis of High Resolution Data

The experimental images in Fig. 7.2 are not suitable for analysis with a Fourier fitting algorithm as the features are too sharp to enable efficient fitting with a polynomial

basis set. In order to obtain an angular distribution from the images and compare with close-coupled quantum (CC QM) calculations, an alternative means of data analysis was employed, suitable only for the forward scattered region. For the analysis, the ion image was divided by the flux-to-density correction determined from the experimental parameters. This only affects the intensity of the angular distribution in the forward scattered direction, as the images recorded were quite symmetric about $\mathbf{k}$. The correction of the instrument function further symmetrises the image and allows additional analysis to be performed. The angular intensity at the edge of the image was then read, neglecting the interior of the image where signal intensity is low. The rim was interpolated with Gaussian weighting over a finite pixel width in order to give increased prominence to the region where scattered signal is strongest. The dotted white lines around the edge of the images in Fig. 7.2 represent the region in which the angular intensity of the rim of the image was read. The obtained angular distributions span from 0° to 360° and are approximately symmetric about the relative velocity vector, $\mathbf{k}$. Due to slightly better signal-to-noise, the slow side of the image was chosen to be compared to theory. The angular distributions obtained from such an analysis are shown in Fig. 7.3, they have been scaled to CC QM calculations by matching the CC QM and experimental cross sections over the angular range of 0 – 40 degrees.

Inspection of the angular distributions in Fig. 7.3 reveals only moderate agreement with the diffraction peaks in the forward scattered region. The oscillations are not clearly identifiable in the angular distributions and there appear to be artefacts in the angular distributions. The imprecise agreement between the experimental and theoretical DCSs is likely a reflection of the imperfect symmetrisation of the experimental images, as well as the blurring sources in the experiment. Although in most of the experimental images, in the region of the theoretically predicted peak, there is some indication of a prominent peak, it cannot be said with confidence that it is observed in the experimental images. The hexapole experimental resolution is capable of resolving an ℓ -type rainbow with an angular spread of 20° [19], but not the irregular feature in the forward direction with an angular spread of 3° .

The images shown in Fig. 7.2 are crushed images. The 3D Newton sphere of

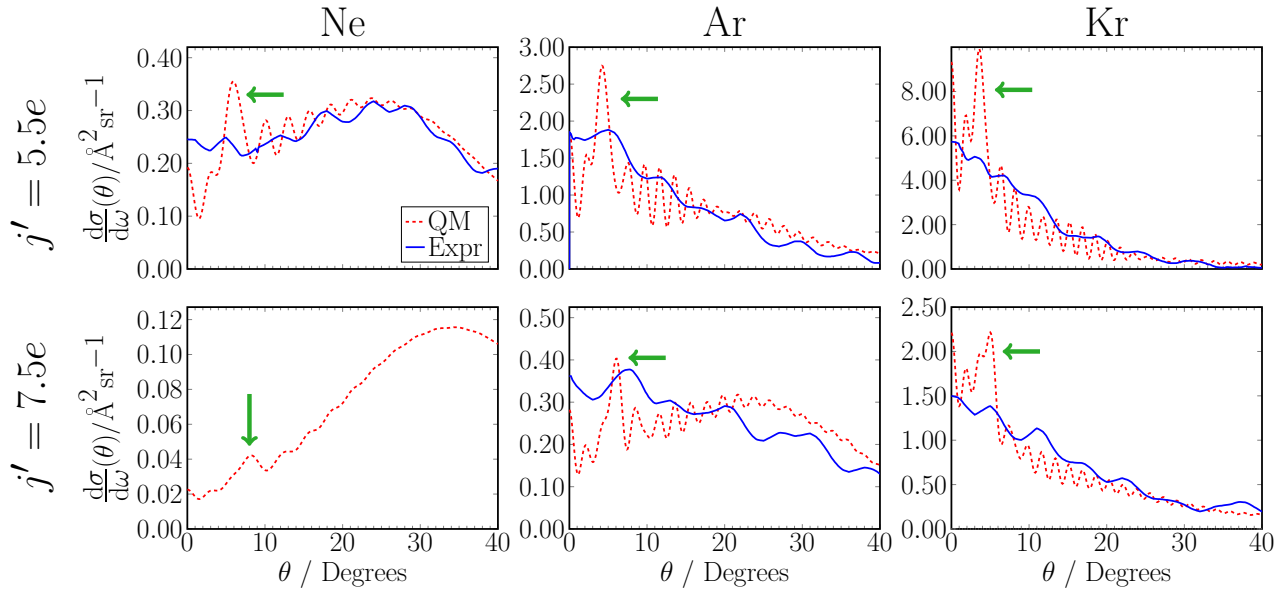


Figure 7.3: Experimental (blue) and theoretical (red) DCSs obtained for ϵ -changing collisions of NO(X) with Ne, Ar and Kr for the $j' = 5.5e$ and $j' = 7.5e$ states on the spin-orbit conserving manifold. The mean collision energies are 661 cm^{-1} , 650 cm^{-1} and 612.0 cm^{-1} for Ne, Ar and Kr respectively. Note the x -axis scale is from 0° to 40° . The green arrows indicate the irregular peak of interest.

ions is projected onto the plane of the MCP leading to a loss in resolution as ions with out-of-scattering-plane components increase the blurring. In order to minimise this effect, the central portion of the Newton sphere should either be (i) resolved in time or (ii) selected using the detector. This may be achieved with hardware, for example a delay line detector [212, 213] or a fast event counting camera [214]. Neither of these is available without significant modifications to the imaging stack (as described in Chapter 8). However, several advanced mathematical reconstruction techniques are available which seek to reconstruct the 3D distribution and thereby allow the central slice of highest angular resolution to be obtained. These algorithms, referred to as inverse-Abel transforms have received much attention, and several different implementations of the algorithms have been presented in the literature [215–220]. Each requires that the image has cylindrical symmetry, which is a good enough approximation for the forward scattered region of the images presented in Fig. 7.2.

The images were rotated so that the relative velocity vector pointed along the principal axis, and the filtered back-projection algorithm of Sato [220] was chosen in order to perform the reconstruction of the 3D distribution due to its satisfactory

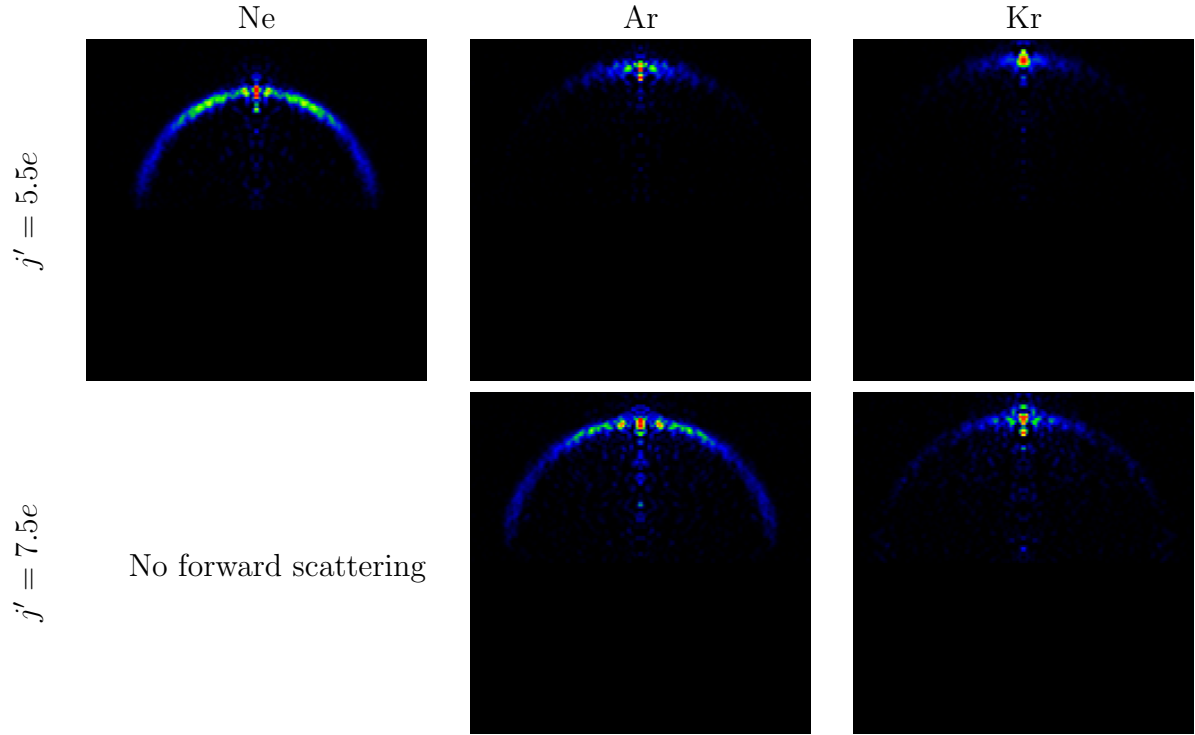


Figure 7.4: Abel-inverted experimental images of Fig. 7.2 obtained from the filtered back-projection technique of Sato [220]. The Abel-inversion causes noise to be moved to the centreline. The images show hallmarks of diffraction with areas of low and high intensity in the very forward scattered direction.

performance when compared to other algorithms. Upon inversion, the images display a much higher angular resolution, demonstrating the power of the numerical filtered back-projection technique. The inverted images are shown in Fig. 7.4. The images contain noticeable noise down the centre line and in the middle of the image. The back-projection algorithm is known to push the noise into the centreline [219]. The angular distributions obtained from the Abel-inversion are revealing, and display the hallmarks of diffraction. The irregular intense peak can be seen in a number of the images, however, the phase and intensities of the other diffraction oscillations is lost. As before, it is useful to compare the angular distributions to theory.

The Abel-inverted images are read in similar way to the raw experimental images. In this case however, the Gaussian weighting of the intensity was not used, and the intensity as a function of angle over the region of highest image intensity was used instead. The Abel-inverted angular distributions are shown in Fig. 7.5.

It can be concluded from these experimental images and extracted angular distributions that the experimental resolution of the hexapole apparatus is insufficient to

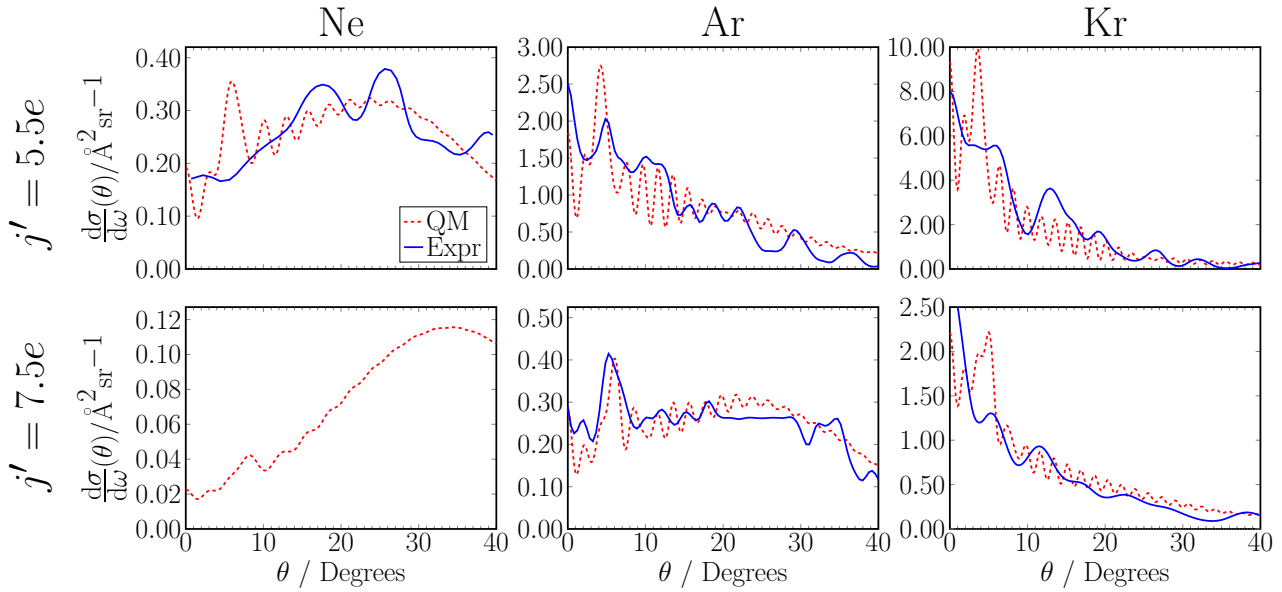


Figure 7.5: The angular distributions obtained from the Abel-inverted ion images (blue) compared to CC QM calculations (red dotted). The Ar images in particular show strong evidence of a peak at the predicted angle of the irregular peak in the diffraction oscillations. Note the x -axis scale is from 0° to 40° .

observe the oscillations with confidence. The Abel-inverted images show hints of the diffraction oscillations, but the number and precise position of the peaks is incorrect, apart from perhaps the irregularly large peak in the midst of the diffraction oscillations which has a slightly larger angular range. Since the collision energy spread in the beams is not the only source of blurring in the experiment, and the experimental resolution can not be sufficiently finely tuned without either modification of the beam sources or detection scheme, another approach is required in order to investigate the irregular peak.

7.1.3 Comparison to Similar Experiments

As has been shown, the lack of collision energy control, coupled with other blurring effects that may not simply be overcome leads to blurring in the hexapole apparatus that causes the oscillations in the DCS in the forward scattered region to remain unobserved in the images obtained from the hexapole apparatus. In order to overcome the limitations from the molecular beams and other sources of blurring, new experimental methods can be applied. Advancements in electrical switching and computer controlled timing systems have allowed the blurring associated with the molecular beams to be

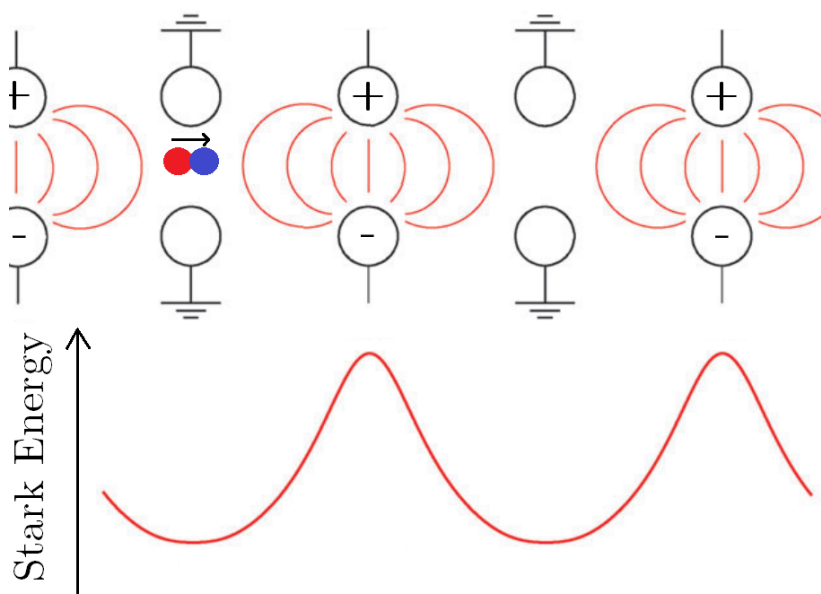


Figure 7.6: A schematic of part of the electrode setup of a stage in a Stark-decelerator. The Stark energy of the NO(X) is shown as a function of position. In order to affect deceleration, the electrodes must be switched before the NO(X) reached the saddle point.

minimised. This has been achieved in the Group of Bas Van der Meerakker by employing a Stark decelerator [204–206]. The Stark decelerator is a large collection of electrodes which utilise the Stark effect to impede the progression of NO(X) through the experiment [204]. A typical setup of the electrodes is shown in Fig. 7.6. The electrodes are switched on as the NO(X) nears them, and the opposing field, by means of the Stark effect causes the NO(X) to slow. As the NO(X) becomes almost level with the electrode, the electrode is switched off so the NO(X) is not accelerated as it passes over the saddle point of the electrode potential. At this time, the next electrode in the array is switched to further slow the NO(X). This continues for some 300 stages and the exact switching time of the electrodes determines the final velocity of the NO(X). By means of this scheme, the velocity of the packet of NO(X) can be precisely controlled and used to tune the collision energy with very high precision (up to 0.3 cm^{-1} [205]).

