

Vector correlations in gas-phase inelastic collision dynamics

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Abstract

This thesis presents a joint experimental and theoretical study of vector correlations in the electronically, vibrationally, and rotationally inelastic collisions of simple molecules with rare-gas atoms.

In the first instance, empirical and calculated data are presented for rotationally inelastic scattering in the $\text{NO}(\text{X})+\text{Ar}$ and $\text{ND}_3(\tilde{\text{X}})+\text{Ar}$ systems at collision energies in the range $405 - 2210 \text{ cm}^{-1}$. These experiments – the first to be conducted on a newly commissioned crossed-molecular beam machine – measured the $\mathbf{k} - \mathbf{k}'$ correlation, *i.e.* that between the vectors describing the relative velocities before and after collision, respectively. The empirical data were subjected to rigorous comparison with both quantum-mechanical and *quasi*-classical trajectory (QCT) calculations. For both the $\text{NO}(\text{X})+\text{Ar}$ and $\text{ND}_3(\tilde{\text{X}})+\text{Ar}$ systems, there is generally good agreement between experiment and theory at all four collision energies investigated.

Two chapters of this thesis focus on the development of trajectory surface-hopping (TSH) QCT models of the $\text{OH}(\text{A}, v=0)+\text{Kr}$ and $\text{OH}(\text{A}, v=0)+\text{Xe}$ systems. Experimental data relating to scalar quantities (rotational energy transfer (RET) and electronic quenching) and to the $\mathbf{j} - \mathbf{j}'$ correlation (which quantifies the depolarisation of the angular momentum of the $\text{OH}(\text{A})$ radical) are compared to variable-collision-energy TSH QCT calculations in which the length of the OH bond is fixed. The algorithms involve all three PESs of the $\text{OH}(\text{A/X})+\text{Kr}$ system, and the full range of electrostatic and roto-electronic mechanisms that couple them, for the first time. The most complete model succeeded in accounting for 93% of experimentally observed quenching. For the $\text{OH}(\text{A/X})+\text{Xe}$ system, coupling matrix elements were estimated from those of $\text{OH}(\text{A/X})+\text{Kr}$, and the most complete model recovered 63% of experimentally observed quenching.

This thesis also presents a novel theoretical study of rotationally inelastic dynamics in the $\text{OH}(\text{A}, v=1)+\text{Kr}$ system. Provisional results from adiabatic calculations in which the OH bond length is allowed to vary over the course of a trajectory are presented alongside experimental data that were reported previously. To date, these calculations continue to underestimate the extent of empirical RET data. Reasons for the observed discrepancy, and suggestions to resolve it, are outlined in detail.

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List of Abbreviations

aug-cc-pVQZ	augmented correlation-consistent polarised valence quadruple zeta basis set
aVQZ-PP	augmented valence quadruple zeta with <i>pseudo</i> -potentials for heavy atoms basis set
aVTZ-DK	augmented valence triple zeta Douglas-Kroll-Hess Hamiltonian basis set
CASSCF	complete active space self-consistent field
CC	close-coupling
CMB	crossed-molecular beam
CCSD(T)	coupled-cluster method with single, double, and perturbative triple excitations
DCS	differential cross-section
FWHM	full width at half-maximum
GFP	green fluorescent protein
ICS	integral cross-section
LIF	laser-induced fluorescence
MRCI	multi-reference configuration interaction
Nd:YAG	neodymium-doped yttrium-aluminium garnet
OODR	optical-optical double resonance
PDDCS	polarisation-dependent differential cross-section
PES	potential energy surface
QCT	<i>quasi</i> -classical trajectory
REMPI	resonance-enhanced multi-photon ionisation
RET	rotational energy transfer
SRP	stimulated Raman pumping
ToF	time-of-flight

TSH		trajectory surface-hopping
VET		vibrational energy transfer
VMI		velocity-map imaging
ZQBS		Zeeman quantum beat spectroscopy

1

Introduction

The field of molecular reaction dynamics is concerned with the study of chemical events on atomic-length distances and over very brief periods of time. At its core, this area of Physical Chemistry is driven by a desire to observe, understand, and predict the various forces that control molecular structure, particle interactions, and – ultimately – chemical change.

Instrumental developments since the 1980s have allowed laboratory measurements to be taken on much shorter timescales: now, attosecond light pulses permit experimental studies to be conducted with exquisite resolution in time and space [1–4], meaning both nuclear and electronic dynamics can be observed in the laboratory. Nonetheless, despite these recent advances in ultrafast spectroscopy, there remains a considerable interest in studying initial and final quantum-state distributions (and the vector correlations that link them) to extract detailed, mechanistic information about a system of interest.

In many areas of Chemistry, it is neither feasible nor necessary to understand observed phenomena on a quantum-mechanical level. For example, it is not necessarily helpful to consider the industrial production of sulfuric acid [5] on a microscopic scale, as to do so would not increase our understanding of the process appreciably or, indeed, make it more profitable. However, through the use of any number of suitable assumptions, complex chemical systems such as this can

often be condensed into much simpler models that allow for easier interpretation and replication of experimental data.

In contrast, however, the fundamental goal of molecular reaction dynamics is actually to use experimental and theoretical tools to unravel, understand, and control the dynamics of molecular collisions on a single-event scale. Indeed, by preparing molecules in a given quantum state, controlling how they are able to interact, and then measuring the quantum-state distribution of the collision/reaction products, it is possible to develop a comprehensive understanding of the dynamical processes at play.

Over the years, the field has benefited enormously from the development of experimental apparatus and theoretical algorithms that are able to investigate high-resolution multi-vector collisions for simple, gas-phase systems, including those reported in this work. In particular, this thesis centres on the use of a number of different experimental techniques, alongside both quantum-mechanical and semi-classical dynamical models, to study the rotationally inelastic collisions of simple molecules with rare-gas species.

1.1 Rotationally inelastic collisions

Collisions that involve the transfer of energy into, or out of, the rotational degrees of freedom of a linear diatomic molecule or a symmetric-top species are of immense importance in this thesis. In all of the systems investigated in this work, the amount of rotational energy possessed by the molecule can increase or decrease as a consequence of its collision with a translationally excited atomic partner. As such, the molecules are said to undergo *rotational energy transfer* (RET) when they interact with atomic colliders.

Rotationally inelastic collisions are ubiquitous in Chemistry and form a key component of the dynamics of many important chemical and biological systems. Even if the products of an inelastic collision are chemically identical to the reagents, rotational energy transfer processes have been shown to compete directly with electronic quenching and radiative processes, as well as with reactive pathways,

and so are crucial in determining the outcome of a given molecule-atom collision. Moreover, it is often the case that inelastic collisions (rotationally, or otherwise) will be the primary mechanism by which non-equilibrium populations are returned to Boltzmann-like distributions following a given physical change or chemical reaction. For example: if OH(X) radicals absorb laser photons of a specific wavelength, this will generate a population of OH(A) molecules in a single $|v, j\rangle$ state that can then be returned to an electronic and rovibrational Boltzmann distribution of energies *via* inelastic collisions [6–8]. Similarly, and in accordance with Polanyi’s rules [9], a reaction with an early potential-energy barrier will lead to the formation of vibrationally excited products (such as the diatomic products in the K + I₂ [10, 11] and O + CS [12] reactions) that are subsequently returned to thermal equilibrium *via* inelastic collisions. Thus, it is very important to investigate the nature, origin, and rates of these mechanistic pathways if we are to improve our understanding of simple molecule-atom collision dynamics before moving on to more complex systems.

This thesis considers the rotationally inelastic collisions of three different molecules – NO(X), ND₃($\tilde{X}$), and OH(A) – with a number of rare-gas atoms – Ar, Kr, and Xe – by looking at three main RET processes:

1. NO(X, $^2\Pi_\Omega$, $v' = 0$, j' , e/f) + Ar $\leftarrow$ NO(X, $^2\Pi_{\frac{1}{2}}$, $v = 0$, j , e/f) + Ar;
2. ND₃($\tilde{X}$, $v = 0$, $j_k'^{\pm}$) + Ar $\leftarrow$ ND₃($\tilde{X}$, $v = 0$, $j_k^{\pm} = 1_1^-$) + Ar;
3. OH(A, $^2\Sigma^+$, $v' = 0/1$, j') + Kr/Xe $\leftarrow$ OH(A, $^2\Sigma^+$, $v = 0/1$, j) + Kr/Xe.

Note that the notation used here is outlined in detail in Chapter 2. A wealth of information about these rotationally inelastic collisions can be gleaned from investigating the vector correlations outlined in Section 1.2.

1.2 Vector correlations in molecule-atom scattering

It is not currently possible to resolve the chemistry of complex systems into correlations between single quantum states. For both experimentalists and theoreticians alike, the sequential addition of atoms to a system leads to an increase in the

number of degrees of freedom that must be modelled, controlled, and/or measured to achieve state-to-state resolution. As a result, for complex systems, any observable quantities that are measured will necessarily be averaged over multiple degrees of freedom, meaning it is often not possible to gain a full insight into the dynamical processes that convert reagents into products. To this end, much attention has been paid to investigating non-reactive collisions between atoms and simple molecules. The collision dynamics of these systems can be fully characterised by four vectors (and the correlations between them) that can be determined both experimentally and theoretically with ever-increasing precision.

For the most part, a collision between two particles can be categorised as either *reactive* or *non-reactive*. In the former case, the product species will be chemically different to the reagents whereas, in the latter, the chemical composition of the colliding pair will remain unchanged over the course of its interaction. However, in both cases, the species that undergo collision may experience a change in one or more of the quantum numbers that define their physical state.

As stated previously, this thesis considers the non-reactive, rotationally inelastic scattering of simple molecules ($\text{NO}(\text{X})$, $\text{ND}_3(\tilde{\text{X}})$, and $\text{OH}(\text{A})$) by rare-gas atoms (Ar , Kr , and Xe). As a helpful illustration, we can discuss the collision of a diatom, AB , with an atom, C , which can be fully specified using the following four vectors (see Figure 1.1): the initial and final relative velocities, $\mathbf{k}$ and $\mathbf{k}'$, respectively; and the initial and final rotational angular momenta of AB , $\mathbf{j}$ and $\mathbf{j}'$, respectively. Notably, the orientation/alignment of the molecule could alternatively be described using the $\mathbf{r}$ and $\mathbf{r}'$ vectors, which quantify the direction of the bond axis before and after collision, respectively. This correlation has been studied previously for both the $\text{NO}(\text{X})+\text{Ar}$ [13–16] and $\text{OH}(\text{X})+\text{Ar}$ systems [17], however, it is not considered further in this work.

A knowledge of the correlations of these vectors, as a function of initial and final quantum states, can provide a wealth of information on the dynamics of the system of interest. It is also the case that the full four-vector correlation can be integrated over various vectors to generate lower-order correlations. These simpler,

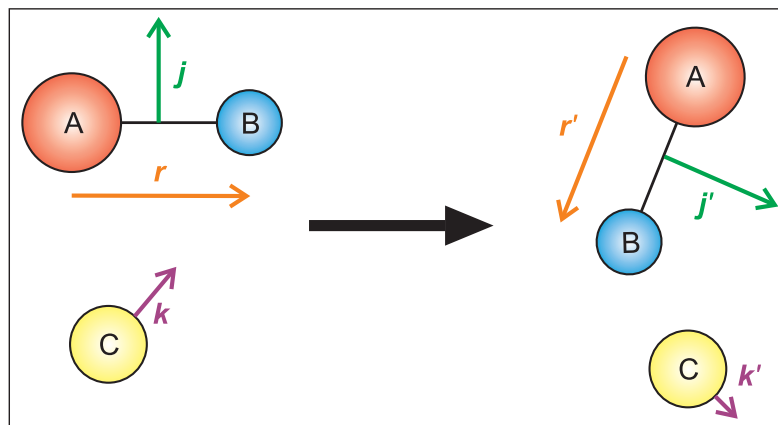


Figure 1.1: Pictorial representation of the full $\mathbf{j} - \mathbf{k} - \mathbf{k}' - \mathbf{j}'$ four-vector correlation that gives all the information about a collision between a diatom, AB, and an atom, C. The vectors that define the AB bond axis before and after collision ($\mathbf{r}$ and $\mathbf{r}'$, respectively) are included here for the sake of completeness, but they are not discussed further in this thesis. See text for details.

integrated correlations are often useful in understanding the observed dynamics, since they allow different aspects of the collision to be investigated separately.

In Chapters 3 and 4, crossed-molecular beam techniques are used to collect empirical data. In these experiments, averaging over the initial and final angular-momentum vectors, $\mathbf{j}$ and $\mathbf{j}'$, respectively, simplifies the full four-vector correlation into the $\mathbf{k} - \mathbf{k}'$ two-vector correlation, which quantifies the intensity of AB scattering as a function of the dihedral angle, θ , between the $\mathbf{k}$ and $\mathbf{k}'$ vectors. These differential cross-sections (DCSs) have been recorded both experimentally and theoretically for the $\text{NO}(\text{X}) + \text{Ar}$ and $\text{ND}_3(\tilde{\text{X}}) + \text{Ar}$ collision systems.

The DCS of a collision can reveal many mechanistic details about the dynamical processes taking place. The distribution of intensity as a function of the scattering angle can shed light on the types of collision that populate certain final quantum states. For example, it will be shown in later chapters that, generally, glancing-blow collisions, which result from large impact parameters, produce forward-scattered maxima in the DCS. The isotropy of the DCS can also be related to the attractiveness of the potential energy surface (PES) that governs the collision [18]: if the atom and molecule enter a deep potential-energy well, they may form a relatively long-lived complex that survives for several rotational periods and generates an isotropic

DCS. In a similar fashion, the anisotropy of the PES can be inferred from the presence, or lack thereof, of rotational rainbows in the DCS, and ℓ -type rainbows can provide information on the attractive regions of the potential [19–24]. Each of these features will be discussed in detail in Chapter 3.

This thesis also presents experimental and theoretical data for the OH(A)+Kr and OH(A)+Xe systems that focus on the $\mathbf{j} - \mathbf{j}'$ correlation [25, 26]. The extent to which the plane or sense of rotation of the rotational angular-momentum vectors in a population of molecules is disturbed over the course of a collision can be directly related to the potential energy of interaction between AB and C. If, then, vector correlations relating to different types of collision are compared (for example, rotationally elastic *versus* rotationally inelastic trajectories), conclusions can be drawn concerning the areas of the PESs that are responsible for the different types of observed dynamics.

To this end, it is necessary to introduce the concept of *angular-momentum polarisation*, *i.e.* a preferred plane or sense of rotation of the rotational-angular-momentum vectors about a reference axis in the laboratory frame. It is possible to preferentially populate or detect a specific quantum state that is defined by the $\mathbf{j}$ or $\mathbf{j}'$ vector by virtue of the correlation between the rotational angular momentum of the molecule and its transition dipole moment. The probability that a molecule absorbs a photon varies as $\cos^2 \theta_{\mu\epsilon}$, where $\theta_{\mu\epsilon}$ is the angle between the electric vector of the light and the transition dipole moment. Thus, polarised light can be used to preferentially excite molecules (either pre- or post-collision) into or from a certain rotational-angular-momentum quantum state. Linearly polarised light can be used to induce/detect angular momentum *alignment*; circularly polarised light can be used to induce/detect angular momentum *orientation*. These concepts are discussed in more detail in Chapter 2.

In Chapter 3, scattered NO(X) molecules are preferentially detected based on the polarisation of the $\mathbf{j}'$ vector. In Chapters 6 and 7, a polarised distribution of $\mathbf{j}$ is created prior to collision, and the loss of this polarisation (to form an isotropic distribution of $\mathbf{j}'$) is monitored over time to shed light on the role played by different

collisional partners in the depolarisation process. The work presented in this thesis complements an extensive series of studies on the collisional depolarisation of angular momentum in the collisions of NO(X) and OH(A) radicals with rare-gas atoms [6–8, 25–29].

1.3 Experimental methods

The discussion in the preceding sections has outlined how a knowledge of the initial and final quantum states of the reagents and products, along with the control of their initial velocity and angular-momentum vectors, provides the maximum amount of information about a given collision process. Thus, an ongoing challenge for experimentalists consists of finding methods by which to isolate, control, and detect single quantum states both before and after collision events. In this way, specific vector correlations can be determined. However, it is equally important that the desired quantum state is unaffected by competing processes, such as collisions with atmospheric gas molecules, or with another molecule of the same species in the molecular-beam pulse. To this end, all the experiments reported in this thesis were conducted under reasonably high-vacuum conditions, such that the outcome of single-collision events can be observed and recorded without interference from secondary events.

1.3.1 Reagent preparation

To achieve the desired experimental aims, a method that is capable of creating a significant population of molecules in a single quantum state is required. There are a range of experimental techniques that can be used to achieve this:

1. **Narrow-bandwidth lasers** can be tuned to excite a specific rovibrational branch of an electronic transition in a molecule. In this way, rotational-level resolution can be achieved for molecules that have undergone electronic [30, 31] and/or vibrational [32, 33] excitation.

2. **Electric and magnetic fields** can be used to selectively guide a specific quantum state of a given molecule into a desired region based on differences in Stark and Zeeman interaction energies [34, 35], respectively. Importantly, these techniques can also be used simultaneously to control and/or select the translational velocity of the gas molecules prior to collision [36–40].
3. **Crossed-molecular beam techniques**, which usually involve the adiabatic expansion of gas pulses with a finite width into a vacuum, allow the direction of the initial relative velocity vector, $\mathbf{k}$, to be defined [41]. The supersonic gas expansion also tends to generate gas pulses with narrow, non-Boltzmann velocity distributions and highly non-thermal rotational-state distributions. The magnitude of $\mathbf{k}$ can be further altered by modifying the angle between the two crossed beams [42]. In most experiments, including those discussed in thesis, the beams intersect at 90° .

1.3.2 Product detection

Once the molecules have undergone collision with a rare-gas atom, a suitably selective method is required to detect a single quantum state in one (or more) of the collision product(s). A range of techniques is also available to achieve this (many of which have been summarised in reference [43]):

1. **Resonance-enhanced multi-photon ionisation** invokes quantum-state-selective ionisation schemes that are commonly used to aid the detection of neutral products using time-of-flight (ToF) techniques [44] or velocity-map imaging (see below). In these multi-photon ionisation schemes, the intermediate state corresponds to an actual electronic state of the atom/molecule, and the efficiency of the ionisation is often increased by several orders of magnitude in comparison to non-resonant alternatives [41].
2. **Velocity-map imaging (VMI)** techniques [45] allow for the determination of the final relative velocity vector, $\mathbf{k}'$, by using a static electric field to focus ions with the same velocity onto the same point on a position-sensitive detector.

When coupled to a camera, these ion-detection events can be recorded over time to build up an image of the velocity distribution within the products of a scattering [15, 46] or photodissociation [47, 48] event.

3. **One-photon-excited-fluorescence** can be measured in polarised laser-induced fluorescence (LIF) [49] and Zeeman Quantum Beat Spectroscopy (ZQBS) [6–8] experiments to measure the loss of excited-state population over time. The *pseudo*-first-order rate constant for collisional fluorescence decay is dependent on the concentration of the collision partner that induces non-adiabatic transitions. Moreover, through the use of a monochromator to resolve fluorescence of a particular wavelength, the loss of population from a single quantum state can be measured.
4. **A second narrow-bandwidth laser** can be used to excite a single quantum state in a product to make it detectable. A second laser is needed in a number of techniques, including (but not limited to): optical-optical double resonance (OODR) [43, 50], $(1 + 1')$ -LIF [51], two-colour resonance-enhanced multi-photon ionisation (REMPI) [25], and Rydberg-tagging [52, 53].
5. **Non-linear spectroscopies**, including four-wave mixing and polarisation spectroscopy, are also in common use [54–56].

1.3.3 This work

Broadly, three different experiments were needed to collect the data reported in this thesis. These are summarised as follows:

1. **NO(X)+Ar**

Reagent preparation using a crossed-molecular beam apparatus, and product detection *via* a two-colour $(1 + 1')$ REMPI scheme and VMI techniques, to measure the $\mathbf{k} - \mathbf{k}'$ vector correlation;

2. **ND₃($\widetilde{\text{X}}$)+Ar**

Reagent preparation using a crossed-molecular beam apparatus with the

application of a hexapole-electric-field state-selector, and product detection *via* a one-colour $(2 + 1)$ REMPI scheme and VMI techniques, to measure the $\mathbf{k} - \mathbf{k}'$ vector correlation;

3. OH(A)+Kr/Xe

Reagent preparation and product detection *via* ZQBS techniques (with the use of a narrow-bandwidth laser and a monochromator) to measure the $\mathbf{j} - \mathbf{j}'$ vector correlation and a number of scalar energy-transfer processes.

The experimental and theoretical results for these systems are presented in Chapters 3 to 7, in the order they are listed here.

1.4 Theoretical methods

Inelastic collisions in simple molecule-atom systems are particularly interesting to study because, unlike most chemical or biological systems, it is possible to generate theoretical algorithms that are capable of modelling the experiment in exquisite detail. Indeed, currently available models can be used to run *ab initio* calculations to generate data that are directly comparable to experimentally determined quantities. The dynamics of inelastic collisions can be modelled either classically or quantum mechanically. However, neither method is without its own set of drawbacks, and there has been a concerted effort to develop hybrid, semi-classical trajectory methods that are capable of rectifying the current discrepancies between experiment and theory.

The different theoretical models described and used in this work all have the same general premise: the initial conditions (including the position, angular momentum, and various quanta needed to describe the internal energy of the molecule) are set, the trajectory is run over a PES, and the final conditions are recorded. The differences between the models arise in how the initial and final conditions are set and recorded, respectively, and whether the motion of the trajectory is described classically or quantum mechanically.

1.4.1 Quantum-mechanical calculations

As will be seen in much of this work, the dynamics of molecule-atom collisions are often subject to quantum-mechanical effects that manifest strongly in experimentally observed data. Thus, a quantum-mechanical theoretical model is necessary if we are to fully capture all the different characteristics of simple molecule-atom collisions, and if we are to achieve quantitative agreement between experimental and calculated data. Quantum-mechanical algorithms uniquely account for the wave-particle duality of the collision partners, and model the system as a set of incoming and outgoing wavefunctions that are related by a scattering matrix through time-independent *close-coupled* equations. The elements of the scattering matrix are probability amplitudes for scattering from an initial state, $|i\rangle$, to a final state, $|f\rangle$, at a given energy; the wavefunction itself is composed of different partial waves with different magnitudes of the total angular momentum, J . The superpositions of these partial waves in quantum-mechanical calculations lead to the interference effects that are not seen in classical simulations.

Although they offer the fullest picture of the collision dynamics for a given system, quantum-mechanical simulations are problematic in that, as the complexity of the system increases, the calculations become too computationally demanding to perform. It is also important to bear in mind that quantum-mechanical trajectories are constrained by the Heisenberg Uncertainty Principle [57, 58], meaning that, for example, both the position and momentum of a given trajectory cannot be specified exactly at any one time.

1.4.2 Classical and semi-classical calculations

In a classical treatment, the initial conditions of the trajectory (position, momentum, and (unquantised) internal energy of the molecule) are set, and Newton’s laws of motion are then used to govern the particles’ motion over the PES. In a purely classical framework, the trajectories are completely independent of each other, and there is no consideration of phase, let alone quantum-mechanical interferences. The outcome of a given trajectory will be a consequence of both the initial conditions

and the path it takes across the PES; for example, whether it samples the attractive potential-energy wells, or rebounds off the repulsive wall. It is, therefore, necessary to average over a large number of trajectories (typically, of the order of $10^5 - 10^6$ in this thesis), with many different initial conditions, to generate a complete picture of the collision dynamics.

Classical models are useful because they allow all the different components of the trajectory (position, momentum, time, and energy) to be specified simultaneously, if desired, since there is no classical analogue of the Uncertainty Principle. Moreover, classical models are generally more amenable to increased system complexity, and can be scaled without a considerable increase in computational demands. However, purely quantum-mechanical effects – such as tunnelling, resonances, and interference – are ignored in classical dynamical calculations, and this means that such models are often unable to provide quantitative agreement between theory and experiment. Of course, it is also the case that purely classical methods do not allow for quantisation in either the initial or final conditions of the trajectories, which is particularly inaccurate for low-energy scattering. In contrast, high-energy experimental data should produce better agreement with classical calculations, and this will be discussed in Chapter 3 of this thesis.

One method by which to introduce quantisation into an otherwise classical dynamical model is to employ *quasi*-classical trajectory (QCT) methods. Here, the trajectory begins in a fully quantised state, and is then allowed to propagate classically over the PES. When finished, the classical, continuous momentum and internal energies of the particles are binned to the nearest discrete, quantum level. Many previous studies have found there to be excellent agreement between experimental data and the results of QCT calculations, however, there remain a number of limitations: QCT models cannot account for interference effects (since the trajectory runs classically, and there is no concept of phase); they do not allow for tunnelling through potential-energy barriers; and quantum-mechanically forbidden energy transfers can occur during the classical phase of the trajectory. An example of the latter is seen when OH(A) is excited with one quantum of vibrational energy

at the beginning of a QCT trajectory: whilst the trajectory is being propagated classically, the vibrational energy may ‘leak out’ into other degrees of freedom, leading to unphysical values of the final rotational and/or translational energy of the particles. This issue is addressed further in Chapter 7.

A number of semi-classical methods are also available that attempt to account for quantum-mechanical effects in classical dynamical models. For example, phase-shifts can be assigned to different classical pathways across the PES to mimic quantum-mechanical interference effects. Though, in many cases, these semi-classical shifts provide a decent estimation of quantum-mechanical effects, they still fail to reproduce experimental data quantitatively, and so are not included in the models used in this work.

1.5 Non-adiabatic electronic quenching

According to the Born-Oppenheimer approximation, the large difference in the masses of nuclei and electrons means that the former may be considered stationary on the timescale of electronic motion [59]. This adiabatic separation of the motions of nuclei and electrons means that the collision dynamics of a given system can be thought to take place on a PES that depends solely on the arrangement of the nuclei in space. As such, the gradient of the resultant surface determines the forces acting on atoms and molecules as they collide and/or react. The majority of chemical systems can be described accurately using a *single* PES and, to that end, are said to show *adiabatic behaviour*. However, in some systems, the Born-Oppenheimer approximation can break down under certain circumstances (for example, when particles possess near-infinite velocities at curve-crossings), and this leads to *non-adiabatic dynamics* [41], a phenomenon discussed in greater detail in Chapter 5.

Non-adiabatic dynamics are of crucial importance in many chemical and biological systems. For example, the reaction of alkali-metal atoms with dihalogen molecules is best described by a harpoon mechanism [41, 60, 61]. In these systems, when the metal atom approaches the dihalogen molecule within a certain, critical distance, the transfer of an electron from the metal atom to the dihalogen becomes

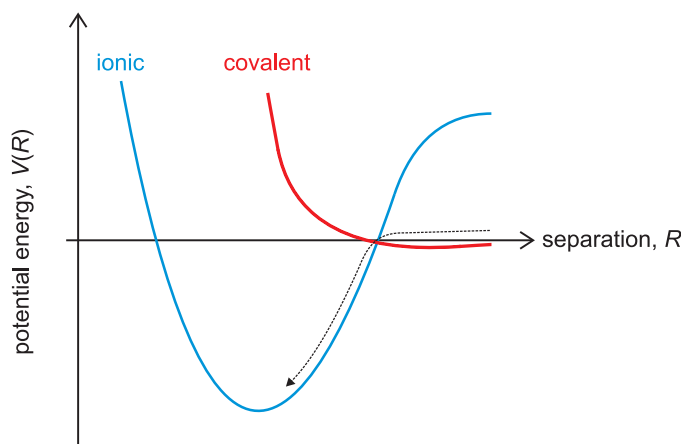


Figure 1.2: Pictorial representation of the the covalent and ionic PESs involved in the harpoon mechanism that governs the reactions of alkali-metal atoms with dihalogen molecules. The potential energy, $V(R)$, is given as a function of the metal-dihalogen separation, R . The black, dotted line shows the path taken by a trajectory that undergoes a non-adiabatic transition from the covalent to the ionic surface.

energetically favourable. This electron-transfer process forms a short-lived X_2^- species (that contains an electron in an anti-bonding orbital) which then dissociates into an X^- ion (and the corresponding X atom). The combination of this nascent X^- species and the M^+ ion produces an MX product molecule. The electron-transfer involves a non-adiabatic transition from a PES of covalent character to one of ionic character at a point of intersection. As can be seen in Figure 1.2, beyond the critical distance for electron transfer, the covalent and ionic PESs are very close in energy (though the covalent surface lies lower in energy than the ionic surface); however, at shorter separations, the Coulombic interaction of the M^+ and X^- ions vastly reduces the energy of the system below that of the covalent surface, leading to the formation of a stable MX product. Further examples of gas-phase, chemical systems in which non-adiabatic effects are important are discussed in Chapter 5.

As noted previously, many biological molecules show significant non-adiabatic dynamics that are often crucial to their physiological function. Examples include, but are by no means limited to:

- **Amino acids** The photostability of a number of amino acids – including those found in the human skin pigmentation protein, melanin [62] – is dependent on the ability to transfer excess energy absorbed on UV excitation to avoid

photo-induced damage. These deactivation pathways often involve several conical intersections and ensure a negligible lifetime for the excited, reactive state of the amino acid [63–65].

- **Photoisomerism in retinal** Many organisms, including humans, make use of the *cis-trans* isomerism of retinal, a rhodopsin protein found in the retina, to optimise vision in both bright and dull environments. The isomerisation process is facilitated by a conical intersection [66].
- **Photoisomerism in green fluorescent proteins** GFPs have been expressed in a wide variety of organisms and have been adapted for multiple uses in molecular and cellular biology and physiology. They have solution-phase fluorescence lifetimes that are strongly dependent on an isomerisation process that accesses a conical intersection between the bright, excited and ground electronic state [67–69].

Previous work on the OH(A)+Kr system has revealed that experimental data are in relatively poor agreement with theoretical calculations run on a single, adiabatic potential energy surface [25]. Studies carried out by Perkins [33] and Herráez Aguilar [70] also confirmed that the agreement is poorer still for the OH(A)+Xe system. In continuation of this work, Chapter 5 of this thesis describes the development of new *quasi*-classical theoretical models that attempt to account for the occurrence of electronic quenching, RET, and the depolarisation of angular momentum when OH(A) molecules collide with heavy rare-gas atoms (Kr and Xe).

In the OH(A)+Kr and OH(A)+Xe systems, quenching of the OH(A) electronic energy is mediated by the non-radiative transfer of population from the higher-energy OH(A)+Kr/Xe PES to the lower-energy OH(X)+Kr/Xe PESs when the triatomic complex exists in near-linear geometries. For those systems in which the OH(A) radical collides with lighter rare-gas atoms, the conical intersection – a point of degeneracy between a higher-energy and a lower-energy PES [71–74] – is located high on the repulsive wall of the upper surface [75]. In contrast, the regions of crossing between the excited-state and ground-state potentials of the

OH+Kr/Xe systems are located in potential-energy minima on the upper surfaces; they are accessible at thermal collision energies and, therefore, are able to act as efficient funnels for the non-radiative transfer of OH(A) population to the ground electronic state [25, 26, 76–78].

Chapters 6 and 7 of this thesis set out the results of various *quasi*-classical models that use electrostatic and rovibrational couplings to model both adiabatic and non-adiabatic OH(A)+Kr/Xe dynamics theoretically [25, 26, 33, 70]. For the first time, these models also give consideration to the effect of including a single quantum of vibrational excitation in the OH(A) radical.

1.6 Outline of this thesis

The initial discussion presented here has outlined the overarching experimental aim of this thesis, namely: to commission, characterise, and optimise a new piece of complex apparatus that is capable of investigating the inelastic scattering of diatomic and simple polyatomic molecules by a range of collision partners. There will be an emphasis throughout on the rigorous comparison of experimental results with quantum-mechanical and *quasi*-classical theoretical data. In addition, the other major aim of this thesis consists of developing accurate computational models of non-adiabatic transitions in OH(A)+Kr and OH(A)+Xe dynamics.

To this end, Chapter 2 will outline the background theory and models that will be used to generate cross-sectional quantities that are directly comparable with experimental data for the NO(X)+Ar system. The chapter will include a detailed discussion of angular momentum, the vectors that define it, and how these vectors are correlated and polarised. There is also a general discussion of the PESs that, together with the kinematics, govern the dynamics of all the different systems investigated in this work. In addition, this chapter will outline the various laboratory techniques that underpin much of the experimental data reported in this thesis, and also includes a detailed account of the data-analysis methods used to extract cross-sectional quantities from experimental images.

Chapter 3 presents experimental and theoretical results for the rotationally inelastic scattering of NO(X)+Ar. This system was studied at a range of collision energies to calibrate the new experimental apparatus, and the data reported here include raw and simulated images and fitted and calculated DCSs. The data collected at 2210 cm^{-1} are of particular interest since this collision energy is significantly higher than any other reported in the literature for the NO(X)+Ar system. In addition, a significant portion of this chapter is spent delimiting the various input parameters needed to simulate accurately the first scattering experiments to be conducted on this apparatus.

Chapter 4 of this thesis discusses experimental and theoretical work carried out in relation to rotationally inelastic scattering of fully quantum-state-selected ND₃($\tilde{X}$)+Ar. This chapter outlines the design and calibration of a hexapole state-selector apparatus that was used to prepare a high-purity beam of molecules in the ND₃($\tilde{X}$, $j_k^\pm = 1_1^-$) state prior to collision. The higher quantum-level resolution of these experimental data means they are amenable to a more rigorous theoretical treatment and, as such, they allow for a thorough appraisal of the accuracy of currently available surfaces and data-analysis algorithms.

Chapter 5 outlines the development of 2D (fixed OH bond length) trajectory surface-hopping *quasi*-classical trajectory (TSH QCT) algorithms that model non-adiabatic transitions in OH(A)+Kr and OH(A)+Xe dynamics. The data reported in Chapter 6 are the result of calculations that included a full set of electrostatic and roto-electronic coupling matrix elements, incorporated into variable-collision-energy algorithms, for the first time. Chapter 7 expands the 2D models to give consideration to the vibrational degree of freedom in OH(A) in a novel theoretical treatment. A discussion of newly calculated PESs for the OH(A, $v = 1$)+Kr system is presented alongside novel theoretical results that are compared with experimental RET data for the first time.

Finally, Chapter 8 summarises the principal findings of this thesis, and offers suggestions regarding the direction to be taken by future experimental and theoretical work.

2

NO(X)+Ar: experimental and theoretical methods

This chapter begins by reviewing the substantial body of work already carried out on the NO(X)+Ar system to give context to the investigation that will be reported in Chapter 3. Following this, the physical properties and spectroscopy of the nitric oxide (NO) radical in its ground electronic state are outlined in detail. This chapter also presents a discussion of the experimental and theoretical methods used in this work to generate and analyse data relating the inelastic scattering of NO(X) by Ar at a range of collision energies. Notably, these data-collection and analysis procedures are also employed to study the inelastic scattering of ND₃($\tilde{X}$) by Ar and, as a result, the content of this chapter is referenced heavily in the remainder of this thesis.

2.1 Review of previous work

The rotationally inelastic scattering of nitric oxide in its open-shell, ground electronic state, NO(X), by a spherically symmetric argon atom, Ar, has been studied extensively. NO(X)+Ar is a particularly interesting diatom-atom system because it lends itself well to experimental investigation at varying levels of quantum-state resolution, and also because it allows for a rigorous comparison of experimental data with high-level theoretical treatments.

This thesis first considers the collision of a primary beam of NO(X) seeded at 10% in Ar with a secondary beam of pure Ar, which gives a collision energy of 469 cm^{-1} . Similar studies investigating NO(X)+Ar inelastic scattering at a collision energy of approximately 500 cm^{-1} are very well documented. Particularly notable publications, which make use of hexapole state-selectors to achieve full quantum-state resolution of $|\text{NO(X)}, \Omega = 0.5, j = 0.5, f\rangle$ prior to collision, include those of Eyles *et al.* (530 cm^{-1}) [22, 79], Brouard *et al.* (532 cm^{-1}) [80], Nichols *et al.* (530 cm^{-1}) [15], van Leuken *et al.* (442 cm^{-1}) [35], and de Lange *et al.* (442 cm^{-1}) [81]. There is also an extensive range of studies performed at similar collision energies that do not make use of hexapole state selection [82–88]. In these latter studies, it is assumed that all the molecules originate in the initial $j = 0.5$ rotational state, and that each of the Λ -doublet levels is equally populated prior to collision.

A sizeable number of studies have also examined the collision of NO(X)+Ar at significantly higher collision energies. Elioﬀ *et al.* [89] considered the scattering of NO(X) by Ar at a collision energy of 1229 cm^{-1} , achieved by colliding a primary beam of NO(X) seeded at 4% in Ar with a secondary beam of Ar seeded at 12% in He. Bontuyan *et al.* [90] investigated NO(X)+Ar scattering at a range of collision energies, the highest of which was 1451 cm^{-1} , achieved by seeding NO(X) at 7% in either H₂, He, or a mixture of He and Ne. Notably, this work did not make use of velocity-map imaging techniques, but rather used time-of-flight ion imaging.

Work by Dixit *et al.* [21] also investigated the same system at 1460 cm^{-1} , with a focus on comparing cross-sectional values for collisions of NO(X, $v = 0$)+Ar with those of NO(X, $v = 5$)+Ar at the same collision energy. Although VMI techniques were used to collect these data, actual images were not presented in reference [21].

Further studies of the same system at relatively high collision energies include those of Suits *et al.* [91] and Lin *et al.* [92], at 1694 cm^{-1} and 1780 cm^{-1} , respectively, however, it should be noted that VMI detection techniques were not employed. It is also important to bear in mind that, for all the studies with a collision energy greater than 500 cm^{-1} that have been presented so far, the NO(X) molecules were not hexapole state-selected.

Interestingly, recent work by van de Meerakker and co-workers involved scattering a Stark-decelerated beam of NO(X) molecules with rare gases to investigate diffraction oscillations in NO(X)+He, Ne, and Ar scattering at collision energies in the range of $450 - 725 \text{ cm}^{-1}$ [38, 93, 94]. More recently, attention has also been paid to NO(X)+Rg scattering at very low collision energies (in the range of $10 - 50 \text{ cm}^{-1}$) to study quantum-mechanical stereodynamics and Fraunhofer scattering [95, 96].

2.2 The coupling of angular momenta

A number of chapters in this thesis concern the dynamics of open-shell, diatomic species that become rotationally excited following collisions with rare-gas atoms. In such systems, a number of different types of angular momenta must be considered to fully describe the dynamics at play. These include:

- $\mathbf{L}$, the electronic orbital angular momentum;
- $\mathbf{S}$, the electronic spin angular momentum;
- $\mathbf{j}$, the total angular momentum;
- $\mathbf{N}$, the total angular momentum excluding electronic spin, *i.e.* $\mathbf{N} = \mathbf{j} - \mathbf{S}$;
and
- $\mathbf{R}$, the nuclear rotational angular momentum, *i.e.* $\mathbf{R} = \mathbf{N} - \mathbf{L} = \mathbf{j} - \mathbf{S} - \mathbf{L}$.

Note that nuclear spin is ignored, since it is unresolved in the experiments that underpin this work.