Further advances in molecular beam technology have allowed the creation of beam sources with high number density and short opening times [203]. These technologies have recently been deployed in an exquisite set of experiments that have allowed the diffraction oscillations in the forward scattered region to be imaged [204,206]. As the apparatus allows fine control of the velocity of the NO(X) beam, it has also been used

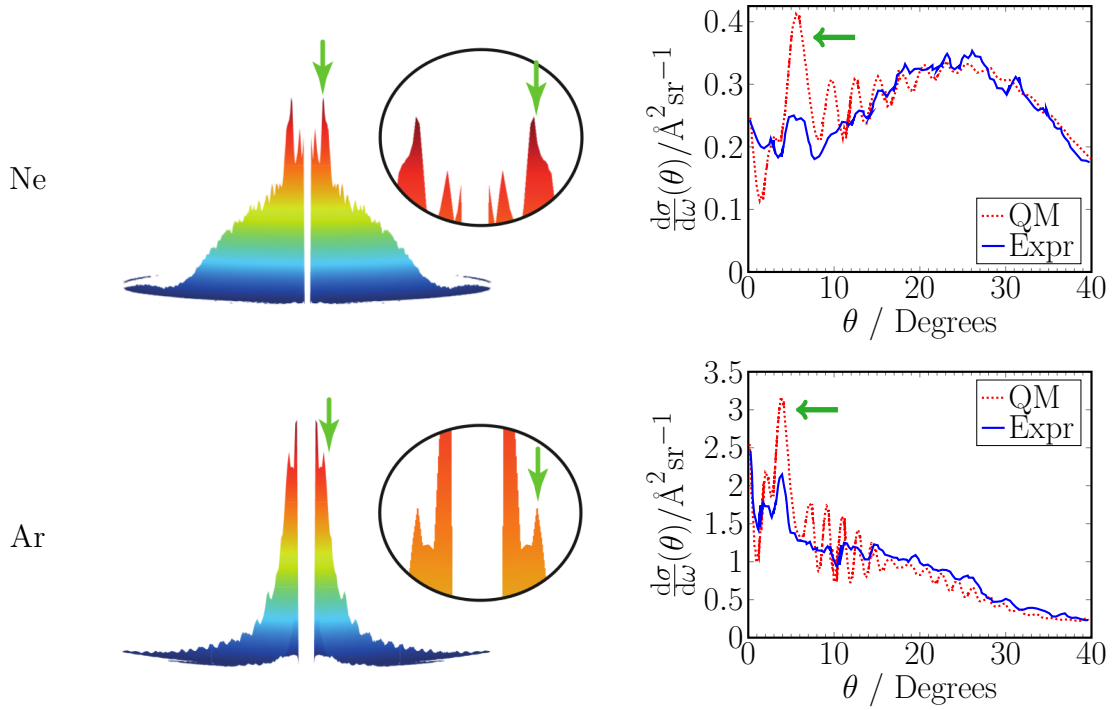


Figure 7.7: Left: the experimental images obtained from inelastic scattering with the NO(X) velocity controlled by a Stark decelerator, adapted from [207]. Right: Angular scattering distributions (blue solid) obtained from the experimental images and compared to CC QM (red solid) calculations. Collisions took place at a collision energy of 715 cm^{-1} for Ne and 725 cm^{-1} for Ar and pertain to ϵ -changing collisions on the spin-orbit conserving manifold to $j' = 5.5$.

in a recent set of experiments that probe resonances as scattering channels open at cold to ultracold collision energies, with a collision energy resolution of 0.3 cm^{-1} [205]. This apparatus, located in the group of Bas Van de Meerakker in Nijmegen, can use an unusual counter-propagating molecular beam geometry [221] which, although increasing the collision energy significantly, can overcome the error associated with an instrument function, as the image is symmetric about the relative velocity vector [206,221]. In such a geometry, the forward scattered direction becomes the region of highest resolution, as opposed to the typical 90° geometry in which the resolution is most sharply defined in the sideways scattered region [204].

During a visit to Nijmegen, a new detection apparatus was installed into the Nijmegen Stark decelerator consisting of a new detector and a gating scheme to enable use of a field-free time-of-flight tube. These advancements in control and precision of the beams pioneered by the Nijmegen group, as well as the improved detection setup, allows the oscillations to be directly visible in the forward scattered direction

by means of velocity mapped ion imaging, as shown in Fig. 7.7. The diffraction peaks, in the forward scattered direction are clearly visible and well defined with respect to the background. By an analysis method superficially similar to the one outlined above and explained in detail by Onvlee [206], the extracted angular distributions display very good agreement to CC QM calculations in the forward scattered direction. The Nijmegen experiment both reproduces the phase and approximate magnitude of the diffraction oscillations in the forward scattered direction. The most intense of these diffraction peaks, highlighted in Fig. 7.7 by a green arrow, will be further investigated due to its particular prominence.

7.2 Understanding the Fraunhofer Peaks

As demonstrated by the Nijmegen experimental data shown in Fig. 7.7, diffraction oscillations in the forward direction are dominated by a single peak of particular prominence. The intense peak in the forward scattered direction can be identified in almost all of the theoretical DCSs that one calculates for collisions of NO(X) with any of the rare gases for either parity conserving, or parity changing collisions on either spin-orbit manifold. In this section, various different theories will be compared to elucidate the mechanism responsible for the appearance of this peak. Of these theoretical models, it will be shown that classical calculations fall short of being able to reproduce the position and prominence of the peak, especially at high j' where the classically forbidden region of the inelastic scattering ends long after the peak appears experimentally and in CC QM calculations. In quantum models, such as the hard shell, CC QM and Fraunhofer theories, the oscillations are clearly apparent at, or near to, the scattering angle predicted by full CC QM calculations and the observed in high resolution experimental data of Van de Meerakker [207].

7.2.1 Classical Calculations

Classical calculations were performed on the V_{sum} potential energy surface for the Ne, Ar and Kr systems of interest. The DCSs are compared to the CC QM DCSs

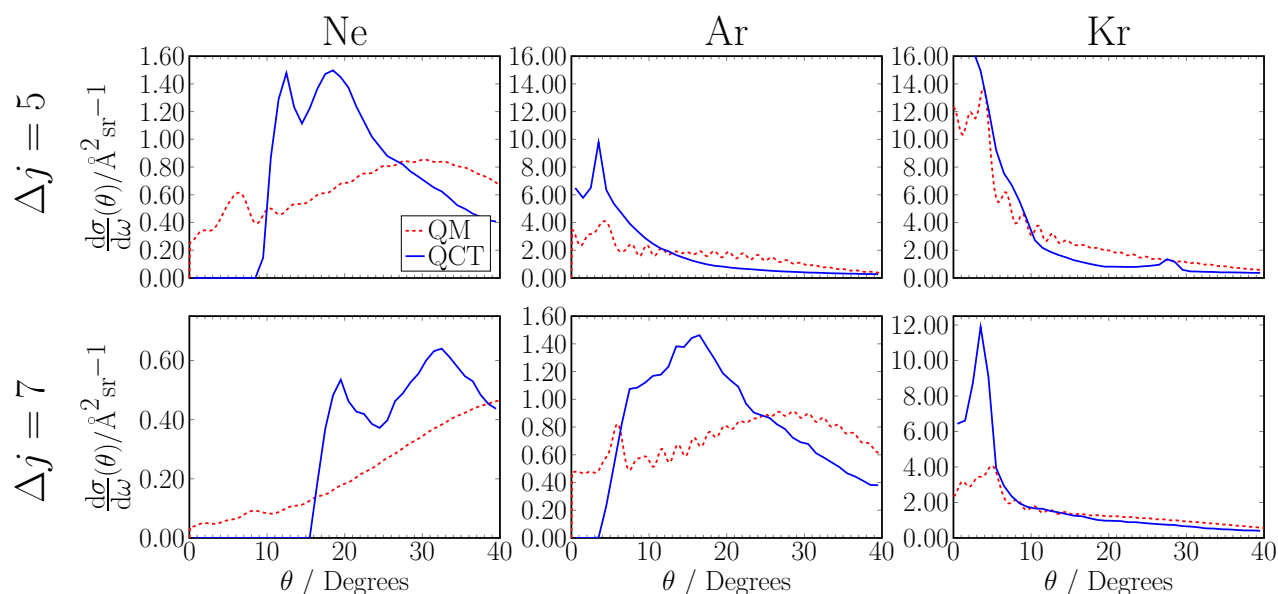


Figure 7.8: Comparison of the classical QCT (blue) and CC QM (red dotted) DCSs recorded for the Ne, Ar and Kr collision systems at energies of 662 cm^{-1} , 650 cm^{-1} and 612 cm^{-1} , respectively. The QM data has been summed and averaged as described in Chapter 2.

for a number of product states. It is already known that the classical calculations perform moderately well, (neglecting parity effects) in the forward scattered region, predicting ℓ -type rainbows and glory scattering with moderate accuracy. To confirm that the appearance of the irregular peak is not due to a classical effect, several different classical calculations can be performed to rule out centrifugal barriers or other classical effects.

The most likely classical explanation for the intense peak is a centrifugal barrier. Collisions that occur with finite orbital angular momentum have a centrifugal component to the rotational energy. The centrifugal barrier can lead to short lived bound states [222], and such features often lead to intense features at low scattering angles. The centrifugal barrier resonances should be apparent in the classical calculations of the opacity functions as sharp features at relatively low impact parameter. Calculations of classical DCSs should then also display an intense feature at low scattering angle corresponding to the centrifugal barrier resonance, if it is present.

From Fig. 7.8, it is clearly seen that the classical DCSs do not consistently contain indications of the irregular peak in the forward scattered region. There are however some notable features. In the DCSs for scattering with Ne, both the $\Delta j = 5$ and

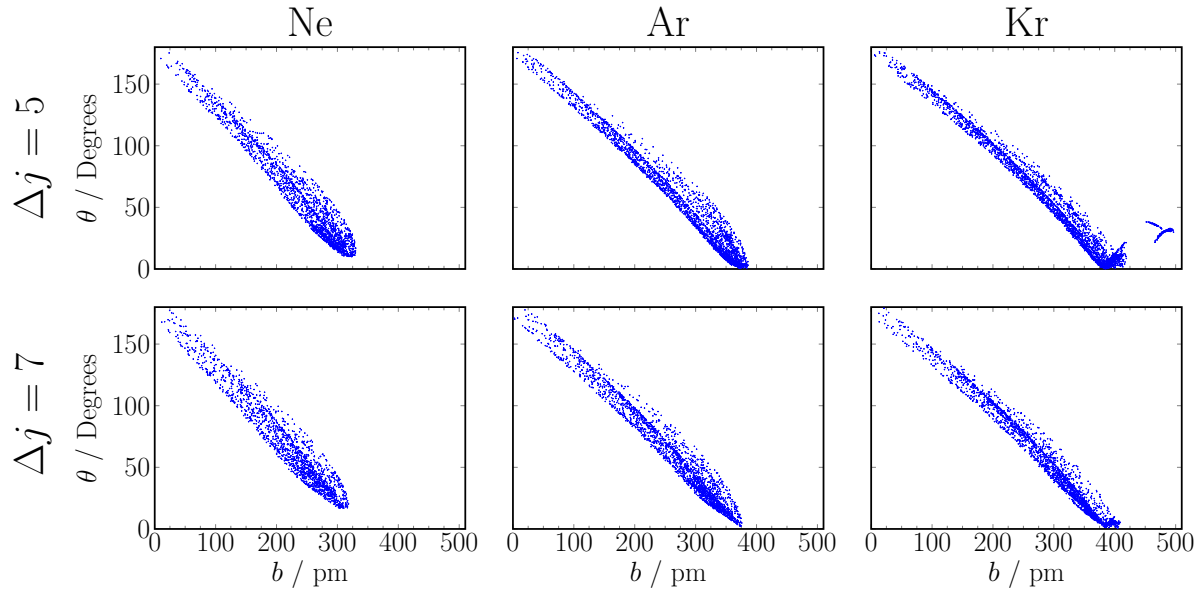


Figure 7.9: Classical deflection functions for the NO(X)–Ne, Ar and Kr collision systems. The upper row displays the deflection function for $\Delta j = 5$ and the lower row for $\Delta j = 7$. No features are present which may explain the oscillations at low scattering angle or the presence of an intense peak.

$\Delta j = 7$ states contain a double peaked feature at $\theta \approx 15^\circ$. This is caused by rotational rainbows, one associated with each end of the NO(X). In the Ar $\Delta j = 5$ state, there is indication of a peak at the same scattering angle as the irregular peak is expected to be observed; this is likely due to an ℓ -type rainbow which appears at low scattering angle due to the relatively low well depth of the Ar. There is also a hint of an ℓ -type rainbow in the Kr system in both $\Delta j = 5$ and $\Delta j = 7$, in the deflection function (Fig. 7.9) at low θ , where the deflection function levels out at approximately the glory impact parameter, $b_g = 400$ pm. The matching of the QCT and QM cross sections over the narrow angular range of the first 40° is poor. The QCT calculations predicts much more forward scattering than is observed in all cases. In addition, the classically forbidden region begins to extend to high impact parameters, preventing low scattering angle (high impact parameter) collisions from applying enough torque to cause high rotational excitation. Typically, in the higher rotationally excited states of the lighter rare gases, the classically forbidden region occurs over the range of scattering angles where the irregular peak is observed. The presence of the classically forbidden region all but rules out a classical origin for the irregular peak.

To further rule out classical effects for the origin of the irregular peak, deflection and

opacity functions from the classical calculations can also be obtained. The deflection functions shown in Fig. 7.9 also do not reveal any specific characteristics that may be associated with the irregular peak in the forward scattered direction. The deflection functions largely display similar characteristics to one another, and in the forward scattered direction there are no remarkable features in any of the deflection functions aside from in Ar $\Delta j = 5$ and Kr $\Delta j = 7$. In these two states, hints of rainbow scattering are displayed by the flattening of the deflection function around the glory impact parameter ($b > 400$ pm). The behaviour of the deflection functions is in general as expected: the larger the impact parameter, the lower the resulting scattering angle. In krypton the relative extent of the attractive part of the potential is more obvious, there is a prediction of an ℓ -type rainbow at a scattering angle of $\approx 28^\circ$, too large a scattering angle to be identified as the irregular feature.

In order to make a comparison to the CC QM calculations, the classical impact parameter can be expressed in terms of the total angular momentum by means of

$$J_{\text{tot}} \approx \ell_{\text{tot}} \approx \frac{b\mu v_{\text{rel}}}{\hbar} = kb, \quad (7.1)$$

where ℓ_{tot} is the classical orbital angular momentum, b is the classical impact parameter, μ is the reduced mass, v_{rel} is the relative velocity. This equation allows comparison between impact parameter and the quantum total angular momentum, J_{tot} and is reasonable at low Δj as the total angular momentum is much bigger than the value of Δj . Opacity functions quantify the scattering probability as a function of J_{tot} which can then be plotted for both classical and CC QM calculations. The classical and quantum opacity functions are shown in Fig. 7.10. There is broadly good agreement between the classical and quantum opacity functions, especially at higher values of J_{tot} . The classical opacity functions, however, do not display sharp features that may be interpreted as a narrow range of impact parameters contributing to a certain feature. Instead, broad features at relatively high impact parameters, mainly contributing to glory scattering are observed.