In papers published in 1926-27 [97–99], Hund outlined idealised situations in which the relative strengths of:

- the electrostatic coupling of $\mathbf{L}$ to the internuclear axis,
- the spin-orbit coupling, and
- the rotational coupling of $\mathbf{L}$ and $\mathbf{S}$ to the total angular momentum, $\mathbf{j}$,

are used to define a given ‘case’. For molecules that are described by a particular case, specific terms of the molecular Hamiltonian will have greater magnitudes than others. Two of these cases, within and between which most diatomic molecules exist, are discussed in the context of this thesis: Hund’s case (a), which relates to the coupling of angular momenta in the ground-state OH(X) and NO(X) molecules, and Hund’s case (b), which best describes the coupling of angular momenta in the excited-state OH(A) molecule. The OH radical, in both its ground and first-excited electronic states, is the focus of Chapters 5-7. Notably, a different coupling scheme is needed to describe the coupling of angular momenta in the symmetric-top ND₃ molecule that is dealt with in Chapter 4.

2.2.1 Hund’s case (a): NO(X)

In low rotational states, the coupling of angular momenta in the NO(X) molecule is best described by Hund’s case (a). Here, $\mathbf{L}$ is coupled strongly and electrostatically to the internuclear axis (the z -axis in the molecule-fixed frame). $\mathbf{S}$ is also coupled relatively strongly to $\mathbf{L}$ by spin-orbit coupling. Both $\mathbf{L}$ and $\mathbf{S}$ have well-defined projections on the internuclear axis, and these are denoted Λ and Σ , respectively. $\mathbf{R}$ exists at a right angle to the internuclear axis. The component of the total electronic angular momentum that lies along the internuclear axis is defined by a vector, $\mathbf{\Omega}$, with magnitude $\Omega = \Lambda + \Sigma$. This vector couples strongly to $\mathbf{R}$ to give the total angular momentum, $\mathbf{j} = \mathbf{\Omega} + \mathbf{R}$, which has a projection of Ω on the internuclear axis. In case (a), the precession of $\mathbf{L}$ and $\mathbf{S}$ around the internuclear axis is assumed to be much faster than the nutation of $\mathbf{\Omega}$ and $\mathbf{R}$ around $\mathbf{j}$ – see Figure 2.1.

The ground-state electronic configuration of NO(X) can be written as

$$1\sigma^2 1\sigma^{*2} 2\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2 1\pi^{*1}.$$

The single, unpaired electron in the π^* orbital of the NO(X) radical gives rise to a projection of $\mathbf{L}$ of $\Lambda = \pm 1$ on the internuclear axis, and a projection of $\mathbf{S}$ of $\Sigma = \pm 0.5$. The coupling of the sum of these angular momenta, $\mathbf{\Omega}$, with

$\mathbf{R}$ results in values of $\bar{\Omega} = 0.5, 1.5$ (where $\bar{\Omega}$ is the absolute value of Ω), which gives rise to two spin-orbit manifolds.

In the limit where Λ -doubling is neglected, there are two contributions to the molecular Hamiltonian that describes the energy of the diatomic molecule: the first arises from nuclear rotation, and the second, from spin-orbit coupling. The latter of these terms quantifies the difference in energy that comes from the electronic spin angular momentum, $\mathbf{S}$, lying either parallel or anti-parallel to the electronic orbital angular momentum, $\mathbf{L}$. The rotational and spin-orbit terms may be separated to produce a factorised Hamiltonian that can be written as [100]:

$$\begin{aligned}\mathcal{H} &= \mathcal{H}_{\text{SO}} + \mathcal{H}_{\text{rot}} \\ &= A(\mathbf{L} \cdot \mathbf{S}) + B(\mathbf{j} - \mathbf{S} - \mathbf{L})^2\end{aligned}\quad (2.1)$$

where $A = 123.13 \text{ cm}^{-1}$ and $B = 1.6961 \text{ cm}^{-1}$ are the spin-orbit and rotational constants, respectively, for NO(X). A knowledge of these constants can be used in conjunction with the above Hamiltonian to calculate the internal energy of a radical in its ground electronic and vibrational states using the following equation [100]:

$$E(j) = B \left[\left(j - \frac{1}{2} \right) \left(j + \frac{3}{2} \right) \pm \frac{X}{2} \right], \quad (2.2)$$

where j is the rotational level, and

$$\begin{aligned}X &= \sqrt{4 \left(j - \frac{1}{2} \right) \left(j + \frac{3}{2} \right) + (Y - 2)^2} \\ &= \sqrt{4 \left(j + \frac{1}{2} \right)^2 + Y(Y - 4)},\end{aligned}\quad (2.3)$$

and

$$Y = \frac{A}{B}. \quad (2.4)$$

The $\pm$ term in Equation (2.2) produces two spin-orbit manifolds that correspond to the $\bar{\Omega} = 0.5$ and $\bar{\Omega} = 1.5$ states. These manifolds form two distinct ladders

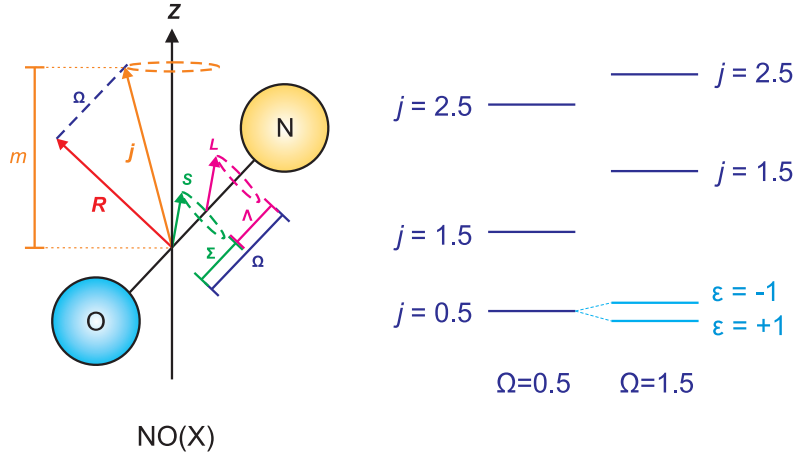


Figure 2.1: The figure on the left-hand side shows the Hund's case (a) angular-momentum coupling scheme for the NO(X) molecule. The coupling of nuclear spin angular momentum is ignored throughout. The figure on the right shows the effect of spin-orbit coupling on rotational energy levels in the NO(X) molecule. The formation of two distinct ladders of rotational energy levels in each of the two spin-orbit manifolds is depicted. Also shown are the two Λ -doublet levels for the $|\Omega = 0.5, j = 0.5\rangle$ state. See text for details.

of rotational energy, as seen in Figure 2.1. For NO(X), the energy of a given rotational level in the $\bar{\Omega} = 0.5$ state is approximately 123 cm^{-1} lower than its counterpart in the $\bar{\Omega} = 1.5$ manifold. The lower and upper manifolds are labelled F_1 and F_2 , respectively.

In the limit of low j , the rotational wavefunctions for each spin-orbit manifold are proportional to the relevant Wigner rotation matrices, and can be written as [100]

$$|j, m, \Omega\rangle = \sqrt{\frac{2j+1}{4\pi}} D_{m\Omega}^{j*}(\phi, \gamma, 0), \quad (2.5)$$

where m is the projection of j onto the space-fixed Z -axis. Importantly, the resultant $|j, m, \bar{\Omega}\rangle$ and $|j, m, -\bar{\Omega}\rangle$ states are not themselves eigenfunctions of the molecular Hamiltonian since they do not possess a well-defined parity with respect to inversion. Thus, within each spin-orbit manifold, the rotational wavefunction is necessarily defined by either a symmetric or an anti-symmetric linear combination of the the two spin-orbit states [100]:

$$|j, m, \Omega, \epsilon\rangle = \sqrt{\frac{1}{2}}(|j, m, \bar{\Omega}\rangle + \epsilon|j, m, -\bar{\Omega}\rangle), \quad (2.6)$$

where $\epsilon = \pm 1$. These $|j, m, \Omega, \epsilon\rangle$ states do have a well-defined parity with respect to inversion, defined as [101]

$$p = (-1)^{j-\epsilon/2}, \quad (2.7)$$

and so are eigenfunctions of the molecular Hamiltonian. The Λ -doublet within a given spin-orbit manifold is then made-up of the pair of symmetric and anti-symmetric states defined by Equation (2.6), and shown in Figure 2.1. Throughout this thesis, the symmetric combination, with $\epsilon = +1$, is referred to as the *e* state, and the anti-symmetric combination, with $\epsilon = -1$, is referred to as the *f* state.

In addition to a symmetry-index label, the Λ -doublet levels can be described with respect to their symmetry of reflection in the plane of nuclear rotation. If the unpaired π^* electron lies in an orbital in the plane of rotation, the state is labelled $\Pi_{A'}$, however, if it lies in an orbital which is perpendicular to this plane, the state is labelled $\Pi_{A''}$.

The splitting of the Λ -doublet is very small, at only 0.01188 cm^{-1} for $j = 0.5$ in the lower $^2\Pi_{\frac{1}{2}}$ state of NO(X) [102]. The splitting can be increased either by the approach of an atom or another molecule (and the resultant reduction in symmetry from $C_{\infty v}$ to C_s), or by excitation of NO to higher j -levels, in which there is mixing with electronically excited states of Σ character. In the limit of Hund's case (a) coupling, the splitting of the Λ -doublet varies linearly with j for the $^2\Pi_{\frac{1}{2}}$ state and as j^3 for $^2\Pi_{\frac{3}{2}}$ [100].

As the value of j increases, Hund's case (a) is no longer a good description of the angular-momentum coupling in NO(X), since $\mathbf{L}$ and $\mathbf{S}$ are no longer strongly coupled to the internuclear axis. Ω ceases to be a good quantum number, so mixing occurs between the two spin-orbit manifolds, and it becomes more accurate to write the respective wavefunctions of NO(X), for example, as [100]:

$$\begin{aligned} |F_1, j, m, \epsilon\rangle &= a|j, m, \bar{\Omega} = 0.5, \epsilon\rangle + b|j, m, \bar{\Omega} = 1.5, \epsilon\rangle, \\ |F_2, j, m, \epsilon\rangle &= a|j, m, \bar{\Omega} = 1.5, \epsilon\rangle - b|j, m, \bar{\Omega} = 0.5, \epsilon\rangle, \end{aligned} \quad (2.8)$$

with the mixing coefficients, a and b , given by

$$\begin{aligned} a &= \sqrt{\frac{X + (Y - 2)}{2X}}, \\ b &= \sqrt{\frac{X - (Y - 2)}{2X}}, \end{aligned} \tag{2.9}$$

and where X and Y are as defined in Equations (2.3) and (2.4). For NO(X) in the highest rotational state that is energetically accessible in the work presented here, $j' = 34.5$, a and b take values of 0.923 and 0.384, respectively, so the Hund's case (a) coupling scheme is approximated throughout [103].

2.3 Experimental methods and design of apparatus

This section outlines the experimental methods and detection schemes used in this thesis to achieve quantum-state-resolved vector correlations for NO(X)+Ar: namely, crossed-molecular beam (CMB) techniques with the application of velocity-map imaging (VMI) and resonance-enhanced multi-photon ionisation (REMPI) detection. These methods, which are used to study the rotationally inelastic scattering of NO(X) by Ar at collision energies in the range $469 - 2210 \text{ cm}^{-1}$, are discussed in detail in this chapter, with an emphasis on the adaption of well-established techniques to generate data for this system of interest.

The experimental data presented in this chapter were all collected using a compact CMB apparatus [104]. This new, compact machine was designed by Dr Scott Seamons. Specific details and dimensions of the rig, and diagrams thereof, can be found in reference [105]. The apparatus was commissioned and characterised by myself at the beginning of this thesis.

Cooling induced by the adiabatic expansion of the gas in the molecular-beam pulse meant it was possible to select molecules in specific electronic, vibrational, and spin-orbit states prior to collision. A small range of rotational states remained populated following the supersonic expansion of the gas pulse. Space constraints meant it was not possible to install a hexapole state-selector of sufficient length to

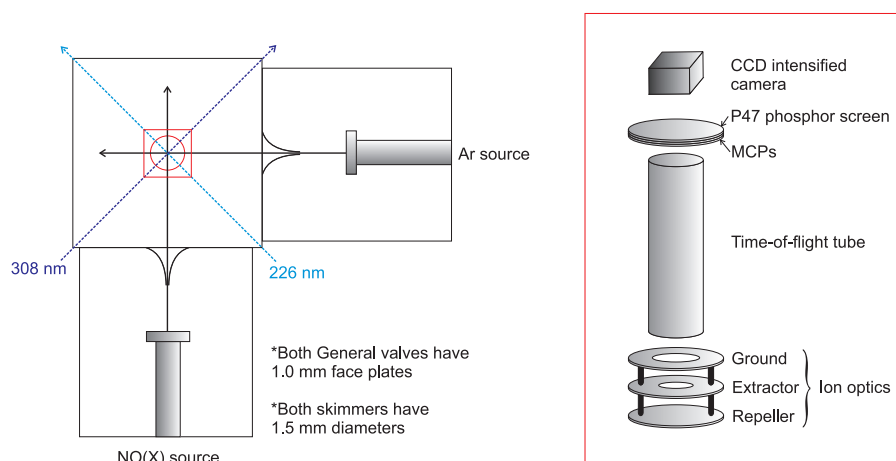


Figure 2.2: Schematic diagram showing the experimental apparatus used to collect data relating to the inelastic scattering of $\text{NO}(\text{X})$ by Ar at variable collision energies. The red box at the centre of the scattering chamber is expanded in the insert figure. Note that the MCPs, phosphor screen, and camera are all positioned above the scattering chamber, parallel to the plane defined by the lasers and molecular beams. The time-of-flight axis is perpendicular to the plane defined by the lasers and molecular beams. See text for further details. The apparatus is not drawn to scale.

achieve Λ -doublet resolution in the initial $\text{NO}(\text{X})$ population. In contrast, the $(1+1')$ REMPI detection scheme employed is selective of the final rotational state and spin-orbit manifold, as well as the final Λ -doublet state. The apparatus used to collect these data is presented in Figure 2.2 and is described in detail in the text that follows.

2.3.1 Rotational temperatures of primary molecular beams

The molecular beams are generated by pulsed General valves, operated at 10 Hz, with a backing pressure of 2 bar. The primary beam contains NO seeded at 10% of the total volume in different carrier gases (Ar, He, and H_2) to aid cooling, discourage cluster formation, and vary the collision energy in the range $469 - 2210 \text{ cm}^{-1}$. The stagnant pressure in the scattering chamber was measured to be $1 \times 10^{-7} \text{ mbar}$. As the gas mixture passes through a 1 mm diameter valve nozzle and expands into a high vacuum, it cools adiabatically to give a reduction in rotational temperature. When seeded in rare gases, the rotational temperature of the $\text{NO}(\text{X})$ beam is reduced to around 10 K; when seeded in hydrogen, the rotational temperature is significantly higher, at around 28 K. These temperatures were determined by comparing experimental $(1+1')$ REMPI scans (shown in Figure 2.3) to the LIFBASE

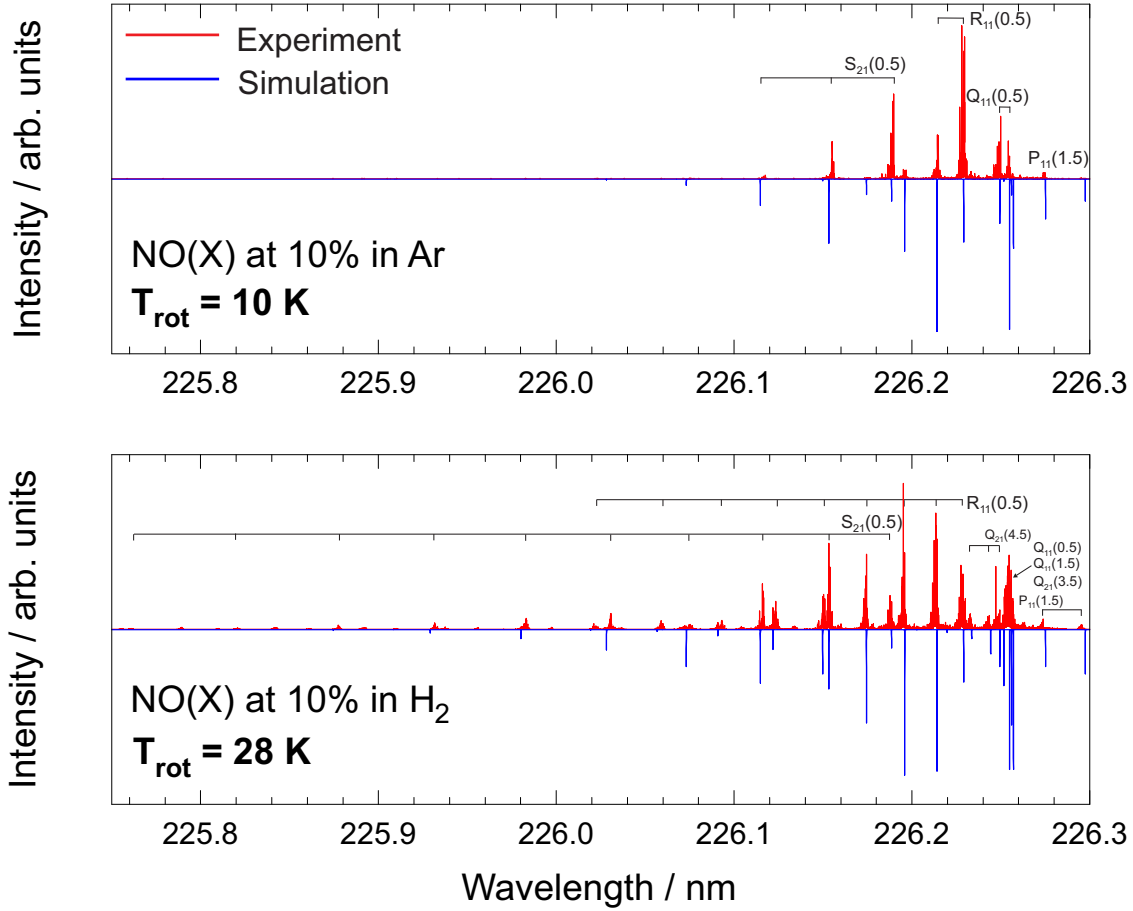


Figure 2.3: $(1+1')$ REMPI scans of the primary molecular beam for different gas mixtures. Experimental spectra were compared to simulations from the LIFBASE spectral database [106] to determine the rotational temperature, T_{rot} . The REMPI scans are overlaid with a selection of spectral branches. Note that not all branches are shown – including labels for overlapping transitions – for the sake of clarity.

spectral database [106]. Note that the use of fluorescence simulation software is appropriate in this instance because the initial excitation of NO(X) in the REMPI detection scheme is a single-photon process.

In the case of a rare-gas seed, collisions between rotationally excited NO(X) molecules and rare-gas atoms induce energy transfer from the former to the latter. The rare-gas atoms act as a heat sink, whereby the internal energy of NO(X) is converted into translational energy of the rare-gas atoms [107]. However, in the case where molecular hydrogen is used as a seed gas, the adiabatic cooling that takes place during the adiabatic expansion is limited by the onset of cluster formation [108]. The exothermic formation of small clusters of hydrogen molecules releases

	rotational-state population / %	
	$T_{\text{rot}} = 10 \text{ K}$	$T_{\text{rot}} = 28 \text{ K}$
$j = 0.5$	16	7
$j = 1.5$	54	28
$j = 2.5$	24	28
$j = 3.5$	16	19
$j = 4.5$	0	12
$j = 5.5$	0	6

Table 2.1: Rotational-state population distributions of the primary molecular beam for two different rotational temperatures, $T_{\text{rot}} = 10 \text{ K}$ and 28 K , achieved by seeding $\text{NO}(\text{X})$ at 10% in Ar and H_2 , respectively.

condensation energy that is then taken up into internal degrees of freedom of the $\text{NO}(\text{X})$ molecules, leading to an increase in the rotational temperature of the beam.

Given that the experiments described in this chapter did not make use of a hexapole state-selector, the rotational-state population distribution of the primary beam is solely determined by how efficiently the beam is adiabatically cooled during the supersonic expansion. Table 2.1 gives the approximate rotational-state population distributions, expressed as a percentage, that were determined from the LIFBASE spectral database for $T_{\text{rot}} = 10 \text{ K}$ and $T_{\text{rot}} = 28 \text{ K}$ [106].

It can be seen in Table 2.1 that, for primary beams in which NO is seeded in rare gases ($T_{\text{rot}} = 10 \text{ K}$), over half of the molecules originate in the $j = 1.5$ state, with evenly populated Λ -doublets levels. Overall, there are significant numbers of molecules in initial rotational levels $j = 0.5 - 3.5$. In contrast, when NO is seeded in H_2 ($T_{\text{rot}} = 28 \text{ K}$), the $j = 1.5$ and $j = 2.5$ states are equally populated, and there are also considerable numbers of NO molecules in the $j = 3.5$ and $j = 4.5$ states (all with evenly populated Λ -doublet levels). These rotational-state distributions have important consequences in terms of how to accurately simulate experimental reality in quantum-mechanical and QCT calculations, and will be discussed further in Section 3.3.4.

Notably, the beams are also passed through a 1.5 mm skimmer, which acts to further select the rotationally coldest and most collinear part. The secondary beam, containing pure Ar, is generated using the same method.

2.3.2 Determination of collision energies

In the first instance, the velocities of the molecular beams were calculated thermodynamically by considering the supersonic expansion of a gas into a vacuum. The velocity of the molecular beam can then be calculated from the thermodynamic limit of the translational energy using the equation [109]

$$|\mathbf{v}| = \sqrt{\frac{2k_{\text{B}}}{m} \left(\frac{\gamma}{\gamma - 1} \right) T}, \quad (2.10)$$

where k_{B} is the Boltzmann constant, m is the mass of the molecule, γ is the ratio of the heat capacity at constant pressure to that at constant volume (C_p/C_v), and T is the temperature. Previous studies have confirmed a valve temperature of around 335 K [110]. A knowledge of the velocities of the primary and secondary beams, which intersect perpendicularly, can be used to calculate their relative velocity (and, hence, the collision energy) by simple Pythagorean geometry. The resultant velocities and energies are given in Table 2.2.

The experimental collision energy can also be determined from the images that are collected (see Figure 2.4). The radius, r , of an image is defined by the velocity of the scattered NO molecules that are detected following collisions with Ar, and is given by

$$r = \frac{1}{p} \times \frac{m_{\text{Ar}}}{(m_{\text{Ar}} + m_{\text{NO}})} \times \sqrt{\frac{2[E_{\text{coll}} - B(j'(j' + 1) - j(j + 1))]}{\mu}}, \quad (2.11)$$

where p is the pixel-to-velocity ratio (determined by the ion optics settings for a given collision energy), m_{X} is the mass of species X, E_{coll} is the total energy available from the collision, B is the rotational constant (in Joules), j and j' are the initial and final rotational states, respectively, and μ is the reduced mass. This fit was applied to the experimental data to generate the collision energies given in the second column of Table 2.2. Note that, unlike in previous studies [15, 22, 80,

Thermodynamic calculations				
System of interest	$v_{\text{pri}} / \text{ms}^{-1}$	$v_{\text{sec}} / \text{ms}^{-1}$	$v_{\text{rel}} / \text{ms}^{-1}$	$E_{\text{coll}} / \text{cm}^{-1}$
NO at 10% in Ar + Ar	609	590	848	515
NO at 10% in He + Ar	1479	590	1592	1816
NO at 10% in H_2 + Ar	2009	590	2094	3141
Experimental images				
System of interest	$v_{\text{pri}} / \text{ms}^{-1}$	$v_{\text{sec}} / \text{ms}^{-1}$	$v_{\text{rel}} / \text{ms}^{-1}$	$E_{\text{coll}} / \text{cm}^{-1}$
NO at 10% in Ar + Ar	554	590	809	469
NO at 10% in He + Ar	1311	590	1437	1480
NO at 10% in H_2 + Ar	1654	590	1756	2210

Table 2.2: Primary-molecular-beam velocities (v_{pri}), secondary-molecular-beam velocities (v_{sec}), relative velocities (v_{rel}), and collision energies for the different $\text{NO}(\text{X}) + \text{Ar}$ scattering experiments investigated in this thesis. The thermodynamic values are calculated as outlined in the text. Collision energies are also calculated from the radius of the experimental images, as given in Equation (2.11), and the velocity of the primary beam is determined retrospectively using the thermodynamic value of $v_{\text{sec}} = 590 \text{ ms}^{-1}$.

110–112], the thermodynamic calculations consistently overestimate the collision energy with respect to that determined from experimental images by as much as 30%. As yet, the reasons for this discrepancy are not well understood, and it is recommended that future work should seek to resolve this. In any case, the experimentally determined energies and molecular-beam velocities are those used in the quantum-mechanical calculations for this thesis.

The extent to which Equation (2.11) can give an accurate reflection of the true collision energy is dependent on the rotational temperature of the molecular beam. In using Equation (2.11), it is assumed that all the NO molecules are in the ground rotational state, $j = 0.5$. As can be seen in the lower plot of Figure 2.3, the most intense transitions in a molecular beam of $\text{NO}(\text{X})$ at 10% in H_2 originate from $j = 1.5$, and, in agreement with the populations reported in Table 2.1, there are significant bands seen in the range $j = 0.5 - 5.5$. However, inclusion of these states in

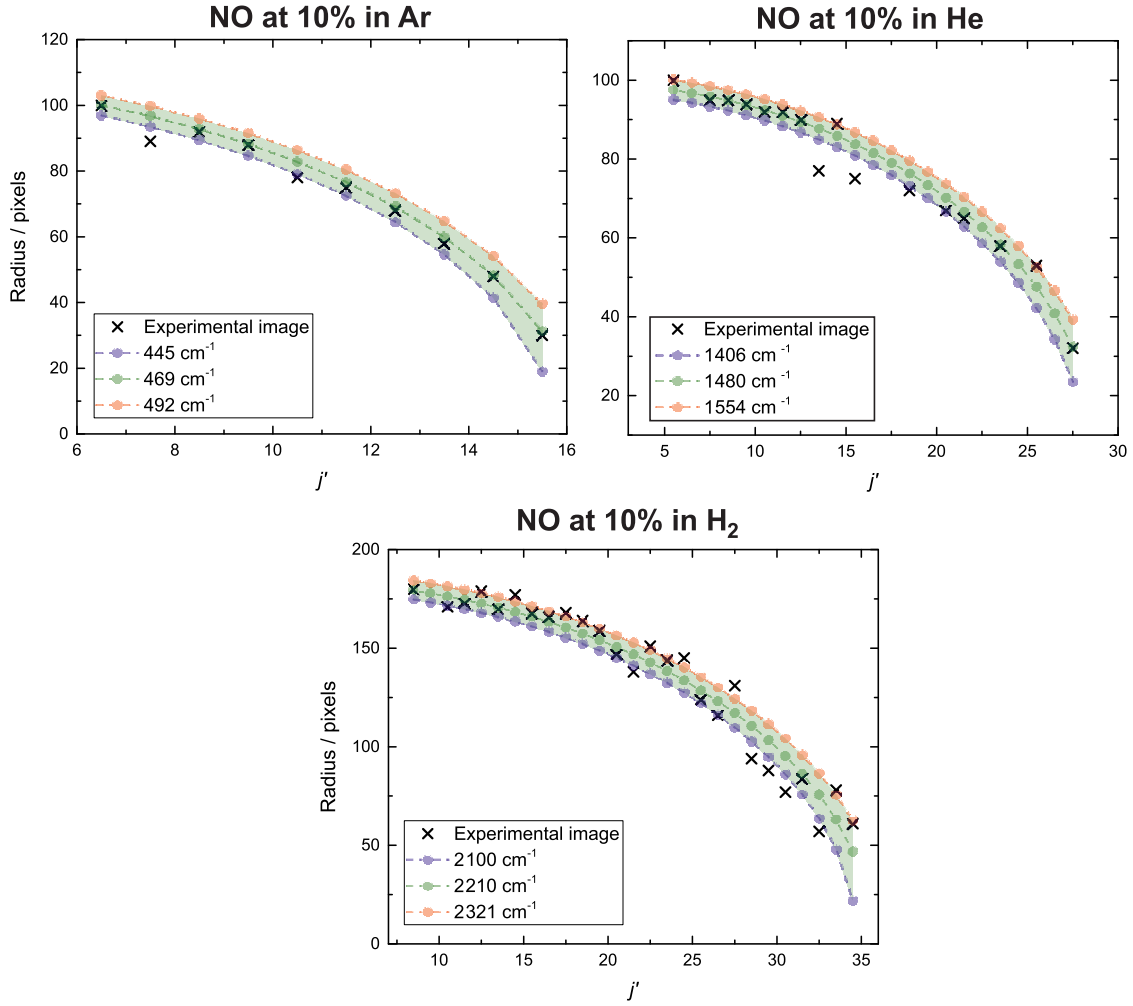


Figure 2.4: Plots of the radii of experimental images against the final rotational state, j' , of the NO(X) molecule after collision with Ar at variable collision energies. The graph titles give the composition of the primary molecular beam (where the proportion of NO is expressed as a percentage of the total volume of the gas mixture) that undergoes collisions with a secondary beam of pure Ar. The collision energy (green line) is determined by fitting a line defined by Equation (2.11) to the experimental data points. The blue and red lines delimit the shaded green area which represents a 5% error margin either side of the predicted value.

Equation (2.11) (by weighting their contributions based on their relative populations in the primary molecular beam at T_{rot}), only causes a 2% reduction in the value of E_{coll} . For this reason, the original value of $E_{\text{coll}} = 2210 \text{ cm}^{-1}$ was used in the quantum-mechanical simulations reported in this chapter. The same treatment was applied for the other two collision energies ($E_{\text{coll}} = 469 \text{ cm}^{-1}$ and $E_{\text{coll}} = 1480 \text{ cm}^{-1}$) investigated, since the primary molecular beams in these experiments show an even narrower rotational-state distribution.

Since the collision energy is fixed for primary and secondary molecular beams with known velocities, the radius of the resultant experimental image is seen to decrease as j' increases. Indeed, the total energy, E , available in the collision system can be expressed as

$$\begin{aligned} E &= E_{\text{coll}} + E_{\text{rot}} + E_{\text{vib}} \\ &= E'_{\text{tr}} + E'_{\text{rot}} + E'_{\text{vib}} - \Delta H(0 \text{ K}), \end{aligned} \quad (2.12)$$

where E_{coll} is the collision energy, E_{rot} and E_{vib} are the rotational and vibrational internal energies before collision, respectively; E'_{tr} , E'_{rot} , and E'_{vib} are the translational, rotational, and vibrational energies after collision, respectively; and $\Delta H(0 \text{ K})$ is the enthalpy of collision at 0 K. For the collisions considered in this thesis, $E_{\text{vib}} = E'_{\text{vib}}$, since $v = v' = 0$, and there is no vibrational excitation in the NO molecule either before or after collision. Therefore, for a fixed collision energy, as the final rotational energy, E'_{rot} , increases, the final translational energy, E'_{tr} , must decrease and, hence, there are smaller radii for the resultant Newton sphere and the velocity-mapped image it produces on the detector [41]. It is also the case that the radius of the image for a particular j' state will increase with collision energy, since more energy is available for translation in the products. If the time-of-flight path of the ions lengthens, the Newton sphere has more time to expand as it travels from the interaction region to the detector, and the image radius will increase as a result. Conversely, if larger voltages are applied to the ion optics, the image becomes smaller, since the ions are focused more intensely onto the detector (see Section 2.3.5).

2.3.3 Vacuum system

As in any CMB experiment, it is very important to maintain a good vacuum in all regions of the apparatus. With the molecular beams turned off, the pressure in the scattering chamber and time-of-flight tube was measured to be around 1×10^{-7} mbar; when both beams were turned on, the pressure rose to approximately 8×10^{-7} mbar. The source chambers for both beams, and the time-of-flight tube (see Figure 2.2), are pumped by turbo pumps (Oerlikon Leybold Vacuum, TURBOVAC

SL80 model), which are backed by rotary pumps. The main scattering chamber is pumped by a larger turbo (Oerlikon Leybold Vacuum, TURBOVAC SL300 model), which is also backed by a rotary pump, to compensate for the larger gas load in this region.

2.3.4 Laser system

The NO(X)+Ar scattering studies discussed in this thesis constitute a two-colour experiment, requiring photons at 226 nm and 308 nm for efficient product detection. To generate light at 226 nm, the frequency-tripled output (355 nm) of a Continuum Surelite III-10 flashlamp-pumped Nd:YAG laser (pulse length: 4 – 6 ns) is used to pump a tunable Lambda Physik LPD 3002 dye laser that contains Coumarin 450 dye in methanol. The fundamental emission is frequency-doubled using a BBO (β -barium borate) crystal to generate light of wavelengths around 226 nm.

To generate light at 308 nm, the frequency-doubled output (532 nm) of another flashlamp-pumped Continuum Surelite III-10 Nd:YAG laser is used to pump a Lambda Physik FL 3002 dye laser that contains Rhodamine 101 dye in methanol. As before, the resultant emission is then frequency-doubled using a BBO crystal to generate light around 308 nm. Both lasers were triggered at 10 Hz.

The bandwidth of the dye laser that produces 226 nm light is 0.36 cm^{-1} [33, 113]. It was also found that the linewidth of the NO(A) $\leftarrow$ NO(X) transition was around 0.40 cm^{-1} . Therefore, it was necessary to scan over a range of wavelengths (of the order of 0.5 cm^{-1}) when recording each image to ensure that the full Doppler profile of the transition was sampled and that there was unbiased detection of the different velocity components within the scattering distribution.

2.3.5 Detection of scattered products

The primary and secondary beams intersect perpendicularly in the middle of the scattering chamber, and are also crossed at 45° by the two lasers, the overlap of which defines the interaction region. The 226 nm light, which is vertically polarised, is unfocused and passes through a 1.5 mm iris. The 308 nm light is

focused just before the interaction region using a lens of focal length 200 mm to increase the density of 308 nm photons here. Assuming that the laser beams have a Gaussian intensity profile [114], the resultant interaction region has dimensions of approximately $1.5 \text{ mm} \times 1.5 \text{ mm} \times 1.5 \text{ mm}$.

Following collisions with Ar atoms, NO molecules in a particular quantum state are scattered onto the surface of a Newton sphere, the radius of which is determined by the internal energy of the scattered products and the collision energy. Within the interaction region, scattered NO molecules are detected state-selectively using a $(1 + 1')$ REMPI scheme. The wavelength of the photon around 226 nm is tuned to selectively excite a final $\text{NO}(\text{X}, \Omega', j', \epsilon')$ state to the electronically excited $\text{NO}(\text{A}^2\Sigma)$ state. The molecule then absorbs another photon at 308 nm and is selectively ionised. Use of a two-colour detection scheme means that the power of the 226 nm laser can be kept low to avoid saturating the transition.

In the experiments carried out in this thesis, different spectroscopic branches at around 226 nm are used to detect $\text{NO}(\text{X})$ molecules scattered into different $|\Omega', j', \epsilon'\rangle$ states. In the following notation, [115]

$$\Delta j_{f_{\Sigma} F_{\Pi}}(j'), \quad (2.13)$$

$f_{\Sigma} = 1, 2$ corresponds to the $j^{\star} = 1.5$ and $j^{\star} = 0.5$ spin-rotation levels of the $\text{NO}(\text{A})$ state, respectively; $F_{\Pi} = 1, 2$ refers to excitation from the $\Omega' = 0.5$ and $\Omega' = 1.5$ spin-orbit manifolds of $\text{NO}(\text{X})$, respectively; and Δj , the change in the value of the rotational quantum number, is assigned the notation $\Delta j = \text{P, Q, R}$ for $\Delta j = -1, 0, +1$, respectively. The detection branches used are:

- overlapping $\text{Q}_{21} + \text{R}_{11}$ branches for $|\Omega' = 0.5, j', e\rangle$;
- overlapping $\text{Q}_{11} + \text{P}_{21}$ branches for $|\Omega' = 0.5, j', f\rangle$;
- overlapping $\text{Q}_{22} + \text{R}_{12}$ branches for $|\Omega' = 1.5, j', e\rangle$;
- overlapping $\text{Q}_{12} + \text{P}_{22}$ branches for $|\Omega' = 1.5, j', f\rangle$.

To generate a single experimental image, batches of 2×10^3 or 2.5×10^3 laser shots were recorded at a time for spin-orbit-conserving and spin-orbit-changing collisions, respectively. The secondary Ar beam was turned off on alternate sets to allow for background subtraction of unscattered NO signal from the primary beam, and to reduce the impact of experimental drift. Images were then produced by summing across a total of 2×10^4 laser shots for spin-orbit-conserving collisions, and 3×10^4 shots for spin-orbit-changing collisions.

The Newton sphere of NO^+ ions was velocity mapped [45, 116] onto a position-sensitive detector. All ions that possessed the same velocity component in the plane defined by the molecular beams (which is parallel to the detector) were mapped onto the same point on the detector, regardless of their initial position. VMI techniques are thus particularly useful because they remove the blurring effects which would otherwise arise from the distribution of spatial coordinates amongst products that share the same velocity. A set of ion optics (see Figure 2.2) acted in much the same way as an optical lens to accelerate the ionised products down a time-of-flight tube using an electric field gradient. The length of the tube affected the size of the image as the Newton sphere expanded over the course of its journey. For the data recorded at 469 cm^{-1} , the apparatus was fitted with a 200 mm time-of-flight tube between the scattering chamber and the detector. However, for the two sets of data collected at higher collision energies, the time-of-flight tube was increased in length by 500 mm to increase experimental resolution. Typical voltages applied to the ion optics were 1200 V on the repeller and 780 V on the extractor. Note that, for the experiments performed at the highest collision energy (2210 cm^{-1}), the voltages on the ion optics had to be increased to 1800 V on the repeller and 1180 V on the extractor so that the images for low j' could fit on the detector. Note also that, in the first instance, the velocity resolution of the ion optics, time-of-flight, and detector apparatus was determined by a series of relatively simple, one-colour experiments that investigated the photodissociation of the NO_2 , OCS , and O_2 molecules. Details of these experiments can be found in reference [105].

The detector used in this thesis (manufacturer: Photonis USA Inc.; model number: APD 2 PS 40/32/25/8 I 40:1 NR AU 6" FM IPB P47) consists of three micro-channel plates (MCPs) and a P47 phosphor screen. Typically, the front MCP was grounded, and voltages in the range of 800 – 900 V and 1600 – 1800 V were applied to the middle and back MCPs, respectively, and 4600 – 4800 V were applied to the phosphor screen. Note that the voltages were always varied such that the ratio of middle MCP : back MCP : phosphor screen was always $x : 2x : (2x + 3000)$.

The MCPs are 40 mm in diameter, and contain around 1×10^6 channels, each of which is 25 μm in diameter. When an ion strikes any given channel on the front face of the MCP, it produces a cascade of electrons that propagates through the stack of MCPs, and the signal is amplified accordingly. The ejected electrons then hit the phosphor screen and generate a flash of light that is recorded by a gated, intensified, charge-coupled device (CCD) camera and relayed to a desktop computer for data analysis.

2.4 Potential energy surfaces

The potential energy surface (PES) quantifies the potential energy of a system as a function of the nuclear coordinates, and is crucial to understanding the dynamics of a given molecule-atom collision. Each point on the surface correlates to a given nuclear geometry in a particular electronic state, however, it is important to bear in mind that, for a given nuclear geometry, it is possible for the nuclei to pertain to several different PESs, each of which corresponds to a given electronic state.

If the potential energy of a system is known, then the forces acting on the particles therein can be determined from:

$$\begin{aligned} \mathbf{F} &= -\nabla V \\ &= -\left(\frac{\partial V}{\partial r_1} + \frac{\partial V}{\partial r_2} + \frac{\partial V}{\partial r_3} + \dots\right) \end{aligned} \quad (2.14)$$

where V is the potential-energy function, ∇ is the gradient operator, and r_x are the various coordinates needed to define the geometry of the system. Thus, it can be seen that the gradient of the PES quantifies the forces acting on the nuclei present

and, as a result, determines their relative motion. The PES, together with the relevant masses and kinematics, therefore completely defines the collision/reaction dynamics for a system with a given set of initial conditions.

2.4.1 PESs for NO(X)+Ar

The collisions of NO(X) molecules with atomic Ar can be described using two non-degenerate PESs [117]. The labels used to differentiate these surfaces depend on the reflection symmetry of the π^* orbital in which the unpaired electron of NO(X) is found with respect to the triatomic plane formed by the approach of Ar towards NO(X). If the π^* orbital containing the electron lies in the triatomic plane, the PES has A' reflection symmetry; if the orbital lies perpendicular to the plane, then the PES has A'' symmetry. Of course, as discussed previously, it is important to remember that the A' and A'' PESs are not the same as the $\Pi_{A'}$ and $\Pi_{A''}$ Λ -doublets.

In reality, the collision of NO(X) with Ar takes place on both the $V_{A'}$ and $V_{A''}$ PESs simultaneously [117]. To this end, it is often more convenient to consider linear combinations of the individual surfaces, defined as [118]

$$\begin{aligned} V_{\text{sum}} &= \frac{1}{2}[V_{A''} + V_{A'}] = \sum_l V_{l0}(R)d_{00}^l(\gamma) \\ V_{\text{diff}} &= \frac{1}{2}[V_{A''} - V_{A'}] = \sum_l V_{l2}(R)d_{20}^l(\gamma) \end{aligned} \quad (2.15)$$

where $d_{\lambda 0}^l(\gamma)$ are reduced Wigner rotation matrix elements and $V_{l\gamma}(R)$ are the radially dependent expansion coefficients [119]. In the limit where the angular-momentum coupling is well described by Hund's case (a), spin-orbit-conserving ($^2\Pi_{\frac{1}{2}} \leftarrow ^2\Pi_{\frac{1}{2}}$) collisions are said to take place on the $V_{\text{sum}}(R, \gamma)$ PES. In contrast, spin-orbit-changing ($^2\Pi_{\frac{3}{2}} \leftarrow ^2\Pi_{\frac{1}{2}}$) collisions are governed by the $V_{\text{diff}}(R, \gamma)$ PES [117, 118].

Figure 2.5 shows PESs for the NO(X)+Ar system as functions of the separation of the rare-gas atom and the centre of mass of the NO radical, R , and the angle, γ , between the vector $\mathbf{R}$ and the NO bond axis; and also as functions of the Cartesian coordinates, X and Y , where $X = R \cos \theta$ and $Y = R \sin \theta$ [120]. Note that $\gamma = 0^\circ$ corresponds to the O-N-Ar geometry and $\gamma = 180^\circ$ corresponds to

N-O-Ar. In calculating the PESs, the bond length of the NO(X) molecule is fixed at its equilibrium value of 1.15 Å [121], and vibrational motion is ignored.

The global minimum of the surface of A' symmetry is found at $R = 3.60$ Å and $\gamma = 95^\circ$, with a well depth of 116 cm^{-1} ; the global minimum of the surface of A'' symmetry is located at $R = 3.65$ Å and $\gamma = 75^\circ$, with a well depth of 111 cm^{-1} [110]. As such, the depths of the attractive potential-energy wells are exceeded by the magnitude of the collision energies investigated in this work ($469 - 2210 \text{ cm}^{-1}$), meaning NO(X)+Ar collisions will tend to sample the repulsive regions of the PESs, especially as the collision energy increases.

The $V_{\text{sum}}(R, \gamma)$ PES is weakly attractive at large R , and contains three minima: two local, shallow minima at $\gamma = 0^\circ$ and $\gamma = 180^\circ$, and a global minimum at $\gamma = 90^\circ$, when the NO-Ar system has a T-shaped geometry. The PES becomes strongly repulsive at low R . The $V_{\text{diff}}(R, \gamma)$ PES is strongly attractive, with two deep wells in near co-linear geometries, and a smaller region of repulsion at $\gamma = 90^\circ$. In general, the $V_{\text{diff}}(R, \gamma)$ potential is much shorter range than $V_{\text{sum}}(R, \gamma)$, and is also more anisotropic. Notably, since $V_{A'}$ and $V_{A''}$ lie very close in energy, calculating the $V_{\text{diff}}(R, \gamma)$ potential will exaggerate any differences between the two combined PESs, whereas calculating $V_{\text{sum}}(R, \gamma)$ will diminish them. This makes the determination of the $V_{\text{diff}}(R, \gamma)$ potential much more challenging. However, it also means that the $V_{\text{diff}}(R, \gamma)$ potential can be used as a more rigorous test of the accuracy of the $V_{A'}$ and $V_{A''}$ surfaces by assessing the agreement of theoretical calculations run on $V_{\text{diff}}(R, \gamma)$ with experimental data.

Notably, both the $V_{\text{sum}}(X, Y)$ and $V_{\text{diff}}(X, Y)$ PESs are slightly asymmetric with respect to reflection in the $X = 0$ plane due to the heteronuclear nature of the NO molecule. The potentials are also slightly longer range towards negative X .

2.5 Quantum-mechanical calculations

In order to test their accuracy, the PESs are used in conjunction with the HIBRIDON suite of codes [122] to run quantum-mechanical calculations for the NO(X)+Ar

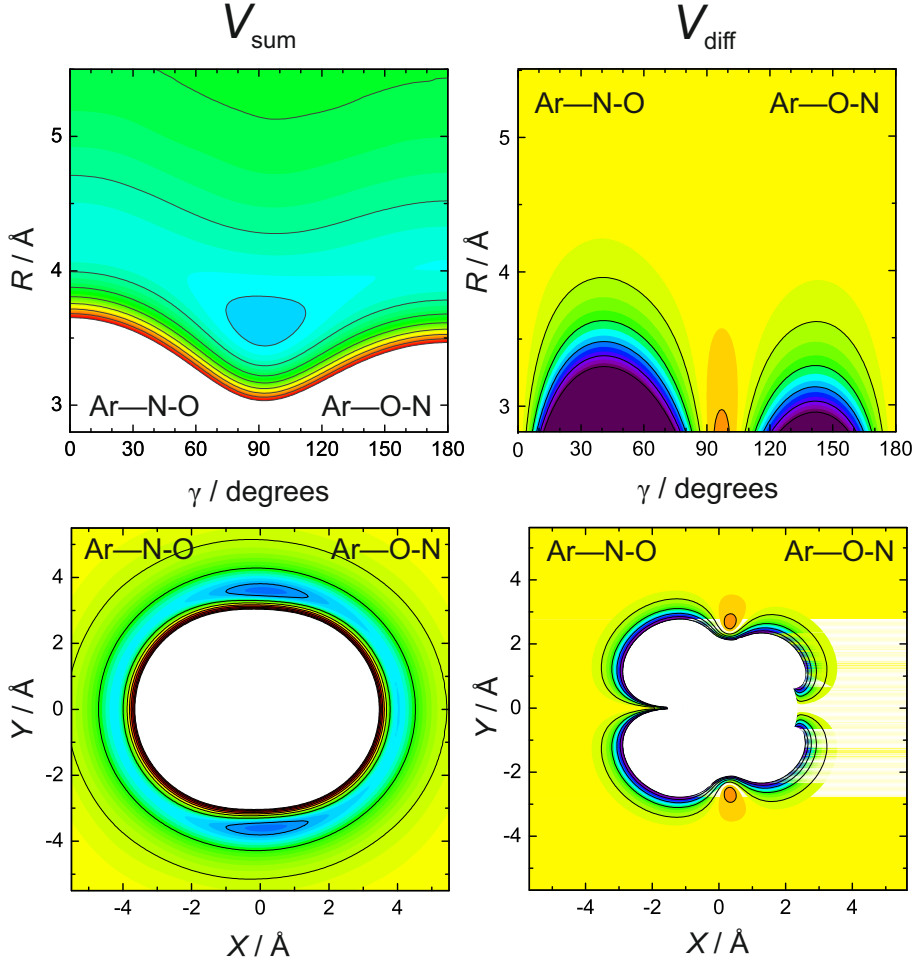


Figure 2.5: $V_{\text{sum}}(R, \gamma)$ and $V_{\text{diff}}(R, \gamma)$ PESs for the NO(X)+Ar system in two different coordinate bases [120] – see text for details. The black lines on the PESs represent contours separated by 40 cm^{-1} , and a potential energy of negligible magnitude is represented by yellow shading.

system. This theoretical treatment is based on full quantum-mechanical, close-coupling, scattering calculations, the output of which is the state-to-state scattering matrix, resolved in all observable angles, that relates the incoming and outgoing wavefunctions. HIBRIDON uses a hybrid operator comprising the Airy propagator [122, 123] in the long-range region and the Log-Derivative propagator [124] in the short-range region.

The plane wave representing the incoming molecule is written as a series of partial waves with an increasing total-angular-momentum quantum number, J . The total number of partial waves, J_{tot} , is chosen such that the opacity function

$P_{if}(J)$ – which gives the probability of a transition from initial state, $|\psi_i\rangle$, to a final state, $|\psi_f\rangle$, as a function of J – converges at a value of $J < J_{\text{tot}}$. The scattering matrix is then defined such that

$$\hat{S}|\Psi_{\text{in}}^J\rangle = |\Psi_{\text{out}}^J\rangle, \quad (2.16)$$

where $\hat{S}$ is the scattering operator. For pure, coherent states, the incoming and outgoing partial waves can be written as a linear combination of the ro-vibrational eigenfunctions of the system [125],

$$|\Psi_{\text{in}}^J\rangle = \sum_i c_i |\psi_i^J\rangle, \quad (2.17)$$

$$|\Psi_{\text{out}}^J\rangle = \sum_f c_f |\psi_f^J\rangle, \quad (2.18)$$

and the wavefunctions are normalised such that $\sum_i |c_i|^2 = 1$ and $\sum_f |c_f|^2 = 1$.

However, when calculating experimentally observable properties, it can be more useful to consider the transition operator, $\hat{T}$, defined such that $\hat{T} = 1 - \hat{S}$. The transition operator can then be applied to the incoming wavefunction such that [101]

$$\begin{aligned} \hat{T}|\Psi_{\text{in}}^J\rangle &= (1 - \hat{S})|\Psi_{\text{in}}^J\rangle \\ &= |\Psi_{\text{in}}^J\rangle - |\Psi_{\text{out}}^J\rangle. \end{aligned} \quad (2.19)$$

The square modulus of the transition matrix element, $|T_{f \leftarrow i}^J|^2$, then gives the quantum-mechanical opacity function, $P_{f \leftarrow i}(J)$, for a given value of J [126]. The $\hat{S}$ -matrix elements are calculated for each value of J , and are then summed over all values of J to recover an experimentally observable quantity.

The calculations presented in the subsequent chapter employed the Log-Derivative propagator [122, 124] between 4.5 and 15 Bohr, and the Airy propagator [122, 123] up to 45 Bohr. Calculations run at 469 cm⁻¹, 1480 cm⁻¹, and 2210 cm⁻¹ used rotational bases for NO(X) up to, and including, $j' = 20.5$, 27.5, and 34.5, respectively, and partial waves up to $J = 160$, 400, and 500, respectively, to ensure convergence. The $V_{\text{sum}}(R, \gamma)$ and $V_{\text{diff}}(R, \gamma)$ potential energy surfaces used for NO(X)+Ar were those of Alexander *et al.* [120].

2.6 Integral and differential cross-sections

As mentioned previously, the accuracy of the PESs used to run theoretical calculations can be assessed by comparing the data they generate with experimental values. To this end, experimentally observable quantities must be extracted from the quantum-mechanical data produced by the HIBRIDON suite of codes.

2.6.1 Integral cross-sections

The integral cross-section can be thought of as the effective area within which an incoming atom must collide with a molecule if it is to scatter the molecule from an initial state, i , to a final state, f .

As discussed in Section 2.5, the quantum-mechanical opacity function, $P_{f \leftarrow i}(J)$, is given by [125]

$$P_{f \leftarrow i}(J) = |T_{f \leftarrow i}^J|^2. \quad (2.20)$$

where $|T_{f \leftarrow i}^J|$ is the transition matrix element, a function of the total-angular-momentum quantum number, J . The integral cross-section is then calculated as [125, 126]

$$\begin{aligned} \sigma_{f \leftarrow i} &= \frac{\pi}{k^2} \sum_{J=0}^{J_{\text{tot}}} \frac{2J+1}{2j+1} [2\min(J, j) + 1] P_{f \leftarrow i}(J) \\ &= \frac{\pi}{k^2} \sum_J \frac{2J+1}{2j+1} [2\min(J, j) + 1] |T_{f \leftarrow i}^J|^2, \end{aligned} \quad (2.21)$$

where $k = p/\hbar$ is the initial wavevector, and j is the rotational-angular-momentum quantum number for the molecule. As mentioned previously, the value of J_{tot} is set such that the magnitude of $P_{f \leftarrow i}(J)$ falls to zero at a value of $J < J_{\text{tot}}$.

2.6.2 Differential cross-sections

The differential cross-section (DCS) quantifies scattering into a conical solid angle, $d\omega = \sin\theta d\theta d\phi$, such that [125]

$$\frac{d\sigma}{d\omega} = \frac{1}{4\pi} \frac{1}{\sin\theta} \frac{d^2\sigma}{d\theta d\phi}. \quad (2.22)$$

Thus, it can also be shown that [125]

$$\sigma_{f \leftarrow i} = \int_0^{2\pi} \int_0^\pi \frac{d\sigma}{d\omega} \sin \theta d\theta d\phi \quad (2.23)$$

returns the integral cross-section by integrating over the surface of the scattering sphere.

Since the molecular scattering is symmetrical about the initial relative velocity vector, $\mathbf{k}$, the DCS shows no dependence on the azimuthal angle, ϕ , and is instead only a function of the scattering angle, θ . To determine the quantum-mechanical DCS, it is useful to calculate the scattering amplitude of a particular $f \leftarrow i$ transition, according to [126]

$$f_{f \leftarrow i}(\theta) = \frac{1}{2ik} \sum_J \frac{2J+1}{2j+1} [2\min(J, j) + 1] P_{f \leftarrow i}(J)(\cos \theta) T_{f \leftarrow i}^J. \quad (2.24)$$

The DCS is then calculated from the scattering amplitude using the equation [127]:

$$\begin{aligned} \frac{d\sigma}{d\omega_{f \leftarrow i}} &= |f_{f \leftarrow i}(\theta)|^2 \\ &= \frac{1}{4k^2} \sum_J \sum_{J'} \frac{2J+1}{2j+1} \frac{2J'+1}{2j+1} [2\min(J, j) + 1] \\ &\quad \times [2\min(J', j) + 1] T_{f \leftarrow i}^J T_{f \leftarrow i}^{J'*} P_{f \leftarrow i}(J)(\cos \theta) P_{f \leftarrow i}(J')(\cos \theta). \end{aligned} \quad (2.25)$$

Notably, individual $\hat{S}$ -matrix elements that correspond to individual partial waves are totally independent of each other. However, the double summation present in Equation (2.25) induces a number of cross-terms that contain the product of $\hat{T}$ -matrix elements with different values of J . This leads to the possibility of interference between different partial waves.

2.6.3 Polarisation-dependent differential cross-sections

In the experiments carried out on the NO(X)+Ar system, the use of vertically polarised 226 nm laser light means that the angular distribution of scattering intensity shows considerable dependence on the polarisation of the final rotational angular momentum of the NO(X) radical. The rotational angular momentum is said to be

polarised [61, 128–130] because the $\mathbf{j}'$ vector distribution is anisotropic with respect to the scattering plane (defined by the crossed molecular beams). The polarisation-dependence of the DCS is defined by the three-vector $\mathbf{k} - \mathbf{k}' - \mathbf{j}'$ correlation.

In a classical description, the distribution of $\mathbf{j}'$ vectors is said to be *oriented* if a particular *sense* of rotation about a reference axis is preferred; the distribution is said to be *aligned* if there is no preference for the sense of rotation, but there is a preferred *plane* of rotation. In a quantum-mechanical picture, the quantum

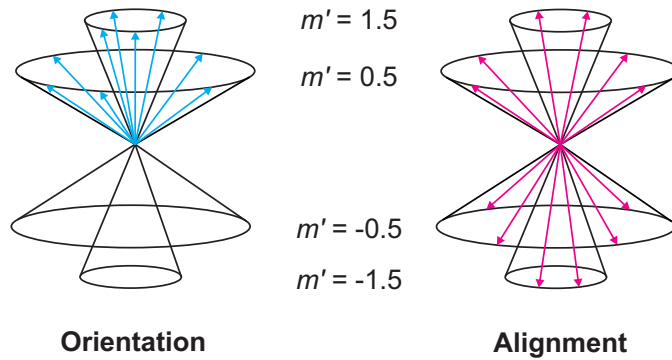


Figure 2.6: Quantum-mechanical depiction of oriented and aligned rotational-angular-momentum distributions.

number, m' , referring to the projection of $\mathbf{j}'$ on a reference axis, is quantised. As such, the polarisation of $\mathbf{j}'$ is achieved when there are unequal populations of m' states. If there is a preference for either positive or negative values of m' , then the distribution is said to be *oriented*; if there is no overall preference for either positive or negative m' , but the distribution in $|m'|$ is unequal, then the distribution is said to be *aligned*. Quantum-mechanical depictions of purely oriented and aligned rotational-angular-momentum distributions are shown in Figure 2.6.

The scattering frame [131] that is used in this work to describe the polarisation of rotational angular momentum is shown in Figure 2.7. The angle θ defines the two-vector correlation of the initial and final relative velocity vectors, $\mathbf{k} - \mathbf{k}'$. As shown on the right of the figure, the direction of the final rotational-angular-momentum vector, $\mathbf{j}'$, is defined fully by two angles: $\theta_{j'}$ and $\phi_{j'}$. In the scattering frame, the initial relative velocity vector, $\mathbf{k}$, is parallel to the principal z -axis. Since the particle is always scattered into the $+xz$ -plane, the direction of the x -axis is

determined by the final relative velocity vector, $\mathbf{k}'$. The direction of the y -axis is then chosen to complete a right-handed set of axes.

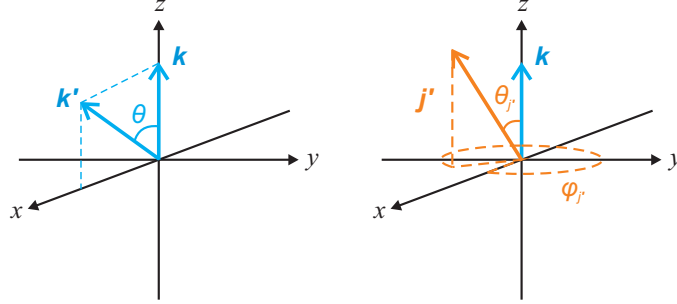


Figure 2.7: The scattering frame in which rotational-angular-momentum polarisation is defined. See text for details.

2.6.4 Quantum-mechanical j' -PDDCSs

In a quantum-mechanical treatment, the wavefunction can be written as a linear combination of $|jm\rangle$ states, such that

$$|\Psi\rangle = \sum_{m=-j}^j c_m |jm\rangle, \quad (2.26)$$

where the density operator can be written as [131, 132]

$$\hat{\rho} = \sum_{m_1, m_2} c_{m_1} c_{m_2}^* |jm_1\rangle \langle jm_2|. \quad (2.27)$$

The individual density matrix elements are, therefore, given by [41, 132, 133]

$$\begin{aligned} \langle jm|\hat{\rho}|jm'\rangle &= \sum_{m_1, m_2} c_{m_1} c_{m_2}^* \langle jm|jm_1\rangle \langle jm_2|jm'\rangle \\ &= c_m c_{m'}^*. \end{aligned} \quad (2.28)$$

It should be noted that, here, the m and m' states do not represent the pre- and post-collision values of the projection quantum number; rather, they are simply used to denote different values of m .

The diagonal elements of the density matrix, for which $m = m'$, describe the population of each $|jm\rangle$ state. The off-diagonal elements define the coherence between different $|jm\rangle$ and $|jm'\rangle$ states. Clebsch Gordan coefficients can then

be used to express the elements of the density matrix. In the case of pure, definite j states [131, 132],

$$\langle jm_1 | \hat{\rho}(\cos \theta) | jm_2 \rangle = \frac{1}{2j+1} \sum_{k=0}^{2j} \sum_{q=-k}^k (2k+1) \left(\frac{2\pi}{\sigma} \frac{d\sigma_q^{(k)}}{d\omega} \right) \langle jm_1, kq | jm_2 \rangle, \quad (2.29)$$

where $\hat{\rho}(\cos \theta)$ is the scattering-angle-resolved density operator, k is the order and q the rank, and $\frac{d\sigma_q^{(k)}}{d\omega}$ are related to the normalised j' -PDDCSs, $n_q^{(k)}(\theta)$, by [131, 132]

$$n_q^{(k)}(\theta) = \frac{2\pi}{\sigma} \frac{d\sigma_q^{(k)}}{d\omega}(\theta). \quad (2.30)$$

Thus, it can be seen that the trace of the density matrix is equal to the probability of being in a particular j' state after scattering through an angle, θ , regardless of the polarisation of the $\mathbf{j}'$ vector. The scattering amplitudes determined by Equation (2.24) are then used to calculate the normalised j' -PDDCSs for transitions from a well-defined $|jm\Omega\epsilon\rangle$ state *via* [131, 132]

$$n_q^{(k)}(\theta) = \frac{2\pi}{\sigma} \frac{1}{4k^2} \frac{1}{2j+1} \sum_{m, m'_1, m'_2} f_{j'm'_1\Omega'\epsilon' \leftarrow jm\Omega\epsilon}(\theta) f_{j'm'_2\Omega'\epsilon' \leftarrow jm\Omega\epsilon}^*(\theta) \langle j'm'_1, kq | j'm'_2 \rangle. \quad (2.31)$$

The complex renormalised j' -PDDCSs, $\rho_q^{(k)}(\theta)$, are given by [131, 132]

$$\rho_q^{(k)}(\theta) = \frac{n_q^{(k)}(\theta)}{n_0^{\{0\}}(\theta)}, \quad (2.32)$$

where $n_0^{\{0\}}(\theta) = \frac{2\pi}{\sigma} \frac{d\sigma}{d\omega}$ is the (real) product angular distribution. The real j' -PDDCSs, $\rho_{q\pm}^{\{k\}}(\theta)$, are then calculated from their complex counterparts *via* the Hertel-Stoll normalisation [134]:

$$\begin{aligned} \rho_0^{\{k\}}(\theta) &= \rho_0^{(k)}(\theta); \\ \rho_{q+}^{\{k\}}(\theta) &= \frac{1}{\sqrt{2}} \left[(-1)^q \rho_{+q}^{(k)}(\theta) + \rho_{-q}^{(k)}(\theta) \right], \quad 1 \leq q \leq k; \\ \rho_{q-}^{\{k\}}(\theta) &= \frac{1}{i\sqrt{2}} \left[(-1)^q \rho_{+q}^{(k)}(\theta) - \rho_{-q}^{(k)}(\theta) \right], \quad 1 \leq q \leq k. \end{aligned} \quad (2.33)$$

In these equations, $k = 1$ describes the orientation of rotational angular momentum and $k = 2$ describes alignment. For the experiments described in this thesis,

which use vertically polarised laser light, the $\rho_0^{\{1\}}(\theta)$, $\rho_{1+}^{\{1\}}(\theta)$, $\rho_{1-}^{\{2\}}(\theta)$, and $\rho_{2-}^{\{2\}}(\theta)$ moments are all zero [112, 131, 135]. The $\rho_0^{\{2\}}(\theta)$, $\rho_{1+}^{\{2\}}(\theta)$, and $\rho_{2+}^{\{2\}}(\theta)$ moments specify the alignment of $\mathbf{j}'$ along the z , $x+z$, and y axes, respectively. $\rho_{1-}^{\{1\}}(\theta)$ is the only non-zero orientation moment, and is defined along the y -axis, but it is not considered any further in this thesis.

2.6.5 Averaging over initial Λ -doublet levels

As discussed previously, the NO(X)+Ar scattering experiments presented in this thesis did not make use of a hexapole state-selector. Therefore, the NO(X) molecules were not resolved into their initial Λ -doublet levels and, because they are almost degenerate in energy, the e and f states were said to be equally populated. In contrast, the detection method used to image scattered products did allow for final Λ -doublet-level resolution.

The theoretical calculations carried out using the HIBRIDON suite of codes are fully resolved in both initial and final Λ -doublet levels. Therefore, it is necessary to average over the two renormalised j' -PDDCSs that correspond to transitions originating in each of the initial e/f states and terminating in a common final e/f state. The following steps outline how the averaged, real, renormalised j' -PDDCSs are determined from the e/f initial Λ -doublet-resolved j' -PDDCSs.

Firstly, the product angular distributions for transitions originating in each of the e/f Λ -doublets are averaged *via*

$$n_0^{\{0\}}(\theta)_{\text{avg}} = \frac{1}{2} \times \left[n_0^{\{0\}}(\theta)_e + n_0^{\{0\}}(\theta)_f \right]. \quad (2.34)$$

The real, renormalised j' -PDDCSs for each initial state are then unnormalised to generate the real, normalised j' -PDDCSs by

$$\begin{aligned} n_{q\pm}^{(k)}(\theta)_{e/f} &= \rho_{q\pm}^{\{k\}}(\theta)_{e/f} \times n_0^{\{0\}}(\theta)_{e/f} \\ &= \frac{n_{q\pm}^{\{k\}}(\theta)_{e/f}}{n_0^{\{0\}}(\theta)_{e/f}} \times n_0^{\{0\}}(\theta)_{e/f}. \end{aligned} \quad (2.35)$$

Then, the resultant normalised j' -PDDCSs are averaged over the initial Λ -doublet state, such that

$$n_{q\pm}^{\{k\}}(\theta)_{\text{avg}} = \frac{1}{2} \times \left[n_{q\pm}^{\{k\}}(\theta)_e + n_{q\pm}^{\{k\}}(\theta)_f \right]. \quad (2.36)$$

Finally, the averaged normalised j' -PDDCS is renormalised by dividing through by the averaged product angular distribution *via*

$$\rho_{q\pm}^{\{k\}}(\theta)_{\text{avg}} = \frac{n_{q\pm}^{\{k\}}(\theta)_{\text{avg}}}{n_0^{\{0\}}(\theta)_{\text{avg}}} \quad (2.37)$$

to generate a real, renormalised j' -PDDCS averaged over the initial Λ -doublet level. In Chapter 3, these averaged, renormalised j' -PDDCSs are used to account for the vertical polarisation of the 226 nm laser light when generating simulated images and fits relating to NO(X)+Ar scattering, according to the method outlined below.

2.7 Data analysis

As explained above, the image collected by the CCD camera is a two-dimensional projection of a three-dimensional Newton sphere of NO⁺ ions. Therefore, the intensity of the images is greatest around the edge of the ring. When measuring the DCS – *i.e.* the scattering intensity into a given angle, θ , for a given $j' \leftarrow j$ transition – it should be the case that the DCS is symmetric about the relative velocity vector, $\mathbf{v}_{\text{rel}}$, since scattering into all azimuthal angles is equally probable. However, as can be seen in Figure 2.8, the intensity is skewed to the left of the vector, which corresponds to the region of the Newton sphere where the NO molecules have relatively slow laboratory-frame velocities. The upper right corner of the sphere denotes a region where molecules are scattered through the same angle, but with a much higher laboratory-frame velocity, as shown in the right panel of Figure 2.8. For this reason, the part of the image to the left of the relative velocity vector is called the ‘slow’ side of the image, and that to the right is referred to as the ‘fast’ side [110]. Molecules with higher laboratory-frame velocities spend less time in the detection region, and the probability of them being ionised on absorbing a laser photon is, therefore, lower.

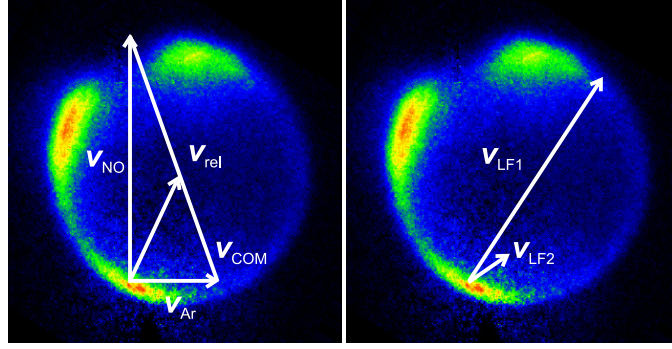


Figure 2.8: The left panel shows an example of an experimental image for the inelastic scattering of $\text{NO}(\text{X})$ by Ar for the $|\Omega' = 0.5, j' = 15.5, f\rangle \leftarrow |\Omega = 0.5, j, e/f\rangle$ transition at 2210 cm^{-1} . The image has been overlaid by the Newton triangle, in which $\mathbf{v}_{\text{NO}}$ and $\mathbf{v}_{\text{Ar}}$ are the laboratory-frame velocities of the NO and Ar before collision, respectively, and $\mathbf{v}_{\text{COM}}$ is the laboratory-frame velocity of the centre of mass of the system. $\mathbf{v}_{\text{rel}}$ is the relative velocity in the laboratory frame. The right panel shows the same image overlaid with laboratory-frame velocity vectors that correspond to the ‘fast’ ($\mathbf{v}_{\text{LF1}}$) and ‘slow’ ($\mathbf{v}_{\text{LF2}}$) sides of the experimental image.

In its most complete form, the equation giving the intensity of scattered signal at point (x, y) on the detector is given by [110, 136]

$$\begin{aligned}
 I(x, y, j, j', j^*, \chi_p) = & \int \int \int \int \int \int \int n_{\text{NO}}(\mathbf{r}_{\text{NO}}, \mathbf{v}_{\text{NO}}, t'_{\text{NO}}) n_{\text{Ar}}(\mathbf{r}_{\text{Ar}}, \mathbf{v}_{\text{Ar}}, t'_{\text{Ar}}) \\
 & \times f_{t_{\text{NO}}}(\mathbf{v}_{\text{NO}}) f_{t_{\text{Ar}}}(\mathbf{v}_{\text{Ar}}) \frac{\mathbf{v}_{\text{rel}}}{\mathbf{v}'_{\text{NO}}} \sigma(\mathbf{v}_{\text{rel}}) P(\mathbf{r}_{\text{det}}) P_{\text{scatt}}(\theta) A(x, y, j', j^*, \chi_p) \\
 & \times \delta(t_{\text{NO}} - t'_{\text{NO}}) \delta(t_{\text{Ar}} - t'_{\text{Ar}}) dt'_{\text{NO}} dt'_{\text{Ar}} d\mathbf{v}_{\text{NO}} d\mathbf{v}_{\text{Ar}} dt_{\text{coll}} d\mathbf{r}_{\text{coll}} d\mathbf{r}_{\text{det}},
 \end{aligned} \tag{2.38}$$

where

- j and j' are the rotational-angular-momentum quantum numbers of the NO molecule before and after collision, respectively;
- j^* is the rotational angular momentum of the $\text{NO}(\text{A})$ molecule in the resonant level of the $(1+1')$ REMPI detection scheme;
- $n_{\text{NO}}(\mathbf{r}_{\text{NO}}, \mathbf{v}_{\text{NO}}, t'_{\text{NO}})$ and $n_{\text{Ar}}(\mathbf{r}_{\text{Ar}}, \mathbf{v}_{\text{Ar}}, t'_{\text{Ar}})$ refer to the number densities in the primary and secondary molecular beams, respectively, which depend on the initial position, $\mathbf{r}$, velocity, $\mathbf{v}$, and time, t ;

- $f_{t_{\text{NO}}}(v_{\text{NO}})$ and $f_{t_{\text{Ar}}}(v_{\text{Ar}})$ are the velocity distributions of the primary and secondary beams, respectively;
- $\sigma(\mathbf{v}_{\text{rel}})$ is the collision cross-section;
- $P(\mathbf{r}_{\text{det}})$ is the probability that the NO molecule will be detected at the position $\mathbf{r}_{\text{det}}$, and is dependent on both the laser position and delay;
- $P_{\text{scatt}}(\theta)$ gives the probability of scattering into the angle defined by θ (and is symmetric about the azimuthal angle, ϕ); and
- the two Dirac functions ensure that the NO molecule and the Ar atom are at the collision position, $\mathbf{r}_{\text{coll}}$, at the time of collision, t_{coll} .

The multiple integral is then performed over all the initial positions, starting times, collision volumes (defined by the overlap of the molecular beams), and detection volumes (defined by the overlap of the laser beams).

It can then be approximated that Equation (2.38) is separable into three components, and can be written as [110, 136]

$$I(x, y, j, j', j^*, \chi_p) = Z(x, y, j, j') P_{\text{scatt}}(\theta) A(x, y, j', j^*, \chi_p), \quad (2.39)$$

where $Z(x, y, j, j')$ is an instrument function that accounts for the variation in probability of detection that comes about as a result of experimental parameters, $P_{\text{scatt}}(\theta)$ is as defined above, and $A(x, y, j', j^*, \chi_p)$ is a term (independent of experimental parameters) that includes all of the polarisation information about the scattering process.

2.7.1 The flux-density correction

As described previously, the instrument function accounts for the effect of experimental parameters on the probability of detection, and can be expressed by collecting

the relevant terms from Equation (2.38), such that [110, 136]

$$\begin{aligned}
 Z(x, y, j, j') = & \int \int \int \int \int \int \int n_{\text{NO}}(\mathbf{r}_{\text{NO}}, \mathbf{v}_{\text{NO}}, t'_{\text{NO}}) n_{\text{Ar}}(\mathbf{r}_{\text{Ar}}, \mathbf{v}_{\text{Ar}}, t'_{\text{Ar}}) \\
 & \times f_{t_{\text{NO}}}(\mathbf{v}_{\text{NO}}) f_{t_{\text{Ar}}}(\mathbf{v}_{\text{Ar}}) \frac{\mathbf{v}_{\text{rel}}}{\mathbf{v}'_{\text{NO}}} \sigma(\mathbf{v}_{\text{rel}}) P(\mathbf{r}_{\text{det}}) \\
 & \times \delta(t_{\text{NO}} - t'_{\text{NO}}) \delta(t_{\text{Ar}} - t'_{\text{Ar}}) dt'_{\text{NO}} dt'_{\text{Ar}} d\mathbf{v}_{\text{NO}} d\mathbf{v}_{\text{Ar}} dt_{\text{coll}} d\mathbf{r}_{\text{coll}} d\mathbf{r}_{\text{det}}.
 \end{aligned} \tag{2.40}$$

A considerable number of experimental parameters are required to calculate the instrument function, including:

- $|\mathbf{v}_{\text{NO}}|$ and $|\mathbf{v}_{\text{Ar}}|$, the mean velocities of the primary and secondary beams, respectively;
- $\sigma_v(\text{NO})$ and $\sigma_v(\text{Ar})$, the FWHM of the Gaussian profiles of the velocity distributions of the primary and secondary beams, respectively;
- $\sigma_t(\text{NO})$ and $\sigma_t(\text{Ar})$, the FWHM of the Gaussian profiles of the temporal distributions of the primary and secondary beams, respectively;
- the FWHM of the Gaussian profile of the spatial widths of the molecular beams;
- the FWHM of the profile of the intensities across the laser beam profiles; and
- the relative positions of the scattering centre, and the laser beam interaction centre.

It is possible to determine the molecular-beam velocities, $|\mathbf{v}_{\text{NO}}|$ and $|\mathbf{v}_{\text{Ar}}|$, in a number of ways. Table 2.2 showed the velocities determined by thermodynamic calculations and from the radii of experimental images. Assuming that the experimentally determined velocity of the primary beam is correct, the FWHM of the Gaussian profile of the velocity distribution of this beam, $\sigma_v(\text{NO})$, is 150 ms^{-1} . The velocity of the secondary beam (which is universally Ar) has been shown in similar systems to be 590 ms^{-1} , with a velocity distribution that has a FWHM,

$\sigma_v(\text{Ar})$, of 75 ms^{-1} [110–112]. Relative values of $\sigma_v(\text{NO})$ and $\sigma_v(\text{Ar})$ were also calculated from velocity-mapped beam spots for each of the systems of interest, and were found to generally reproduce the ratio of the velocities obtained from the experimental image radii.

Notably, as the experiment is modelled with increasing accuracy, evaluating the integral in Equation (2.40) analytically becomes increasingly complex. In practice, it is often more efficient to perform the integral as a sum over many trajectories. In this work, this was achieved using Monte Carlo methods [110], whereby a map of the position-dependent detection efficiency was constructed point-by-point. Examples of the input files for the algorithms used to simulate experimental images for both the $\text{NO}(\text{X})+\text{Ar}$ and $\text{ND}_3(\tilde{\text{X}})+\text{Ar}$ systems are included in Appendix B.

2.7.2 Fitting experimental DCSs

Recalling Equation (2.39), it can be approximated that the effect of laser polarisation on the probability of detection is independent of the effect of other experimental parameters. Thus, since vertically polarised light was used to collect the empirical data that are presented in Chapter 3, it is necessary to determine the polarisation-dependent term, $A(x, y, j', j^*, \chi_p)$, that is derived from the averaged, renormalised j' -PDDCSs, $\rho_{q\pm}^{\{k\}}(\theta)_{\text{avg}}$. For a given excitation branch, and a given $j' \leftarrow j$ transition [137, 138],

$$A(x, y, \chi_p) = 1 + \sum_{kq\pm} F_{q\pm}^{\{k\}}(\chi_p) \rho_{q\pm}^{\{k\}}(\theta)_{\text{avg}}. \quad (2.41)$$

In this thesis, linearly polarised light is used, so there are contributions from $k = 2$, $q = 0, 1$ and 2 . The $F_{q\pm}^{\{k\}}(\chi_p)$ functions contain the geometric information needed to calculate the individual contributions from each of the averaged, renormalised

j' -PDDCSs according to [137, 138]

$$F_0^{\{2\}}(\chi_p) = \frac{1}{4}h^{(2)}(j', j^\star)c_2(j')[3\sin^2\Theta\cos 2\chi\cos 2\beta - (3\cos^2\Theta - 1)], \quad (2.42)$$

$$F_{1+}^{\{2\}}(\chi_p) = \frac{\sqrt{3}}{4}h^{(2)}(j', j^\star)c_2(j')[2\sin\Theta\cos\phi\sin 2\chi \\ + 2(\sin\Theta\cos\Theta\sin\phi\cos 2\chi - \sin 2\Theta\cos\phi)\cos 2\beta], \quad (2.43)$$

$$F_{2+}^{\{2\}}(\chi_p) = \frac{\sqrt{3}}{4}h^{(2)}(j', j^\star)c_2(j')[[(1 + \cos^2\Theta\cos 2\phi\cos 2\chi \\ - 2\cos\Theta\sin 2\phi\sin 2\chi]\cos 2\beta - \sin^2\Theta\cos 2\phi)]. \quad (2.44)$$

In these expressions, $h^{(2)}(j', j^\star)$ is a line-strength factor for the alignment moments of order $k = 2$. $c_2(j')$ are normalisation factors that act as proportionality constants for the polarisation moments and the averaged, renormalised j' -PDDCSs, and are given explicitly as [131, 137, 138]

$$c_2(j') = \left[\frac{(2j' + 3)(2j' - 1)}{j'(j' + 1)} \right]^{\frac{1}{2}}. \quad (2.45)$$

The three Euler angles of which $F_{q+}^{\{2\}}(\chi_p)$ is a function – Θ , ϕ , and χ – describe the relative orientations of the detector frame (defined by the laser propagation axis) and the scattering frame (described by the relative velocity). The angle β is the polarisation angle of the electric vector of the laser light. If the light is linearly polarised, then $\beta = 0^\circ$.