From the classical calculations, it is clear that the oscillation in the forward scattered

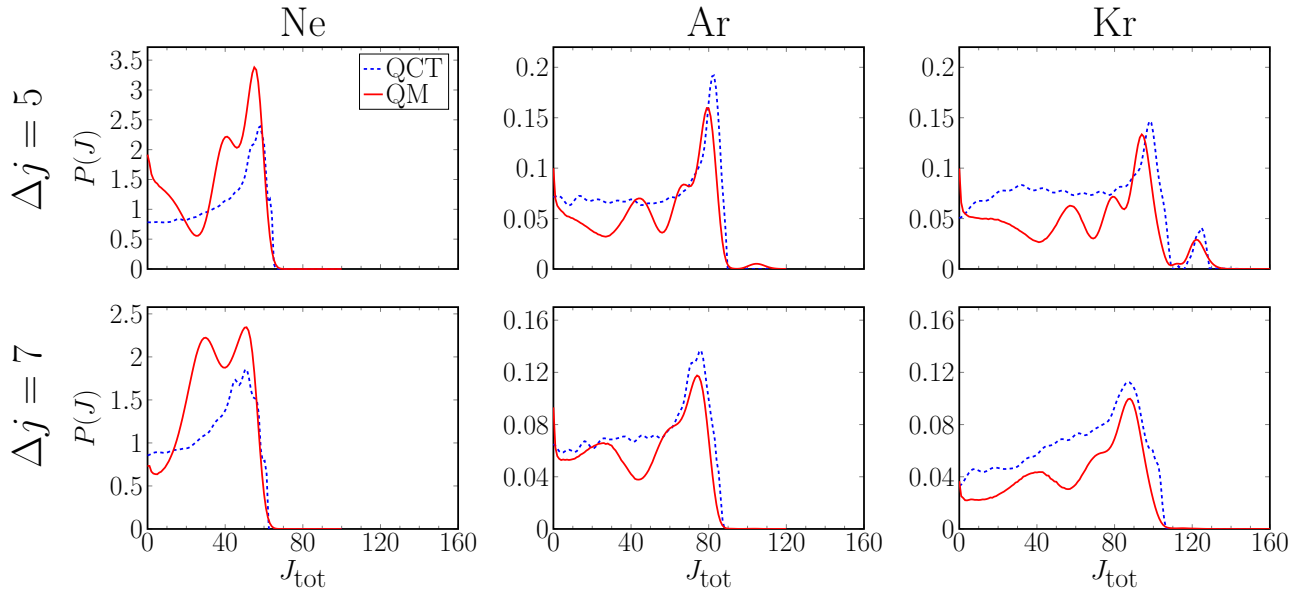


Figure 7.10: Comparison of the classical (blue dashed) and Λ -doublet averaged CC QM (red) opacity functions for the Ne, Ar and Kr collision systems. The opacity functions show no features in the averaged QM or QCT calculations that may lead to the observation of the irregular diffraction peak.

direction are not caused by a classical effect such as a centrifugal barrier or by the attractive part of the potential. Since the intense oscillation is present in the CC QM calculations, it can be concluded that the oscillation has no classical analogue and is likely due to a quantum effect.

7.3 Quantum Models

7.3.1 Partial Wave Analysis

It has been determined that the intense peak in the forward direction is not caused by classical effects. Partial wave analysis can be used to determine which partial waves make up the peak. In order to investigate this, the partial waves which make up the fully converged CC QM DCS were investigated using the HIBRIDON [97] suite of codes.

The opacity functions for each of the systems were calculated and are displayed in Fig. 7.11. The DCSs were calculated using the full range of partial waves (red lines, Fig. 7.11) and from $J_{\text{tot}} = 0$ to the beginning of the shaded region shown in the top panels of Fig. 7.11. The resulting DCSs shown in the middle panel of Fig. 7.11, display the irregular peak after scaling. The position and phase of the diffraction peaks is also in

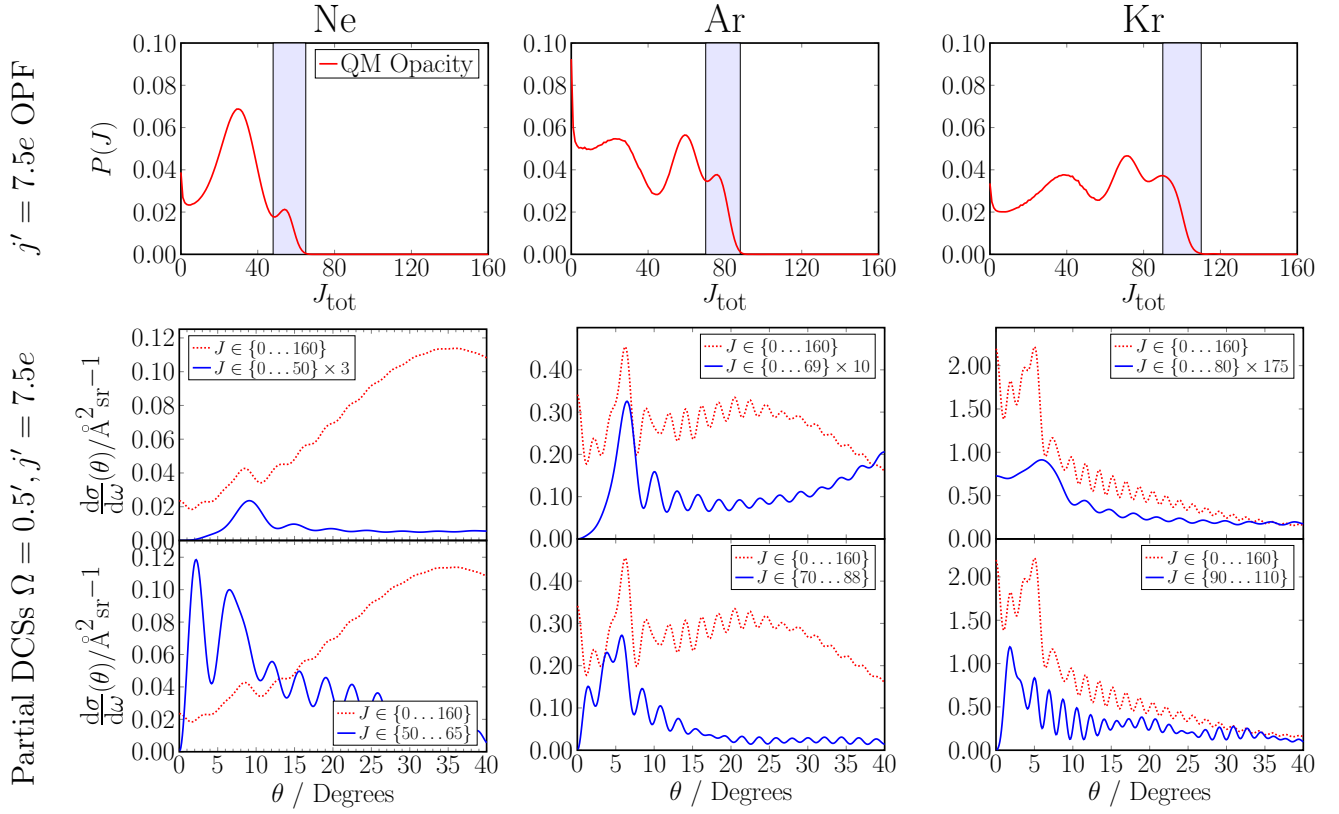


Figure 7.11: Top panels: the quantum opacity function as a function of total angular momentum, J_{tot} , the highlighted area indicates the region responsible for the oscillations and corresponds to the outermost part of the repulsive potential. Middle panels: the (scaled) partial DCSs (blue) made up of partial waves up to the beginning of the shaded area plotted with the full DCS (red). Bottom panels: the (unscaled) partial DCSs (blue) made up only of the partial waves in the shaded area plotted against the full DCS (red). These show the intense forward scattered feature and the fast oscillations are almost completely caused by partial waves in the shaded region.

close agreement with the full $J_{\text{tot}} \in \{0 \dots 160\}$ calculations. When the DCSs associated with the partial waves in the shaded region are calculated according to Eqn. (2.32) in Chapter 2, the intense oscillation is clearly visible and does not require scaling in order to be seen, indicating that the largest contribution comes from relatively high J_{tot} . In the case of neon, the peak is much stronger when calculated in this region than in the full potential.

Even though the shaded region shows the largest contribution to the irregular peaks intensity, all ranges of J_{tot} display evidence for the irregular peak and diffraction oscillations indicating that the partial waves interact with one another to form the observed peak. Since the peak is visible in DCSs resulting from any range of J_{tot} , we may draw two conclusions regarding the nature of the oscillations. The first is that even

the interference between a small subset of partial waves contributes to the irregular peak and diffraction oscillations, and that the attractive part of the potential seems to have little role, since features of the attractive part of the potential are usually seen at higher J_{tot} in the opacity functions (especially at lower Δj). Additionally (in the case of neon), the relative magnitude of the forward scattered peaks when summed between the $J_{\text{tot}} \in \{50 - 65\}$ is greater than the total DCS. This is due to coherences between partial waves leading to a reduction in the total DCS in certain angular ranges when the sum over all J_{tot} is performed in Eqn. (2.32).

The J_{tot} range in which the oscillations appear most strongly in terms of the scattering flux per steradian, corresponds to the highest values of J_{tot} , and hence for a given collision energy and rotational state, the range at which the oscillation appears shifts to higher J_{tot} for the larger rare gas systems, as seen in the top panel of Fig. 7.11. The partial wave analysis reveals that the peak is present at all J_{tot} values and that the largest contribution appears to come from large values of J_{tot} , before the $P(J_{\text{tot}})$ drops to negligibly small values.

7.3.2 Comparison of CC QM and QMHS Models

It has been shown in Fig. 7.7 that the CC QM calculations on the full potential reproduce well the experimentally observed position of the diffraction oscillations. The partial wave analysis has shown that all values of J_{tot} contribute to the observed irregular peak and diffraction oscillations. To confirm that the attractive part of the potential can be neglected and the irregular peak still recovered, quantum mechanical hard shell (QMHS) [103] calculations were performed and compared with the full CC QM calculations. Calculations can also be performed on the truncated potential where the attractive part is removed in the CC QM calculations. It was found, however, that the truncation function distorted the repulsive wall slightly, causing the contour expansion coefficients to be too different from the full potential to be able to draw any firm conclusions.

The results of the calculations are shown in Fig. 7.12. The agreement between the QMHS and CC QM calculations are compared in the forward scattered region, and

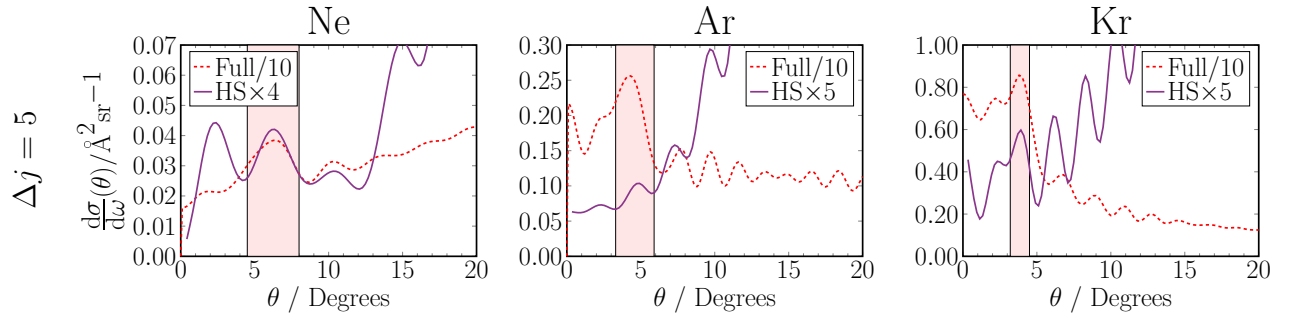


Figure 7.12: A comparison of the quantum models for three collision systems. The Λ -doublet averaged CC QM on the full potential is given by the red dotted line, the QMHS of Hornung is the purple line. Both of the models display the characteristic oscillations associated with diffraction in the forward scattered region. The highlighted areas in red contain the irregular peak.

display moderate agreement, especially in the region of the irregular peak. The effect of the attractive part is shown by the red dotted lines indicating scattering on the full potential. As can be seen in the first few degrees of scattering angle, the irregular peak is clearly present in both of the calculations, confirming the feature appears in a repulsive quantum model which does not include an attractive region. This agrees with the results of the partial wave analysis undertaken above, that showed the feature forming from interactions at all values of J_{tot} . Since repulsive interactions on the contour which lead to low scattering angle collisions are the cause of the irregular peak in the QMHS calculations, and the peak is not observed in classical calculations, a quantum effect is responsible for the prominent peak.

The irregular peak is affected by parity, but it is present regardless of the parity of the initial and final states. The CC QM calculations performed in Fig. 7.12 have been averaged over initial and summed over final parity states, and the irregular feature can still be seen. Additionally, the QMHS model used in Fig. 7.12 is closed shell and therefore the parity depends only on j' , the oscillations can still be seen at a very similar phase to those in the full CC QM calculations, even though the magnitude is diminished.

It can be concluded then that the oscillation is not caused by a parity effect. However, from these results it can also be concluded that the origin of the irregular peak is quantum mechanical. Since the oscillations are not caused by parity, other quantum effects must be responsible. It then remains to show that the oscillation is

formed by molecular diffraction, a purely quantum mechanical effect [208].

Several different models of diffraction have been created [204, 209, 223]. The next section will explore the analytical Fraunhofer model. Investigations of the irregular peak lead to deep insights into the dynamics and shape of the molecular potential when posed in terms of the Fraunhofer model, they also highlight the breakdown of the classical kinematic apse model in the low angle region.

7.4 Origin of the Fraunhofer Peak

The partial wave analysis coupled with classical calculations clearly points to a quantum mechanism being responsible for the irregular peak in the forward scattered direction. The mechanism that leads to the fast forward scattered peaks is, like the other narrow oscillations in the forward scattered direction, due to molecular diffraction. The matter waves of the incoming rare gas atom scatter off the hard shell of the target and lead to narrow constructive and destructive interference patterns from waves sampling differing molecular geometries. The interference pattern that results are the diffraction oscillations and were shown by Onvlee to be caused by the Huygen's principle, that all points on a wave front are sources of secondary waves which allow the interacting matter waves to bend around one another into the classical shadow of the object [207, 224], as shown in Fig. 7.1.

The Fraunhofer model was adapted for inelastic scattering from models developed by Drozdov [225] and Blair [226] by Faubel in 1984 [209] in order to describe rotational energy transfer in the very forward scattered direction during an atomic collision. Lemeshko and Friedrich later extended the model [208] to allow open-shell scattering amplitudes to be computed on either spin-orbit manifold. The analytical Fraunhofer model allows the computation of the scattering amplitudes, and then by means of standard scattering theory described in Chapter 2, the DCSs and PDDCSs can be obtained.