Combining Equations (2.39) and (2.41), it can be written, to a good approximation, that [131, 137, 138]

$$I(x, y, \chi_p) = P_{\text{scatt}}(\theta)Z(x, y) \left[1 + \sum_{kq\pm} F_{q\pm}^{\{k\}}(\chi_p)\rho_{q\pm}^{\{k\}}(\theta)_{\text{avg}} \right], \quad (2.46)$$

where $Z(x, y)$ is the instrument function (see Equation (2.40)) that is independent of the laser polarisation. The DCS can be expanded as a series of Legendre polynomials, such that [131, 137, 138]

$$P_{\text{scatt}}(\theta) = \sum_n \frac{2n+1}{2} a_n P_n(\cos\theta), \quad (2.47)$$

where a_n are the expansion coefficients, and $P_n(\cos \theta)$ is the n^{th} Legendre polynomial. A linear combination of the corresponding basis functions can then be used to fit the intensity observed in the experimental image using [131, 137, 138]

$$I(x, y, \chi_p) = \sum_n \frac{2n+1}{2} a_n B_n(x, y, \chi_p), \quad (2.48)$$

where the basis functions, $B_n(x, y, \chi_p)$, are given by

$$B_n(x, y, \chi_p) = P_n(\cos \theta) Z(x, y) \left[1 + \sum_{kq\pm} F_{q\pm}^{\{k\}}(\chi_p) \rho_{q\pm}^{\{k\}}(\theta)_{\text{avg}} \right]. \quad (2.49)$$

In reality, the experimental image is not fit in two dimensions; instead, it is fit as a one-dimensional series of Fourier moments. The images, and corresponding basis functions, $I(x, y)$, are converted to polar coordinates, $I(r, \theta_r)$, and are then written as a sum of their Fourier moments *via* [110, 136, 139, 140]

$$I(r, \theta_r) = f_0(r) + 2 \left(\sum_{-m}^0 f_m(r) \sin m\theta_r + \sum_0^m f_m(r) \cos m\theta_r \right), \quad (2.50)$$

where the Fourier moments are given by [110, 136]

$$f_m(r) = (2 - \delta_{0m}) \int_0^{2\pi} F(r, \theta_r) \cos m\theta_r r d\theta_r, \quad (2.51)$$

$$f_{-m}(r) = 2 \int_0^{2\pi} F(r, \theta_r) \sin m\theta_r r d\theta_r. \quad (2.52)$$

These Fourier moments describe the radial anisotropy of the image. It was found that the series of moments in the range $m = -12, 12$ was sufficient to fully reproduce the observed experimental detail.

The Fourier moments are subsequently fit using a genetic algorithm to minimise the value of χ^2 , which is given by [110, 136]

$$\chi^2 = \frac{1}{2m_{\text{max}} + 1} \sum_{-m_{\text{max}}}^{+m_{\text{max}}} \int \frac{(f_m^{\text{exp}}(r) - \sum \frac{2n+1}{2} a_n f_m^n(r))^2}{f_{m=0}^{\text{exp}}(r)} dr, \quad (2.53)$$

where $f_m^{\text{exp}}(r)$ is the m^{th} Fourier moment of the experimental image, $f_m^n(r)$ is the m^{th} moment of the n^{th} basis image, and a_n is the corresponding expansion coefficient of the DCS that is allowed to vary iteratively during the fit to minimise the value of χ^2 . The optimised value of a_n is then used to reconstruct the fitted DCS using Equation (2.47).

2.7.3 Specifying the detection region and experimental time delays

As outlined in the previous section, the generation of simulated images from quantum-mechanical calculations requires a knowledge of the relative position of the laser with respect to the scattering centre, x_{det} and y_{det} (in m, where ‘det’ refers to the detection region delimited by the lasers), and of the time delay between the triggers of the molecular beams and the laser, t_{det} (in s). To this end, and to further the aim of quantifying the instrument function of this new CMB apparatus, simulated images were generated using a range of possible laser positions and time delays to find those that best reproduced the experimental data. These images, which simulate scattering into $j' = 15.5f$ on the spin-orbit-conserving manifold at a collision energy of 2210 cm^{-1} , are shown in Figures 2.9 and 2.10. The same test was carried out on a selection of images, at each collision energy, to confirm that the values of x_{det} , y_{det} , and t_{det} worked well for all final states and collision energies.

A qualitative appraisal of the data shown in Figure 2.9 reveals that the laser positions that give the best correlation between the simulated and experimental images are $x_{\text{det}} = 0.005 \text{ m}$, and $y_{\text{det}} = -0.001 \text{ m}$. Using these values of x_{det} and y_{det} , a second set of simulations was run that sampled over the range $t_{\text{det}} = 0 - 8 \times 10^{-5} \text{ s}$, in increments of $0.5 \times 10^{-5} \text{ s}$. The images, which are shown in Figure 2.10, suggest an optimum value of $t_{\text{det}} = 4 \times 10^{-5} \text{ s}$.

2.8 Error analysis

The flux-density correction, and the parameters that are used to calculate it, are the most likely source of error in determining fitted experimental DCSs, since even minor changes in the instrument function are likely to affect the resultant cross-sections. The error analysis should, therefore, reflect the confidence with which the parameters underpinning the flux-density correlation are determined.

To this end, the errors included on plots of the DCS are calculated by fitting both the fast and slow sides of the experimental image and determining the standard deviation of the resultant DCSs from that obtained by fitting the whole image at

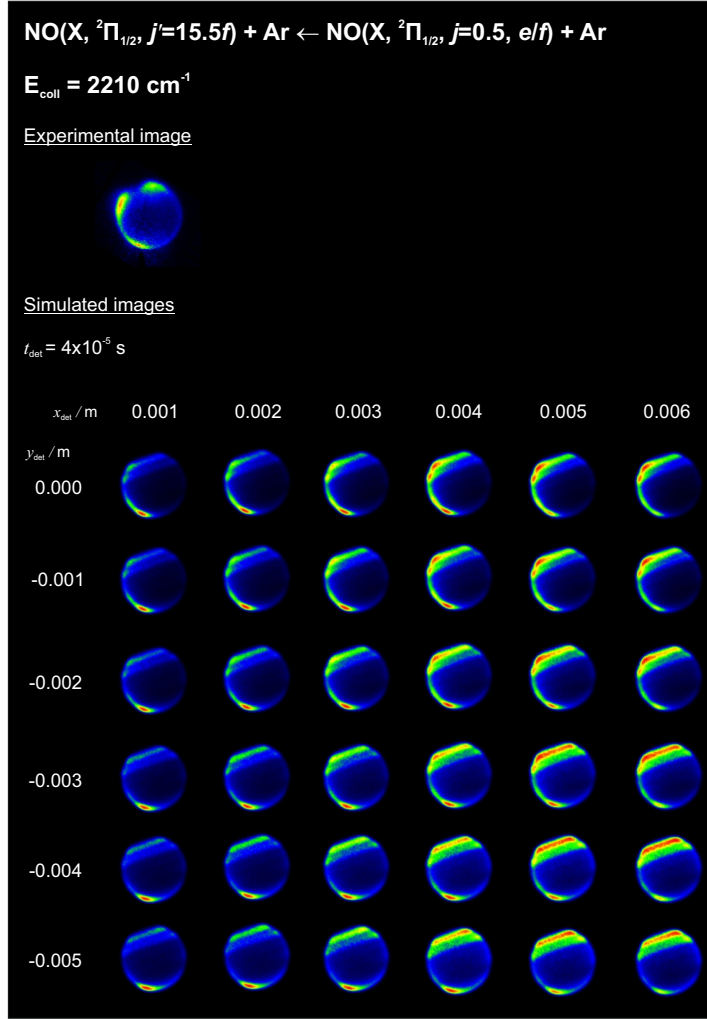


Figure 2.9: Simulated images for the inelastic scattering of NO(X)+Ar at a collision energy of 2210 cm^{-1} . The data presented here are for the spin-orbit-conserving $j' = 15.5f \leftarrow j = 0.5e/f$ collision. The images show the effect of varying the x_{det} and y_{det} coordinates that define the centre of the detection region. Values of $x_{\text{det}} = 0.005 \text{ m}$ and $y_{\text{det}} = -0.001 \text{ m}$ were chosen based on a comparison of the simulations with the experimental image shown in the figure.

once. In the case where a series of experimental images for the same $j' \leftarrow j$ transition was recorded numerous times, the standard deviation between the corresponding DCSs was also calculated. In doing so, the error bars reflect both the internal error generated in the flux-density correction and the external error associated with the reproducibility of experimental images.

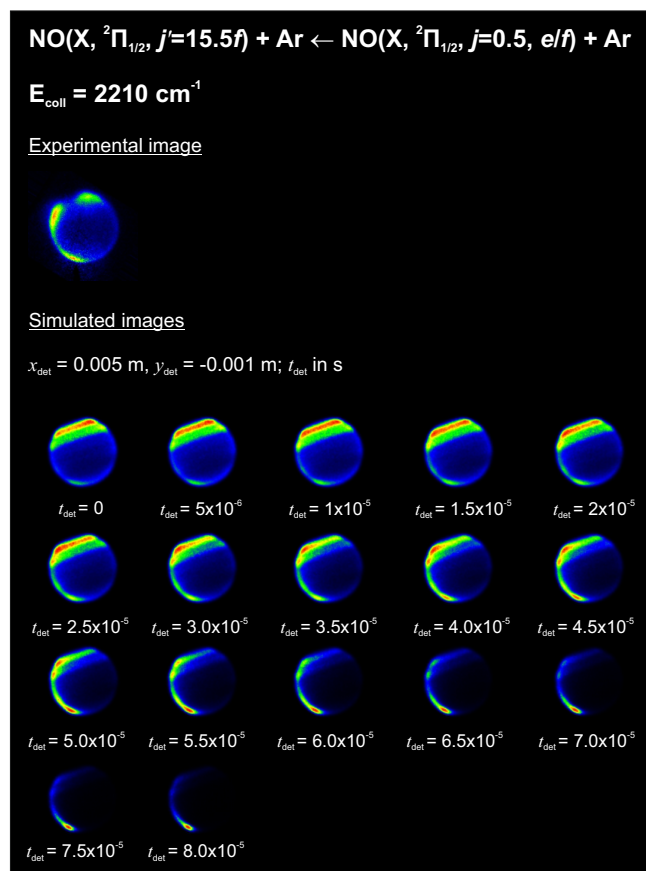


Figure 2.10: Simulated images for the inelastic scattering of $\text{NO}(X)+\text{Ar}$ at a collision energy of 2210 cm^{-1} . The data presented here are for the spin-orbit-conserving $j' = 15.5f \leftarrow j = 0.5e/f$ collision. The images show the effect of varying t_{det} , the time delay between triggering the primary molecular beam valve and the 226 nm laser. A value of $t_{\text{det}} = 4 \times 10^{-5} \text{ s}$ was chosen based on a comparison of the simulations with the experimental image shown in the figure.

2.9 Summary

This chapter began by describing the spectroscopy of the $\text{NO}(X)$ radical and outlining the main experimental techniques used in this work – namely, a crossed-molecular beam apparatus with product detection by velocity-map imaging and resonance-enhanced multi-photon ionisation techniques. Following this, a general description of the nature and importance of the PESs that are used in the quantum-mechanical calculations reported in this work was provided. These surfaces, together with the kinematics of the system of interest, govern the collision dynamics observed during an inelastic scattering event and, as such, are crucial to understanding both

the experimental and theoretical data reported in this thesis.

This chapter concluded by outlining the quantum-mechanical algorithms used to generate the theoretical data presented in Chapter 3. The methods by which integral cross-sections, differential cross-sections, and polarisation-dependent differential cross-sections are then extracted from these calculations were also described. In the subsequent chapter, the DCSs are subjected to a rigorous comparison with experimental data to assess how well currently available theoretical models can reproduce experimental measurements.

3

Inelastic scattering of NO(X)+Ar at variable collision energies

This chapter presents data collected from the first sets of scattering experiments carried out on a new crossed-molecular beam machine. The system of interest, NO(X)+Ar, has been studied extensively, and was thus chosen as a suitable candidate for the calibration and optimisation of the experimental apparatus.

The data reported here relate to the rotationally inelastic scattering of NO(X) by Ar at variable collision energies, achieved by seeding NO(X) in various carrier gases to alter the primary-beam velocity. Experimental images were collected for the scattering of $|\text{NO(X)}, \Omega = 0.5, j, e/f\rangle$ into a range of final states, defined in terms of the final spin-orbit manifold, rotational level, and Λ -doublet level. Fits of the experimental images, simulations, and extracted differential cross-sections of both are also presented and discussed. Notably, the data collected at the highest collision energy investigated in this thesis (2210 cm^{-1}) quantify the scattering of NO(X) by Ar with a larger relative velocity than any other work published previously, and so are of particular interest in this thesis.

3.1 Results: experimental and simulated images

This section presents raw experimental images, analytical fits, and simulations generated from quantum-mechanical calculations for the inelastic scattering of NO(X)+Ar at three different collision energies: 469 cm^{-1} , 1480 cm^{-1} , and 2210 cm^{-1} . A comprehensive set of images, spanning the full range of energetically accessible final rotational quantum states, is presented for each collision energy. In all cases, data relating to spin-orbit-conserving collisions are reported, however, images for spin-orbit-changing collisions were also collected at the highest collision energy. Notably, this energy – some 2210 cm^{-1} – is considerably higher than any other reported in the literature.

All the simulated images reported in this section were generated from sets of quantum-mechanical calculations that were run at a single collision energy. Furthermore, it was also assumed that all the NO molecules were in the ground electronic, vibrational, spin-orbit, and rotational ground states (with equally populated Λ -doublet levels) prior to collision. Although the discussion in Section 2.3.1 revealed that the NO molecules in the various primary-beam mixtures occupied a distribution of rotational states prior to collision, the decision not to simulate the experimental images using a j -weighted quantum-mechanical DCS is justified in the discussion of the high-collision-energy data at the end of this section.

As noted previously, the 226 nm laser light that was used to collect the experimental images presented in this chapter was vertically polarised. The effect of this polarisation on the fitted images, and the DCSs extracted from them, was accounted for by considering the averaged, renormalised, j' -PDDCSs, generated by the quantum-mechanical calculations, using the method outlined in Section 2.7.2.

3.1.1 NO(X)+Ar scattering at 469 cm^{-1}

The data shown in Figure 3.1 refer to the inelastic scattering of NO(X) by Ar at a collision energy of 469 cm^{-1} . These experimental images were amongst the first to be recorded on a newly commissioned CMB apparatus, and this collision

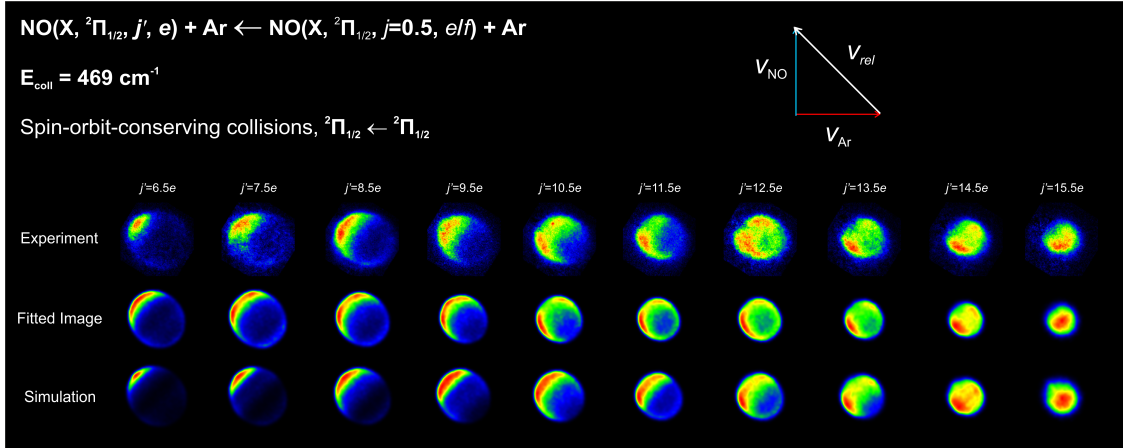


Figure 3.1: Experimental, fitted, and simulated images for the inelastic scattering of $\text{NO}(\text{X}) + \text{Ar}$ at a collision energy of 469 cm^{-1} . The data presented here refer to spin-orbit-conserving collisions (${}^2\Pi_{1/2} \leftarrow {}^2\Pi_{1/2}$). The Newton triangle for the collision system is also shown. As explained in the text, the simulated images shown here were generated assuming that all of the $\text{NO}(\text{X})$ molecules are in the $j = 0.5$ rotational state prior to collision.

energy was purposely chosen because it is so well documented in the literature [15, 16, 22, 35, 38, 79–85, 87–89, 141, 142].

The images, fits, and simulations presented here are for spin-orbit-conserving collisions (for which $\Omega = 0.5$ and $\Omega' = 0.5$). The initial Λ -doublet levels of $\text{NO}(\text{X})$ are equally populated, and all the images shown are for scattering into a final e state (by virtue of the Λ -doublet-selective detection scheme). At this collision energy, $j' = 16.5$ is the highest accessible rotational state, however, poor signal-to-noise ratios for scattering into very low and very high j' limited image acquisition to the range $j' = 6.5 - 15.5$.

For collisions between $\text{NO}(\text{X})$ and Ar that scatter into low final rotational states, j' , the products are primarily forward-scattered; in contrast, collisions that induce high rotational excitation in $\text{NO}(\text{X})$ lead to predominantly backward-scattered images. For collisions that result in low rotational excitation, there is only a small amount of rotation energy transfer (RET) – these collisions result from large impact parameters, and are referred to as *glancing-blow collisions*. In the event of low levels of RET, the $\text{NO}(\text{X})$ molecules deviate very little from their original trajectories, have small scattering angles, θ , and generate images that

show a predominance of forward scattering.

As the magnitude of j' increases, collisional RET occurs to a greater extent, and the product distribution becomes increasingly sideward- and then backward-scattered. To bring about a greater transfer in rotational angular momentum, collisions must become increasingly direct or *head-on*, so the post-collision $\text{NO}(\text{X})$ molecules fly away at large scattering angles in the opposite direction to that in which they approached the Ar atoms originally. It is also important to note that the experimental fits successfully capture the asymmetry of the scattering intensity about the relative velocity vector, $\mathbf{k}$, lending confidence to both the basis functions used (including the effect of the vertical polarisation of the 226 nm laser light) and the number of Legendre polynomials included in the fitting algorithms.

The agreement between the experimental and simulated images is generally good, however, there are a number of notable discrepancies. Several images – for example, those for $j' = 8.5e$, $10.5e$, and $12.5e$ – appear to show a secondary, less intense ring at a larger radius than the peak intensity. It is possible that these outer rings represent unwanted ionisation from a lower j' state as a result of overlap in the respective spectroscopic transitions. The Newton spheres that result from scattering into these two different j' states have different volumes, because the molecules have dissimilar translational energies, meaning they produce rings of different radii when crushed onto the detector.

It is also noticeable that the images presented here are not totally circular; rather, they appear to be stretched along the direction of $\mathbf{k}$. It is possible that this distortion is due to incorrect VMI settings. It is important to acknowledge that the images presented in this section are of particularly poor quality, since they are the result of some of the first scattering experiments to be performed on this apparatus, and many experimental parameters had not yet been optimised.

3.1.2 $\text{NO}(\text{X})+\text{Ar}$ scattering at 1480 cm^{-1}

A comprehensive set of experimental images was recorded at a collision energy of 1480 cm^{-1} , and is presented in Figure 3.2. Although the inelastic scattering of

$\text{NO}(\text{X})+\text{Ar}$ has been studied previously at a similar collision energy, the work in reference [21] focused on the effects of vibrational excitation on the DCS and did not report an extensive set of images that fully demonstrated the gradual change in the $\mathbf{k} - \mathbf{k}'$ vector correlation with rotational excitation. Moreover, more recent advances in experimental techniques and design have allowed higher quality images to be collected and presented in this thesis in comparison to those in reference [21].

The images presented here were collected for spin-orbit-conserving collisions that mostly scattered into final e states; for higher j' states, final f states were recorded, since these transitions occur at lower wavelengths, with a higher signal-to-noise ratio. From energy conservation, the highest accessible final state is $j' = 29.5$, however, the highest recordable state was found to be $j' = 27.5$.

As for the first set of images, reported at 469 cm^{-1} , the number and angular distribution of the peaks in the radial intensity of the experimental images is reproduced relatively well in both the fits and the simulations. The poorest agreement is for low j' states, where the quantum-mechanical data predict significantly more forward scattering than is seen experimentally. Indeed, this phenomenon of underpredicting the level of forward scattering for low j' states is also seen for other data sets, and is discussed further in Section 3.1.3.

In general, however, it can be said that the quality of the images recorded at a collision energy of 1480 cm^{-1} shows a marked improvement compared to those recorded at 469 cm^{-1} . This is most likely a consequence of experimental optimisation and increased resolution brought about by the installation of a longer time-of-flight tube (see Section 2.3.5). In particular, the images are much more circular at this higher collision energy – this is thought to be due, at least in part, to an improvement in the quality of the velocity-map imaging. Furthermore, the images reported here show no evidence of the double-ring formation that resulted from overlapping transitions at 469 cm^{-1} . For these reasons, it was decided to continue studying the $\text{NO}(\text{X})+\text{Ar}$ system at an even higher collision energy, in order to probe the collision dynamics further, and to test the ability of currently available theoretical calculations to model high-energy dynamics.

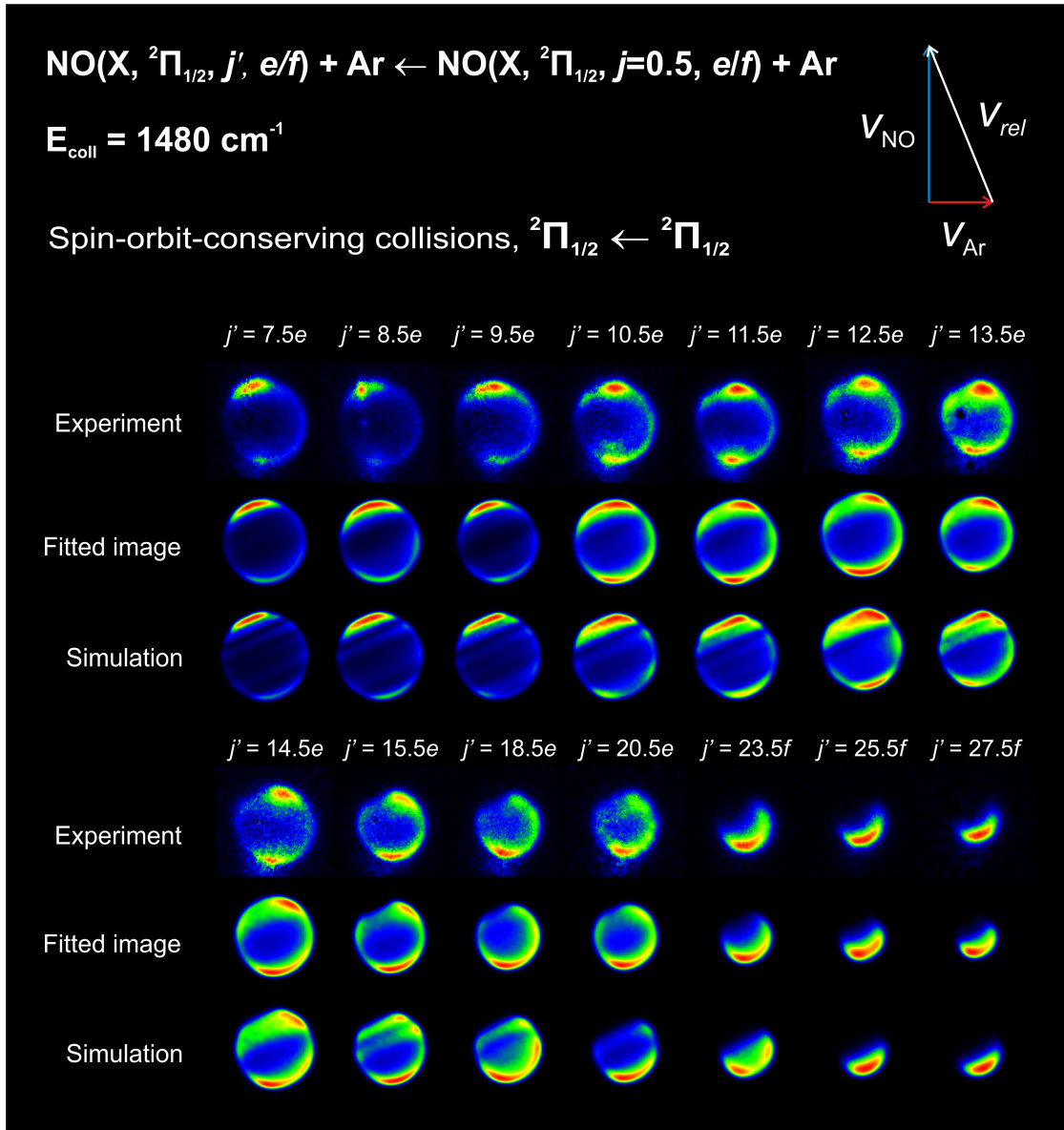


Figure 3.2: Experimental, fitted, and simulated images for the inelastic scattering of $\text{NO}(X) + \text{Ar}$ at a collision energy of 1480 cm^{-1} . The data presented here refer to spin-orbit-conserving collisions (${}^2\Pi_{1/2} \leftarrow {}^2\Pi_{1/2}$). The Newton triangle for the collision system is also shown. As explained in the text, the simulated images shown here were generated assuming that all of the $\text{NO}(X)$ molecules are in the $j = 0.5$ rotational state prior to collision.

3.1.3 $\text{NO}(\text{X}) + \text{Ar}$ scattering at 2210 cm^{-1}

This section presents images for the inelastic scattering of $\text{NO}(\text{X})$ by Ar at the highest collision energy investigated in this thesis: 2210 cm^{-1} . This energy, which is considerably higher than any previously reported in the literature, is achieved by seeding $\text{NO}(\text{X})$ at 10% in molecular H_2 in the primary beam and colliding it with a secondary beam of pure Ar. In contrast to the data presented in earlier sections, images for both spin-orbit-conserving (${}^2\Pi_{\frac{1}{2}} \leftarrow {}^2\Pi_{\frac{1}{2}}$) and spin-orbit-changing (${}^2\Pi_{\frac{3}{2}} \leftarrow {}^2\Pi_{\frac{1}{2}}$) transitions were recorded at this collision energy. The vast majority of images collected show final f states, which undergo transitions at lower wavelengths. Final e states were recorded or, indeed, the j' state was omitted entirely, if overlapping transitions prevented the collection of a given $|j', f\rangle$ image. $j' = 35.5$ and $j' = 34.5$ are the highest theoretically accessible final rotational states for spin-orbit-conserving and spin-orbit-changing collisions, respectively, where the difference originates from the 123 cm^{-1} separation between the $\text{NO}(\text{X})$ spin-orbit manifolds. Decent signal-to-noise ratios allowed data to be recorded up to $j' = 34.5$ and $j' = 33.5$ for spin-orbit conserving and spin-orbit-changing transitions, respectively, as shown in Figures 3.4 and 3.5. Notably, a total of 2×10^4 laser shots were recorded for each spin-orbit-conserving image, whereas 3×10^4 laser shots were recorded for each spin-orbit-changing image due to lower signal-to-noise ratios.

As discussed in Section 2.3.1, whilst the simulations reported in previous sections all assumed that all $\text{NO}(\text{X})$ molecules are in the initial $j = 0.5$ state, in experimental reality, there is significant population in a number of higher j states. To investigate the effect of the initial rotational-state distribution on the simulations, Figure 3.3 presents three simulated images that were generated using a quantum-mechanical DCS that was calculated assuming that all $\text{NO}(\text{X})$ molecules originated in the $j = 0.5$ state and compares them to a further three simulated images that were generated using a composite, j -weighted quantum-mechanical DCS that takes into account the relative population of initial j states in $\text{NO}(\text{X})$ at $T_{\text{rot}} = 28 \text{ K}$. In general, it can be seen that the agreement between the two sets of simulated images is good. One notable consequence of including the higher- j -state DCSs in the

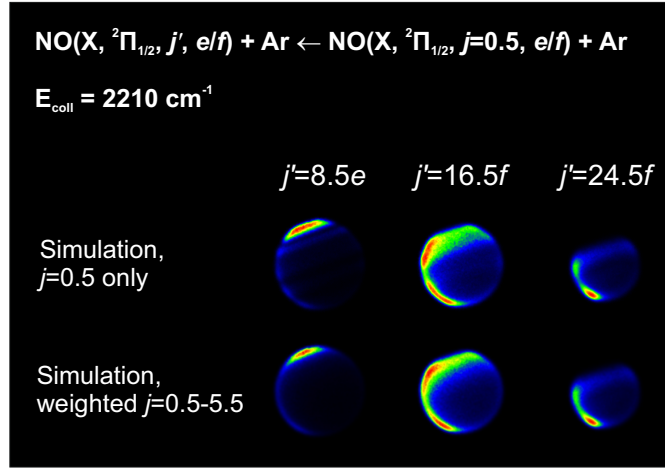


Figure 3.3: Simulated images for the inelastic scattering of $NO(X)+Ar$ at a collision energy of 2210 cm^{-1} . The data presented here refer to spin-orbit-conserving collisions (${}^2\Pi_{1/2} \leftarrow {}^2\Pi_{1/2}$). The first row of simulated images was generated assuming that all of the $NO(X)$ molecules are in the $j = 0.5$ rotational state prior to collision. The second row of simulated images was generated from j -weighted DCSs. See text for details.

simulation algorithms is an increase in the intensity of scattering in the forward direction, especially for the $j' = 8.5e$ state. However, as has been seen in the images already presented in this chapter, simulations that were generated using only the $j = 0.5$ DCS already overestimate the extent of forward scattering that is observed experimentally. It is, therefore, believed that, as far as generating simulated images is concerned, neglecting to incorporate higher- j DCSs (which are computationally costly and time-consuming to generate) in the simulation algorithms is not responsible for the current discrepancy between experiment and theory. To that end, separate consideration is given to the effect of the rotational-state distribution on the agreement between experimental and calculated DCSs, and this is discussed in Section 3.3.4.

Spin-orbit-conserving collisions

As can be seen in Figure 3.4, there is generally good agreement between the experimental, fitted, and simulated images for spin-orbit-conserving collisions. The number, relative intensity, and angular distributions of the peaks in the raw experimental images are largely reproduced in the corresponding fits and simulations.

Indeed, broadly speaking, the agreement between experiment and theory is much better for these data sets than for the lower collision energies presented previously. This is most likely due to improvements in experimental resolution (by adding an extended time-of-flight tube) and also due to the optimisation of several parameters (most notably, the molecular-beam and laser time delays and positions) that makes the inputs for the fitting and simulation algorithms much more accurate. These optimisations were possible due to the large body of data recorded at this particular collision energy.

The experimental images collected at 2210 cm^{-1} appear to show a notable absence of intensity in the forward-scattered region, particularly for $j' < 14.5$, and a more moderate excess of backward-scattered intensity in the range $j' = 16.5 - 27.5$, when compared to theoretical predictions. It was shown in Section 2.7.3 that the lack of scattering into low θ at low j' observed experimentally cannot be explained by altering the instrument-function parameters. The deterioration in the agreement between experiment and theory for the backward-scattered region of the image at medium j' may also stem from the decrease in the integral cross-section for scattering into higher j' states: the poorer-quality experimental images that result are more difficult to fit accurately, and this could contribute to the notable discrepancy between theory and experiment at high j' . In addition, it is thought that the inability of the simulations to fully replicate the experimental images may be linked to inherent issues with how well the current input parameters reflect experimental reality. To that end, particular discrepancies between experiment and theory are now discussed in detail in the context of the high-collision-energy data.

Spin-orbit-changing collisions

Figure 3.5 shows the images collected for spin-orbit-changing collisions at 2210 cm^{-1} . As for the data collected for spin-orbit-conserving collisions, the agreement between the experimental, fitted, and simulated images is generally good. However, the raw experimental images themselves are of a poorer quality than those recorded for spin-orbit-conserving collisions, despite the fact that 1×10^4 more laser shots were recorded

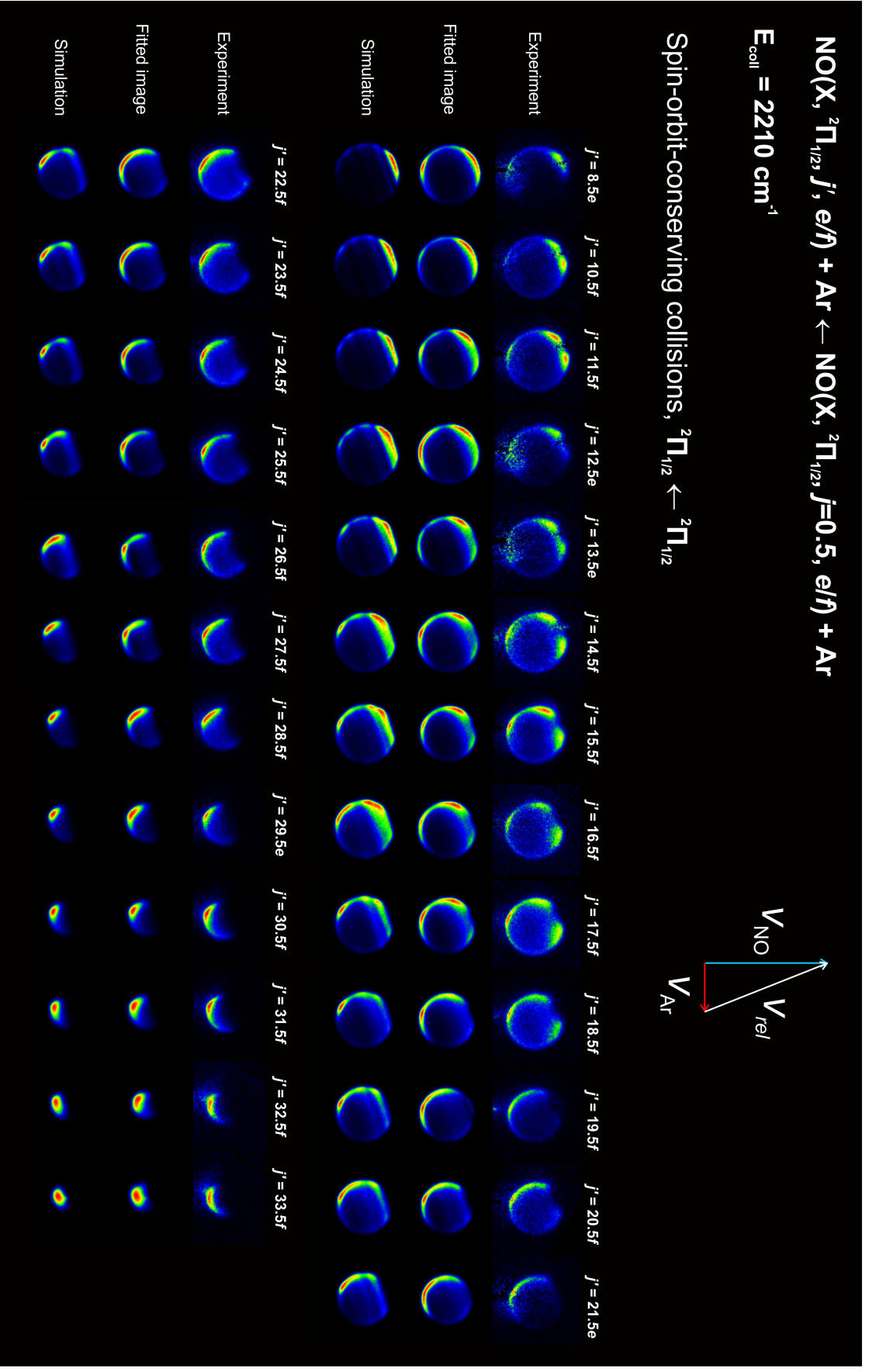


Figure 3.4: Experimental, fitted, and simulated images for the inelastic scattering of $\text{NO}(X)+\text{Ar}$ at a collision energy of 2210 cm^{-1} . The data presented here refer to spin-orbit-conserving collisions (${}^2\Pi_{1/2} \leftarrow {}^2\Pi_{1/2}$). The Newton triangle for the collision system is also shown. As explained in the text, the simulated images shown here were generated assuming that all of the $\text{NO}(X)$ molecules are in the $j = 0.5$ rotational state prior to collision. The images here are drawn to the same scale as those in Figure 3.5.

per image for the former. This is due to the lower integral cross-section for spin-orbit-changing collisions, meaning a higher number of laser shots are needed to converge the data. It should also be noted that, for a given j' state, the spin-orbit-changing image has a slightly smaller radius than the corresponding spin-orbit-conserving image: an additional 123 cm^{-1} are needed to achieve the ${}^2\Pi_{\frac{3}{2}} \leftarrow {}^2\Pi_{\frac{1}{2}}$ transition, meaning there is less translational energy available to the scattered products.

As noted in Section 2.4.1, spin-orbit-changing collisions can be thought of as taking place on the $V_{\text{diff}}(R, \gamma)$ PES, whereas spin-orbit-conserving collisions can be considered to take place on the $V_{\text{sum}}(R, \gamma)$ PES. The $V_{\text{diff}}(R, \gamma)$ PES, by virtue of the subtraction operation required to generate it, is more likely to highlight inaccuracies in the calculated $V_{\text{A}'}$ and $V_{\text{A}''}$ surfaces. As such, spin-orbit-changing data can be seen as a more rigorous probe of the agreement between experiment and theory. Thus, given that the agreement for the spin-orbit-changing data presented here is, in general, as good as that seen for spin-orbit-conserving collisions at this (and lower) collision energies, it can be concluded that the $\text{NO}(\text{X})+\text{Ar}$ PES used in this work [120] is indeed able to model high-energy dynamics accurately.

3.2 Results: differential cross-sections

The DCS for rotationally inelastic diatom-atom collisions can provide a wealth of information regarding the classical and quantum-mechanical dynamics that underpin the scattering event. The general structure of the DCS can be related to classical regions of attraction and repulsion in the PES, and quantum-mechanical interference effects can lead to oscillations that are observable in experimental and theoretical images, and in the DCSs extracted from them. The DCS for a given collision, therefore, provides a rigorous probe of the ability of currently available PESs and theoretical models to accurately predict a range of experimentally observable quantities.

This section presents DCSs that were extracted from the experimental images and quantum-mechanical calculations discussed in the previous sections. The data shown relate to spin-orbit-conserving collisions of $\text{NO}(\text{X})+\text{Ar}$ at 469 cm^{-1} ,

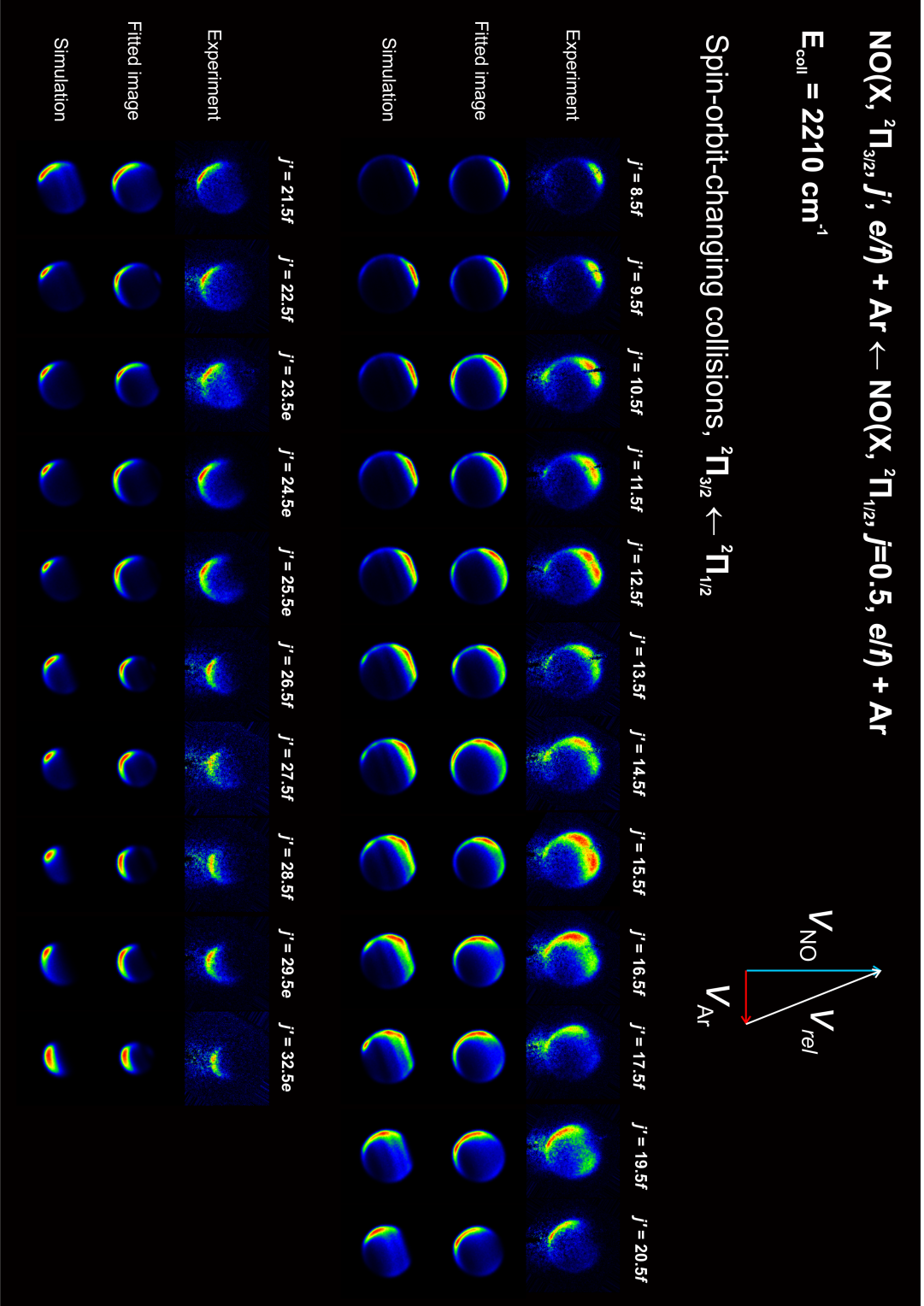


Figure 3.5: Experimental, fitted, and simulated images for the inelastic scattering of $\text{NO(X)} + \text{Ar}$ at a collision energy of 2210 cm^{-1} . The data presented here refer to spin-orbit-changing collisions ($^2\Pi_{3/2} \leftarrow ^2\Pi_{1/2}$). The Newton triangle for the collision system is also shown. As explained in the text, the simulated images shown here were generated assuming that all of the NO(X) molecules are in the $j = 0.5$ rotational state prior to collision. The images here are drawn to the same scale as those in Figure 3.4.

1480 cm^{-1} , and 2210 cm^{-1} , and also to spin-orbit-changing collisions at 2210 cm^{-1} . A number of different features in the DCSs are discussed, with the emphasis throughout placed on the agreement between experiment and theory, and on the effect of increasing collision energy on the observed collision dynamics. Note that, for the data collected at 469 cm^{-1} and 1480 cm^{-1} , the quantum-mechanical DCSs assume that 100% of the NO(X) molecules are in the $j = 0.5$ rotational state prior to collision. In contrast, the quantum-mechanical DCSs for scattering at 2210 cm^{-1} are a j -weighted average of the DCSs for trajectories that originated in each of the j levels in the range $j = 0.5 - 5.5$, based on the rotational-state distribution at 28 K (see Table 2.1). The effect on the DCS of modelling the rotational-state distribution accurately is discussed in Section 3.3.4.

In broad terms, there is reasonable agreement between the experimental and quantum-mechanical DCSs presented in the following sections. The calculated data tend to reproduce the number, angular distribution, and relative intensity of the peaks in the DCS, lending confidence to the basis functions employed and the number of Legendre polynomials included in the fits. It is also important to bear in mind that the experimental data presented here only provide information on the relative intensity of the scattering-angle distribution. Since the absolute magnitude of the cross-section cannot be known, the experimental DCSs are scaled to have the same integral as the quantum-mechanical data. Each set of DCSs is now discussed in turn.

3.2.1 NO(X)+Ar scattering at 469 cm^{-1}

Despite the fact that the experimental images recorded at the lowest collision energy are generally of a poorer quality than those from higher-energy data sets (see Figure 3.1), there is still relatively good agreement between the fitted and quantum-mechanical DCSs in Figure 3.6. Indeed, since the structure of the DCS can act as a sensitive probe of the PES, given that the angular distribution of scattering intensity will depend intimately on the anisotropy of the surface, the good agreement between the experimental and theoretical data shown suggests that the Alexander PES [120] employed in the calculations is relatively accurate at this collision energy.



$$E_{\text{coll}} = 469 \text{ cm}^{-1}$$

Spin-orbit-conserving collisions, ${}^2\Pi_{1/2} \leftarrow {}^2\Pi_{1/2}$

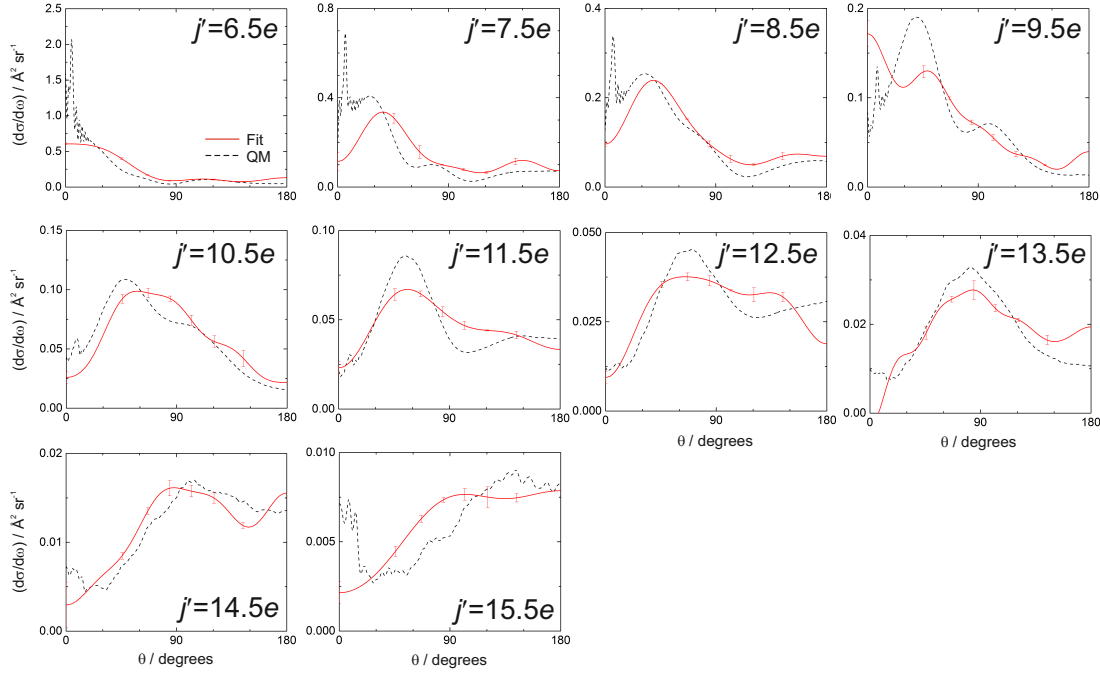


Figure 3.6: Fitted and quantum-mechanical DCSs for the inelastic scattering of $\text{NO}(\text{X}) + \text{Ar}$ at a collision energy of 469 cm^{-1} . The data presented here refer to spin-orbit-conserving collisions (${}^2\Pi_{1/2} \leftarrow {}^2\Pi_{1/2}$). As explained in the text, the quantum-mechanical DCSs shown here were generated assuming that all of the $\text{NO}(\text{X})$ molecules are in the $j = 0.5$ rotational state prior to collision. Note the difference in scale of the y -axes.

One notable difference between the experimental and theoretical data shown in Figure 3.6 is that the quantum-mechanical calculations predict a considerably greater number and magnitude of oscillations in the DCS structure than is observed experimentally – especially for $j' \leq 9.5$. The nature and origin of these oscillations, and their influence on the experimental and quantum-mechanical DCSs, is discussed in the context of the high-collision-energy data in Section 3.3.2.

3.2.2 $\text{NO}(\text{X}) + \text{Ar}$ scattering at 1480 cm^{-1}

Figure 3.7 shows fitted and quantum-mechanical DCSs for spin-orbit-conserving collisions at 1480 cm^{-1} . As with the data collected at 469 cm^{-1} , there is generally



$$E_{\text{coll}} = 1480 \text{ cm}^{-1}$$

Spin-orbit-conserving collisions, ${}^2\Pi_{1/2} \leftarrow {}^2\Pi_{1/2}$

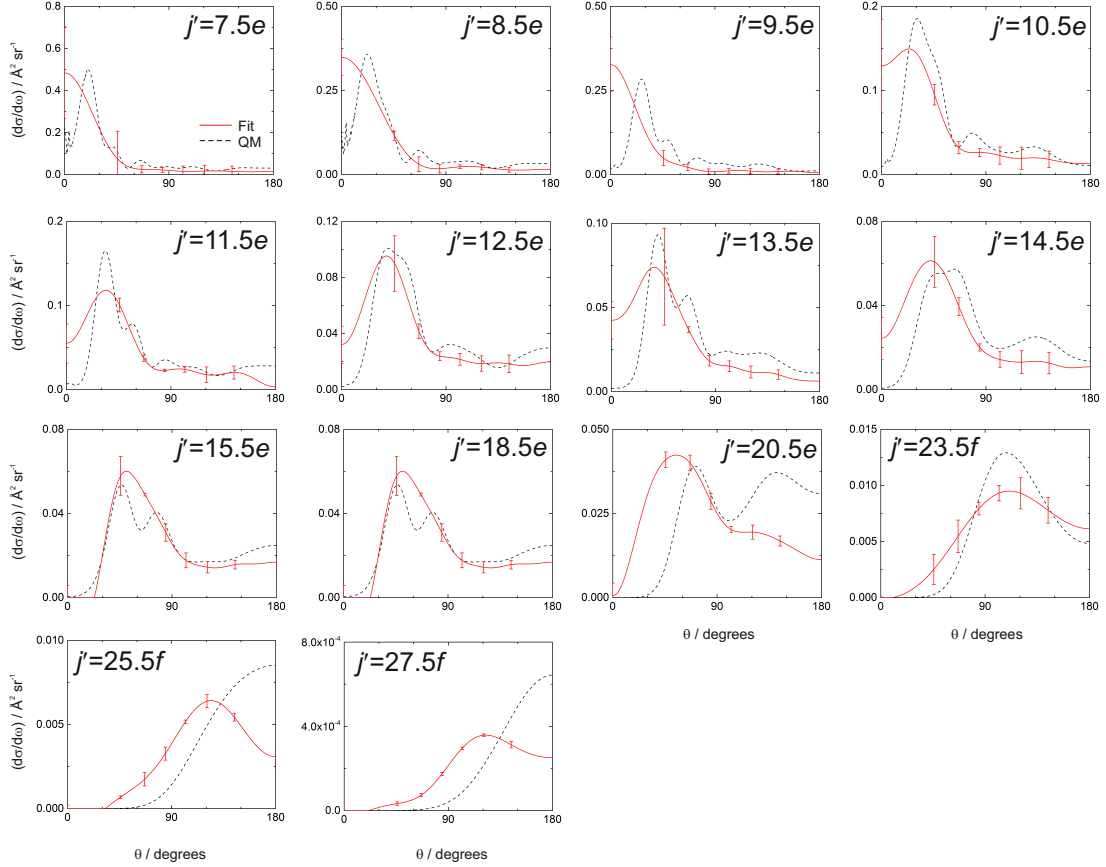


Figure 3.7: Fitted and quantum-mechanical DCSs for the inelastic scattering of $\text{NO}(\text{X}) + \text{Ar}$ at a collision energy of 1480 cm^{-1} . The data presented here refer to spin-orbit-conserving collisions (${}^2\Pi_{1/2} \leftarrow {}^2\Pi_{1/2}$). As explained in the text, the quantum-mechanical DCSs shown here were generated assuming that all of the $\text{NO}(\text{X})$ molecules are in the $j = 0.5$ rotational state prior to collision. Note the difference in scale of the y -axes.

good agreement between experiment and theory, lending confidence to the accuracy of the PES employed in terms of its ability to reproduce the experimental scattering distribution at this collision energy. The data are also free of systematic error, and only a few final states show notable discrepancies between experiment and theory.

Unlike the data recorded at a lower collision energy, the DCSs presented here are largely devoid of rapid oscillations in the forward-scattered region. High

levels of background signal at low j' , where forward scattering is usually most intense, prevented the collection of decent images for the j' states most affected by diffraction. The DCSs for scattering into $j' = 7.5e$ and $j' = 8.5e$ do, however, show small diffraction oscillations at $\theta < 20^\circ$. A further, notable feature of the data collected at this collision energy is that the simulations consistently over-predict the magnitude of backward scattering for the highest states recorded ($j' = 20.5e$, $25.5f$, and $27.5f$). Disagreement in the high- θ region of the DCS be discussed further in the context of the data collected at 2210 cm⁻¹, which have undergone a more rigorous analysis and interpretation.

3.2.3 NO(X)+Ar scattering at 2210 cm⁻¹

The data shown in Figures 3.10 and 3.11 represent fitted and calculated DCSs for spin-orbit-conserving and spin-orbit-changing collisions of NO(X)+Ar at 2210 cm⁻¹. As mentioned previously, seeding NO(X) in H₂ produced a primary beam with a considerably higher rotational temperature (28 K) than those discussed previously (10 K), and since there is a much larger body of higher-quality data to analyse at this previously unstudied collision energy, the DCSs reported in this section were calculated as the j -weighted average of the individual DCSs for trajectories that originated in each of the $j = 0.5 - 5.5$ rotational levels.

As outlined in Chapter 2, the simulation and fitting procedures that were used to analyse the data collected at 469 cm⁻¹ and 1480 cm⁻¹ consider the full 360° range of the scattering distribution. However, for many j' states, fitting the full experimental image collected at 2210 cm⁻¹ produced a DCS that disagreed strongly with quantum-mechanical calculations in the high- θ , backward-scattered region. This was particularly true in the $j' = 14.5 - 30.5$ range for both spin-orbit-conserving and spin-orbit-changing collisions. To investigate this further, the ‘fast’ and ‘slow’ sides of the image (see Section 2.7) were fitted separately, and the extracted DCSs were compared to that from a fit of the full image, as shown in Figure 3.8.

The data in the figure show clearly that there is notable disagreement between experiment and theory for the j' levels shown in the $\theta > 140^\circ$ range. It can also

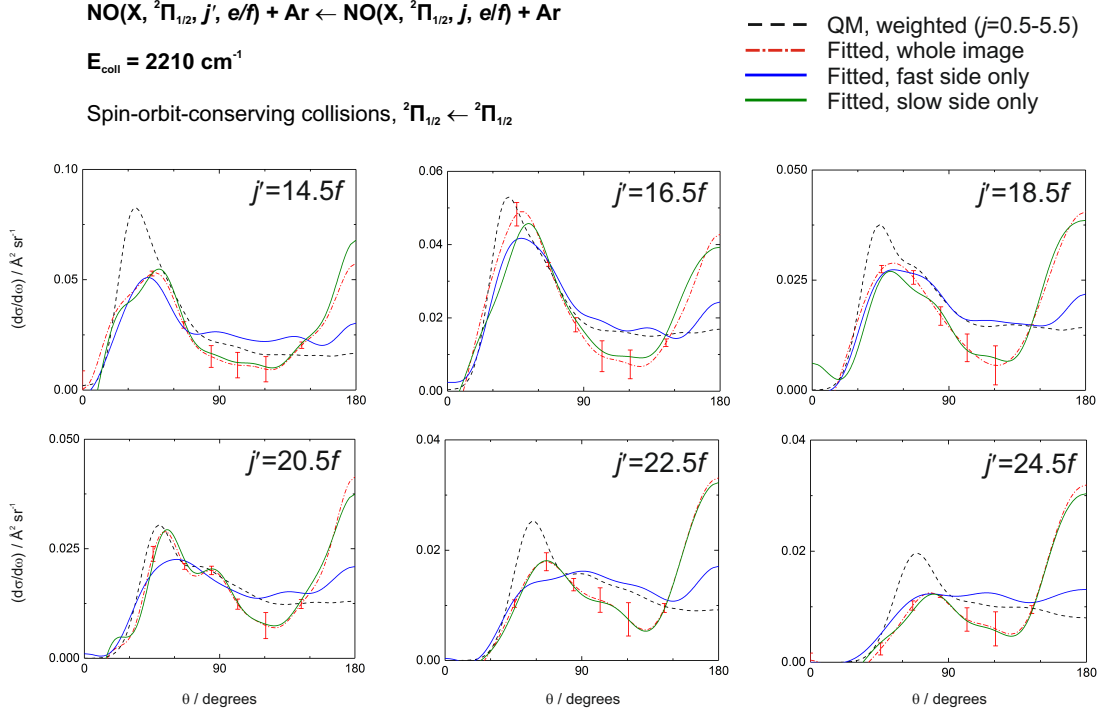


Figure 3.8: Fitted and quantum-mechanical DCSs for the inelastic scattering of $\text{NO}(X)+\text{Ar}$ at a collision energy of 2210 cm^{-1} . The data presented here refer to spin-orbit-conserving collisions (${}^2\Pi_{1/2} \leftarrow {}^2\Pi_{1/2}$). The DCSs shown by black, dashed lines are j -weighted quantum-mechanical DCSs. DCSs extracted from fits of the whole experimental image are shown in red; DCSs extracted from fits of the fast side of the experimental image only are shown in blue; DCSs extracted from fits of the slow side of the experimental image only are shown in green. See text for details.

be seen that the prominent backward scattering in the fit of the whole image can largely be attributed to that which corresponds to the slow side. Such an observation suggests that, even though the instrument function that is used in the simulation algorithms has been optimised to account for various experimental parameters (see Section 2.7.3), there is still an accumulation of scattered signal in the high- θ region of many experimental images that has not been accounted for theoretically. Thus, when DCSs are extracted from fits of the full experimental images that are generated from these simulations, there is a strong peak at high θ that is absent in the quantum-mechanical DCSs.

The origin of this region of high intensity in the slow side of the experimental images can be explained by considering Figure 3.9. Here, the Newton triangles for the $\text{NO}(X, j = 0.5)+\text{Ar}$ system at collision energies of 469 cm^{-1} , 1480 cm^{-1} , and

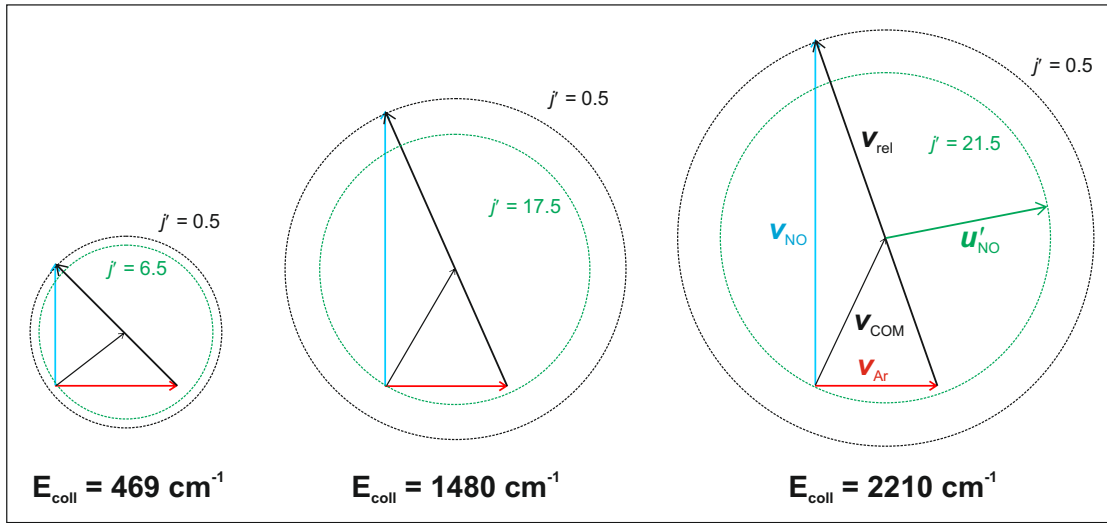


Figure 3.9: Newton triangles for the $\text{NO}(X, j = 0.5)+\text{Ar}$ system at collision energies of 469 cm^{-1} , 1480 cm^{-1} , and 2210 cm^{-1} that have been drawn to scale. The various vectors that define the Newton triangles in each case are labelled on that for 2210 cm^{-1} . The black, dashed circles superimposed on the Newton triangles correspond to the radii of the experimental images that result from a rotationally elastic collision (for which $j' = j = 0.5$). The green, dashed circles give the radii of the experimental images for which the post-collision centre-of-mass-frame velocity of NO, $\mathbf{u}'_{\text{NO}}$, is most similar to the laboratory-frame velocity of the centre of mass of the system, $\mathbf{v}_{\text{COM}}$. The corresponding final rotational state of NO, j' , is also labelled in green.

2210 cm^{-1} have been drawn to scale. The black, dashed circles superimposed on the Newton triangles correspond to the radii of the experimental images that result from a rotationally elastic collision (for which $j' = j = 0.5$). The green, dashed circles give the radii of the experimental images for which the post-collision centre-of-mass-frame velocity of NO, $\mathbf{u}'_{\text{NO}}$, is most similar to the laboratory-frame velocity of the centre of mass of the system, $\mathbf{v}_{\text{COM}}$. The corresponding final rotational quantum state of NO, j' , is also labelled in green.

As outlined in Section 2.7, particles that scatter into the bottom-left of the Newton triangle will have near-zero velocity in the laboratory frame. Since they are travelling more slowly, they spend longer in the detection region, have a higher probability of ionisation, and thus are more likely to contribute to the detected signal. This *slow-side bias* will be most prominent for those particles with the slowest lab-frame velocities, *i.e.* those at, or near to, the laboratory-frame origin. Thus, it would be expected that those rotational states for which the post-collision centre-of-

mass-frame velocity of NO, $\mathbf{u}'_{\text{NO}}$, corresponds most closely to the laboratory-frame velocity of the centre of mass, $\mathbf{v}_{\text{COM}}$, will show a region of very high intensity at the laboratory origin. This is because, in this instance, the magnitude of $\mathbf{u}'_{\text{NO}}$, which defines the radius of the post-collision Newton sphere, also coincides with the velocity most likely to be detected in the experiment.

The disagreement in the backward-scattered region of the DCS between fits of the full experimental image and quantum-mechanical calculations is clearly seen for many j' states at a collision energy of 2210 cm^{-1} . However, a similar problem is not observed in the data collected at 469 cm^{-1} and 1480 cm^{-1} . This is not particularly surprising for the data at 469 cm^{-1} since, in this case, the final rotational state for which $\mathbf{u}'_{\text{NO}}$ passes through the laboratory origin on the Newton triangle ($j' = 6.5$) is predominantly forward scattered. Thus, very few NO molecules are scattered in the direction of the laboratory-origin. Furthermore, as j' increases, and the angular distribution shifts to higher θ such that more NO particles are scattered into the bottom-left of the Newton triangle, the magnitude of $\mathbf{u}'_{\text{NO}}$ will also decrease and move away from the laboratory origin. To that end, the experimental images are less affected by the slow-side bias as j' increases.

For the data collected at 1480 cm^{-1} , the final rotational state for which $\mathbf{u}'_{\text{NO}}$ passes through the laboratory origin on the Newton sphere ($j' = 17.5$) lies within the range of recorded j' states. Thus, for many of the images collected at similar j' , there will be a strong laboratory-origin bias. In this case, the instrument function employed in the simulation algorithm proved able to account for such bias. Thus, DCSs extracted from fits of the full images are devoid of a strongly backward-scattered peak that is also not predicted by theory. However, the same cannot be said for the data recorded at 2210 cm^{-1} , when the final rotational state for which $\mathbf{u}'_{\text{NO}}$ passes through the laboratory origin on the Newton sphere ($j' = 21.5$) also lies within the range of j' states recorded. In this range of j' , many of the DCSs extracted from fits of the whole image do show strong disagreement between experiment and theory in the backward-scattered region. This can be attributed to the fact that the full extent of the laboratory-origin bias was not successfully

predicted by the instrument function. It is possible that the laboratory-origin effect will be underestimated considerably by the simulation if, for example, a significant number of particles spend a long time in the detection region before being swept out by a successive gas pulse in the experimental apparatus [143]. To that end, it is recommended that, in future, the instrument function be optimised for the high-energy data to attempt to account for the intense signal observed at the laboratory-frame origin. Effort should also be made to understand the cause of this issue in the experimental apparatus itself.

Indeed, in light of this issue, and based on the observation that the DCSs extracted from fits of the fast side of the images show generally good agreement with those generated from quantum-mechanical calculations, it was decided to use fast-side-only fits in the final data sets for $E_{\text{coll}} = 2210 \text{ cm}^{-1}$.

Spin-orbit-conserving collisions

The fitted and calculated DCSs for spin-orbit-conserving collisions show generally good agreement across the full range of j' recorded. However, despite a considerable improvement in the quality and resolution of the experimental images (in comparison to those collected at lower collision energies), there are a number of discrepancies between theory and experiment that ought to be addressed.

As for lower collision energies, the quantum-mechanical calculations tend to overestimate the extent of forward scattering measured at low j' , particularly for $j' \leq 14.5$. In a similar fashion, there appears to be a systematic underestimation of the intensity of backward scattering thereafter, particularly in the range $j' = 19.5 - 27.5$. In these cases, altering the basis functions and the number of Legendre polynomials used in the fitting of the experimental data did not successfully resolve the disagreement observed when theoretical data were compared to either a fit of the whole image or a fit of the fast side of the image.

For the images recorded for $j' = 12.5e$ and $j' = 13.5e$, it is believed that the relatively poor agreement between the theoretical and fitted data can be attributed to the relatively low quality of these experimental images. For both, there is a

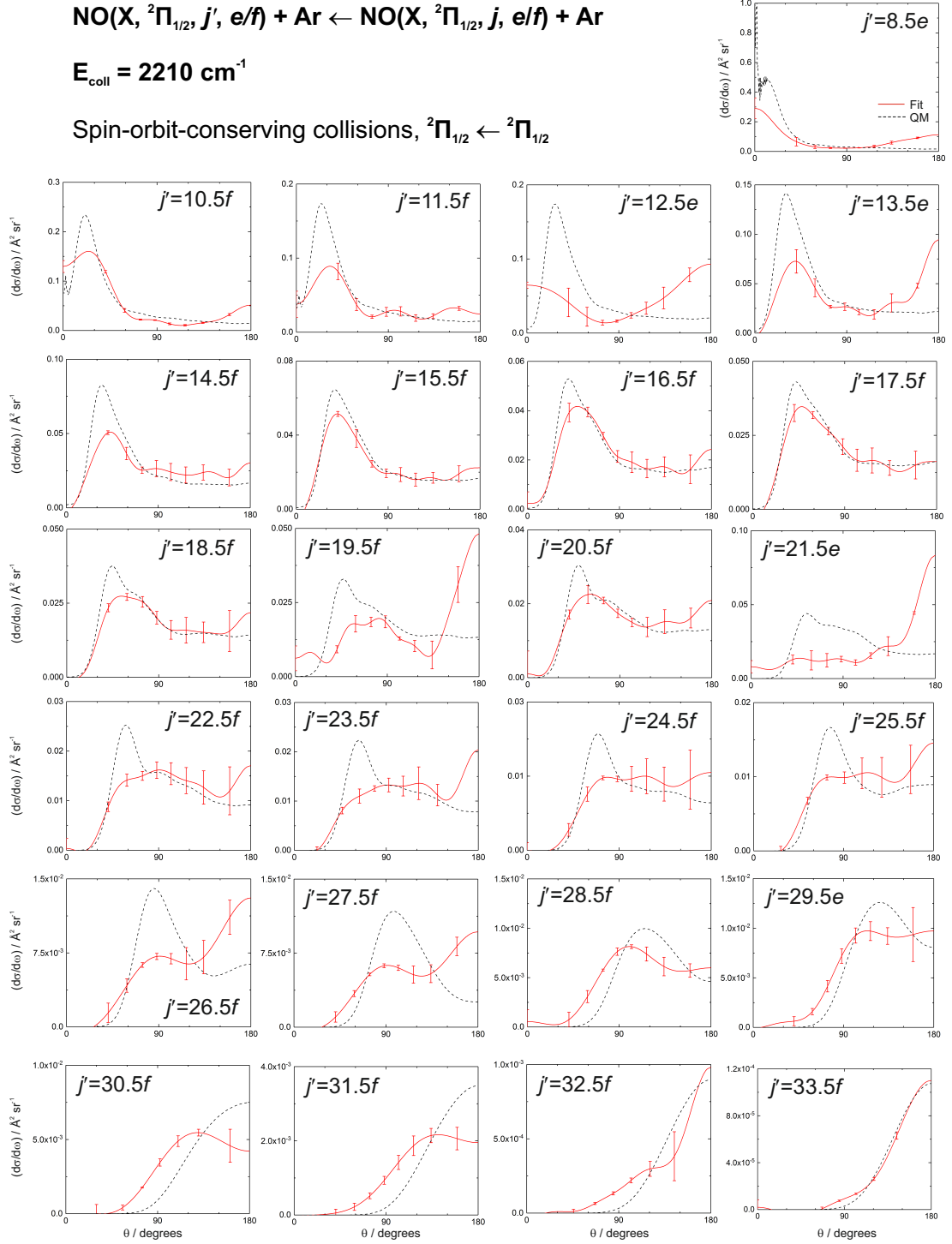


Figure 3.10: Fitted and quantum-mechanical DCSs for the inelastic scattering of $\text{NO}(X) + \text{Ar}$ at a collision energy of 2210 cm^{-1} . The data presented here refer to spin-orbit-conserving collisions (${}^2\Pi_{1/2} \leftarrow {}^2\Pi_{1/2}$). As explained in the text, the quantum-mechanical DCSs shown here were calculated from a j -weighted average of the individual DCSs for trajectories that originated in each of the $j = 0.5 - 5.5$ rotational states. Note the difference in scale of the y -axes.

notable quantity of poorly subtracted background signal in the backward-scattered signal that will impact negatively on the accuracy of the fitting process.

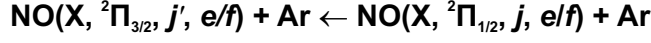
In general, the scattering distributions recorded experimentally and predicted theoretically show the strongest disagreement in the range $j' = 20 - 30$: the quantum-mechanical calculations consistently predict a more sideward-scattered distribution than that measured experimentally. It is also the case that these images, which are small and uniformly show a strong slow-side bias, are more difficult to fit, since the angular distribution of the DCS is exquisitely sensitive to how well the geometric centre of the image is defined prior to fitting. As outlined in the previous discussion, the images collected in this range of j' will also be the most sensitive to the laboratory-origin bias. As such, it is possible that, even when only the fast side of the image is fitted, the effect of the laboratory-origin bias is still seen in the extracted DCS, producing a more intense backward-scattered peak than is predicted by theory.

Spin-orbit-changing collisions

Figure 3.11 presents the fitted and quantum-mechanical DCSs for spin-orbit-changing collisions at 2210 cm^{-1} . The trends observed are largely the same as for the spin-orbit-conserving collisions and, in general, the agreement between experiment and theory for spin-orbit-changing collisions is very good. As before, forward scattering is overestimated by theory for $j' \leq 17.5$. It is also the case that backward scattering is underestimated by theory for $j' = 17.5 - 22.5$. However, it is thought that this observation can largely be rationalised using the same arguments that were outlined in the previous discussion of the spin-orbit-conserving data.

3.3 Further discussion

It has been noted that the quality of the experimental data improved significantly as the apparatus was characterised and optimised. As such, the data relating to the inelastic scattering of NO(X) by Ar at 2210 cm^{-1} are believed to be the most reliable and accurate of those reported in this thesis. In spite of this, some of the data reported at this collision energy still show appreciable disagreement between



$$E_{\text{coll}} = 2210 \text{ cm}^{-1}$$

Spin-orbit-changing collisions, ${}^2\Pi_{3/2} \leftarrow {}^2\Pi_{1/2}$

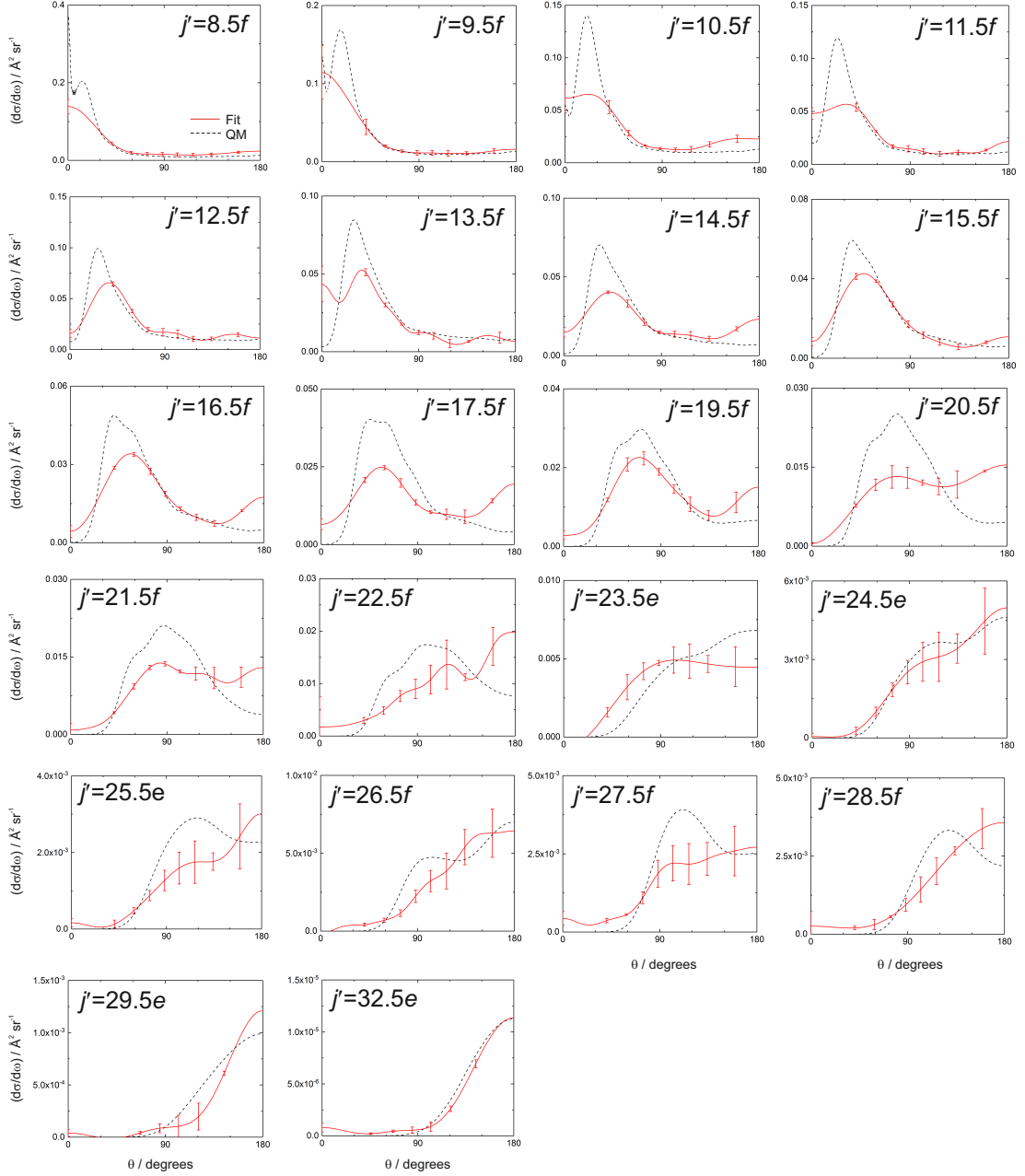


Figure 3.11: Fitted and quantum-mechanical DCSs for the inelastic scattering of $\text{NO}(\text{X}) + \text{Ar}$ at a collision energy of 2210 cm^{-1} . The data presented here refer to spin-orbit-changing collisions (${}^2\Pi_{3/2} \leftarrow {}^2\Pi_{1/2}$). As explained in the text, the quantum-mechanical DCSs shown here were calculated from a j -weighted average of the individual DCSs for trajectories that originated in each of the $j = 0.5 - 5.5$ rotational states. Note the difference in scale of the y -axes.

experiment and theory. Section 2.7 outlined how, when generating fitted and simulated images, and the corresponding DCSs, it is crucial to derive the correct set of parameters that will give the most accurate representation of experimental reality. However, there is also a need to balance the demands of input accuracy with that of computational time, without compromising the quality of the data that result.

Many of the experimental images reported for all three collision energies that were investigated in this thesis suffer from a notable lack of scattered signal in the intensely forward-scattered region of the DCS. For low j' states in particular, this leads to a decrease in scattering intensity exactly where the quantum-mechanical calculations predict it to be strongest. In the first instance, it is likely that the use of batch (rather than shot-by-shot) subtraction of background signal in recording the empirical data makes a significant contribution to the observed discrepancy between experiment and quantum-mechanical theory. This is due to the effects of experimental drift (in, for example, laser position and time delay) as an image is acquired over time. To combat this, steps were taken to improve the quality of experimental background subtraction before recording the $\text{ND}_3(\tilde{\text{X}})+\text{Ar}$ data presented in Chapter 4, and the issue is addressed in further detail there. However, it is also the case that, as outlined in Section 3.3.2, QCT calculations do predict a distinct lack of scattered intensity in the forward-scattered, classically forbidden region.