In a field free region, the Fraunhofer scattering amplitudes for a $^2\Pi$ molecule in a

collision with a structureless atom are given by [223]

$$f_{f \leftarrow i}(\theta) = \frac{ikR_0}{4\pi} \sqrt{\frac{2}{2j'+1}} J_{\Delta m}(kR_0\theta) \sum_{\kappa \neq 0} \Xi_{\kappa 0} F_{\kappa \Delta m} \langle jm, \kappa \Delta m | j'm' \rangle \langle j|\Omega|, \kappa 0 | j'|\Omega' \rangle \times \left\{ \begin{array}{l} (-1)^\kappa - (-1)^{\Delta j} \\ (-1)^\kappa + (-1)^{\Delta j} \end{array} \right\}, \quad (7.2)$$

where the values m and m' are the projections of the angular momenta, $\mathbf{j}$ and $\mathbf{j}'$ onto the wavevector, $\mathbf{k}$, κ is the potential expansion coefficient defined in Eqn. (2.12). The function $F_{\kappa \Delta m}$ takes the form

$$F_{\kappa \Delta m} = \begin{cases} 2\pi [(-1)^\kappa (-1)^{\Delta m}] \sqrt{\frac{2\kappa+1}{4\pi}} \frac{\sqrt{(\kappa+1)! (\kappa-\Delta m)!}}{(\kappa+\Delta m)!! (\kappa-\Delta m)!!} & \kappa + \Delta m \text{ even \& } \kappa \geq \Delta m \\ 0 & \text{else,} \end{cases} \quad (7.3)$$

and $J_{\Delta m}(kR_0\theta)$ is a Bessel function of the first kind and $!!$ is the double factorial function. The parenthesis in Eqn. (7.2) represents the two possible final parities, starting from the f Λ -doublet level, the top bracket represents ϵ -changing collisions and the bottom ϵ -conserving collisions. The coefficients κ are related to the shape of the object from which the incoming wave scatters. The contour of the object is defined by the potential energy surface and is expanded as a series of spherical harmonics with expansion coefficients $\Xi_{\kappa 0}$ by

$$R_{E_{\text{coll}}}(\theta, \phi) = \sum_{\kappa=0}^{\kappa_{\text{max}}} \Xi_{\kappa 0} Y_{\kappa 0}(\theta, \phi), \quad (7.4)$$

with $\kappa = 0$ corresponding to a sharp edged disk of radius $R_0 = \Xi_{00}/\sqrt{4\pi}$. Contributions with $\kappa > 0$ describe the deviations from this spherical shape. In the case of scattering from an initial $j = 0.5$ state, as considered in this thesis, it can be shown *via* the Clebsch-Gordan triangle relations [57] that

$$|j - \kappa| \leq j' \leq j + \kappa. \quad (7.5)$$

Upon combination of Eqn. (7.5) with the rules governing $F_{\kappa \Delta m}$ from Eqn. (7.3), it is

found that each rotational state-to-state transition is exclusively governed by a single value of κ . The rule is that of any direct scattering model [91] and is given by [207,224]

$$\kappa = j' - \frac{1}{2}\epsilon\epsilon'. \quad (7.6)$$

The model naturally leads to two types of collision, those with even $\kappa = \Delta j$ and those with $\kappa = \Delta j + 1$. These two types of collision will be further explored in the subsequent sections.

In order to compare the Fraunhofer model to the CC QM model, two scaling factors must be applied to the Fraunhofer model. The diffraction peaks in the Fraunhofer DCSs are shifted with respect to the CC QM predicted positions. In order to correct for this slight shift ($\ll 1^\circ$), the radius R_0 of the object in the Fraunhofer model is multiplied by a correction factor, this correction factor was found to take a value of 1.20. This scaling of the radius accounts for the finite range of the repulsive potential and the effects resulting from the attractive part [207], and it was found by investigating the phase shifts of the systems over a range of collision energies. The second factor multiplies the DCSs themselves. This factor can be very large and increases in magnitude with the mass of the rare gas atom. The scaling is performed so that the intensity of the most prominent peak matches that of the CC QM calculations. Each of the plots will have this scaling factor indicated in the legend.

The Fraunhofer model DCSs obtained from the square moduli of the scattering amplitudes (Eqn. (7.2)) are shown in Fig. 7.13 for the $j' = 5.5$ collision. Remarkably good agreement is demonstrated in the forward scattered direction for all of the product rotational states, agreement becomes less good at higher scattering angle due to the influence of the attractive part of the potential. After scaling, the DCSs and R_0 , the model shows excellent agreement with the CC QM calculations, and accounts for all of the diffraction peaks. The DCSs in Fig. 7.13 show both the parity conserving and parity changing collisions. The energy difference between the nearly degenerate Λ -doublet states is tiny compared to the collision energy, indicating the large difference in diffraction pattern is not an energetic effect.

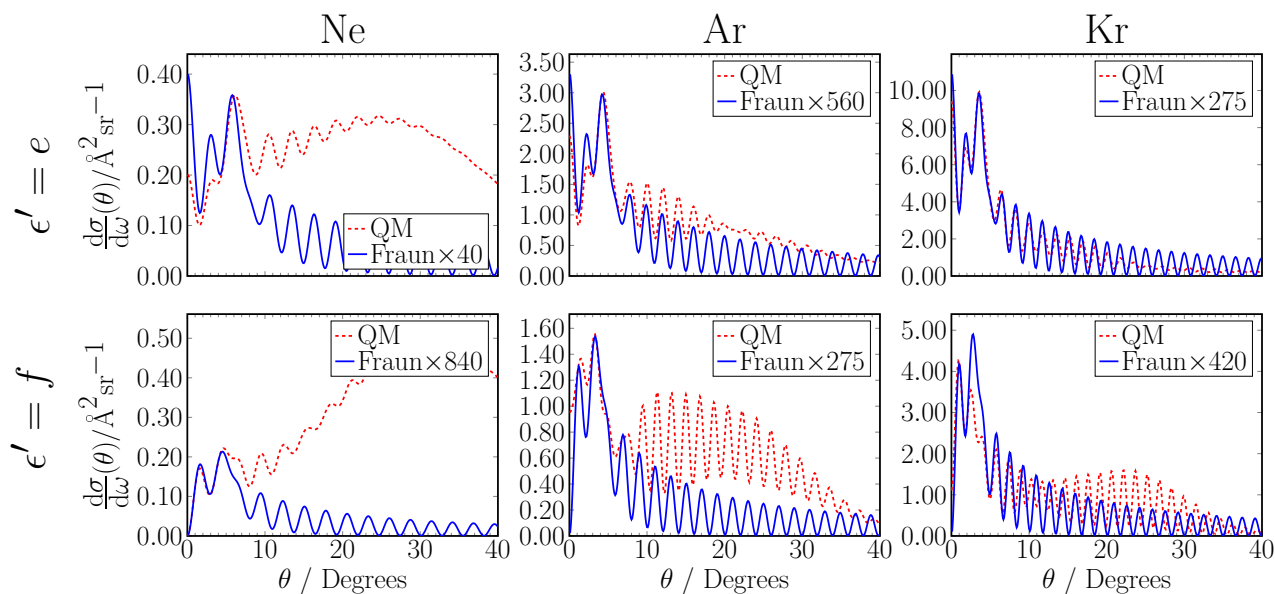


Figure 7.13: CC QM (red dotted) and Fraunhofer (blue solid) calculations performed for the $j' = 5.5$ collision on the spin-orbit conserving manifold at a collision energy of 610 cm^{-1} . In the forward direction, excellent agreement between the Fraunhofer and CC QM calculations is demonstrated.

In the forward scattered direction, the molecules are diffracted into the classical shadow of the object as the colliders display wave-particle duality. Onvlee related this² to Huygen's principle [224]; each point on a wavefront is comprised of wavelets which spread in the forward direction. The new wavefronts propagate into the classical shadow of the object, interfere with one another, and create interference fringes. By Babinet's principle [207, 224], the interference effect yields an identical diffraction pattern as scattering from a slit with an aperture of the shape of the object. Following the Huygen's principle, the diffraction peaks are most intense when the phase difference between different parts of the object is as large as possible, this occurs from scattering at the N and the O-end of the NO(X) [207, 224].

7.4.1 Angular Momentum

The Fraunhofer DCSs reveal that the simple analytical model accurately reproduces the irregular peak and the diffraction oscillations in the forward scattered direction. The physical origin of the large peak has been shown by Onvlee to be related to the Huygen's principle [207, 224]. The construction of the Fraunhofer model suggests that more

²This interpretation was discovered by the Nijmegen group, and is expanded upon in reference [207].

information about its appearance can be obtained from considering the magnetically resolved DCSs which are obtained from the Fraunhofer scattering amplitudes by means of

$$\frac{d\sigma_{j,m,\epsilon \rightarrow j',m',\epsilon'}}{d\omega}(\theta) = \frac{|f_{j,m \rightarrow j',m',\epsilon'}(\theta)|^2}{k^2(2j+1)} \quad (7.7)$$

without summation over the m and m' sub-states. The possible values for m are $m \in \{-j \dots +j\}$ and for m' are $m' \in \{-j' \dots +j'\}$, in integer steps. The total DCS is the sum of the different $m \rightarrow m'$ contributions. In the scattering frame, the quantum numbers m and m' are the projections of $\mathbf{j}$ and $\mathbf{j}'$ onto the initial wavevector, $\mathbf{k}$.

The kinematic apse model [64, 161] has been successful at producing an alignment correction to the experimental ion images of NO scattering with small rare gases such as He [24, 227], Ne [11], and it has also been applied to Ar [122]. In this thesis it was found to be deficient in the low angle region by comparison to Xe (see Chapter 4). Since the Fraunhofer model is based on an impulsive, hard shell model, it might be expected that the kinematic apse model can reproduce some of the dynamic features of the Fraunhofer model. The core assumption of the kinematic apse model is that the projection of $\mathbf{j}$ onto the kinematic apse, $\hat{\mathbf{a}}$ is conserved during the collision, leading to the propensity for $\Delta m_a = 0$. Additionally, $\mathbf{j}$ is assumed to be cylindrically symmetric about $\hat{\mathbf{a}}$. Even though collisions of NO with a rare gas do not resemble a hard ellipse collision as prescribed by the kinematic apse model, the model is surprisingly good at predicting the collision-induced rotational alignment of the NO molecule when compared to CC QM calculations (see Chapter 4). The reason for this is that the plane of rotation is primarily governed by the impulsive interactions and is only slightly perturbed by the attractive part of the potential (as shown in Chapter 4).

The Fraunhofer DCSs were calculated in the scattering frame as in Eqn. (7.7), but to investigate the degree of apse direction projection preserving propensity, in the low angle scattering region, the scattering amplitudes were rotated to the apse frame by means of [207]

$$f_{j,m_a,\epsilon \rightarrow j',m'_a,\epsilon'}^{\text{apse}}(\theta) = \sum_{m=-j}^j \sum_{m'=-j'}^{j'} f_{j,m,\epsilon \rightarrow j',m',\epsilon'}^{\text{scat}}(\theta) d_{m,m_a}^{(j)}(\beta) d_{m',m'_a}^{(j')}(\beta) \quad (7.8)$$

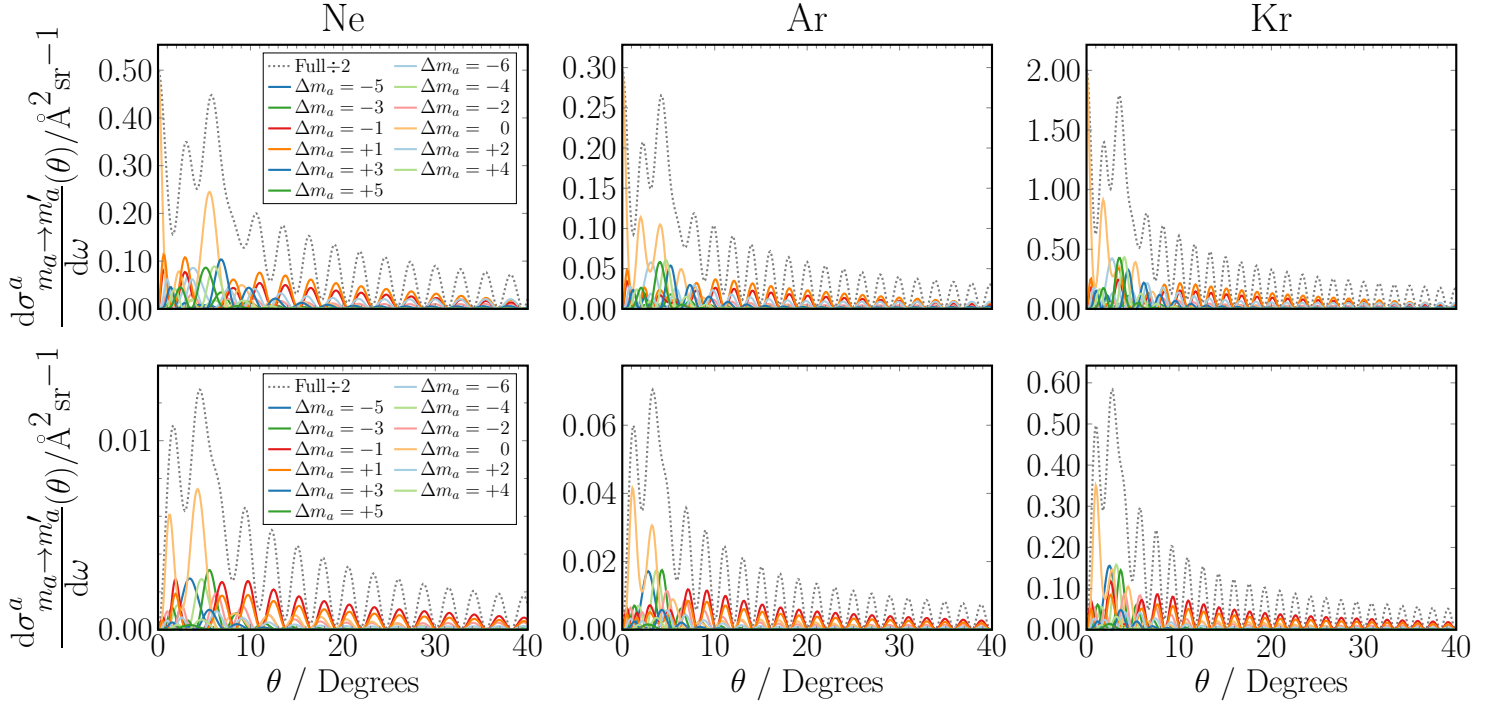


Figure 7.14: Magnetically resolved DCSs from the Fraunhofer model rotated to the kinematic apse frame. There is some degree of $\Delta m_a = 0$ propensity over the intense peak, however there are large contributions from many other magnetic sub-states.

where m and m' are the projections of $\mathbf{j}$ onto $\mathbf{k}$ and m_a and m'_a are the initial and final projections of $\mathbf{j}$ onto $\hat{\mathbf{a}}$. The function $d_{m',m_a}^{(j')}(\beta)$ is a reduced rotation matrix element [57]. After rotation, the magnetic DCSs in the kinematic apse frame are recovered by means of Eqn. (7.7).

As can be seen from the kinematic apse frame magnetically resolved DCSs (Fig. 7.14), the state with $\Delta m_a = 0$ contributes to approximately half of the observed total DCS in the region of the intense diffraction oscillation. It is also important outside of this range, contributing to each of the subsequent diffraction peaks. A mixture of different sub-states contributing to the intense peak is observed for each system. This suggests that the projection preserving propensity onto the apse direction is not valid in the forward scattered region where the large Fraunhofer peak is present, in agreement with the results presented in Chapter 4. As the kinematic apse model itself does not provide state-to-state DCSs, the effect can be further investigated by calculating the renormalised PDDCSs, which can be obtained from the kinematic apse model by means of Eqn. (4.2) in Chapter 4. The Fraunhofer model renormalised PDDCSs have been formulated by Lemeshko and Jambrina [210] and can be obtained from the Fraunhofer

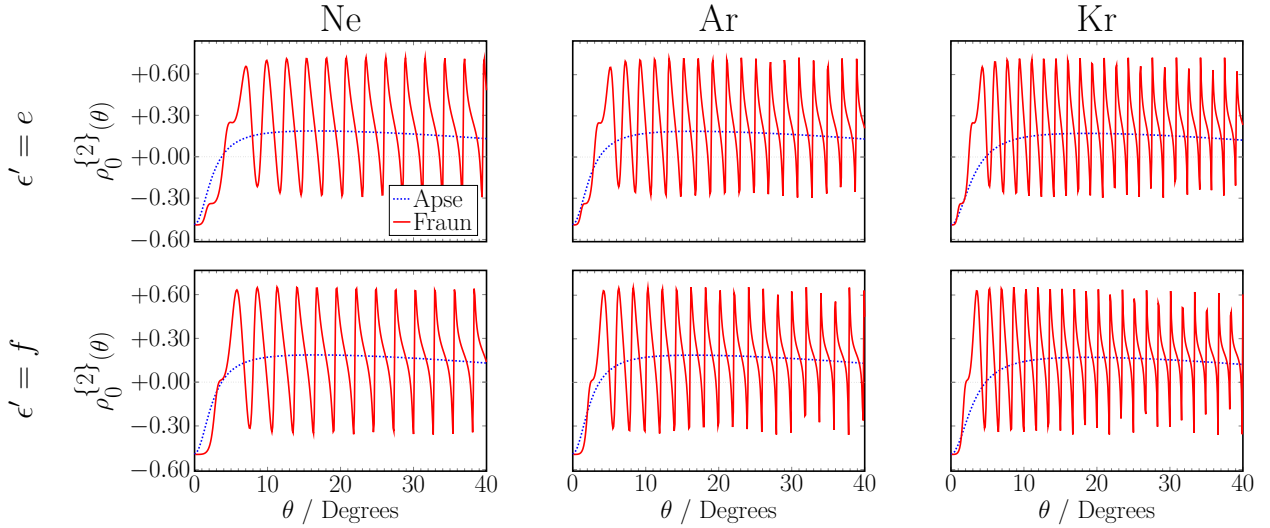


Figure 7.15: The kinematic apse (blue dotted) $\rho_0^{\{2\}}(\theta)$ renormalised PDDCSs compared to the Fraunhofer model (red) PDDCSs. The Fraunhofer model does not display strict m_a preserving propensity and only agrees with the kinematic apse model PDDCSs on average.

scattering amplitudes by

$$\rho_{q\pm}^{\{k\}}(\theta) = \sum_{m=-j}^j \sum_{m_1=-j'}^{j'} \sum_{m_2=-j'}^{j'} \frac{1}{\frac{d\sigma}{d\omega}(\theta)} f_{j,m,\epsilon \rightarrow j'm_1\epsilon'}(\theta) f_{j,m,\epsilon \rightarrow j'm_2\epsilon'}^*(\theta) \langle j'm_1, kq | j'm_2 \rangle, \quad (7.9)$$

with $\langle \dots | \dots \rangle$ a Clebsch-Gordan coefficient. The calculated renormalised PDDCSs are shown in Fig. 7.15. Inspection of Fig. 7.15 shows that the Fraunhofer $\rho_q^{\{k\}}(\theta)$ renormalised PDDCSs agree with the kinematic apse model $\rho_q^{\{k\}}(\theta)$ renormalised PDDCSs only on average. The lack of agreement between the kinematic apse and Fraunhofer model PDDCSs in the low angle region shows that in the Fraunhofer model, the propensity for the projection of $\mathbf{j}$ onto the apse direction to be conserved is not rigorous, however at scattering angles larger than $\theta = 10^\circ$ where the Fraunhofer model is no longer applicable, the apse model is again expected to strongly influence $\rho_0^{\{2\}}(\theta)$. The lack of apse preserving propensity is further demonstrated by Fig. 7.14 in the subsequent section for the Kr system, where the intense peak has effectively zero $\Delta m_a = 0$ component. This demonstrates that the intense diffraction peak generally does not follow the $\Delta m_a = 0$ propensity rule.

7.4.2 Scattering Frame m_j Resolved DCSs

The kinematic apse frame magnetically-resolved DCSs shows that the $\Delta m_a = 0$ propensity rule is not rigorously conserved in the Fraunhofer model and offers no compelling explanation for the irregular peak. Examination of the scattering frame magnetic DCSs can also be instructive, and the magnetically resolved DCSs, obtained from Eqn. (7.7), are shown in Fig. 7.16. This figure contains plots for the Ne, Ar and Kr systems, with both parity changing (bottom), and parity conserving (top) collisions shown for each possible value of $\Delta m = m' - m$. It can be seen in this figure that the largest diffraction peak is mainly caused by a single Δm contribution, with relatively high m' purity.

The figure also reveals a relationship which can be derived from the analytical Fraunhofer model; that the Δm value that will contribute most to the intense diffraction peak is related to the rotational state and the system parity by [207]

$$\Delta m = j'\epsilon\epsilon' - \frac{1}{2}. \quad (7.10)$$

For the parity conserving $j' = 5.5e$ collision, the dominant Δm contribution given by Eqn. (7.10) is the $\Delta m = -6$ contribution, which agrees with Fig. 7.16. In order to affect this state-to-state transition, the initial m sub-state is either ± 0.5 and transitions to a magnetic sub-state with $m' = \mp 5.5$. The parity conserving transition consists of only even Δm with the $\Delta m = -6$, $m = \pm 0.5 \rightarrow m' = \mp 5.5$ transitions dominating. Conversely, for the parity changing transition, the initial m sub-state can either be ± 0.5 , and transitions to a magnetic sub-state with $m' = \pm 5.5$ (with only the odd Δm transitions being non zero) and the $\Delta m = 5$, $m = \pm 0.5 \rightarrow m' = \pm 5.5$ transition dominates. Note that in the parity conserving case, the $\pm m \rightarrow \mp m'$ contributions are always identical, and in the parity changing case the $\pm m \rightarrow \pm m'$ contributions are always identical. In order to display the magnetically resolved DCSs succinctly, the full DCS in Fig. 7.16 has been scaled by half in order to facilitate comparison, as each Δm transition contains two identical magnetic sub-level transitions.

From these calculations, and the physical basis of the Fraunhofer model lying in wave-particle duality, it is likely that the occurrence of the large peak should be general

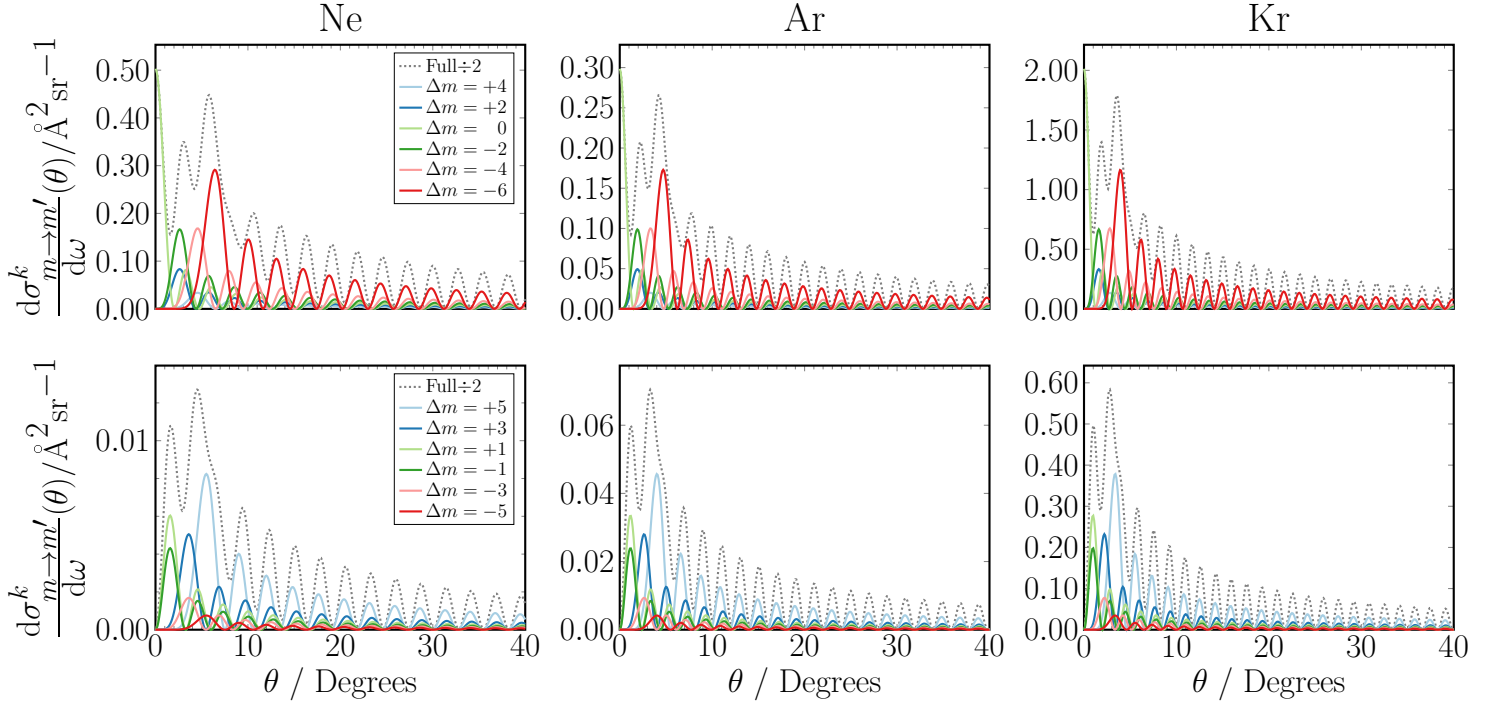


Figure 7.16: Magnetically resolved DCSs for the $j' = 5.5$ collision for a variety of systems. The top panels show state-to-state transitions resulting in the $\epsilon' = e$ state (parity conserving) and the bottom panel to the $\epsilon' = f$ parity changing state. The most intense diffraction peak is caused by a relatively pure $m \rightarrow m'$ collision in each of the systems for both parity-conserving and parity-changing collisions.

in inelastic scattering. It is found however that it is most prominent in intermediate values of j' [207,224], where the assumptions of the Fraunhofer model are most valid. For low rotational excitation, the peak is obscured by the attractive part of the potential leading to strong glory type scattering. For high rotational excitation, the direct scattering model breaks down due to transitions occurring *via* tiers of virtual states and the influence of the V_{diff} potential becomes more important as Hund's case (a) is no longer a good description of the coupling in NO(X). The manifestation of the irregular peak in the DCSs can be thought of as relying on the balance between repulsion and attraction on the PES. For the heavier rare gases with a larger attractive surface, such as the NO(X)–Kr potential, features originating from the attractive part of the potential (for instance ℓ -type rainbows) shift to higher scattering angle, allowing the peak to be clearly seen.

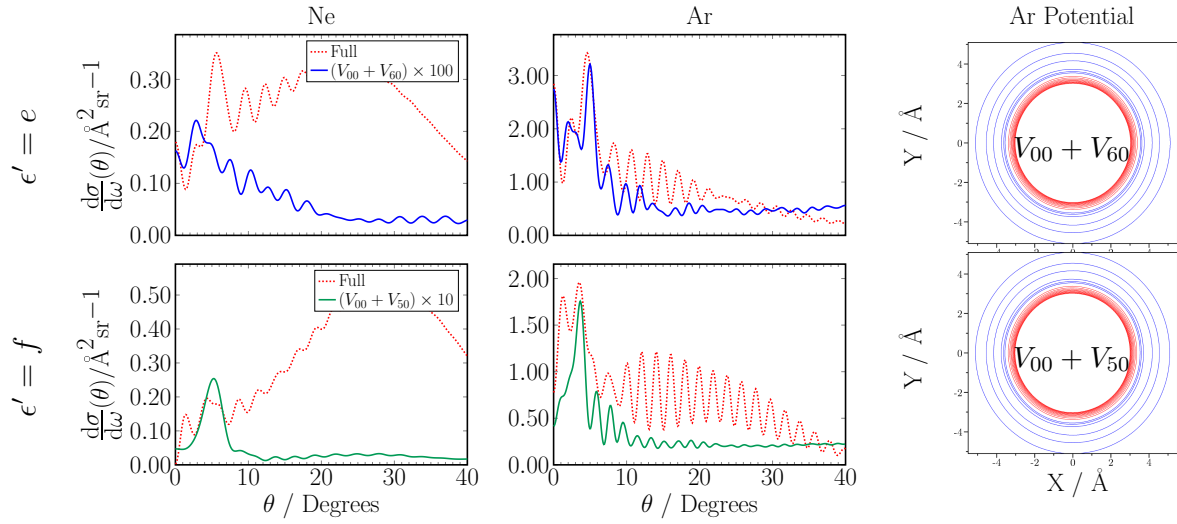


Figure 7.17: Left & middle: CC QM calculations performed with only the potential term predicted by the Fraunhofer model to affect the transition to a $j' = 5.5$ state used ($\kappa = 5$ green, $\kappa = 6$ blue). The full potential (red dotted) displays good agreement, demonstrating that the QM calculations are well approximated by the Fraunhofer model in the region of the diffraction oscillations. Right: The modified Ar potentials upon which the CC QM calculations are performed, red contours are spaced at 100 cm^{-1} and signify repulsion whereas blue contours are spaced at 10 cm^{-1} and signify attraction.

7.4.3 Potential Terms

It was established in Eqn. (7.6) that the Fraunhofer model always predicts scattering by one potential term only. It is therefore desirable to test how faithfully the CC QM calculations reproduce the Fraunhofer model when scattering by only one potential term is possible. The quantum mechanical potential expansion given in Eqn. (2.12) (Chapter 2) was modified by setting all the expansion coefficients, κ , to zero for a given j' transition with the exception of those satisfying Eqn. (7.6). The resulting potentials can then have scattering calculations performed upon them. The shape of the potential deviates only slightly from a sphere (as shown for the NO(X)–Ar system in Fig. 7.17). The zeroth order $\kappa = 0$ term is much larger than the $\kappa = 5$ or $\kappa = 6$ terms, and according to the Fraunhofer model, the $\kappa = 5$ and $\kappa = 6$ terms are responsible for the diffraction oscillations appearing in the parity changing and parity conserving $j' = 5.5$ state respectively – in accordance with Eqn. (7.6).

Upon calculation of the parity conserving and parity changing DCSs using the modified potentials, it is found that the diffraction peaks do appear in the CC QM calculations in a similar manner to those in the full potential when the correct coupling

term prescribed by Eqn. (7.6) is used. Figure 7.17 shows a comparison for the neon and argon collision systems. If the incorrect term is used, the DCS is typically negligibly small. There are obvious differences between the full CC QM calculations and those performed on the truncated potentials. These are caused by the modification itself, when the expansion given in Eqn. (7.4) is performed, the values of the $\Xi_{\kappa 0}$ coefficients change leading to a different potential contour. However, we may conclude that the diffraction peaks in the forward scattered region are generally dominated by direct scattering in which one potential term couples the initial to the final state.

7.5 Summary

The hexapole apparatus was modified to achieve the highest resolution possible without employing a full Newton sphere slicing technique or exerting further control over the molecular beams. Despite promising resolution enhancements, the apparatus could not conclusively resolve features in the forward scattered direction. Comparison to the Nijmegen group's Stark decelerator were then performed, in which the diffraction patterns in the forward scattered region were observed.

A particular intense peak can be seen in the theoretical and experimental DCSs that has unusual intensity compared to the other diffraction peaks. The origins of this peak were investigated with a number of theoretical techniques. These investigations showed the peak is not due to a classical phenomenon and is instead purely quantum mechanical in origin with no classical analogue. It results from interference effects resulting from the wave-particle nature of the colliding species. As was shown by Onvlee *et al.* [207], this is a manifestation of Huygen's principle, in which the matter waves scatter into the geometric shadow of the NO(X). The resulting angular distributions are well reproduced by the analytical Fraunhofer scattering model. The model itself has a simple formulation, and allows deep insight into the dynamics in the forward scattered direction. Investigation of the magnetically resolved DCSs showed the peak is formed by a single pair of $m \rightarrow m'$ transitions and that a simple equation governs which contribution will dominate the large peak.

The propensity for scattering from a single Δm is related to the shape of the potential, as the Fraunhofer model (being a direct scattering model) predicts scattering from only a single potential term. This was confirmed to also be true in the CC QM scattering calculations by undertaking modification of the potential energy surfaces. Furthermore, The peak was also shown to not be caused by propensity for conservation of the projection of $\mathbf{j}'$ onto $\mathbf{a}$, as the kinematic apse and Fraunhofer model renormalised PDDCSs only agree on average with one another. Lastly, the scattering frame DCSs were rotated to the kinematic apse frame where it was confirmed that the Δm_a contributions that dominate the scattering to the angle of the irregular peak were not always the ones with $\Delta m_a = 0$. However, the $\Delta m_a = 0$ contribution was non-zero and contributes more to the total DCS in the larger angle Fraunhofer diffraction oscillations.