It may also prove interesting to study the scattering of fully hexapole-state-selected $\text{NO}(\text{X})$ by Ar at high collision energy to help determine the extent to which the observed discrepancy with theory is quantum-mechanical and/or parity-dependent in nature. To that end, future experimental work on high-energy hexapole-state-selected $\text{NO}(\text{X})+\text{Ar}$ scattering could, therefore, help elucidate the contributions from classical and quantum-mechanical dynamics in the low- θ region of the DCS and, by extension, allow for a better understanding of the disagreement in the data reported here. To that end, this section offers a fuller consideration of a number of factors that affected the trends shown by and accuracy of the theoretical results reported in this chapter.

3.3.1 Quantum-mechanical oscillations: parity dependence and diffraction

The quantum-mechanical calculations carried out in this thesis treat the set of $\text{NO}(\text{X})+\text{Ar}$ trajectories coherently. As such, the wave-particle character of the scattered molecules leads to purely quantum-mechanical interference effects that are manifested as oscillations in the experimental and calculated DCSs.

j -dependent alternations in the integral cross-section (ICS) for diatom-atom collisions have long been observed for near-homonuclear molecules [144]. They arise from the constructive or destructive interference of trajectories that scatter off either end of the diatomic molecule (or, indeed, off a given point along the bond axis itself), since the bond orientation of the diatom is not selected prior to collision. In a similar fashion, the DCS is affected by interference between different trajectories that scatter into the same value of θ .

Parity-dependent oscillations

As has been seen in the various data sets presented in this chapter, many DCSs show more than one peak in intensity over the full range of scattering angles. Previous work on $\text{NO}(\text{X})+\text{Ar}$ has shown that these oscillations can be explained using a relatively simple, hard-shell model that consists of four interfering pathways [38, 93, 94]. These four pathways are either head-on ($\gamma = 0^\circ, 180^\circ$) or side-on ($\gamma = 90^\circ, 270^\circ$) in nature, and are associated with the Jacobi angles shown in parentheses. The scattering amplitude is then written as a function of the relative phase shifts for the different paths [38, 145, 146],

$$f_{f \leftarrow i}(\theta) \propto 1 + e^{-i(\Delta\phi_N - \pi\Delta p/2)} + e^{+i\pi\Delta p/2} + e^{-i\Delta\phi_O}, \quad (3.1)$$

where $\Delta\phi_N$ and $\Delta\phi_O$ are the phase shifts between a trajectory that scatters off either end of the NO molecule and one that scatters perpendicularly off the bond axis into a given angle, θ . $\Delta p = p' - p$ is the change in the parity of $\text{NO}(\text{X})$, such that $\Delta p/2 = 0$ for parity-conserving collisions and $\Delta p/2 = 1$ for parity-changing

collisions. For a near-homonuclear molecule, such as NO, the phase shifts can then be expressed as [38, 145, 146]

$$\Delta\phi_x = (\Delta j_{\theta,x}^2 - j'^2)^{\frac{1}{2}} - j' \cos^{-1} \left(\frac{j'}{\Delta j_{\theta,x}} \right), \quad (3.2)$$

where $\Delta j_{\theta,x}$ is the magnitude of the angular momentum transferred when the molecule is scattered through a given angle, θ , after being struck at either the $x = \text{N}$ or $x = \text{O}$ end of the molecule, and is defined as

$$\Delta j_{\theta,x} = \Delta j_{\max,x} \sin \left(\frac{\theta}{2} \right). \quad (3.3)$$

$\Delta j_{\max,x}$ is the angular momentum transferred when the molecule is scattered though $\theta = 180^\circ$ which, in the limit of a hard-shell potential, can be defined as

$$\Delta j_{\max,x} = 2k(A_x - B), \quad (3.4)$$

where A_x is the major semi-axis for the x -end of the ellipsoid, B is the minor semi-axis, and $k = p/\hbar$ is the wavevector that is associated with the linear momentum of the molecule, p , and is also related to the inverse of the de Broglie wavelength of the particles.

Equation (3.1) can then be adapted for the parity-conserving and parity-changing cases, such that [38]

$$\begin{aligned} f_{\text{cons}}(\theta) &\propto 2 + e^{-i\Delta\phi_{\text{N}}} + e^{-i\Delta\phi_{\text{O}}}, \\ f_{\text{chang}}(\theta) &\propto e^{-i(\Delta\phi_{\text{N}} - \pi)} + e^{-i\Delta\phi_{\text{O}}}. \end{aligned} \quad (3.5)$$

Taking the square modulus of the of the corresponding scattering amplitude will, therefore, generate the DCS, *via* [38, 146]

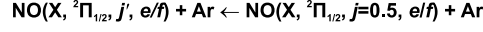
$$\begin{aligned} \frac{d\sigma_{\text{cons}}}{d\omega_{f \leftarrow i}} &\propto |f_{\text{cons}}|^2 \\ &\propto 6 + 4(\cos \Delta\phi_{\text{N}} + \cos \Delta\phi_{\text{O}}) + 2 \cos (\Delta\phi_{\text{N}} - \Delta\phi_{\text{O}}); \end{aligned} \quad (3.6)$$

$$\begin{aligned} \frac{d\sigma_{\text{chang}}}{d\omega_{f \leftarrow i}} &\propto |f_{\text{chang}}|^2 \\ &\propto 2 - 2 \cos (\Delta\phi_{\text{N}} - \Delta\phi_{\text{O}}). \end{aligned} \quad (3.7)$$

The dominant contribution to the parity-conserving DCS arises, therefore, from the interference that originates in the second term of the above equation. In contrast, the DCS for parity-changing collisions only depends on the difference of the interference terms that relate to scattering from either end of the molecule. In the homonuclear case, these two terms will be equivalent, and the DCS for parity-changing collisions will go to zero, as expected. Values of A_x and B can be obtained directly from the NO(X)+Ar PES by measuring the appropriate distance from the centre of the plot to the hard-ellipse contour defined by the collision energy.

Multiple-peaked oscillations in the DCS may then be attributed to the quantum-mechanical interference of phase differences from parity-conserving trajectories that scatter off either end of the NO molecule rather than the bond axis. In contrast, the near-homonuclear nature of the NO(X) molecule means that the phase difference terms from scattering off either end of the molecule largely cancel for parity-changing collisions, producing a single-peaked DCS with no observable oscillations. The number of peaks observed in parity-conserving DCSs is determined by two factors: the anisotropy of the potential and the de Broglie wavelength of the system. If the de Broglie wavelength is large compared to the phase shift, the quantum-mechanical interference is seen as a gradual increase or decrease in scattering intensity with respect to the scattering angle, meaning fewer oscillations are observed. For NO(X)+Ar, the dimensions of the ellipse along the semi-major and semi-minor axes are quite similar, meaning the PES is relatively isotropic [111].

In the experiments presented in this chapter, there is no quantum state-selection of the initial Λ -doublet level, so both the e and f levels are approximately equally populated. In contrast, the detection method of the scattered products is able to discriminate between final Λ -doublet states. In any case, the DCS for scattering into a given j' state will, in reality, be the average of the parity-conserving and parity-changing transitions from both initial Λ -doublet states. As a consequence, for many j' states, the parity-conserving oscillations will be washed out by averaging with the single-peaked, parity-changing DCS. This can be seen very clearly in the DCSs presented in Figure 3.12. Here, quantum-mechanical DCSs for parity-conserving



$$E_{\text{coll}} = 469 \text{ cm}^{-1}$$

Spin-orbit-conserving collisions, ${}^2\Pi_{1/2} \leftarrow {}^2\Pi_{1/2}$

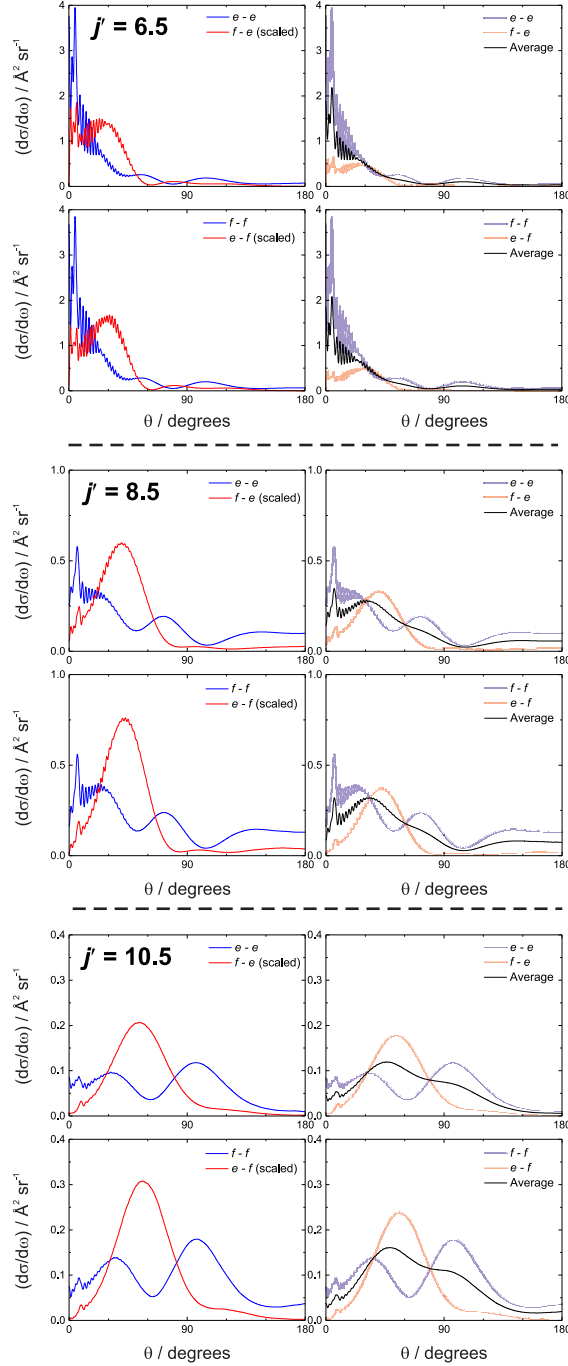


Figure 3.12: Comparison of quantum-mechanical DCSs for parity-conserving (blue) and parity-changing (red) spin-orbit-conserving collisions that scatter $\text{NO}(X, j = 0.5)$ molecules into a range of final rotational states at $E_{\text{coll}} = 469 \text{ cm}^{-1}$. To aid the comparison of structure, each pair of DCSs in the left-hand column has been scaled to give equal integrals. In the right-hand column, the DCSs in black are the average of the corresponding (unscaled) parity-conserving and parity-changing pair.

and parity-changing spin-orbit-conserving collisions that scatter $\text{NO}(X, j = 0.5)$ molecules into a range of final rotational states at $E_{\text{coll}} = 469 \text{ cm}^{-1}$ are presented alongside the DCSs generated by averaging over the initial Λ -doublets. It is important to note that, even though such averaging diminishes the observed magnitude of parity effects, there is still evidence (albeit muted) of parity-dependent oscillations in the DCSs shown in Figure 3.12 and, more broadly, in the experimental and theoretical data reported in Figures 3.6 to 3.11 for all collision energies.

Diffraction oscillations

Quantum-interference effects also give rise to rapid oscillations in the forward-most scattered region (typically, $\theta < 20^\circ$) of the DCS. The wave-particle duality of the Ar particles means that, on striking the NO molecule, the incoming matter-beam is diffracted. The resultant, diffracted waves can interfere either constructively or destructively to produce areas of relatively high and low scattering intensity, respectively. This phenomenon is known as Fraunhofer diffraction [147, 148] and is represented pictorially in Figure 3.13. Recent experiments carried out by von Zastrow *et al.* have successfully resolved Fraunhofer diffraction oscillations in experimental DCSs that result from the scattering of a Stark-decelerated beam of $\text{NO}(X)$ by He, Ne, and Ar [38, 93, 94]. However, it is important to note that the resolution of the experiment described in this thesis is not sufficiently high to resolve the quantum-mechanical interferences predicted theoretically. Further consideration of the parity-resolved DCSs for scattering into $j' = 6.5$ and $j' = 8.5$ in Figure 3.12 shows clear evidence of diffraction oscillations in the forward-scattered region. As with the parity-dependent effects, averaging over the initial Λ -doublet levels does seem to diminish the magnitude of the resultant oscillations, however, they remain easily observable. Diffraction oscillations are evident in many of the DCSs reported in Figures 3.6 to 3.11.

As with parity-dependent oscillations, a hard-shell model can be used to estimate the spacing between the diffraction peaks in the DCS, such that the angular

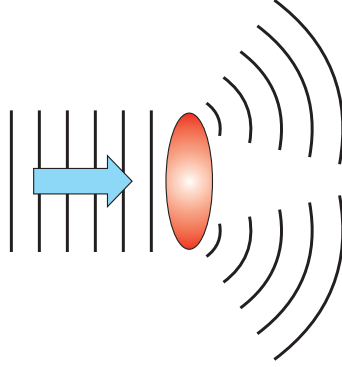


Figure 3.13: A simple diagram showing how a matter-wave is diffracted when it strikes either end of a hard ellipse. The blue arrow denotes the direction of travel of the incoming matter-wave.

spacing, $\Delta\theta$, is given by

$$\Delta\theta = \frac{\pi}{kR}, \quad (3.8)$$

where k is the wavevector of the collision – related to the inverse of the de Broglie wavelength – and R is the radius of the target molecule, calculated as the average of the A_x and B ellipsoidal radii. Previous work has confirmed that this relatively simple, hard-shell model shows good agreement with the Fraunhofer oscillations predicted by the HIBRIDON suite of codes [111, 122]. The agreement is particularly good when the values of A_x and B have relatively similar magnitudes, since this increases the accuracy of the effective radius, R , used in Equation (3.8).

3.3.2 Classical oscillations: ℓ -type and rotational rainbows

Rainbows are present in many of the quantum-mechanical DCSs reported in this chapter. These correspond to minima in the deflection function, $\chi(b)$, and to maxima in the scattering angle, θ , as a function of the impact parameter, b , since DCSs are only sensitive to the absolute value of the deflection angle, $\theta = |\chi|$, because of the cylindrical symmetry about the relative velocity vector [24]. Two types of rainbows are observed in DCSs: ℓ -type rainbows and rotational rainbows. Figure 3.14 is referenced throughout this section.

ℓ -type rainbows appear as maxima in the DCS as a function of the orbital angular momentum, ℓ , or the impact parameter, b , which are related by $\ell \propto b^2$

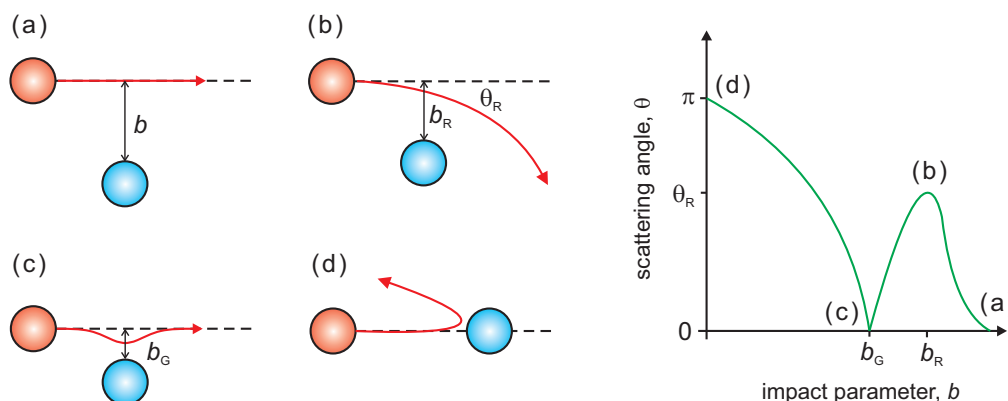


Figure 3.14: Diagram (adapted from [41]) showing how variation in impact parameter, b , leads to the formation of ℓ -type rainbows. The left-hand figure shows representations of several trajectories that lead to different types of scattering; the corresponding deflection plot is shown on the right. In the experiment at hand, the blue sphere represents an Ar atom and the red sphere represents an $\text{NO}(X)$ molecule. See text for details.

[24, 85]. At large impact parameters (Figure 3.14 (a)), the collisions are largely glancing-blow in nature, and produce intensely forward-scattered peaks in the DCS. As the impact parameter is lowered, the particles begin to feel the attractive part of the potential and the approaching particle is drawn towards the stationary collision partner. This generates a minimum in the deflection plot and, therefore, a local maximum in the DCS at the *rainbow angle*, θ_R , and an impact parameter of b_R (Figure 3.14 (b)). Notably, at θ_R , there are two values of b that lead to scattering at the given angle; below θ_R , there are three values of b that result in scattering into a certain value of θ , and this gives rise to interference effects [41].

As the impact parameter is reduced further, the particles also begin to sample the repulsive part of the potential, the approaching particle is deflected, and the scattering angle is seen to decrease (Figure 3.14 (c)). At a certain impact parameter, b_G , the attractive and repulsive potentials cancel exactly, and the net deflection of the particle is zero. This is known as *glory scattering*. If the impact parameter is reduced further still, the repulsive part of the potential dominates, and the collisions become increasingly head-on. The result is that the scattering angle increases steadily to its maximum value, $\theta = \pi$ rad (Figure 3.14 (d)).

Rotational rainbows originate from the repulsive part of the potential [149]. The anisotropy of the repulsion can give rise to an interference effect, whereby different

initial conditions (namely, the impact parameter and the relative orientation of the particles) can lead to the same scattering outcome (namely, the final rotational state and the scattering angle). Double rotational rainbows are particularly common for heteronuclear molecules, since they do not possess a mirror plane perpendicular to their principal symmetry axis. Scattering from each end of the diatomic molecule gives rise to two separate, single-peaked DCSs that sum constructively to give a double-peaked DCS. At low j' , the overlap of the two peaks is often masked by glory scattering, however, the double-peaked structure is more easily seen as j' increases [84].

Figure 3.15 compares j -weighted scattering-angle distributions for NO(X)+Ar inelastic collisions at 2210 cm^{-1} calculated using quantum-mechanical and *quasi*-classical trajectory (QCT)¹ algorithms. Note that all the scattering-angle distributions shown were calculated by scaling the quantum-mechanical and QCT DCSs to have the same integral. Since QCT calculations are, by their nature, closed-shell, a direct comparison with quantum-mechanical data requires that the latter be averaged over the initial Λ -doublet levels and summed over the final Λ -doublet levels so that the two sets of calculations are presented at the same resolution. Prior to scaling, the closed-shell quantum-mechanical DCSs, $\frac{d\sigma^{\text{CS}}}{d\omega}$, are calculated *via*:

$$\frac{d\sigma^{\text{CS}}}{d\omega} = \frac{1}{2} \times \left[\frac{d\sigma^{f-f}}{d\omega} + \frac{d\sigma^{f-e}}{d\omega} + \frac{d\sigma^{e-f}}{d\omega} + \frac{d\sigma^{e-e}}{d\omega} \right], \quad (3.9)$$

where $\frac{d\sigma^{x-y}}{d\omega}$ are the open-shell, quantum-mechanical DCSs for $x - y$ parity-resolved transitions. It should also be stressed that, since the QCT values of j' are integer (whereas the corresponding quantum-mechanical values are half-integer), each set of angular distributions is labelled in terms of Δj relative to $j = 0.5$, *i.e.* $\Delta j = j' - 0.5$.

As discussed previously, the oscillatory structure that is observed in parity-resolved, quantum-mechanical DCSs is much less pronounced after averaging over the initial Λ -doublet levels, though there is still some evidence of very minor oscillations in the DCSs of medium j' . For the most part, the QCT angular distributions show

¹The reader is referred to Section 5.5 for a detailed discussion of the nature, assumptions, advantages, and limitations of QCT calculations.

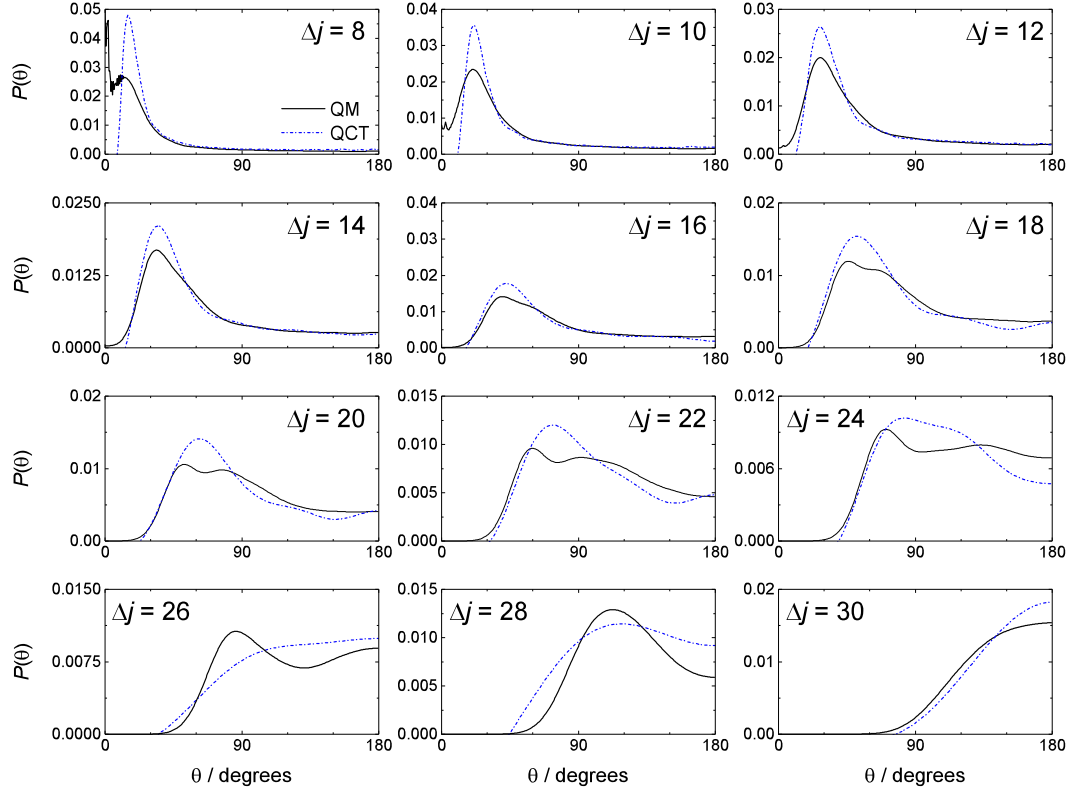


Figure 3.15: Comparison of j -weighted scattering-angle distributions for a range of Δj collisions that were generated from quantum-mechanical (QM) and *quasi*-classical trajectory (QCT) calculations run for the $\text{NO}(X) + \text{Ar}$ system at $E_{\text{coll}} = 2210 \text{ cm}^{-1}$. The open-shell quantum-mechanical angular distributions were averaged over the initial Λ -doublet levels and summed over the final Λ -doublet levels for comparison with closed-shell QCT theory.

a single peak, the maximum of which shifts to progressively larger values of θ as j' increases and the intensity distribution becomes predominantly backward-scattered. Overall, it can be said that there is generally good agreement in the positions of the maxima in both the quantum-mechanical and QCT angular distributions.

For $\Delta j = 8 - 10$, a comparison of the distributions elucidates the existence of a classically forbidden region at low scattering angles, where the QCT DCS intensity falls to zero. In contrast, the quantum-mechanical distribution for the lowest ($\Delta j = 8$) transition shows intense, rapid oscillatory structure in this region, as discussed previously. In general, however, neither the quantum-mechanical nor the QCT data shown in Figure 3.15 provide clear evidence of ℓ -type rainbows in the DCS structure, as would be expected at high collision energy. To investigate this further,

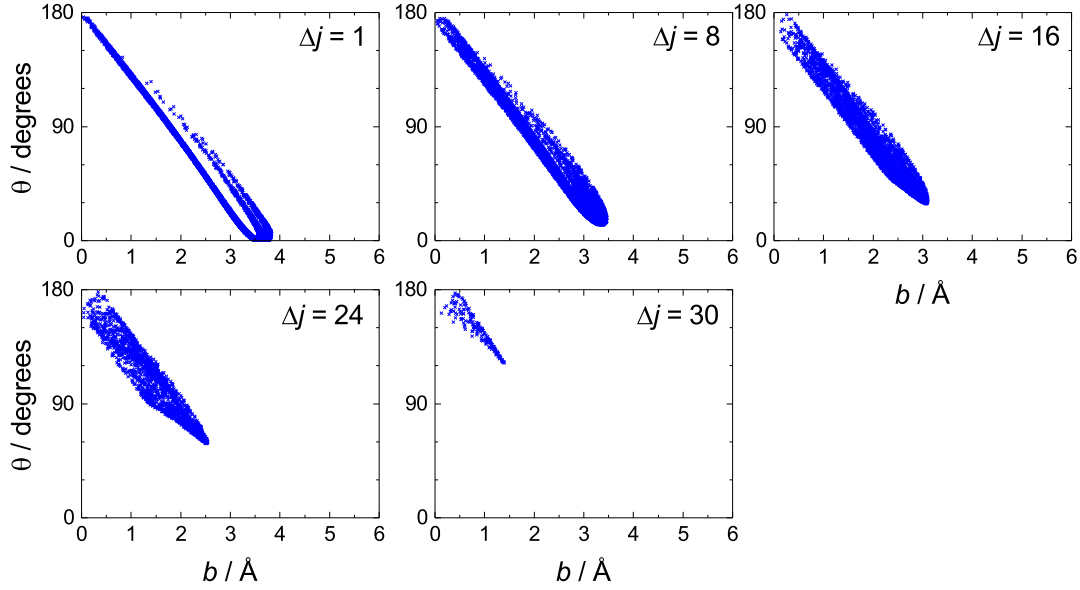


Figure 3.16: Deflection functions for a range of Δj collisions that were generated from *quasi*-classical trajectory (QCT) calculations run for the NO(X)+Ar system at $E_{\text{coll}} = 2210 \text{ cm}^{-1}$. In this instance, all trajectories originated in $N = 1$, such that, in the notation used here, $\Delta j = j' - 1.5$.

Figure 3.16 shows deflection functions for batches of QCT calculations, run at 2210 cm^{-1} , in which the NO(X) molecules originated in $N = 1$ (one of the two most populated N levels at $T_{\text{rot}} = 28 \text{ K}$) and underwent various Δj transitions on collision with Ar. From the deflection functions, it can be seen that, classically, no trajectories with impact parameters greater than $b = 3.8 \text{ Å}$ contribute to the DCS. In fact, the vast majority of collisions are head-on and occur at low impact parameters that sample the repulsive region of the NO(X)+Ar PES. As such, there is no secondary maximum in the the deflection function and no ℓ -type rainbow in the DCS.

This observation can be explained classically, based on the fact that the NO(X)+Ar PES is not particularly attractive in nature and that the collisions investigated in this section take place at high collision energy. Both Nichols [111] and Eyles [110] report ℓ -type rainbows for very low- Δj NO(X)+Rg scattering at collision energies around 500 cm^{-1} [150]. However, such features are not observed by for collisions of $\Delta j \geq 6$, *i.e.* the lower limit of the transitions reported at 469 cm^{-1} in this work. Similarly, the rainbows – which are a feature of collisions that sample the attractive part of the PES – will undoubtedly become less pronounced as the collision

energy increases. Nichols also presents evidence of much more prominent rainbows for DCSs relating to inelastic scattering in the $\text{NO}(\text{X})+\text{Kr}$ system [111], for which the PES is markedly more long-range and attractive [151, 152] than that of $\text{NO}(\text{X})+\text{Ar}$.

The fact that the QCT DCSs reported in this section do not show oscillatory structure – whereas the quantum-mechanical and, in some instances, experimental DCSs reported in Figures 3.6 to 3.11 do – suggests that the oscillations are quantum-mechanical in nature.

3.3.3 Collision-energy distribution

The variation in translational velocities within the molecular beam is best described by the Boltzmann distribution, whereby

$$n(v) \propto v^2 e^{[-\alpha_v(v-\bar{v})^2]}, \quad (3.10)$$

where $n(v)$ is the number of molecules with a given velocity, v ; $\alpha_v = -4 \ln(0.5)/\sigma^2$ (σ is the FWHM of the Gaussian distribution of molecular-beam velocities); and $\bar{v}$ is the mean velocity of the molecular beam. Given that $E_{\text{coll}} \propto v^2$, it can also be said that the collision energy that characterises the system of interest is, in reality, best described by a distribution of energies.

Reproducing this distribution of energies in quantum-mechanical calculations requires individual scattering matrices to be generated for a large number of collision energies. The resultant DCSs are then used to produce a weighted average according to the Boltzmann distribution. Figure 3.17 compares the quantum-mechanical DCSs for the scattering of $\text{NO}(\text{X})$ into three final rotational states: $j' = 6.5e$, $11.5e$, and $15.5e$. DCSs in black are from a single calculation run at 469 cm^{-1} , and those in red are expressed as a Boltzmann-weighted average of thirteen different DCSs calculated at collision energies in the range $409 - 529 \text{ cm}^{-1}$, at increments of 10 cm^{-1} .

The single-energy and weighted DCSs for $j' = 6.5e$ and $j' = 11.5e$ show excellent agreement. The same cannot be said for $j' = 15.5e$, where there is significantly greater discrepancy between the two DCSs shown. However, it should be noted that the angular distribution of intensity within the $j' = 15.5e$ DCSs is largely the same:

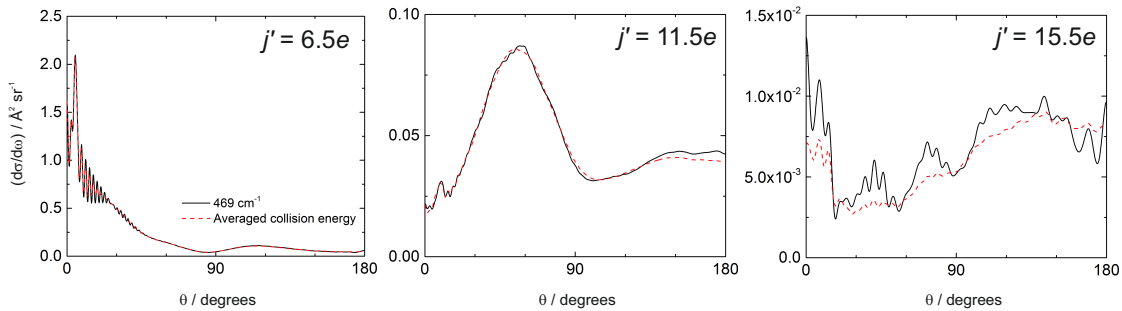


Figure 3.17: Quantum-mechanical DCSs for the inelastic scattering of NO(X)+Ar. The data presented here refer to spin-orbit-conserving collisions ($^2\Pi_{\frac{1}{2}} \leftarrow ^2\Pi_{\frac{1}{2}}$). DCSs in black are from a single calculation run at 469 cm^{-1} , and those in red are expressed as a Boltzmann-weighted average of thirteen different DCSs calculated at collision energies in the range $409 - 529\text{ cm}^{-1}$, at increments of 10 cm^{-1} .

the main difference lies in the overall intensity, and in the number of oscillations observed. Given that the agreement between single-energy and weighted DCSs shown in Figure 3.17 is generally good, it was decided that quantum-mechanical calculations would be run at a single collision energy for the higher-energy (1480 cm^{-1} and 2210 cm^{-1}) experiments. This is particularly advantageous for these higher-energy calculations, which require significantly greater numbers of channels to achieve convergence in J , making them particularly lengthy and expensive.

Of course, the collision energy at which the quantum-mechanical calculations are run depends on whether the full initial rotational-state distribution is taken into account. The method by which the experimental collision energy is determined was discussed in Section 2.3.1, and the collision energies reported in this chapter are generated using Equation (2.11) by assuming that all the molecules in the beam originate in $j = 0.5$, giving a value of $E_{\text{coll}} = 2210\text{ cm}^{-1}$ for NO(X) seeded at 10% in H_2 . If, instead, proportional contributions from higher initial j levels are also included, the value of E_{coll} now becomes 2163 cm^{-1} . Notably, this value of E_{coll} lies well within the 95% confidence limits of the collision energy shown in Figure 2.4. For this reason, and for the sake of consistency, all collision energies are calculated assuming that 100% of the molecules originate in $j = 0.5$.

3.3.4 Initial rotational-state population distribution

As discussed previously, the significantly hotter rotational temperature of the primary molecular beam when NO was seeded in H_2 meant that the quantum-mechanical DCSs for this collision energy were adapted to account for the initial rotational-state distribution of the molecular beam. Figure 3.18 compares the j -weighted DCSs to those that assume that 100% of the molecules originate in $j = 0.5$. As can be seen, the differences between the j -weighted and $j = 0.5$ DCSs are mostly minimal, especially for high j' states, when the number, distribution, and intensity of peaks is in very good agreement. In a similar fashion, the simulated images presented in Figure 3.3 generally showed negligible differences when derived from either the $j = 0.5$ DCS or the j -weighted DCS for high j' states.

However, as can also be seen in Figure 3.18, there is a significant difference between the $j = 0.5$ and j -weighted DCSs with respect to the intensity of the forward-scattered region for $j' = 8.5e$. Given that the $j = 0.5$ DCS already over-predicts the extent of forward-scattering observed in the experimental data presented here, modelling the rotational-state distribution more accurately would not resolve the observed disagreement between experiment and theory. Therefore, based on the fact that the $j = 0.5$ and j -weighted DCSs for the majority of states are largely similar, and in consideration of the vastly reduced computational demands in only calculating a single DCS for $j = 0.5$, a j -weighted DCS was not used to generate the simulated images presented in this chapter.

3.4 Summary

This chapter has presented data from the first sets of rotationally inelastic scattering experiments to be carried out on this new, compact, crossed-molecular beam machine. As such, the role of this study was to select a suitable candidate system with which to calibrate and optimise this new experimental apparatus.

Experimental, fitted, and simulated images were presented alongside fitted and quantum-mechanical DCSs for the rotationally inelastic scattering of $\text{NO}(X)$ by Ar

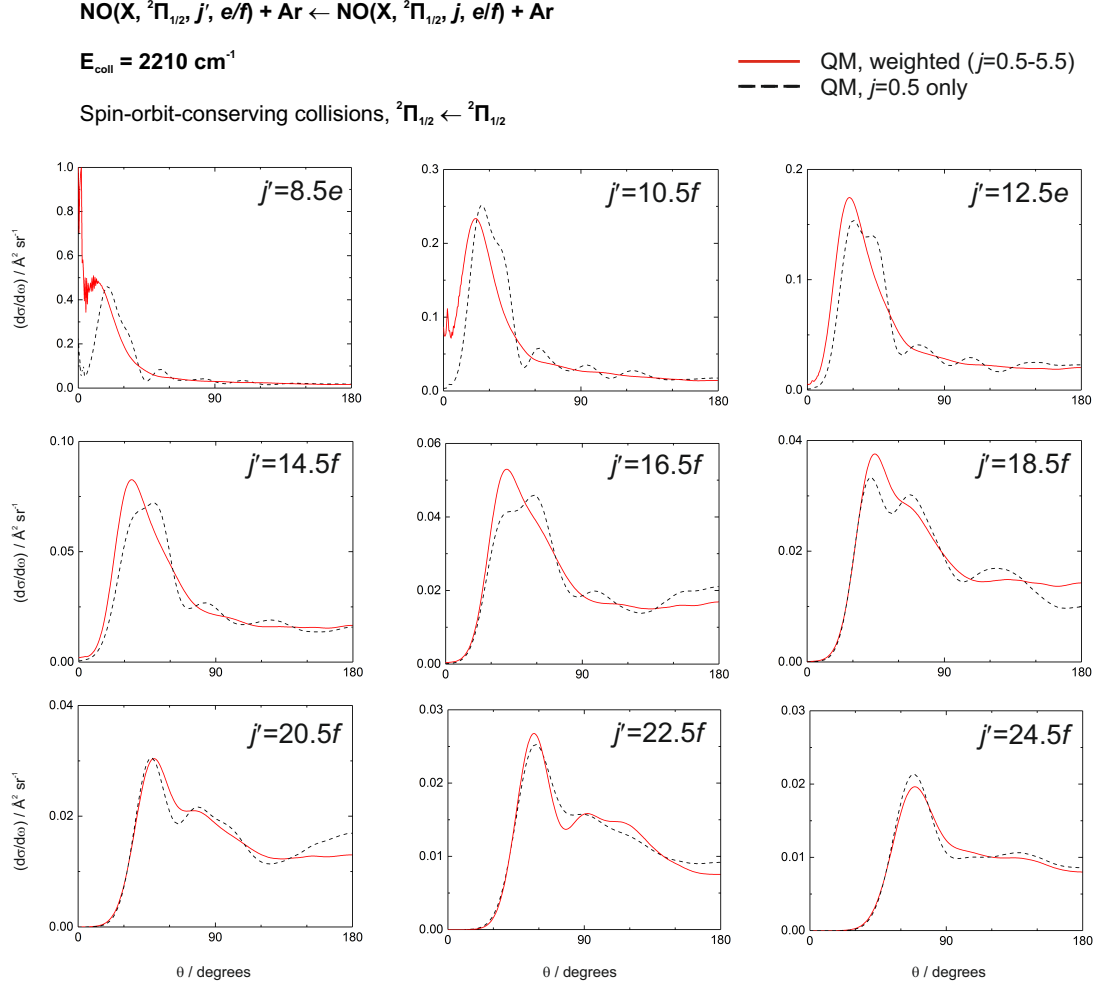


Figure 3.18: Quantum-mechanical DCSs for the inelastic scattering of NO(X)+Ar at a collision energy of 2210 cm^{-1} . The data presented here refer to spin-orbit-conserving collisions ($^2\Pi_{1/2} \leftarrow ^2\Pi_{1/2}$). The DCSs shown by black, dashed lines were generated assuming that all of the NO(X) molecules are in the $j = 0.5$ rotational state prior to collision. The DCSs shown by red lines were generated from a weighted average of the DCSs for collisions that originate in each of the initial rotational states in the range $j = 0.5 - 5.5$. See text for details.

at collision energies of 469 cm^{-1} , 1480 cm^{-1} , and 2210 cm^{-1} . The latter collision energy is considerably higher than any other reported in the literature, and so is of particular interest in this thesis.

All the experimental data were subjected to a rigorous comparison with full, close-coupled, quantum-mechanical calculations (run using the HIBRIDON suite of codes [122]) in order to assess the ability of currently available PESs to model the inelastic scattering of NO(X) by Ar. The data at 2210 cm^{-1} were also compared to

closed-shell QCT calculations. The origin and nature of several important features of the images and DCSs (including, but not limited to, the effect of collision energy and the anisotropy of the PES on the dynamics, the angular distribution of scattering intensity, and the nature and occurrence of classical and quantum-mechanical oscillations) were discussed in detail.

The agreement between experiment and theory was found to be reasonably good, especially for the experiments carried out at 469 cm^{-1} and 1480 cm^{-1} , in that theory correctly reproduces the number, angular range, and relative intensity of peaks in the fitted DCSs (within the limit of current experimental resolution). For the data recorded at 2210 cm^{-1} , the agreement between experiment and theory was also found to be generally good, however, there was also a more appreciable level of disagreement between the empirical and calculated DCSs for several low and medium values of j' . To that end, it is also hoped that future experimental and theoretical work on high-energy diatom-atom collisions will help better our understanding of the scattering dynamics observed in the current experimental data.