The prominence of the large peak is caused by a relatively pure Δm collision. As was shown by Onvlee *et al.*, in accordance with Huygen's principle, the peak occurs at an angle where there is a maximum in constructive interference, which occurs when the matter waves scatter with maximum phase shift, corresponding to the N-end and O-end of the molecule [207,224]. It is therefore expected that the diffraction oscillations will be highly sensitive to the bond axis orientation, and such investigations should be the focus of future work.

Conclusion

8.1 Summary

Experimental and theoretical studies of NO(X) rare gas collisions have been undertaken. A series of two and three-vector correlations have been presented involving collisions with Ne, Ar, Kr and Xe. In the simplest case, differential cross sections pertaining to a $\mathbf{k}-\mathbf{k}'$ correlation were determined. The differential cross sections quantify the scattering cross section as a function of scattering angle. The Kr and Xe systems both display strong secondary maxima at high scattering angle in the low rotational final states which is characteristic of ℓ -type rainbow features. Parity dependent effects were also investigated by extending a semi-classical four path model and comparing to classical calculations.

By making use of polarised laser light, the rank one renormalised polarisation dependent differential cross sections (PDDCSs), $\rho_{1-}^{\{1\}}(\theta)$, which describe the molecular orientation as a function of scattering angle after a collision, and the rank two $\rho_{q+}^{\{2\}}(\theta)$ renormalised PDDCSs, which describe rotational alignment, could be determined. These showed that the attractive part of the potential strongly augments the collision-induced polarisation. In the case of Xe, it was shown that the attractive part of the

potential affects the forward scattered region, where low angle scattering is dominated by long-range interactions. This caused a reduction in the observed alignment. Previously the alignment has been shown to be caused mainly by impulsive interactions. The kinematic apse model, which assumes that the projection of the angular momentum, $\mathbf{j}$, onto the kinematic apse, $\hat{\mathbf{a}}$, is conserved, describes the experimentally determined and quantum mechanical alignment very well; apart from in the forward scattered direction in the heavier rare gases.

Investigations into the NO(X)–Kr collision system were undertaken by measurement of the $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs. The $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs are strongly affected by the attractive part of the potential. In the regions where the attractive part is most dominant, such as where an ℓ -type rainbow is present, the orientation is shown to be positive. In the backward scattered direction, the orientation is negative. By integration over scattering angle, the $a_{1-}^{\{1\}}$ polarisation moments were obtained which demonstrated parity dependent oscillations and a general decrease as a function of j' . This decrease was explained in terms of limiting classical mechanisms based on long range interactions at low Δj and impulsive interactions at high Δj . The renormalised PDDCSs themselves were investigated further, revealing that orientation is strongly affected by the parity, and the de Broglie wavelength of the system.

The experiment was then reconfigured by placing a set of four guiding rods in the interaction region, the guiding rods essentially adiabatically orient the NO(X) in the electric field allowing classical N or O-end collisions to take place. By integrating the N-end and O-end images over scattering angle and taking a normalised difference of the result, the dependence of the scattering cross sections on the initial orientation could be obtained. This quantity, representing the $\mathbf{r-k}$ correlation is known as the steric asymmetry and displays highly non-linear behaviour as a function of j' . The interference effects displayed are related to semi-classical interference between scattering off the N-end and O-end of the molecule. However, at low j' , the attractive part of the potential plays an important role in causing a consistent N-end preference. At middle j' the semi-classical interference mechanism leads to large oscillations in the sign of the steric asymmetry. Finally, at high j' a classical mechanism dominates in which

sufficient torque can only be applied by trajectories hitting the N-end of the molecule, as it is further from the NO(X) centre of mass. The steric preference was seen to be relatively insensitive to the high-order terms in the potential, and could be qualitatively reproduced by simply using the first and second order expansion terms.

Finally, the experiment was re-configured to improve the angular resolution of the detection setup. The oscillations predicted in the differential cross sections (DCSs) at low scattering angle were measured, unfortunately the experimental resolution remains insufficient to unambiguously image the oscillations without further modifications to either the molecular beam sources or detection setup. A new apparatus in Nijmegen has been built with sufficient control of the molecular beams to allow imaging in these challenging conditions. A collaboration between the Nijmegen and Oxford groups set about trying to understand the prominence of a particularly intense diffraction peak. Classical methods were used to rule out centrifugal barrier resonances and other classical effects. An analytical Fraunhofer diffraction model was then applied which was shown to almost quantitatively match the close-coupled quantum (CC QM) calculations. It predicts several surprising features, the first was that the propensity for preserving the projection of $\mathbf{j}$ onto the kinematic apse is not valid in the forward scattered direction, and the second was that a particular $m \rightarrow m'$ contribution to the total DCS would dominate a collision, based on the final parity and rotational state of the collision system. The Fraunhofer model provides information on the molecular shape of NO(X) and was shown by Onvlee *et al.* [207, 224] to be sensitive to the relative orientations of the NO(X).

These experimental and theoretical investigations have highlighted the importance of the attractive region of the PES and its influence on the observable quantities both at low scattering angle and at high scattering angle. The role of the repulsive part has also been shown to be important in the $\mathbf{r-k}$ correlation and for predicting the behaviour of the $\rho_{q+}^{\{2\}}(\theta)$ renormalised PDDCSs.

Although all the observations could be reproduced by the CC QM calculations, additional mechanistic insight has been provided by a multitude of theoretical calculations, ranging from classical QCT to quantum hard shell (QMHS) calculations, as

well as modified *ab initio* potential energy surfaces. These calculations highlight the richness of the dynamics of the ‘simple’ NO(X) rare gas systems and the powerful analytical framework provided by the use of vector correlations.

8.2 Future Work

Recent advances in theoretical techniques and the versatility of the hexapole apparatus open up a series of possible new experiments which can, or have already been designed and implemented. These involve scattering with exotic species, fast switching electric fields and state-of-the-art sensor technology.

8.2.1 High-Order Vector Correlations

The orientation and steric geometries can be combined in order to investigate high-order vector correlations; those pertaining to the $\mathbf{r}-\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ correlations. In this geometry, the laser runs perpendicular to the plane of the beams, and probes the rank one orientation renormalised PDDCS ($\rho_{1-}^{\{1\}}(\theta)$) as a function of scattering angle. This geometry (shown in Fig. 8.1) is particularly challenging to implement as the velocity mapping along the time-of-flight axis is known to be poor with the orientation rods in place. To overcome this, a cylindrical lens will be placed in front of the 308 nm ionisation laser in order to ensure that only molecules scattered in the plane of the beams are ionised, and hence imaged. This will create an oblate disk of ions rather than an approximate sphere as in previous experiments, fewer ions will form along the ToF axis, reducing blurring.

The forward scattered region is of particular interest in the orientation resolved DCSs. The oscillations in the DCS in the region of the diffraction oscillations and irregular peak are out of phase for the N-end and O-end. In order to assess this, the Fraunhofer scattering amplitude can be modified to allow the probing of 4-vector correlations [223]. In the analysis of the steric asymmetry presented in Chapter 6, the interference resulting in the characteristic change in sign as a function of j' was shown to be activated by the $\kappa = 1$ and $\kappa = 2$ terms in the potential. However, the field-free Fraunhofer model always couples initial to final states by only one term (see

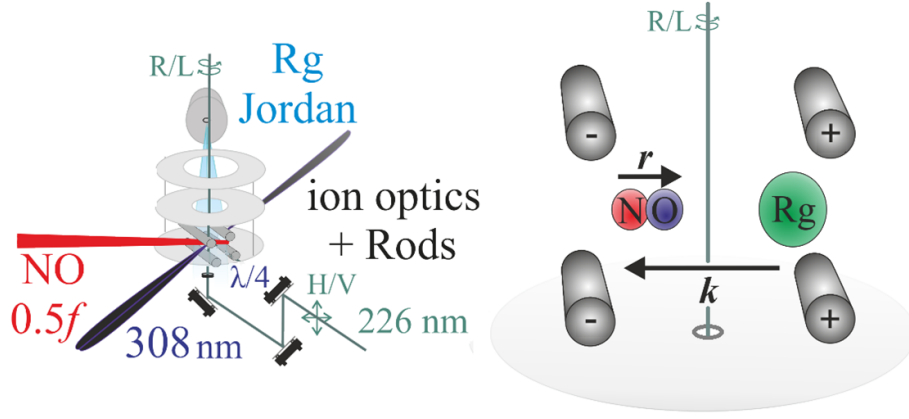


Figure 8.1: The modifications to the experimental apparatus necessary to measure the rank one multipole of the $\mathbf{r}\text{--}\mathbf{k}\text{--}\mathbf{k}'\text{--}\mathbf{j}'$ 4-vector correlation. Left: the laser and beam setups. Right: The behaviour of NO(X) in the interaction region.

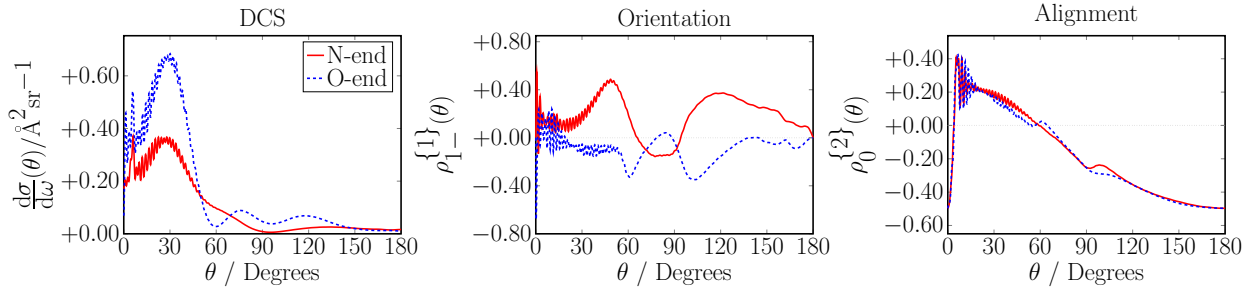


Figure 8.2: The steric resolved DCSs and PDDCSs calculated for scattering of NO(X) with Ar to a $j' = 7.5e$ state. The red solid lines are calculations for the N-end and blue dashed for the O-end. Left: the CC QM DCS. Middle: the $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCS. Right: the $\rho_0^{\{2\}}(\theta)$ renormalised PDDCS.

Chapter 7). The Fraunhofer scattering amplitude in the field is given by [223]

$$f_{f \leftarrow i}^{E \neq 0}(\theta) = \frac{ikR_0}{4\pi} \sqrt{\frac{2}{2j'+1}} J_{\Delta m}(kR_0\theta) \sum_{\kappa \neq 0} \Xi_{\kappa 0} F_{\kappa \Delta m} \langle jm, \kappa \Delta m | j'm' \rangle \langle j|\Omega|, \kappa 0 | j'|\Omega' \rangle \quad (8.1)$$

$$\times \left\{ \beta [(-1)^\kappa + (-1)^{\Delta j}] + \alpha [(-1)^\kappa - (-1)^{\Delta j}] \right\} \\ \times \left\{ \alpha [(-1)^\kappa + (-1)^{\Delta j}] + \beta [(-1)^\kappa - (-1)^{\Delta j}] \right\},$$

where the mixing coefficients α and β are as defined in Eqn. (6.4) of Chapter 6, the top bracket represents scattering to an ϵ -conserving, and the bottom bracket an ϵ -changing state. In the electric field, equation (7.10) which governs the largest Δm contribution to the irregular peak are no longer valid as the initial parity is ill defined. Analysis of the Fraunhofer model compared to the full CC QM calculations should provide insight into the differential steric effect in the forward scattered region.

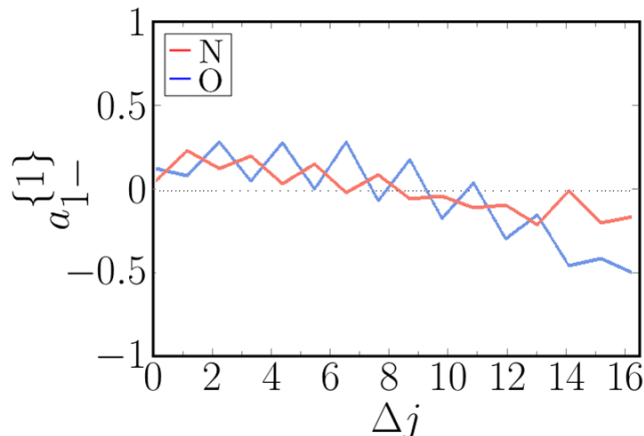


Figure 8.3: Integration of the oriented $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs as a function of scattering angle. The oriented $a_{1-}^{\{1\}}$ moments display the same overall trend as a function of Δj as presented in Chapter 5, however the initial parity is mixed, hinting at a non-parity dependent mechanism for the oscillations as a function of Δj .

The orientation rods allow the steric preference to be determined as a function of scattering angle. As is shown in the left hand panel of Fig. 8.2, there is a large difference between the DCSs for N-end and O-end collisions, as has been observed experimentally [25]. As well as these large differences in the DCS, the $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCS are predicted by the CC QM calculations shown in the middle panel of Fig. 8.2 to be extremely sensitive to the orientation of the molecule. Upon integration, as shown in Fig. 8.2, the orientation dependence for the N-end and O-end collisions are inverted, with strong oscillations in the intensity but a decreasing trend. Interestingly, the O-end of the molecule displays greater oscillations in magnitude and leads to much more negative orientation at high Δj .

When the $\rho_{1-}^{\{1\}}(\theta)$ renormalised PDDCSs are integrated over scattering angle, the resulting quantities yield the $\mathbf{r-k-j'}$ correlation, the steric polarisation parameters. The polarisation parameters of Fig. 8.3 show an oscillation reminiscent of the parity dependent oscillations presented in Chapter 5, however, as the adiabatic orientation mixes the initial parity states, the interference mechanism responsible for the Δj dependent oscillations remains of interest. Measurement of a multipole of the full 4-vector correlation would represent a significant experimental achievement, and in recent publications has been described as ‘forbidden fruit’ by Herschbach [3].

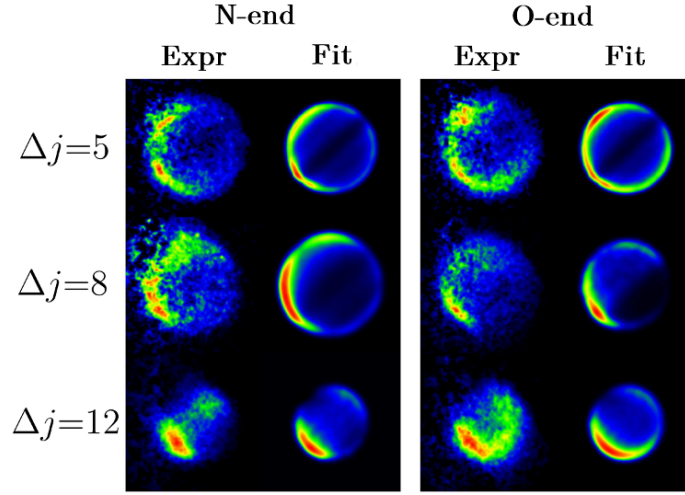


Figure 8.4: Experimental and fitted ion images recorded on the spin-orbit changing manifold for NO(X) scattering with Ar into $\epsilon' = e$. The S/N ratio is low, reflecting the very low integral cross sections of the spin-orbit changing states.