4

Inelastic scattering of state-selected $\text{ND}_3(\tilde{\text{X}})+\text{Ar}$ at 405 cm^{-1}

Deuterated ammonia, ND_3 , is a molecule of notable interest for dynamicists: it is a relatively simple, symmetric-top species that is amenable to experimental manipulation and observation and rigorous theoretical treatments [46, 153–160]. It is also of significant astrochemical importance, being the first triply-deuterated molecule identified conclusively in space [161]. This chapter presents a comparative experimental and theoretical study of the fully quantum-state-selected, rotationally inelastic scattering of $\text{ND}_3(\tilde{\text{X}})$ by Ar. The experiments described in this chapter were the first to employ a newly designed hexapole state-selector that was used to generate a well-defined beam of $\text{ND}_3(\tilde{\text{X}}, j_k^\pm = 1_1^-)$ molecules.

Once prepared, the beam of $\text{ND}_3(\tilde{\text{X}}, j_k^\pm = 1_1^-)$ (seeded at 5% in Ar) interacted with a secondary beam of pure Ar to undergo rotationally inelastic collisions at an energy of 405 cm^{-1} . During collision, the $\text{ND}_3(\tilde{\text{X}}, j_k^\pm = 1_1^-)$ molecules were excited into various final rotational states, most of which lie higher in energy than $j_k^\pm = 1_1^-$, and velocity-map images were obtained for several $\text{ND}_3(\tilde{\text{X}}, j_{k'}'^-)$ states using a well-known (2+1) REMPI detection scheme *via* the two-photon $\tilde{\text{B}}, v_2 = 5 \leftarrow \text{X}$ transition at around 317 nm. The rotationally inelastic dynamics of the $\text{ND}_3(\tilde{\text{X}}, j_k^\pm = 1_1^-)+\text{Ar}$ system have already been studied at a collision energy

very similar to that reported in this thesis [160], and so the set of data reported here served to calibrate the new hexapole state-selector apparatus. The experimental data are also compared to quantum-mechanical calculations.

This chapter begins by outlining the spectroscopy of the ND_3 molecule, including an explanation of the notation used throughout. The calibration of the hexapole state-selector apparatus is then discussed in detail. The main body of this chapter will focus on a rigorous comparison of experimental and theoretical data relating to rotationally inelastic scattering in the $\text{ND}_3(\tilde{X}, j_k^\pm = 1_1^-) + \text{Ar}$ system. This chapter ends by summarising the main conclusions drawn from this work and highlighting their relevance to future experimental and theoretical studies.

4.1 The spectroscopy of $\text{ND}_3(\tilde{X})$

Before considering the rotationally inelastic scattering of $\text{ND}_3(\tilde{X})$ by Ar, it is important to understand the spectroscopy of the ND_3 molecule in its ground electronic state, which has an electronic configuration given by

$$1a_1^2 1e_1^4 2a_1^2. \quad (4.1)$$

As such, the molecule can be classified as closed-shell (with term symbol $^1\Sigma$); it has no unpaired electrons and an electronic spin angular momentum of zero. $\text{ND}_3(\tilde{X})$ may be classified as an oblate, symmetric-top molecule. In this case, $I_a = I_b < I_c$, where I_a , I_b , and I_c are the moments of inertia ($I_x = m_x r_x^2$) about three mutually perpendicular axes through the centre of mass, where I_c is assigned to the largest moment of inertia. Each moment of inertia corresponds to a rotational constant – A , B , and C – such that $X \propto I_x^{-1}$; however, these constants do not relate explicitly to individual bond lengths within the molecule.

In general, a given rotational level in an oblate top is labelled j_k . j is the rotational-angular-momentum quantum number, and k (which can be assigned a value in the range $-j \leq k \leq j$, where k is an integer) is the quantum number that corresponds to the projection of $\mathbf{j}$ onto the unique c axis of the molecule. For ND_3 , the c axis is the C_3 axis of rotation – see Figure 4.1. Notably, each j level has

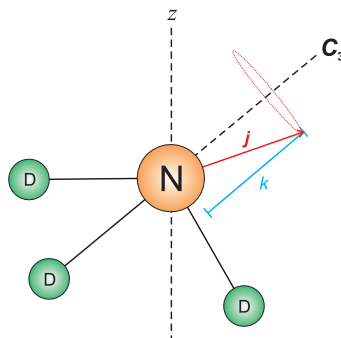


Figure 4.1: The $\mathbf{j}$ vector and the k projection that, along with the inversion symmetry, are used to define the rotational state of the ND_3 molecule.

$2j + 1$ degeneracy that arises from the projection of $\mathbf{j}$ onto the space-fixed Z -axis, denoted m . In addition, each level of k (except $k = 0$) has two-fold degeneracy due to the inversion symmetry of the ν_2 vibrational mode of ND_3 . As such, the energy levels of ND_3 are labelled with an additional quantum number, $+$ or $-$, that corresponds to the symmetric and antisymmetric components, respectively, of the linear combination of the wavefunctions that describe the ‘up’ or ‘down’ position of the nitrogen atom with respect to a triatomic plane of deuterium atoms – see Figure 4.2. The energy splitting between these the inversion-symmetry states is small, with the j_k^+ state being found 0.053 cm^{-1} lower in energy than the corresponding j_k^- state [162]. Although both inversion-symmetry states are mirror images of each other, and exist in the C_{3v} point group, there is high fluxionality of the inversion under the experimental conditions reported in this thesis due to a low inversion splitting, a small activation barrier to inversion, and the viability of quantum-mechanical tunnelling. To account for this, the ND_3 molecule is assumed to have D_{3h} symmetry in the calculations reported in this thesis [163].

The energy of a given j_k level will depend on the values of both j and k , and also on a number of rotational and centrifugal distortion constants. The most complete expression for the rotational energy, $F(j, k)$, can be written as [164]:

$$F(j, k) = Bj(j + 1) + (C - B)k^2 - D_j j^2(j + 1)^2 - D_{jk} j(j + 1)k^2 - D_k k^4 \quad (4.2)$$

where B and C are the rotational constants outlined above, and the various constants labelled D are attributed to centrifugal distortion. In the limit that the molecule

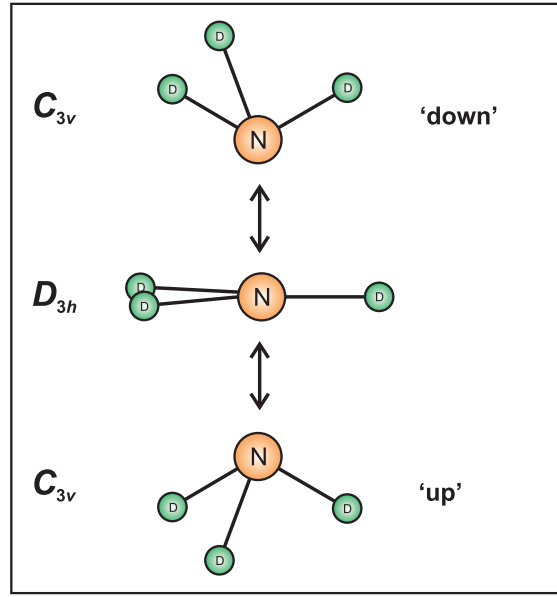


Figure 4.2: Inversion in the ND_3 molecule.

can be treated as a rigid rotor, only the first two terms in the equation above contribute to the molecular energy, such that:

$$F(j, k) = Bj(j+1) + (C - B)k^2. \quad (4.3)$$

Notably, and in contrast to a prolate, symmetric top, the energy of a given j level in an oblate, symmetric-top molecule will decrease as k increases.

Since $\text{ND}_3(\tilde{X})$ is a closed-shell molecule, the absence of spin-orbit coupling means that the molecular Hamiltonian can be simplified into one term for nuclear rotation, as outlined in Equations (4.2) and (4.3). Furthermore, the specific, symmetry-adapted eigenstates of ND_3 can be derived from generic symmetric-top eigenstates, given by [165, 166]:

$$|j, k, m, \epsilon\rangle = \frac{1}{[2(1 + \delta_{k0})]^{\frac{1}{2}}} (|j, k, m\rangle + \epsilon|j, -k, m\rangle), \quad (4.4)$$

where ϵ is the inversion index and the various other constants are as defined previously. $\delta_{k0} = 1$ when $k = 0$ and $\delta_{k0} = 0$ when $k \neq 0$. In general, $\epsilon = \pm 1$, except for the $k = 0$ states, for which $\epsilon = +1$ only [165]. The inversion index, ϵ , is linked to the inversion quantum number, $\pm$, as: $\pm = -\epsilon(-1)^j$, and the overall parity of the rotational inversion states is given by [165]:

$$\hat{i}|j, k, m, \epsilon\rangle = -\epsilon(-1)^{j+k}|j, k, m, \epsilon\rangle, \quad (4.5)$$

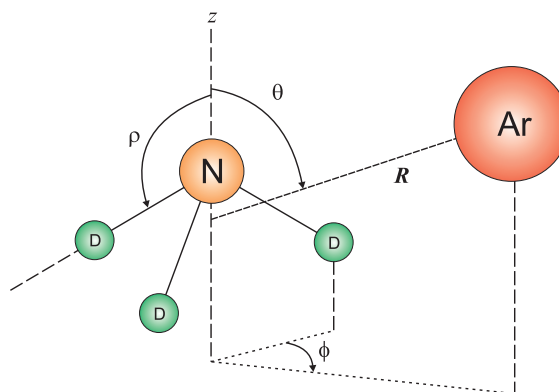


Figure 4.3: Coordinate system used to define the $\text{ND}_3(\tilde{X}) + \text{Ar}$ system in terms of $\mathbf{R}$, θ , ϕ , and ρ . The origin of the coordinate system is taken to be the centre-of-mass of the ND_3 molecule.

where $\hat{i}$ is the inversion operator. There are three possible nuclear spin modifications for the ND_3 molecule: A_1 , A_2 , and E . Broadly, when $k = 0$ or $3n$, where n is any integer, the nuclear spin has either A_1 symmetry, A_2 symmetry, or a combination of the two; otherwise, the nuclear spin state is of E symmetry [166]. The degeneracies of each of the three coupled deuterium spin states are calculated from the irreducible representations to give statistical weights of: $g_{A_1} = 10$, $g_{A_2} = 1$, and $g_E = 16$ [167].

4.2 Potential energy surface

Figure 4.3 shows the coordinate system used in this chapter to define the $\text{ND}_3(\tilde{X}) + \text{Ar}$ configuration. The origin of the coordinate system is set as the centre-of-mass of the ammonia molecule; $\mathbf{R}$ is the vector between the centre-of-mass of ND_3 and the Ar atom; and the various angles – θ , ϕ , and ρ – are defined in the diagram. The N–D bond length was fixed to its vibrationally averaged value in the ground electronic state ($r_0 = 1.016 \text{ \AA}$) [168].

Figure 4.4 shows the PES of the $\text{ND}_3(\tilde{X}) + \text{Ar}$ system that was calculated by Loreau *et al.*, using the coordinate system described above, at the CCSD(T) (coupled-cluster method with single, double, and perturbative triple excitations) level of theory with a Hartree-Fock reference wavefunction [168]. The calculations used an aug-cc-pVQZ (augmented correlation-consistent polarised valence quadruple zeta) basis set, and scalar relativistic effects were included *via* the Douglas-Kroll-Hess

Hamiltonian, with energy correction in the case of geometric basis-set superposition. The PES was expanded in tesseral spherical harmonics, $S_{\lambda\mu}(\theta, \phi)$, such that [160]

$$V(R, \theta, \phi, \rho) = \sum_{\lambda, \mu} \nu_{\lambda\mu}(R, \rho) S_{\lambda\mu}(\theta, \phi), \quad (4.6)$$

where the $S_{\lambda\mu}(\theta, \phi)$ functions are real-valued combinations of spherical harmonics, $Y_{\lambda\mu}(\theta, \phi)$. The R -dependence of the expansion coefficients, $\nu_{\lambda\mu}(R, \rho)$, was fitted using cubic splines in the interaction region ($R \leq 15.87$ Å) and the appropriate inverse powers of R in the long-range region ($R > 15.87$ Å). The ρ -dependence was fitted to a polynomial expansion [160, 168].

In the contour plots shown, the potential energy of interaction is given as a function of two coordinates, R and θ , at fixed values of ρ and ϕ . In both cases, the inversion angle, ρ , is fixed at its equilibrium value, $\rho_e = 112.1^\circ$, and $\phi = 0^\circ$ or $\phi = 60^\circ$, corresponding to the approach of the Ar atom in the plane defined by one of the three N–D bonds and the C_3 axis or midway between the planes defined by a pair of N–D bonds and the C_3 axis, respectively. Note that these surfaces have been adapted, within the Born-Oppenheimer approximation, from those of $\text{NH}_3(\text{X}) + \text{Ar}$ by changing the isotopic mass of hydrogen.

The figure illustrates that the potential is generally more attractive when $\phi = 60^\circ$, such that the Ar atom approaches the ND_3 molecule between the planes defined by two N–D bonds and the C_3 axis. Indeed, the global minimum of the surface is found in this geometry when the Ar atom is located just above the N atom of the ammonia molecule, at $\theta = 85.1^\circ$. When $\phi = 0^\circ$, and the Ar atom approaches the ammonia molecule in the plane defined by one of the N–D bonds and the C_3 axis, the distance of closest approach is reduced and the local minimum becomes less deep.

The long-range behaviour of the system in the two geometries is also quite different. For $\phi = 0^\circ$ and a fixed value of R , the local minimum lies along $\theta = 112.1^\circ$. This arrangement, which corresponds to the direct approach of the Ar atom towards and along one of the N–D bonds, maximises the dispersion interaction and stabilises the configuration. However, as R is decreased, this structure becomes less favourable, and the minimum shifts towards progressively smaller values of θ . In contrast, when

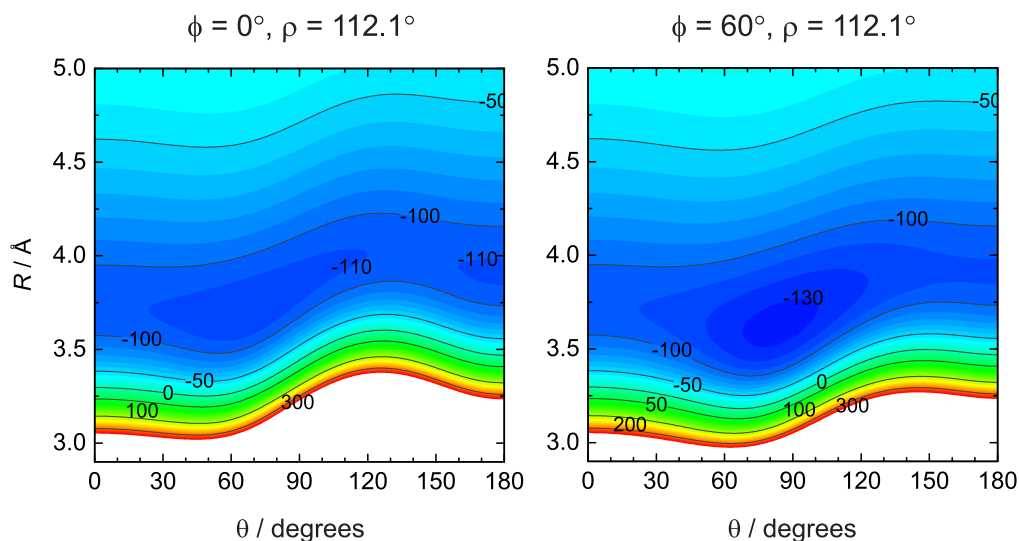


Figure 4.4: CCSD(T) PES of the $\text{ND}_3(\tilde{X}) + \text{Ar}$ system, as a function of $\mathbf{R}$ and θ , with $\rho = \rho_e = 112.1^\circ$ [168]. The values on the surfaces give the potential energy in cm^{-1} . The left-hand plot shows the PES when $\phi = 0^\circ$; the right-hand plot shows the PES when $\phi = 60^\circ$. Note that these PESs have been adapted from those of $\text{NH}_3(\text{X}) + \text{Ar}$ by changing the isotopic mass of hydrogen.

$\phi = 60^\circ$, there are two local minima at $\theta = 0^\circ$ and $\theta = 135^\circ$ in the long range. When R decreases, the minimum can be found when $\theta = 85.1^\circ$, as noted previously. In effect, a configuration with $\phi = 0^\circ$ is more favourable in the long range, whereas that with $\phi = 60^\circ$ minimises the interaction energy in the short range.

A final consideration is given to the relative stability of the two symmetric-top configurations. When $\theta = 0^\circ$, and the Ar atom approaches the ammonia molecule along the z -axis and towards the N atom, the potential energy of interaction is some 13.5 cm^{-1} lower than that found when $\theta = 180^\circ$ and the Ar atom approaches from below. As such, the interaction with Ar is said to perturb the otherwise-symmetric double-well inversion potential of free ammonia, and this will have important consequences for the inversion tunnelling splitting in the rovibrational states of the complex [168].

4.3 Quantum-mechanical calculations

Quantum-mechanical scattering calculations were performed by Loreau *et al.* [160, 168], on the PES described above, using the close-coupling (CC) method [158]

in the body-fixed frame. The CC equations were solved at a collision energy of 410 cm^{-1} , using the renormalised Numerov algorithm, on an equidistant grid of 250 points in the range $R = 4.3 - 22.0 \text{ a}_0$. Note that this collision energy is very similar to that of the experiments carried out in this thesis (405 cm^{-1}). The basis set consisted of rotational states up to, and including, $j = 11$, and all partial waves up to a total of $J = 120$ were taken into account.

4.4 Experimental apparatus

Figure 4.5 is a schematic diagram of the experimental apparatus used to collect data for the inelastic scattering of $\text{ND}_3(\tilde{\text{X}}, j_k^\pm = 1_1^-)$ by Ar. The apparatus is similar in parts to that described in Chapter 2, however, a number of important modifications have been made. Most notably, the new apparatus includes the addition of a hexapole state-selector to fully quantum-state-select molecules in the $\text{ND}_3(\tilde{\text{X}}, j_k^\pm = 1_1^-)$ state before collision. Specific details and dimensions of the experimental apparatus used to collect the data reported in this chapter can be found in reference [169]. The purpose, design, and calibration of this hexapole state-selector are described in detail in the sections that follow.

4.4.1 State selection: the linear Stark effect

As outlined above, each rotational level, j , comprises $2j + 1$ degenerate, space-quantised m levels in the absence of an external field. However, the application of an external electric (or magnetic) field can lift this degeneracy – this is known as the Stark (or Zeeman) effect. In the presence of an electric field (such as that generated by a hexapole state-selector), the ND_3 dipole moment, $\boldsymbol{\mu}$, points along the C_3 axis, and the angle, α , between the $\mathbf{j}$ vector and $\boldsymbol{\mu}$ is given by:

$$\cos \alpha = \frac{\epsilon |k|}{\sqrt{j(j+1)}}. \quad (4.7)$$

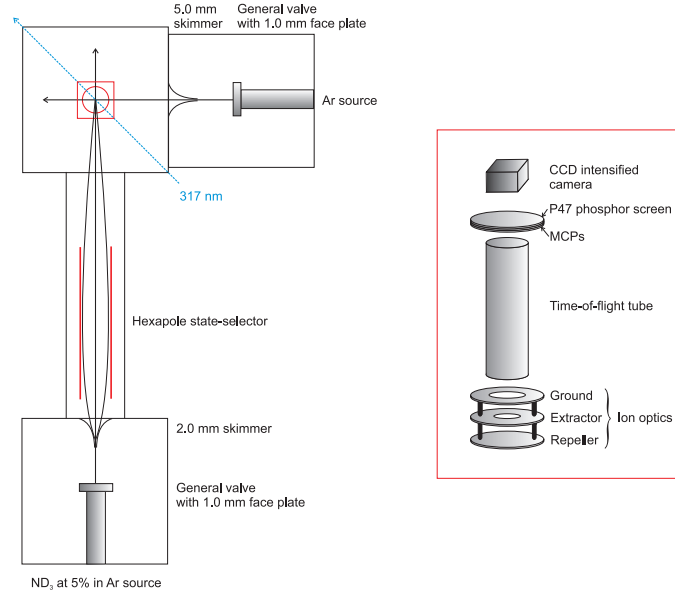


Figure 4.5: Schematic diagram of the experimental apparatus used to collect data relating to the inelastic scattering of $\text{ND}_3(\tilde{X}, j_k^\pm = 1_1^-)$ by Ar. The red box at the centre of the scattering chamber is expanded in the insert figure. Note that the MCPs, phosphor screen, and camera are all positioned above the scattering chamber, parallel to the plane defined by the lasers and molecular beams. The time-of-flight axis is perpendicular to the plane defined by the lasers and molecular beams. The apparatus is not drawn to scale. See text for details.

As $\mathbf{j}$ precesses about the C_3 axis, the component of $\boldsymbol{\mu}$ that is perpendicular to $\mathbf{j}$ cancels out, leaving only μ_j , which is given by

$$\begin{aligned}\mu_j &= \mu \cos \alpha \\ &= \mu \frac{\epsilon |k|}{\sqrt{j(j+1)}}.\end{aligned}\tag{4.8}$$

The interaction of a polar, symmetric-top molecule with an external electric field, E – the electric vector of which can be found at an angle, β , to $\mathbf{j}$ – will lead to an interaction energy of

$$\begin{aligned}E_{\text{Stark}}(j, k, m) &= -\mu_j E \cos \beta \\ &= -\mu \frac{\epsilon |k|}{\sqrt{j(j+1)}} E \frac{|m|}{\sqrt{j(j+1)}} \\ &= -\frac{\mu E \epsilon |km|}{j(j+1)}.\end{aligned}\tag{4.9}$$

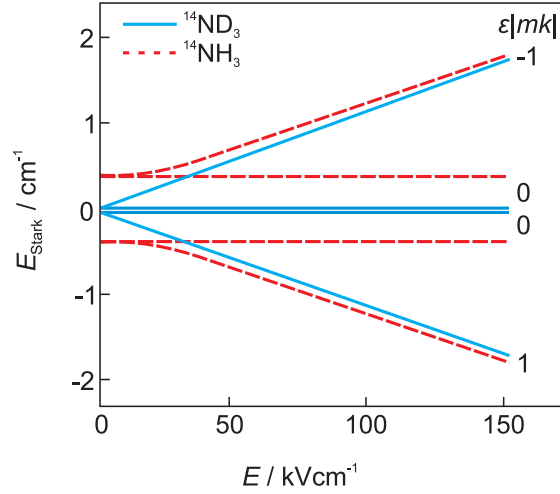


Figure 4.6: Stark splitting of the $|j, k\rangle = |1, 1\rangle$ level of $^{14}\text{NH}_3$ and $^{14}\text{ND}_3$ as a function of the strength of the electric field applied. This figure is adapted from that in reference [170].

It is this Stark interaction energy that allows for the isolation and differential focusing of specific $\text{ND}_3(\tilde{X}, j_k^\pm)$ states using the electric field created by a hexapole state-selector. This phenomenon is discussed in more detail in the section to follow. Notably, the choice of ND_3 over NH_3 is made because the magnitude of the inversion energy splitting is significantly reduced upon deuteration: 0.79 cm^{-1} for NH_3 and 0.053 cm^{-1} for ND_3 [162]. This leads to a more linear Stark effect in the range of voltages sampled in these experiments (see Figure 4.6).

4.4.2 Calibration of hexapole state-selector apparatus

Hexapole state-selectors [171–173] make use of the linear Stark effect to differentiate high- and low-field-seeking molecules. The apparatus is formed of six, stainless steel, cylindrical rods with rounded ends, in a hexagonal arrangement. The rods are 140 mm long, have a radius $R_{\text{rod}} = 1.50 \text{ mm}$, and the hexagon they form has an inner radius $R_0 = 2.65 \text{ mm}$. These dimensions were chosen to obey the relationship $R_{\text{rod}} = 0.565R_0$, and thus produce an ideal hexapole field (see Figure 4.7) [174]. Positive and negative potential differences are applied to all six rods such that alternate rods carry the same magnitude of voltage, but with different polarity. Figure 4.8 shows computer-aided designs (CADs) of the hexapole used in this thesis [175].

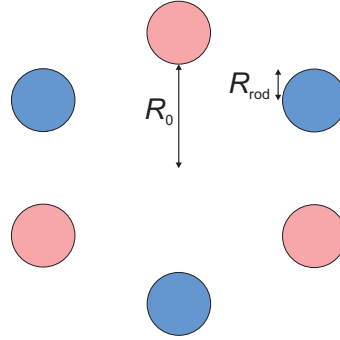


Figure 4.7: An ideal hexapole electric field is best approximated when $R_{\text{rod}} = 0.565R_0$ [174]. In this work, $R_0 = 2.65$ mm and $R_{\text{rod}} = 1.50$ mm. Rods coloured red and blue carry positive and negative voltages, respectively.

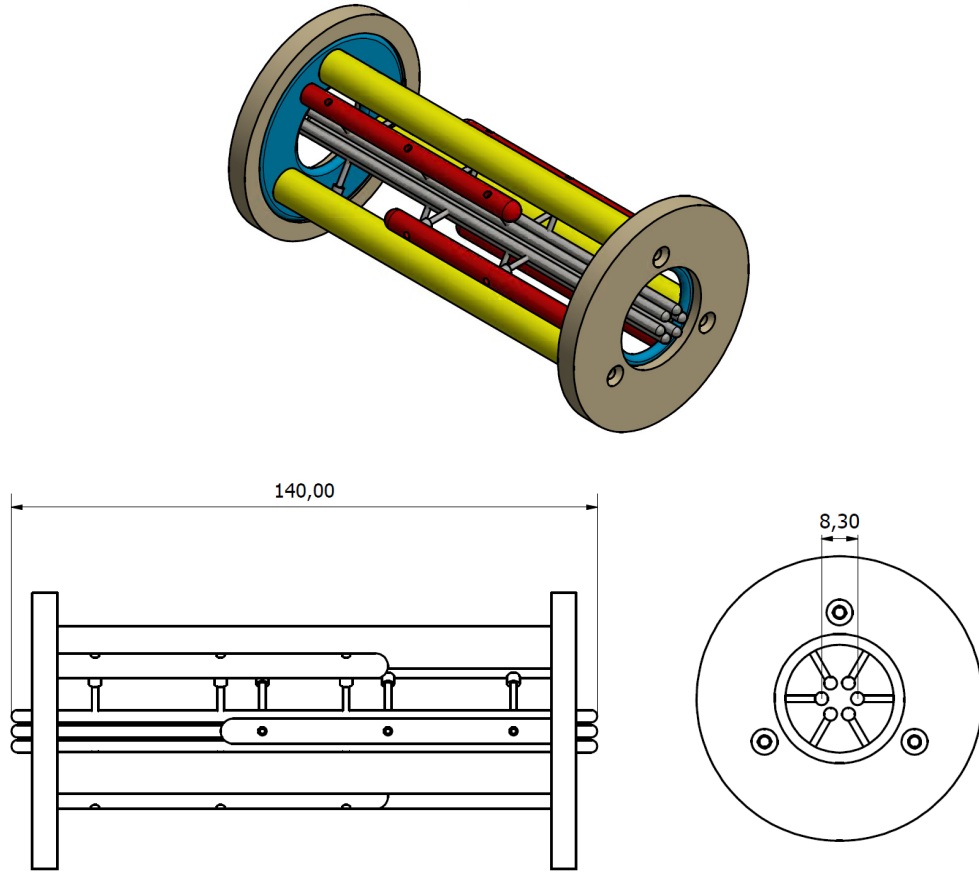


Figure 4.8: CAD drawings of the hexapole state-selector designed and built in-house and used in the experiments described in this chapter [175]. In the upper drawing: the yellow supports and brown end-pieces are made of MACOR®; the red supports, blue end-pieces, and hexapole rods are made of stainless steel. Red supports that are attached to a given end-piece will carry a voltage of equal magnitude and opposite polarity to those attached to the end-piece opposite. Thus, alternate hexapole rods have voltages of opposite polarity. The hexapole rods are 140 mm long, and have a centre-to-centre separation of 8.30 mm, as shown.

The electric field produced by a hexapole has three-fold axial symmetry, and the potential energy is given by

$$V(R) = V_0 \left(\frac{R}{R_0} \right)^3 \cos 3\phi, \quad (4.10)$$

where R and ϕ are two of the coordinates that define a cylinder, R_0 is the inner radius of the hexapole, and V_0 is the voltage applied to the rods. For a given radial distance, R , the magnitude of the hexapole field is given by

$$\begin{aligned} E(R) &= - \frac{dV}{dR} \\ &= - 3V_0 \frac{R^2}{R_0^3}. \end{aligned} \quad (4.11)$$

This equation can be combined with Equation (4.9) to generate the following expression for the force experienced at R :

$$\begin{aligned} F(R) &= \frac{\mu\epsilon|km|}{j(j+1)} \frac{dE_{\text{Stark}}}{dR} \\ &= \frac{6V_0R}{R_0^3} \frac{\mu\epsilon|km|}{j(j+1)}. \end{aligned} \quad (4.12)$$

It follows, therefore, that the low-energy $\epsilon = +1$ state will be high-field-seeking and will diverge from the path of the hexapole rods; the high-energy $\epsilon = -1$ state will be low-field-seeking and will undergo harmonic motion along the length of the hexapole. By tuning the potential applied to the rods, the resultant electric field can be used to selectively focus molecules in the $\text{ND}_3(\tilde{X}, j_k^\pm = 1_1^-)$ state into the interaction region and defocus all other states for which $k \neq 0$. The frequency of the harmonic motion is determined by the j , k , and m quantum numbers of the ND_3 molecule, and the voltages applied to the rods are selected such that the molecules in the desired state undergo one half-wavelength of harmonic motion that focuses them into the interaction region. In the case that $j = 0$ and/or $k = 0$, the molecules are unperturbed by the application of an electric field and will travel on-axis through the hexapole apparatus. Initially, a beam stop was fitted immediately after the hexapole to block any molecules travelling on-axis and increase the purity of the resultant

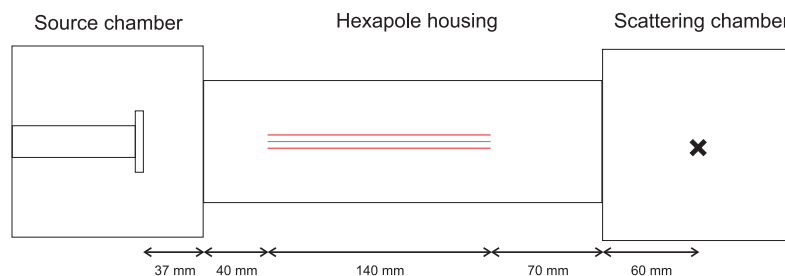


Figure 4.9: Cross-sectional diagram of the primary-beam source chamber, hexapole housing, and scattering chamber. The distances noted indicate that the hexapole apparatus should focus the $\text{ND}_3(\tilde{X}, j_k^\pm = 1_1^-)$ molecules 347 mm downstream from the face-plate of the General valve, in the geometric centre of the scattering chamber, labelled $\times$.

state-selected beam. However, the presence of the beam stop was found to reduce the magnitude of the scattered signal without improving the quality of the image, and so it was removed during the collection of the data reported in this chapter.

The large dipole moment of ND_3 (around 1.47 D [170]) means that it interacts strongly with the hexapole electric field, and this results in a high frequency of oscillation. For this reason, it is possible to use relatively short rod lengths and low voltages in comparison to those needed to state-select less polar molecules. For example, the experiments in this thesis use a 140 mm long hexapole with ± 2400 V applied; in reference [80], a 1660 mm long hexapole with ± 10000 V applied is used to state-select NO, which has a much smaller dipole moment of 0.16 D [176].

As noted previously, a single hexapole state-selector is used in this work. This contrasts with the experimental apparatus reported in references [46, 160], where a double hexapole was employed. In these cases, a pair of 120 mm long hexapole apparatus was placed in sequence along the beam path, separated by a small aperture, and ± 18500 V were applied to the rods. As such, the ND_3 molecules underwent one half-wavelength of harmonic motion along each of the two hexapole state-selectors (*i.e.*, one full wavelength in total) and crossed the beam-propagation axis as they passed through the origin. Generally, the use of a double hexapole serves to increase the purity of the molecular beam pulse that reaches the interaction region: even if higher j_k^- states are focused by the hexapole, the voltages applied to the rods can be chosen to ensure that the half-wavelength focal length of these states does not coincide with that required for passage through the aperture. However,

it is also the case that the use of a double hexapole and aperture will inevitably lead to lower signal levels, since not all molecules in the $j_k^\pm = 1_1^-$ state will follow an ideal trajectory path that passes through the aperture and terminates in the interaction region. As will be discussed in Section 4.4.3, the $j_k^\pm = 1_1^-$ -state purity of the molecular beam focused by the single hexapole used in this experiment is calculated at 99.9% in the interaction region. Therefore, in the interest of maximising number densities in the interaction region, it was decided to use a single hexapole state-selector apparatus in the work presented here.

Since the experiments reported in this chapter are the first to use this piece of apparatus, the hexapole state-selector required careful design, construction, and calibration. A cross-section of the primary-beam source chamber, hexapole housing unit, and scattering chamber is shown in Figure 4.9. The distances included in the figure indicate that the $\text{ND}_3(\tilde{X}, j_k^\pm = 1_1^-)$ molecules need to be focused at a point 270 mm after the beginning of the hexapole rods (and 347 mm after the face-plate of the primary-beam General valve). This point in space is the geometric centre of the cubic scattering chamber, and the $\text{ND}_3(\tilde{X}, j_k^\pm = 1_1^-)$ molecules must be focused here to ensure that the interaction region and the detection volume are coincident. A set of programs (written in Fortran 77 by Jack Langley [169]) that simulate the passage of trajectories of $\text{ND}_3(\tilde{X}, j_k^\pm = 1_1^-)$ molecules through an ideal-hexapole electric field was used to predict the voltage required to focus the molecules in the interaction region. Figure 4.10 shows the paths of six such trajectories along the length of the cross-section shown in Figure 4.9.

Figure 4.11 compares the calculated probability of transmission through the detection volume for $\text{ND}_3(\tilde{X}, j_k^\pm = 1_1^-)$ molecules and the normalised intensity of the experimental signal from the primary beam as a function of the voltage applied to the hexapole rods. The calculated transmission probability agrees well with the experimental tuning curve, and both suggest a peak in the transmission probability at around ± 2400 V. Notably, the agreement between theory and experiment is worse at low voltages. In this case, the molecules experience a smaller displacement force, deviate less from their field-free trajectory, and are able to approach the hexapole

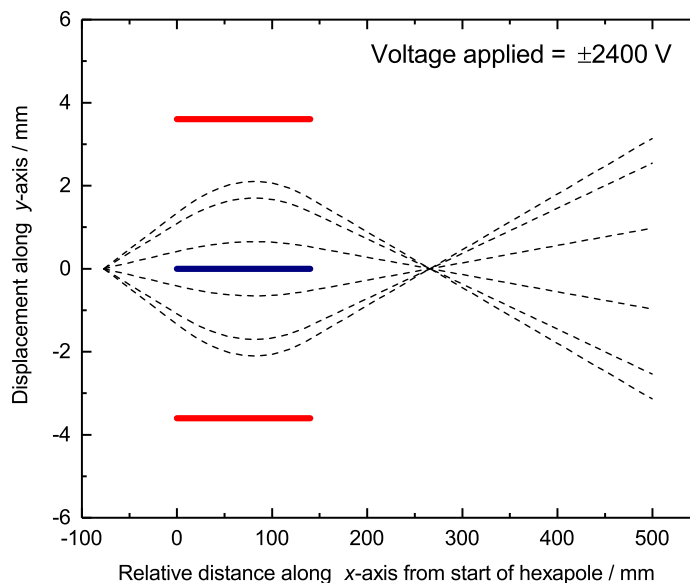


Figure 4.10: Simulated trajectories of $\text{ND}_3(\tilde{X})$ molecules in the $j_k^\pm = 1_1^-$ state through the hexapole state-selector apparatus when ± 2400 V are applied to the rods. The focal point of the hexapole corresponds to the geometric centre of the scattering chamber.

rods more closely. Hence, the ideal-hexapole approximation is no longer valid, since the molecules experience the anisotropy of the electric field, and the agreement between calculated and experimental data is correspondingly poorer [111].

Of course, as noted previously, it is possible to focus ND_3 molecules in different $|j, k, m\rangle$ states by varying the voltage that is applied to the hexapole rods. However, as will be discussed further in Section 4.4.3, the rotational temperature of the primary beam is sufficiently low (approximately 4 K) such that the population of states for which $j > 1$ is negligible. Thus, even if these states were to be focused into the interaction region by the hexapole apparatus, their population is small enough to ignore the resultant effect on the images that are collected. Figure 4.12 shows the observed experimental REMPI signal from $\text{ND}_3(\tilde{X}, j_k^\pm = 1_1^-)$ molecules that comes about when the hexapole apparatus is turned on. Note that the application of ± 2400 V to the rods ensures that only signal from the $j_k^\pm = 1_1^-$ state is enhanced (by a factor of around 10, in comparison to the intensity of the transitions from $j_k^\pm = 1_1^-$ when the hexapole is turned off – see Figure 4.13).

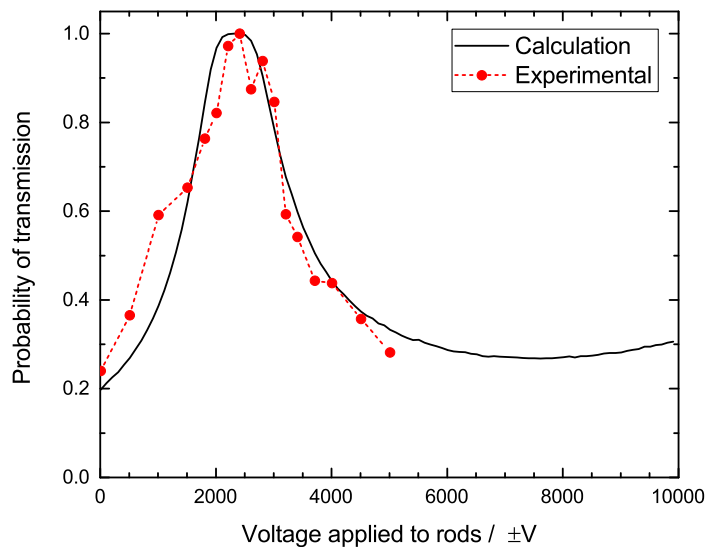


Figure 4.11: Comparison of the normalised experimental tuning curve and the calculated probability of transmission of $\text{ND}_3(\tilde{X}, j_k^\pm = 1_1^-)$ molecules through the detection volume. Both curves suggest an optimised hexapole voltage of ± 2400 V.