8.2.2 Spin-Orbit Changing Differential Steric Effect

The steric asymmetry on the spin-orbit changing manifold has been shown in Chapter 6 to have many unusual features. The differential steric effect can also be probed by analysing the angular distributions of the N-end and O-end images. The experimental ion images used in the determination of the integral steric asymmetry for the NO(X)–Ar spin-orbit changing collisions found in Chapter 6 are shown in Fig. 8.4. As is the case with the angular distributions presented in Chapter 4 and 5, the oriented images also contain the angular distribution, this provides a three vector $\mathbf{r}-\mathbf{k}-\mathbf{k}'$ correlation. The experimentally determined angular distributions for images with sufficient S/N were obtained for the N-end and O-end collisions using the algorithm described in Chapter 3. As noted in Chapter 6, experimental data for these states is challenging to collect as the cross sections for spin-orbit changing collisions are significantly smaller than those for spin-orbit conserving collisions (see Fig. 6.9 of Chapter 6). Fig. 8.4 shows the experimentally determined ion images for the $\Delta j = 5$, $\Delta j = 8$ and $\Delta j = 12$ collisions to the $\Omega' = 1.5$ manifold. Also shown are the fitted images. General trends similar to those seen in the spin-orbit conserving collisions presented in Chapter 4 and 5 can be observed. The products of the collisions (shown in Fig. 8.4) which scatter to low states, $\Delta j = 5$, are forwards and sideways scattered, scattering to $\Delta j = 8$ is mostly

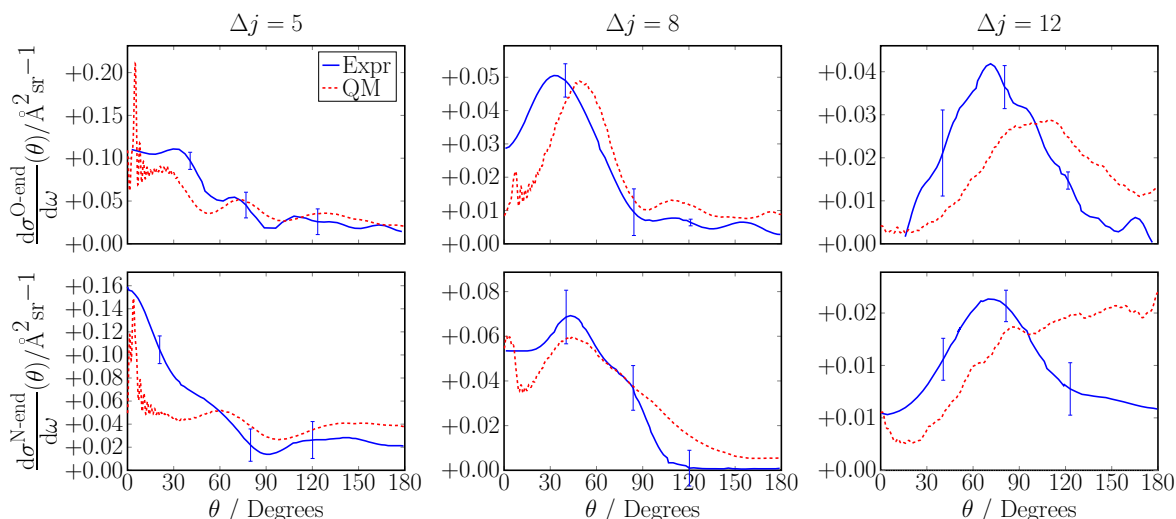


Figure 8.5: The NO(X)–Ar steric resolved angular distributions (blue) obtained from the ion images shown in Fig. 8.4 at a collision energy of 650 cm^{-1} . The QM calculations (red) show moderate agreement to the experimental data. The top panels display the O-end angular distributions and the bottom panels the N-end angular distributions.

side scattered while collisions to $\Delta j = 12$ are shifted towards backward scattering. As has been explained, this is due to more impulsive collisions leading to these higher rotational states. A decrease in the size of the image between $\Delta j = 8$ and $\Delta j = 12$ can also be observed: more energy is transferred to achieve rotational excitation of the molecule and less energy is available to be partitioned into recoil velocity.

The differences between the N-end and O-end images are quite strong, especially in the case of $\Delta j = 12$ where there is significantly more backward scattering from the O-end of the molecule than the N-end. The agreement between experiment and theory is quite unsatisfactory, possibly due to the low signal-to-noise in the images, incorrect α and β or incorrect basis function parameters. Images with better signal-to-noise are being obtained in order to test the accuracy of the three and four vector correlations on the spin-orbit changing potential surface.

8.2.3 Scattering of NO(X) with O₂(X)

The scattering of NO(X) with oxygen represents a significant theoretical and experimental challenge. Not only is it possible to excite rotational degrees of freedom in the O₂(X), but many more potential energy surfaces are needed to accurately model the collision. Despite this degree of complexity, study of such systems remains an

attractive field of investigation as the nuclear spin statistics forbid population of the even $N(\text{O}_2)$ states¹. By studying the rotational energy transfer between two diatomic molecules, correlations between the internal states of the products, as well as new vector correlations, can be determined. Some recent work has been performed scattering with oxygen [228–230], however little has been attempted on diatom-diatom collision systems. Typically, studies on these inelastic collisions have focused on systems in which only a single molecule is open shell in nature, for example $\text{O}_2 + \text{H}_2$ [231] or $\text{OH}(\text{X}) + \text{HCl}$ [232]. These systems have attracted more attention as there are no spin-coupling effects for the closed shell partner, and the number of PESs required to describe the system is therefore reduced, and theoretically accessible.

Potential energy surfaces for the $\text{NO}(\text{X}) - \text{O}_2$ system are currently too undeveloped to perform scattering calculations [233]. However, some speculation has been made about possible features of the potential energy surfaces and the energetic ordering of the four coupled surfaces that describe the $\text{NO}(\text{X}) - \text{O}_2$ system. The total electron spin angular momentum for the interaction complex can be defined as

$$\mathbf{S} = \mathbf{S}_{\text{NO}} + \mathbf{S}_{\text{O}_2}, \quad (8.2)$$

where $\mathbf{S}_{\text{NO}}$ and $\mathbf{S}_{\text{O}_2}$ are the electron spin for the NO and O_2 molecules respectively. In total, between the NO and O_2 , there are three unpaired electrons which can interact during the course of the collision. Therefore, $|\mathbf{S}|$ can take values of 0.5 or 1.5. This gives rise to the possibility of both a doublet state, in which two of the spins are paired, and a quartet state, in which the spins all remain unpaired. Hund's first rule predicts that the quartet state will be lower in energy due to the lower electron-electron repulsion, however, Hund's rules were originally developed to be applied to atoms.

On the other hand, Heitler–London theory [234] predicts that the doublet surface will be lower in energy [233]. Heitler–London theory is problematic as it predicts a covalent bond between the $\text{NO}(\text{X})$ and $\text{O}_2(\text{X})$ which is not observed [233]. The Heitler–London theory was originally formulated to explain bonding in hydrogen, which

¹Here the quantum number N is used for the oxygen molecule instead of j order to clearly distinguish its Hund's case (b) character.



Figure 8.6: The two minima of the NO(X)-O₂ potential energy surface. One is a linear geometry, which is lowest energy at large separations whereas the T-shaped geometry is preferred when electron-electron repulsion is important at close range.

is a very different species to either NO(X) or O₂(X). Economides found from performing several different *ab initio* calculations that no theoretical method gave consistent results for the ordering of the potential surfaces [233]. For this reason, scattering calculations can not be performed, even in the classical regime, as the lowest energy surface has yet to be identified.

Bacon and co-workers [229] noted that it is expected for the NO+O₂ system to have a relatively deep attractive potential well due to the possibility of spin pairing in the collision partners. Due to the relatively low masses involved in this system, the spin-orbit coupling term is quite small and it is unlikely that significant mixing will occur between the doublet and quartet surfaces [229]. This may open up the possibility of running classical trajectory calculations on just one surface, if the ground state surface can be correctly identified. Fig. 8.6 shows the geometries which have been predicted by Lee and Wright [235] to be the potential energy minima on the quartet surfaces. It was also predicted by Economides [233] that at long range, a linear orientation with ⁴Π symmetry would be the preferred orientation of the minimum of the surface as dipole-induced dipole interactions are expected to dominate (left panel Fig. 8.6). However, at low molecular separation it is thought that electron-electron repulsion is likely to become the dominant force and so a ‘T-shaped’ geometry would be favoured [233], shown in the right panel of Fig. 8.6. This geometry can have either ⁴A₁ or ⁴A₂ symmetry, depending on whether the NO electron is in or out of the plane of the bond axis. The outermost electrons in both molecules are in π* orbitals, and so an ‘end-on’ approach (linear) or ‘side-on’ approach (molecules parallel) of the NO(X) will result in a large interaction between these electrons. Nevertheless, these interactions

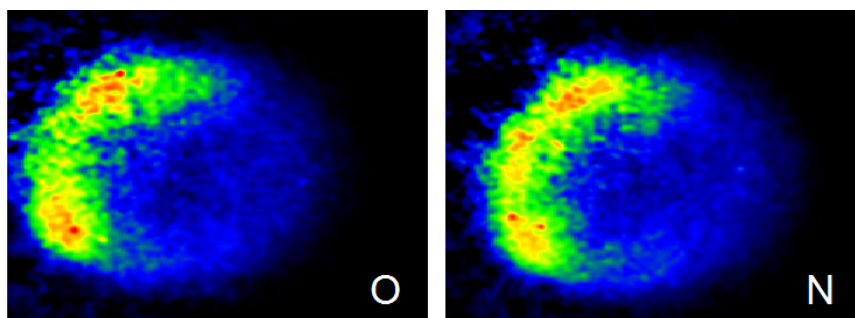


Figure 8.7: Images of NO(X) scattered with oxygen recorded in the steric geometry (left: N-end, right: O-end) for a collision resulting in the $j' = 7.5e$ state. Slight differences can be observed in the images, however the resolution is too low to observe product pair correlations.

are predicted to be weak, and so it is likely that a wide range of bond axis orientations in both the NO(X) and O₂ will be sampled.

There are two main photolysis channels for NO₃ in the visible region [236], however, the energy barrier for the reverse of the photolysis reaction is around 16 000 cm⁻¹ [233, 237], which is far too high to be accessible at the collision energy of the beams.

Integral steric asymmetry

As discussed, the collision can induce rotational excitation in both collision partners. This also leads to increased complexity in ion image analysis. Within each ion image, multiple rings of intensity are predicted to be observed due to the presence of the many different occupied rotational states of the oxygen and the NO(X). Each of these rings, an effective ion image for each $[j(\text{NO}), N(\text{O}_2)]$ pair, must be analysed separately to obtain the angular distribution for each product pair. There are many methods available for the analysis of multiple nested rings within an ion image, including Abel-inversion [217, 218, 220, 238], ‘onion-peeling’ [216] and numerical methods [239]. The nested Newton spheres make analysis extremely challenging, and recovering statistically meaningful data from the images is difficult. A new analysis algorithm in which the image is deconvoluted and resimulated is in development, however it is possible to obtain some information directly from the scattered images by integration over scattering angle.

The hexapole apparatus was configured for scattering oxygen in the steric geometry (see Chapter 3). Collisions of NO(X) with oxygen were then undertaken with steric

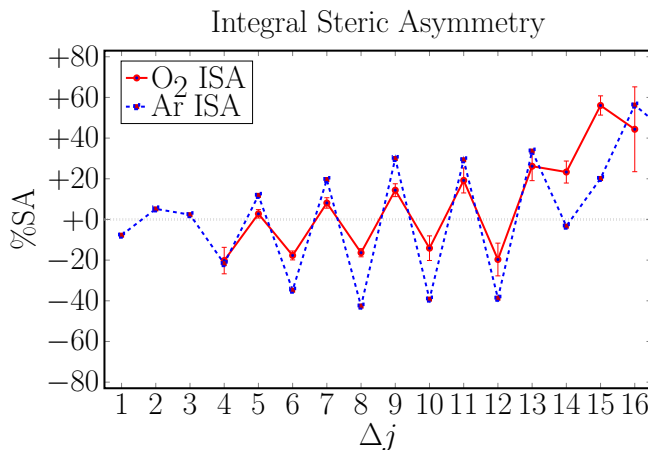


Figure 8.8: Integral steric asymmetry obtained for the NO(X)–O₂ collision system (red) compared to the steric asymmetry of the NO(X)–Ar system (blue dashed). The collisions shown are to $\epsilon' = e$ states on the spin-orbit conserving manifold. The main features present in the NO(X)–Ar system are reproduced with the oxygen collision partner.

resolution in the NO(X). Note that the oxygen is unoriented, but has the possibility to be aligned by the molecular beam [240–242]. The integral steric asymmetry was then calculated from the complete ion images (an example of one of the experimental ion images is shown in Fig. 8.7). These images have the N-end and O-end intensities taken, and then the summed and weighted steric asymmetry from all the product pair rotational states is calculated. The steric asymmetry for scattering of NO(X) with oxygen is shown in Fig. 8.8. The Δj dependent oscillations are still observed, indicating that the interference mechanism responsible for the oscillations is still in effect with the diatomic collision partner. It is however slightly diminished. Analysis of lower lying Δj states may indicate a strong attractive region in the NO(X)–O₂ system which has been speculated to be caused by a large attractive well due to spin-pairing in the collision partners. At higher Δj , the steric asymmetry increases again, with N-end collisions favoured. This is the same behaviour as in a collision with argon, indicating that the mechanisms responsible for the steric asymmetry in the atom diatom collisions are also present in the NO(X)–O₂ system. Further investigation of the oriented angular distributions with a new image analysis method should provide estimates of well depths (*via* ℓ -type rainbows) and provide experimental angular distributions which may be able to guide theory in the production of high quality PESs. The ultimate goal would be to obtain a complete set of $\mathbf{r}\text{--}\mathbf{k}\text{--}\mathbf{k}'\text{--}\mathbf{j}'$ measurements for the NO(X)–O₂ collision system,



Figure 8.9: A diagram of the slicing apparatus designed to observe the pairwise correlations in the hexapole. The ion optics are the same as in the Townsend [243] DC slicing experiment. In the flight tube a set of inverting electrodes are used in order to stretch the Newton Sphere.

each with product pair resolution. In order to achieve this, the blurring associated with the orientation rods would need to be overcome.

Improving resolution

The simplest way to recover the full 3D distribution of ions from a ‘crushed’ 2D image is to perform an Abel inversion, which is a mathematical transformation that requires images to have cylindrical symmetry. Unfortunately, as the apparatus uses molecular beams that cross at 90° , the experimental scattering distribution possesses a flux-to-density factor and such does not possess the necessary cylindrical symmetry, and so direct mathematical recovery of the product distribution is not possible. The flux-density correction can be applied to symmetrise the experimental images, however, this process is not exact when products recoil with multiple velocities (as is the case for diatom-diatom scattering), and so it is preferable to directly extract the information from the full 3D distribution. A promising alternative is slice imaging. Slicing methods aim to increase the stretch of Newton spheres in the time-of-flight (ToF) direction in order to sample a smaller proportion of azimuthal angles ϕ , and so reduce the blurring in the image.

A new slicing method was developed and electrodes deployed into the experiment, as depicted in Fig. 8.9. Initially, the ions are extracted by the field gradients between the first four plates, as in the Townsend DC slicing setup [243]. The Newton sphere of ions begins to expand as the ions progress towards the detector and the temporal width of the ion cloud grows. At a specific point in the ToF tube, the ions pass through

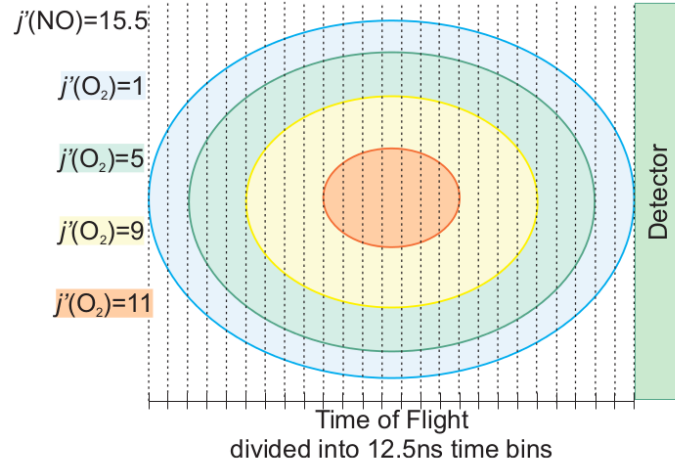


Figure 8.10: Theoretical maximum Newton Sphere elongation from the slicing setup. The concentric rings are the expected time differences between different product pairs arriving on the detector. With 12.5 ns slicing, it is expected that the full 3D representation of the product pairs can be recovered.

a grounded electrode and are near a grounded grid (far right Fig. 8.9). At this point, a high voltage (around 2 kV) is applied to the pulsed grid, creating a field gradient between the two electrodes, which has the effect of inducing differential acceleration in the Newton sphere. Ions which are close to the pulsed potential are accelerated more than those furthest away, as at the pulse time, they experience a greater acceleration field than those closer to the detector. Ions at the back of the Newton sphere advance upon the ions at the front, and so the temporal width is decreased. This process continues until the Newton sphere is pancaked, such that the temporal width is as small as possible. Following this, ions that were previously at the back of the Newton sphere overtake those previously at the front, and the ions again begin to stretch in the ToF direction, this time with much greater differences in velocity. Having left the pulsed region, this process of temporal stretching continues until the ions impact the detector.

The temporal stretch that can be achieved is expected from simulation to be very large in comparison to conventional DC slice imaging methods such as those of Liu [244] or Townsend [243], at around 1.3 μ s for a pulsed voltage of 2500 V. Increasing the pulsed voltage beyond 2500 V magnifies the image, eventually causing it to be too large to fit onto the detector. In order to compensate for this, the aperture sizes of the pulsed and ground electrodes can be varied in order to straighten the field lines after the

pulsed plate, and hence reduce the magnification of the resulting image to fit the small (40 mm) detector currently in place on the experiment.

With this method it should be possible to enhance the Newton sphere arrival time long enough to employ the PImMS sensor [214] to perform 3D imaging [245] of the Newton sphere as it impacts the detector. This will provide sufficient resolution to view the pairwise correlations in NO(X)-O₂(X) scattering. Other experimental considerations are also important. For instance, by slicing the effective signal level is reduced. In order to compensate for this, the repetition rate of the experiment should be increased, the maximum repetition rate before instability in the molecular beams becomes problematic is between 30 Hz and 50 Hz.

By utilising the experiment's modularity, combined with advanced sensors and electric field switching schemes, new frontiers of reaction dynamics can be explored. By scattering complex diatomics such as NO(X) with O₂(X), the experiment can be used to guide theory in the production of high quality PESs and obtain rich information about the mechanism of rotational energy transfer between the two species.

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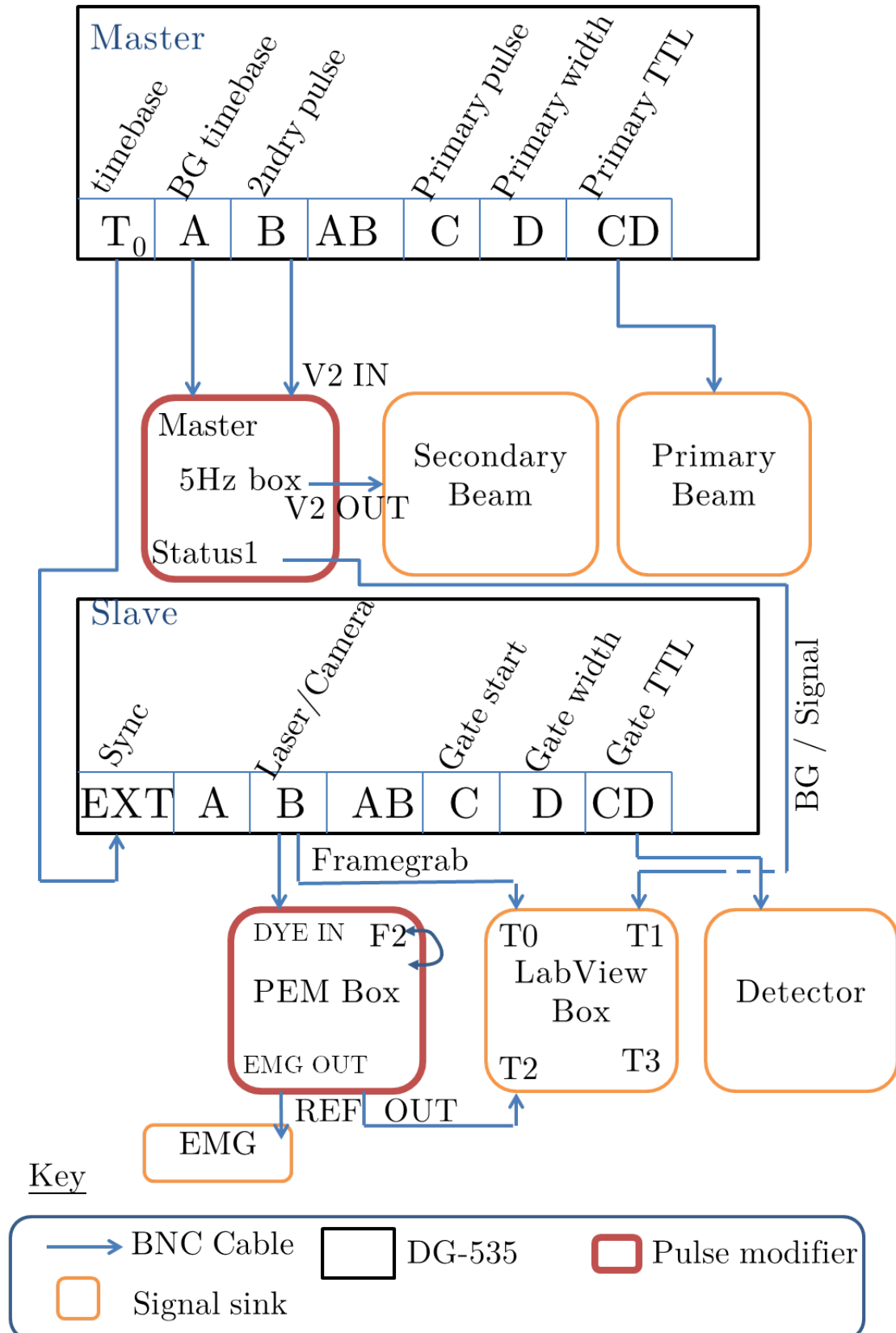


Triggering Schemes

In this appendix, the triggering schemes for each experimental geometry is reported. The steric geometry requires a different timing setup to the alignment geometry as the orienting field must be changed to velocity mapping conditions as close as possible to the laser firing. If the field is changed at too early, the molecules are not oriented before collision, and if the field is changed too late, the velocity mapping can not be achieved. In the alignment and steric geometries, the photo-elastic modulator is used to control the polarisations of the excitation laser.

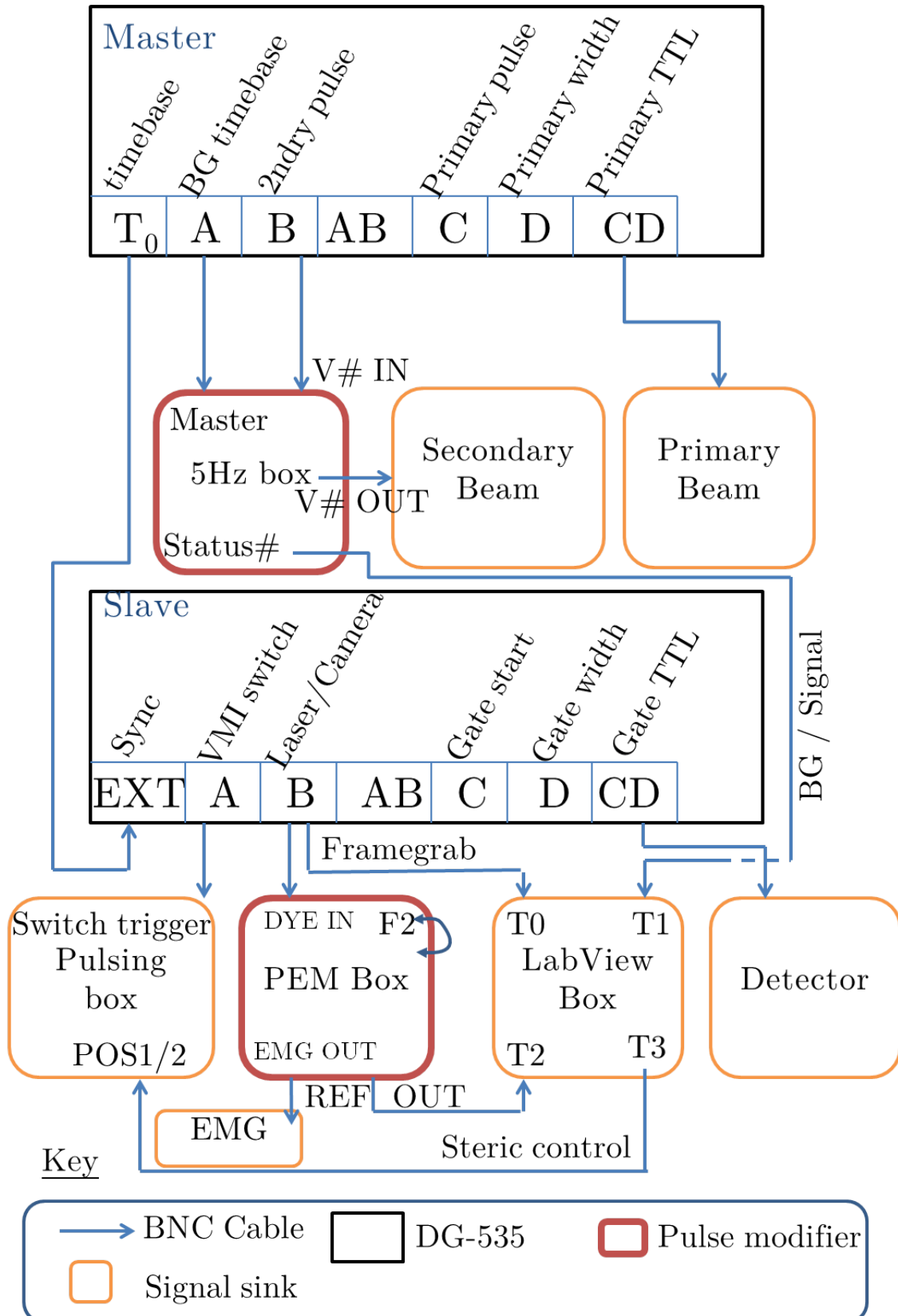
A.1 The Alignment or Orientation Geometry

Polarisation (H/V S/BG)



A.2 The Steric Geometry

Steric Geometry (NO/ON H/V S/BG)



B

Glossary of Terms

Many different terms and abbreviations are introduced in this thesis. Some of the most common have been placed here for reference.

HS Hard shell, uses the contour at E_{coll} as the target shape.

CCD Charge couple device camera.

MCP Microchannel plate electron multiplier.

QM Quantum mechanical.

QCT quasi-classical trajectory.

CC QM close-coupled quantum mechanical. Refers to calculations where the potential changes smoothly.

QMHS Quantum mechanical hard shell.

QM av CC QM calculations averaged over initial and summed over final Λ -doublet and spin-orbit states.

PES Potential Energy Surface.

PIXTOV Pixel to velocity ratio, dimensionless.

DCS Differential Cross Section, a measure of the $\mathbf{k}$ – $\mathbf{k}'$ correlation.

ICS The Integral Cross Section.

ISA The Integral Steric asymmetry given in terms of %SA. Spans from 100% indicating all collisions proceed by hitting the N-end to -100% which indicates all collisions proceed by hitting the O-end.

PDDCS (j') Polarisation Dependent Differential Cross Section.

R-PDDCS Polarisation Dependent Differential Cross Section, they represent the distribution of $\mathbf{r}$ with respect to $\mathbf{k}$ and $\mathbf{k}'$.

V_{sum} The adiabatic surface that spin-orbit conserving collisions primarily sample. It is the half-sum of the A' and A'' diabatic surfaces.

V_{diff} The adiabatic surface that spin-orbit changing collisions primarily sample. It is the half-difference of the A' and A'' diabatic surfaces.

V_{tot} A modified potential made up of parts of the V_{sum} and V_{diff} potentials.

Truncated potential A modified potential that has had the attractive part removed.



Glossary of Symbols

Any symbol with a prime (') refers to the quantum number or quantity associated with the product state. For example, j' would indicate the rotational quantum number of the scattered NO(X) molecules after interacting with the collision partner. Whereas m' would indicate the projection quantum number of $\underline{j'}$ onto $\underline{k}$.

Ω The spin-orbit quantum number, takes values of $\frac{1}{2}$ or $\frac{3}{2}$.

v The vibrational quantum number.

j The rotational quantum number.

Δj The change in rotational quantum number due to the collision, $j' - j$. As all the collisions presented here start with $j = 0.5$, Δj is an integer. Δj is usually used when comparing to closed-shell calculations.

m The magnetic quantum number. Spans from $-j$ to $+j$ in integer steps. It is the projection of $\underline{j}$ onto $\underline{k}$.

ϵ The spectroscopic index, related to the system parity by $\epsilon = p(-1)^{j-\frac{1}{2}}$.

- $\mathbf{J}_{\text{tot}}$ The total angular momentum, includes nuclear rotation and electron spin as well as orbital angular momentum.
- κ The index of the potential expansion for either V_{sum} or V_{diff} .
- Λ The electronic angular momentum.
- $\mathbf{r}$ (bold in text) The bond axis orientation vector.
- $\mathbf{j}$ (bold in text) The angular momentum vector.
- $\mathbf{E}$ (bold in text) The electric field vector.
- $\mathbf{k}$ (bold in text) The relative velocity vector.
- $\mathbf{k}$ One of two meanings. (i) the wavevector (ii) the rank of the polarisation moment which spans from 0 to $2j$.
- q The index of the moment spans from 0 to k .
- $\theta_{\mu E}$ The angle of the electric field with respect to the dipole moment.
- θ The scattering angle, defined as the angle between $\mathbf{k}$ and $\mathbf{k}'$.
- ϕ The polar scattering angle.
- $\rho_{q\pm}^{\{k\}}(\theta)$ The real, renormalised PDDCS of immediate directional significance.
- $n_{q\pm}^{\{k\}}(\theta)$ The real, normalised PDDCS.
- $a_{q\pm}^{\{k\}}$ The real, polarisation moment. The scattering intensity integrated normalised PDDCS.
- $\rho_{q\pm}^{(k)}$ The complex, renormalised PDDCS. Has no *immediate* directional significance.
- % $\mathbf{SA}$ The integral steric asymmetry, the normalised difference between collisions at the head and tail of a molecule.
- A The spin-orbit energy.
- B The rotational constant.

$E(j)$ The rotational energy of the j^{th} state.

ΔE_{rot} The change in rotational energy from the collision.

p The parity, the symmetry with respect to inversion of the state.

$Z(x, y)$ The instrument function or density-to-flux conversion factor.

P_{scat} The angular distribution.

$A_{V/H}(\theta; \Gamma)$ The quantity which contains the polarisation dependent transition probabilities, in turn depends on the probe polarisation and the polarisation dependence of the system.

Rg Rare gas; can be He, Ne, Ar, Kr or Xe.

$d\omega$ Shorthand for $d\theta d\phi$.

$\frac{d\sigma}{d\omega}$ The differential cross section, given here in units of $\text{\AA}^2 \text{sr}^{-1}$.

ℓ The orbital angular momentum quantum number.

$P_l(\cos \theta)$ The associated Legendre polynomial. The index l is always an integer.

$C_{kq}(\theta, \phi)$ The modified spherical harmonic function defined as $C_{kq}(\theta, \phi) = \sqrt{\frac{4\pi}{(2k+1)}} Y_{kq}(\theta, \phi)$.