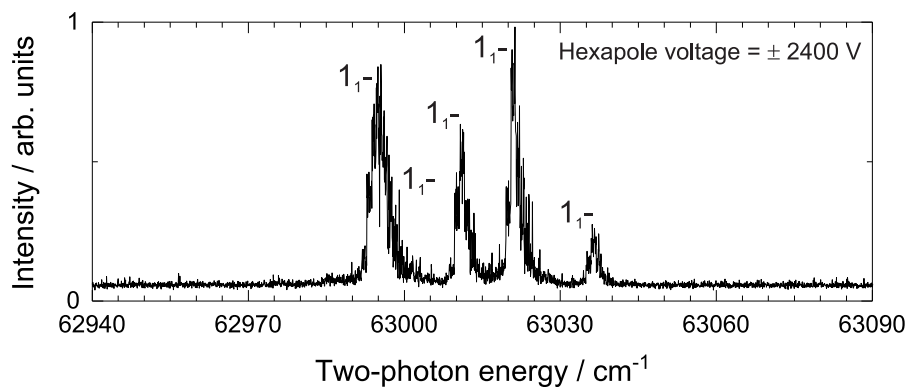


Figure 4.12: (2+1) REMPI spectrum of the primary beam with the hexapole voltage set at ± 2400 V. The peaks are labelled with $j_k^\pm$ notation. See text for details.

The effect of the hexapole apparatus on the rotational-state purity of the beam is discussed further in the section that follows.

4.4.3 Molecular beams and collision energies

The molecular beams in these experiments are produced using General valves that are fitted with 1 mm valve nozzles and operated at 10 Hz with a backing pressure of 2 bar. The primary beam contained ND_3 seeded at 5% of the total volume in Ar and the rotational temperature of the beam was measured to be around 4 K. This

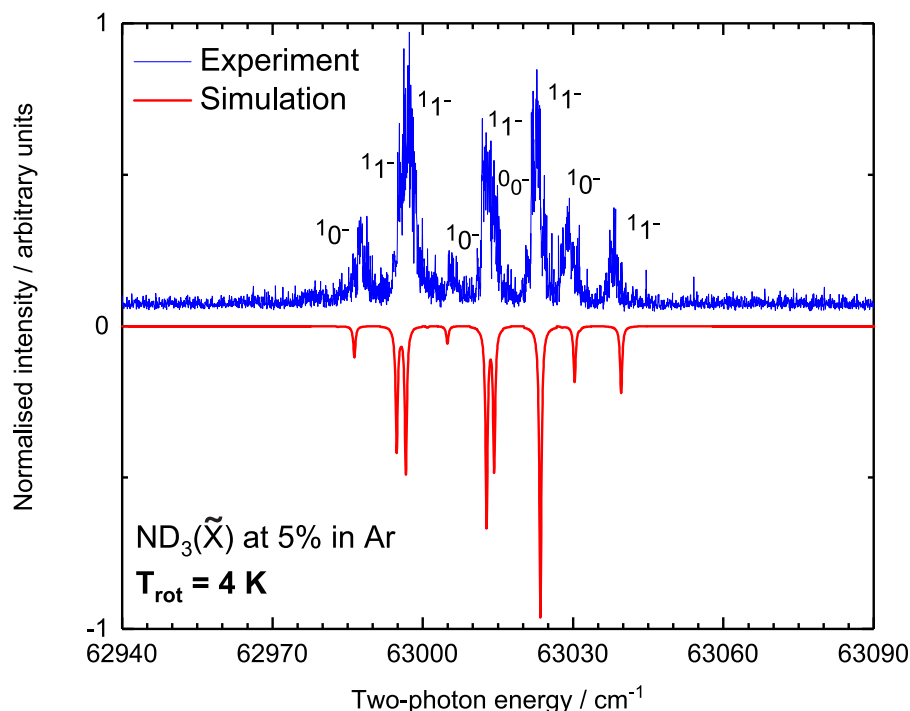


Figure 4.13: Comparison of an experimental (2+1) REMPI spectrum at 317 nm with the output of the PGOPHER spectral simulation software [177]. Note that the experimental spectrum was recorded with the hexapole turned off.

temperature was determined by comparing experimental (2+1) REMPI scans at 317 nm (in the absence of the hexapole apparatus) to the output of the PGOPHER spectral simulation software [177] – see Figure 4.13.

Note that, as a consequence of both symmetry- and nuclear-spin constraints, only transitions originating from the $-$ inversion component appear in bands for which the vibrational quantum number in the $\text{ND}_3(\tilde{\text{B}}, v_2)$ state is odd. This is the case for the (2+1) REMPI scheme at 317 nm that was used to measure the rotational-state distribution of the primary beam, which excites molecules into the $\text{ND}_3(\tilde{\text{B}}, v_2 = 5)$ state.

At a rotational temperature of 4 K, the PGOPHER software predicts that different $j_k^\pm$ states will have the populations given in Table 4.1. The data highlight that only the $j_k = 0_0$, 1_1 , and 1_0 levels are significantly populated, with a mere 0.7% of the population in higher rotational levels. It is possible to calculate the $j_k^\pm = 1_1^-$ -state purity of the beam pulse as it reaches the interaction region. In the first instance, it is assumed that the number densities of molecules for which

	Rotational state population / %
	$T_{\text{rot}} = 4 \text{ K}$
$j_k^\pm = 0_0^-$	3.5
$j_k^\pm = 0_0^+$	34.4
$j_k^\pm = 1_1^-$	29.1
$j_k^\pm = 1_1^+$	29.6
$j_k^\pm = 1_0^-$	2.6
$j_k^\pm = 1_0^+$	0.2

Table 4.1: Rotational state population of the primary molecular beam at $T_{\text{rot}} = 4 \text{ K}$, achieved by seeding $\text{ND}_3(\tilde{\text{X}})$ at 5% in Ar.

$j = 0$ and/or $k = 0$ vary as d^{-2} , where d is the distance travelled along the beam-propagation axis, independently of the hexapole-electric-field strength. Moreover, the probability of transmission through the interaction region when voltages of $\pm 2400 \text{ V}$ are applied to the hexapole rods can be calculated for the various j_k^- states that populate the primary molecular beam at 4 K using the simulation algorithms described in Section 4.4.2. It is also assumed that all j_k^+ are ejected from the molecular beam pulse as it passes along the hexapole apparatus such that they are not present in the interaction region. Applying the relevant treatments to the molecular-beam populations reported in Table 4.1 gives a $j_k^\pm = 1_1^-$ -state purity of 99.9% for the primary molecular beam.

As for the $\text{NO}(\text{X}) + \text{Ar}$ scattering experiments described in Chapter 2, the collision energy of the $\text{ND}_3(\tilde{\text{X}}) + \text{Ar}$ scattering experiments reported in this chapter was determined from both thermodynamic calculations and also from the experimental images that were collected (see Figure 4.14). In both cases, the collision energy was determined to be 405 cm^{-1} , which also agrees with values quoted in the literature for similar experiments [160].

To calculate the collision energy from the radii of the experimental images for $\text{ND}_3(\tilde{\text{X}}) + \text{Ar}$, a modified version of Equation (2.11) is used:

$$E_{\text{coll}} = \eta + \Delta E_{\text{rot}}, \quad (4.13)$$

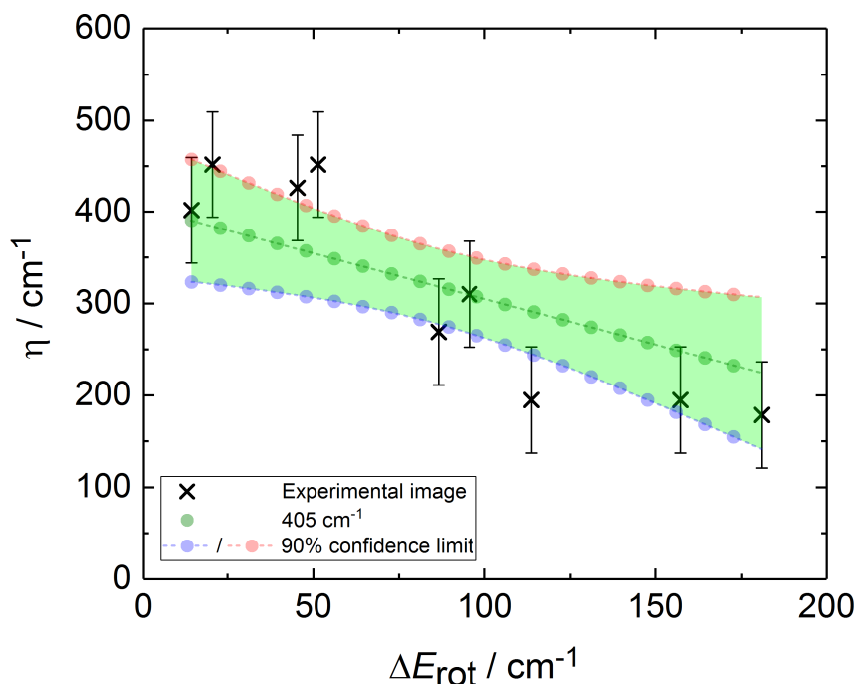


Figure 4.14: Determination of the experimental collision energy, E_{coll} , from the radii of experimental images. The green line denotes a collision energy of 405 cm^{-1} . The red and blue lines denote upper and lower 90%-confidence limits, respectively. See text for details.

where

$$\eta = \left(r \times p \times \frac{(m_{\text{Ar}} + m_{\text{ND}_3})}{m_{\text{Ar}}} \right)^2 \left(\frac{\mu}{2} \right), \quad (4.14)$$

and, as in Chapter 2, E_{coll} is the collision energy of the system, r is the radius of the image, p is the pixel-to-velocity ratio, m_X is the mass of species X, and μ is the reduced mass of the system. In this instance, ΔE_{rot} is the difference in energy between the final and initial rotational quantum states of the ND_3 molecule that is calculated using Equation (4.3). Figure 4.14, which shows a straight-line plot of η against ΔE_{rot} , highlights that, although the line of best-fit predicts a collision energy of 405 cm^{-1} , some of the experimental data points do not fall within the 90%-confidence error limits. This is likely due, in part, to the considerable difficulty of determining the radii of images that are intensely forward scattered. However, as the resultant collision energy agrees well with both thermodynamic

calculations and values reported in the literature [160], it was decided to assign a value of $E_{\text{coll}} = 405 \text{ cm}^{-1}$ to the data reported in this work.

4.5 Laser system, product detection, and data analysis

A one-colour experiment is used to study the inelastic scattering of $\text{ND}_3(\tilde{X}) + \text{Ar}$ in the laboratory, making use of a three-photon (2+1) REMPI detection scheme. To generate light at 317 nm, the frequency-doubled output (532 nm) of a flashlamp-pumped Continuum Surelite III-10 Nd:YAG laser, operating at 10 Hz, is used to pump a Lambda Physik FL 3002 tunable dye laser that contains DCM dye in methanol. The resultant emission is then frequency-doubled to generate light of the desired wavelength. Notably, the linewidth of the $\text{ND}_3(\tilde{B}) \leftarrow \text{ND}_3(\tilde{X})$ transition is approximately 0.10 cm^{-1} , which is much narrower than the bandwidth of the laser (0.40 cm^{-1}), meaning that the images were recorded at a fixed wavelength and did not make use of scanning over the Doppler profile.

The interaction region and detection volumes are as defined in Chapter 2, with the 308 nm laser beam being replaced by one at 317 nm, and the 226 nm beam being removed entirely. The 317 nm light is focused by a spherical lens of 150 mm focal length just before the interaction region to increase photon density. The resultant detection region has a volume of approximately $8 \times 10^6 \text{ mm}^3$ (assuming that the laser beam has a Gaussian intensity profile [114] and that the molecular beam is focused ideally by the hexapole).

To generate a single experimental image, batches of 5×10^4 shots were recorded at a time for a fixed wavelength. The secondary Ar beam was turned off on alternate shots and the resultant background signal was subtracted from the final image. The VMI optics, detector, and camera used were as described in Chapter 2. Notably, when recording images for ND_3 scattering, the voltage on the repeller was set at 1800 V and that on the extractor was set at 1180 V. At this point, the reader is also referred to Chapter 2, where the data-analysis methods used in this chapter are outlined in detail. Note that, where appropriate, the equations outlined there

were modified to include the additional k rotational-angular-momentum projection quantum number needed to describe the ND_3 molecule.

The work presented in Chapter 3 revealed that the use of Boltzmann-weighted DCSs, averaged over a range of collision energies, in place of a single-collision-energy DCS, did not significantly improve the agreement between experiment and theory for the $\text{NO}(\text{X})+\text{Ar}$ system. For this reason, and in the interest of reducing the computational demand of running multiple quantum-mechanical calculations, DCSs from a single calculation (run by Loreau [160]) at 410 cm^{-1} were used to generate the simulated and fitted images presented in this chapter. Furthermore, and as outlined in the previous sections, the use of a hexapole apparatus allowed for the full quantum-state selection of molecules in the $\text{ND}_3(\tilde{\text{X}}, j_k^\pm = 1_1^-)$ state prior to collision in order to successfully generate a high-purity beam. As a result, the quantum-mechanical calculations reported in this chapter assumed that 100% of molecules were in the $\text{ND}_3(\tilde{\text{X}}, j_k^\pm = 1_1^-)$ state at the beginning of each trajectory. The errors included on plots presented in this chapter have been generated in the same way as described in Chapter 2.

4.6 Specifying the detection region and experimental time delays

As for the $\text{NO}(\text{X})+\text{Ar}$ system, a series of simulated images was generated over a range of the two coordinates, x_{det} and y_{det} , that define the centre of the detection region, and over a range of values of t_{det} , the time delay between triggering the primary-molecular-beam valve and the 317 nm laser. A selection of these simulations for scattering into the $j_k'^\pm = 2_1^-$ state is presented in Figures 4.15 and 4.16. Based on several iterations for different final states, it was decided that values of $x_{\text{det}} = -0.001\text{ m}$, $y_{\text{det}} = 0.001\text{ m}$ and $t_{\text{det}} = -2 \times 10^{-5}\text{ s}$ produced the best agreement with the experimental data. These parameters were then used to generate the final set of simulated images that is presented and discussed in Section 4.9.

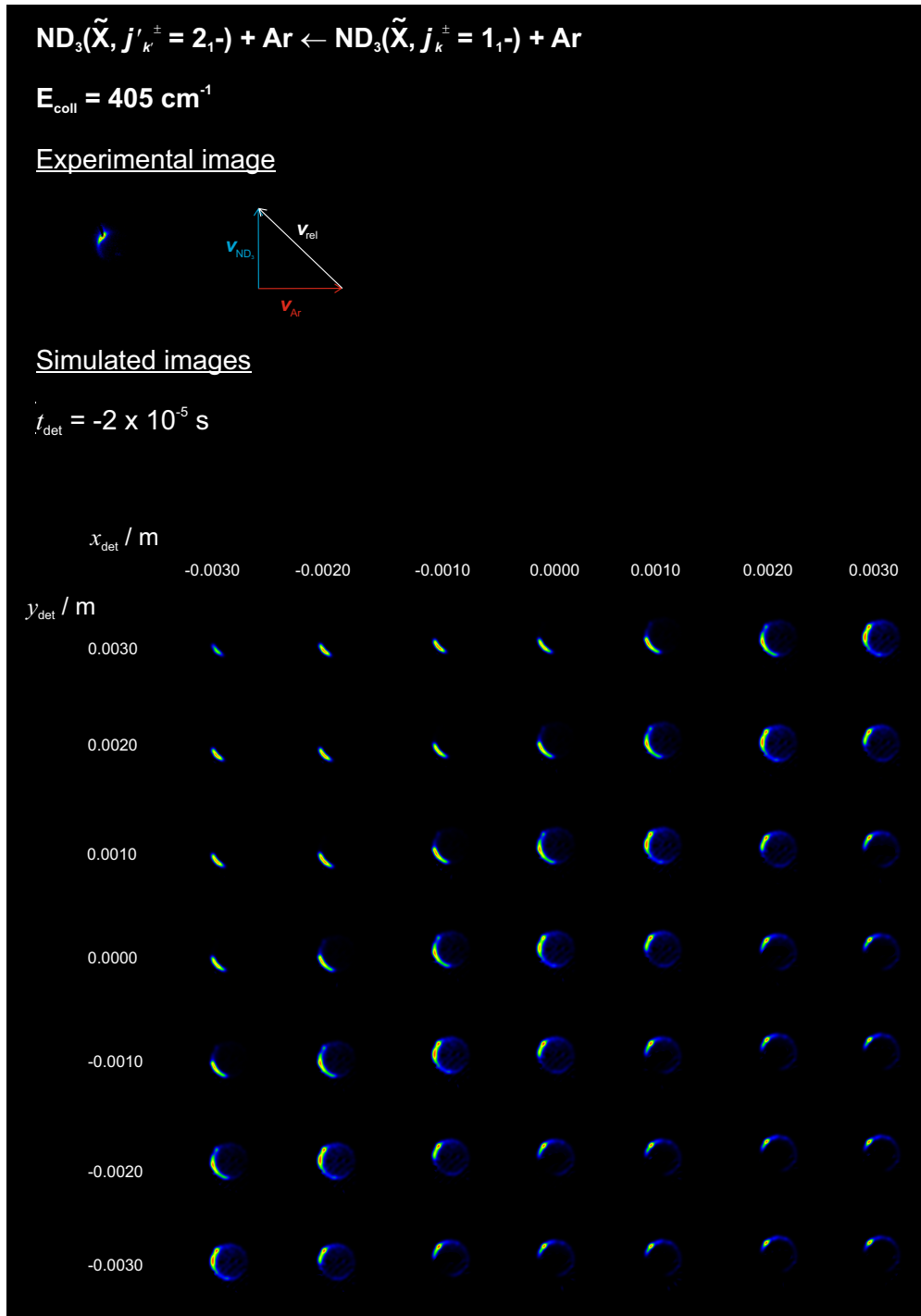


Figure 4.15: Simulated images for the inelastic scattering of $\text{ND}_3(\tilde{X}) + \text{Ar}$ at a collision energy of 405 cm^{-1} . The data presented here are for the $j'_{k'}^\pm = 2_1^- \leftarrow j_k^\pm = 1_1^-$ collision. The simulations show the effect of varying the x_{det} and y_{det} coordinates that define the centre of the detection region. Values of $x_{\text{det}} = -0.001 \text{ m}$ and $y_{\text{det}} = 0.001 \text{ m}$ were chosen based on a qualitative comparison of the simulations with the experimental image shown in the figure.

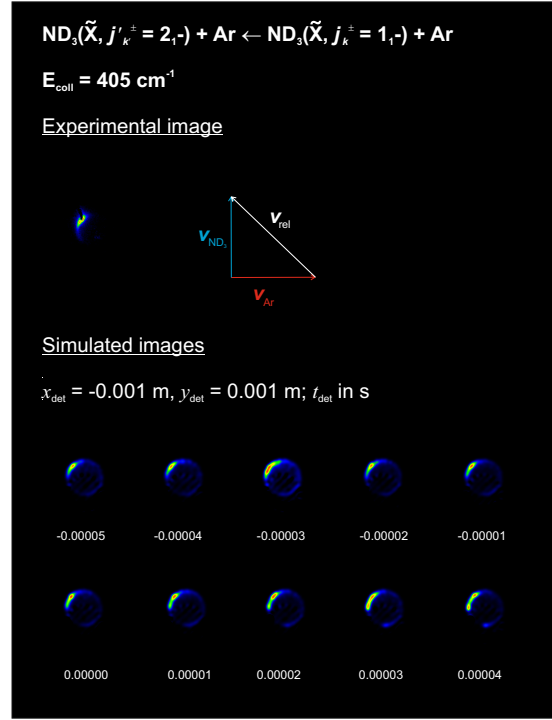


Figure 4.16: Simulated images for the inelastic scattering of $\text{ND}_3(\tilde{X}) + \text{Ar}$ at a collision energy of 405 cm^{-1} . The data presented here are for the $j'_{k'} = 2_1^- \leftarrow j_k = 1_1^-$ collision. The simulations show the effect of varying t_{det} , the time delay between triggering the primary-molecular-beam valve and the 317 nm laser. A value of $t_{\text{det}} = -2 \times 10^{-5} \text{ s}$ was chosen based on a qualitative comparison of the simulations with the experimental image shown in the figure.

4.7 Camera thresholding

The data-acquisition software used to collect the experimental images reported in this thesis makes use of a thresholding parameter for the CCD camera. If the intensity of an ion hit does not exceed this value, it is not included in the output file. Ideally, the value of the thresholding parameter should be chosen to maximise the signal-to-noise ratio. Figure 4.17 shows a series of images recorded for scattering into the $j'_{k'} = 5_5^-$ state. The value of the thresholding parameter was changed for each image, though all other experimental parameters were kept the same.

As can be seen in the figure, the intensity of the resultant image is exquisitely sensitive to the magnitude of the thresholding parameter in the 143 – 150 range. At values lower than 143, signal and noise are virtually indistinguishable: the camera pixels are saturated by ion hits and very little scattered signal is detected. At

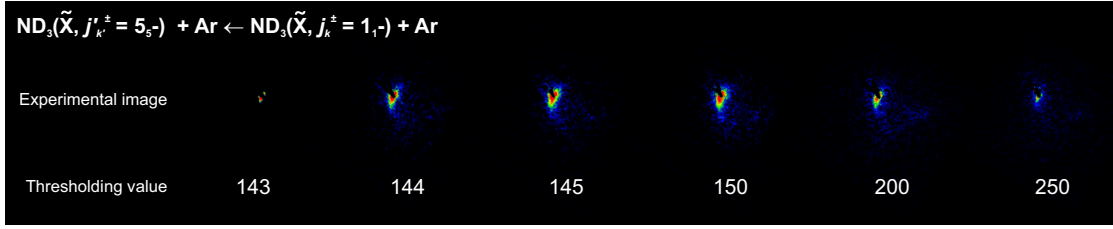


Figure 4.17: Comparison of experimental images for scattering into the $j_{k'}^{\pm} = 5_5^-$ state. The thresholding value in the data-acquisition software was changed for each image whilst all other experimental parameters were kept the same.

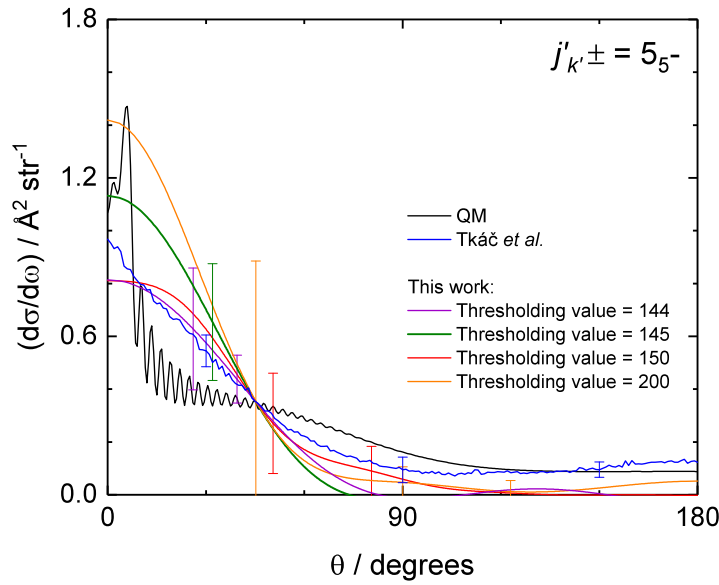


Figure 4.18: Qualitative comparison of the quantum-mechanical DCS for scattering into the $j_{k'}^{\pm} = 5_5^-$ state with experimental DCSs recorded using various camera-thresholding values and with the experimental DCS reported by Tkáč *et al.* [160]. Each set of DCSs has been normalised to have the same magnitude at $\theta = 45^\circ$. Note that DCSs were not extracted from the experimental images with thresholding values of 143 and 250 due to a lack of scattered signal.

values greater than 150, there is a gradual decrease in the intensity of scattered signal. Based on the data shown in Figure 4.17, the final images reported in this thesis were all recorded with a thresholding value of 150, since this value maximises the signal-to-noise ratio. To confirm the visual trends shown by the experimental images, DCSs were extracted from fits of the empirical data and compared to both quantum-mechanical calculations and the relevant experimental DCS reported by Tkáč *et al* [160]. To that end, the data reported in Figure 4.18 reveal a good level

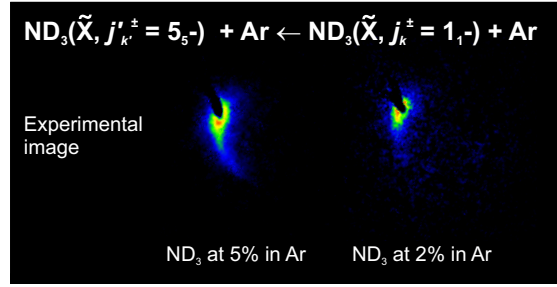


Figure 4.19: Qualitative comparison of experimental images for scattering into the $j_{k'}^{\pm} = 5_5^-$ state when ND_3 is seeded at 5% and 2% of the total volume in Ar in the primary molecular beam.

of agreement and confirm that any discrepancies between the DCSs for different thresholding values lie within experimental error.

4.8 Seed ratio of primary molecular beam

In addition to selecting an appropriate camera threshold, it is also the case that the level of signal recorded during a single acquisition cycle will depend on the seed ratio of ammonia in argon in the primary molecular beam. If the concentration of ammonia is too high, too many ions will hit the detector per laser shot and, consequently, too many camera pixels will light up during a single acquisition cycle, leading to saturation in the resultant image. In a similar fashion, the MCP pores or phosphor screen can become saturated by if successive ions arrive during the dead time of either component. To determine whether the 5%-mix used to collect the images presented in Section 4.9 risked such saturation, the primary-molecular-beam seed ratio was diluted to 2% ND_3 in Ar. Figure 4.19 shows a qualitative comparison of two images recorded for scattering into the $j_{k'}^{\pm} = 5_5^-$ state for both 5%- and 2%- ND_3 -in-Ar seed ratios. The figure confirms that diluting the concentration of ammonia in the primary molecular beam simply reduces the intensity of scattered signal observed and does not improve the quality of the image in the forward-scattered region.

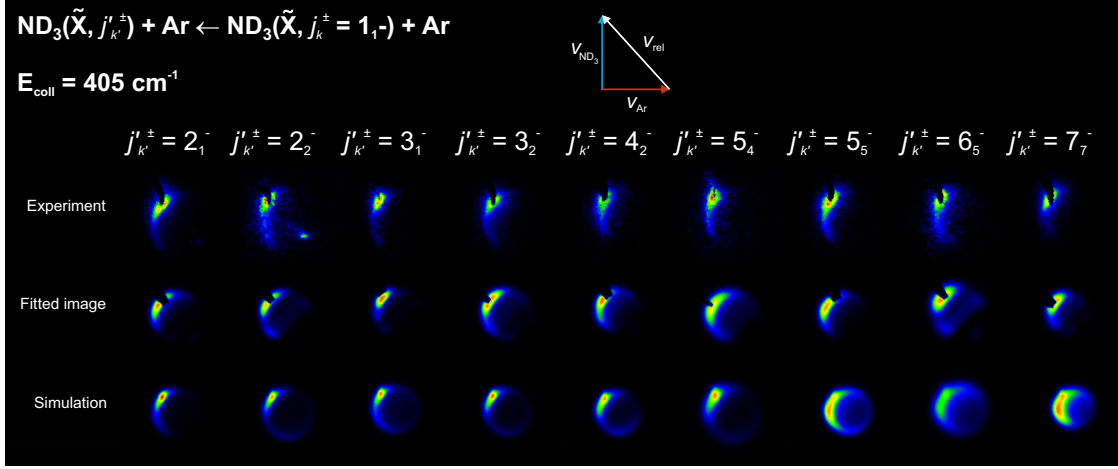


Figure 4.20: Experimental, fitted, and simulated images for the inelastic scattering of $\text{ND}_3(\tilde{\text{X}}, j_k^\pm = 1_1^-) + \text{Ar}$ at a collision energy of 405 cm^{-1} . The Newton triangle for the collision system is also shown. As explained in the text, the simulated images shown here were generated assuming that all of the hexapole-state-selected $\text{ND}_3(\tilde{\text{X}})$ molecules are in the $j_k^\pm = 1_1^-$ rotational state prior to collision.

4.9 Results: images and DCSs

Figure 4.20 presents experimental, fitted, and simulated images for the rotationally inelastic scattering of $\text{ND}_3(\tilde{\text{X}}, j_k^\pm = 1_1^-) + \text{Ar}$ at a collision energy of 405 cm^{-1} . In general, there is good agreement between experiment and theory in that all three sets of images show a gradual increase in the extent of sideward scattering as the final $j_{k'}^\pm$ level of the $\text{ND}_3(\tilde{\text{X}})$ molecule increases.

Notably, and as seen in previous work on the $\text{NO}(\text{X}) + \text{Ar}$ system, the subtraction of background, unscattered signal from the intensely forward-scattered region continues to be problematic, despite the use of shot-by-shot (rather than batch) subtraction. This manifests in the experimental images as a distinct lack of scattered signal intensity along $\mathbf{k}$, precisely where quantum mechanics predicts many images to be most intense. Such disagreement between experiment and theory also caused issues during the fitting of the raw data, as discussed below.

Figure 4.21 compares quantum-mechanical DCSs with those extracted from fits of the experimental images. To aid more rigorous analysis, the data recorded in this work are also compared directly with those of Tkáč *et al.* [160] where possible. To that end, the magnitudes of the experimental DCSs in both sets of data were

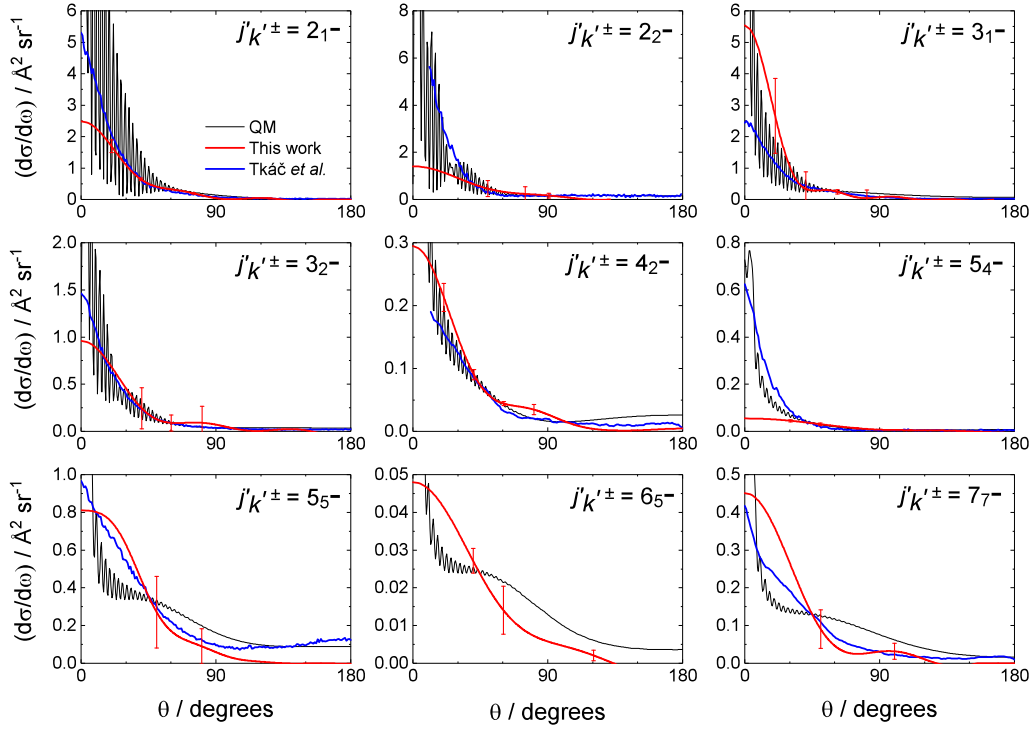


Figure 4.21: Fitted experimental and quantum-mechanical DCSs for the inelastic scattering of $\text{ND}_3(\tilde{X}, j_k^\pm = 1_1^-) + \text{Ar}$ at a collision energy of 405 cm^{-1} . Where possible, a direct comparison is also made to the data of Tkáč *et al.*, which related to the inelastic scattering of $\text{ND}_3(\tilde{X}, j_k^\pm = 1_1^-) + \text{Ar}$ at an almost identical collision energy (410 cm^{-1}) [160]. Each set of DCSs has been normalised to have the same magnitude at $\theta = 45^\circ$.

normalised to match the corresponding theoretical value at $\theta = 45^\circ$. As for the images presented earlier, there is generally good agreement between experiment and theory, neglecting the fact that the experimental resolution was not high enough to capture the intense diffraction oscillations predicted by the quantum-mechanical calculations. For all the final $j_{k'}^\pm$ states recorded, the DCS is dominated by an intensely forward-scattered peak, governed by the long-range, attractive region of the PES. The agreement between experiment and theory is particularly strong for most of the states recorded in the $j' = 3 - 5$ range, where both sets of data display very sharp, forward-scattered peaks that do not extend beyond $\theta = 60^\circ$.

On a first attempt, the lack of scattered signal along $\mathbf{k}$ caused significant problems during the fitting procedure and generated DCSs that were in extremely poor agreement with fits of the quantum-mechanical data. To overcome this, a

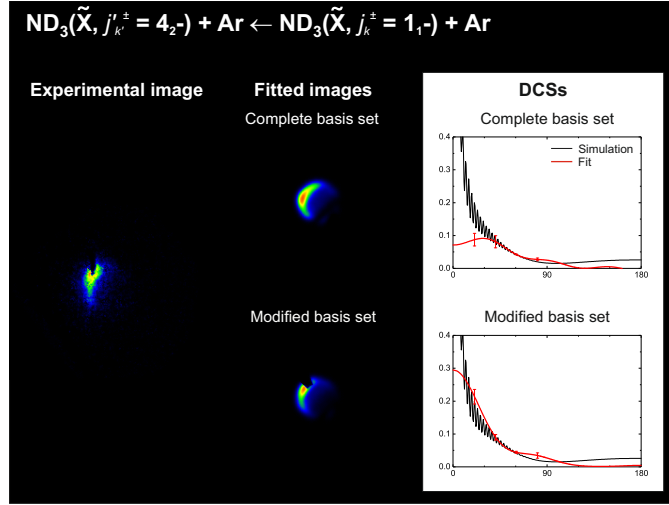


Figure 4.22: Comparison of the complete and modified Fourier-moment basis sets, and extracted DCSs, for scattering into the $j_{k'}^{\pm} = 4_2^-$ state. The DCSs have been normalised to have the same magnitude at $\theta = 45^\circ$. The data shown emphasise the significant improvement in the agreement between experiment and theory when a modified basis set is used.

portion of the Fourier-moment basis set was subtracted prior to fitting to mirror the lack of intensity in the corresponding experimental data. For the majority of the images, use of these modified basis sets served to vastly improve the agreement between experiment and theory. Figure 4.22 shows a comparison of complete and modified Fourier-moment basis sets, as well as the extracted DCSs, for scattering into the $j_{k'}^{\pm} = 4_2^-$ state. The data shown emphasise the significant improvement in the agreement between experiment and theory when over-subtraction of the background is accounted for in the basis sets. However, for those images (*e.g.*, that for scattering into the $j_{k'}^{\pm} = 2_2^-$ state) that required the largest subtraction along $\mathbf{k}$, the overall effect was to significantly reduce the height of the forward-scattered peak in the experimental fitted DCS relative to that in the quantum-mechanical data. Therefore, it is clear that, despite moving from batch to shot-by-shot subtraction, there are still issues with over-subtraction of background signal during data acquisition, and future experimental work should seek to resolve this.

Apart from the forward-scattered peak, the most notable feature of the DCSs shown in Figure 4.21 is a broad shoulder of scattering intensity for higher final $j_{k'}^{\pm}$ states. Though predicted by the quantum-mechanical calculations for scattering

into $j' \geq 5$, this feature of the DCSs is not reproduced in the fit. Instead, the experimental images and DCSs generally show a somewhat broader and less intense forward-scattered peak than is predicted by theory. Equivalent features are seen in the data reported in reference [160], where the authors have suggested that the disagreement between experiment and theory is likely due to the fact that the experimental resolution is not sufficient to resolve both features: instead, the two distinct peaks merge into one broader, less intense maximum. It is thought that a similar explanation can be offered for the discrepancy in the data reported here. Indeed, it is important to remember that the skimmer placed in front of the secondary molecular beam in the experimental apparatus described in this chapter has a diameter of 5 mm, whereas that placed in front of the primary molecular beam has a diameter of 2 mm. Thus, by the time the gas pulse arrives in the interaction region, the secondary molecular beam will be relatively poorly collimated (at least in comparison to the primary beam), and this will reduce the experimental resolution.

The relative intensity of the ICS and DCS for scattering into a particular state is a consequence of the j' and k' quantum numbers and also of the inversion symmetry of the final state of the ND_3 molecule. Indeed, for scattering into final levels with – inversion symmetry, 80% of the scattering occurs into $j' \leq 4$ [160]. The probability of scattering into a certain state (*i.e.* the magnitude of the ICS) is determined largely by how strongly the initial and final quantum states of the $\text{ND}_3(\tilde{X})$ molecules are coupled by the expansion coefficients in Equation (4.6) [160, 168]. As a point of comparison, the $j_{k'}^{\pm} = 3_1^-$ state is directly coupled to the initial $j_k^{\pm} = 1_1^-$ state by the $v_{\lambda 0}$ coefficients (where $\lambda = 0 - 3$), and the resulting ICS and DCS for a transition between the two are relatively large. In contrast, the $j_{k'}^{\pm} = 3_2^-$ state is only coupled to the $j_k^{\pm} = 1_1^-$ state by the smaller v_{33} and v_{53} coefficients, generating a much smaller ICS and DCS. Similar explanations can be offered for the other states recorded. To that end, the ICSs for energetically accessible $j_{k'}^{\pm}$ states at 405 cm^{-1} that may also be focused by a hexapole apparatus and detected using a (2+1) REMPI scheme at 317 nm are reported in Figure 4.23.

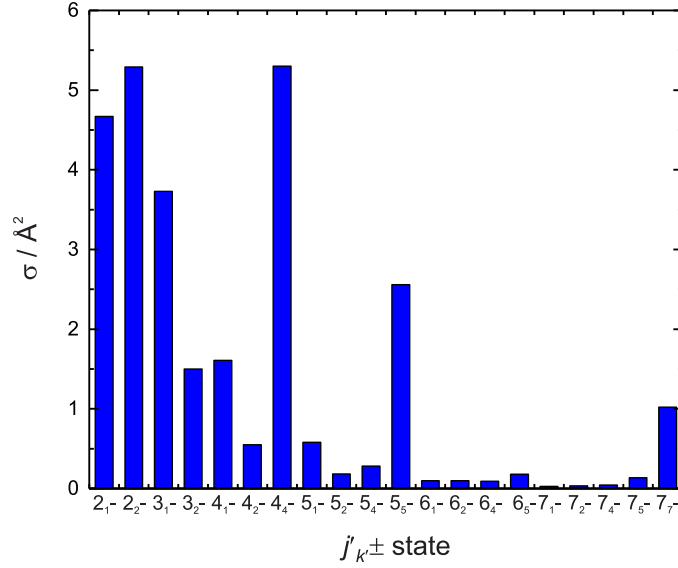


Figure 4.23: Comparison of ICSs for scattering into the range of energetically accessible $j'_{k'}^{\pm}$ states at 405 cm^{-1} that may also be focused by a hexapole apparatus and detected using a (2+1) REMPI scheme at 317 nm .

4.10 Further discussion of fitting procedures

The raw experimental and theoretical data presented in this chapter were analysed using the same fitting procedures that were outlined in Chapter 2. These methods have been used successfully on other systems and, in the work presented here, serve to generate fitted images and extracted DCSs that show reasonable agreement between the empirical and calculated data and also in comparison to those of Tkáč *et al.*. However, given that the data presented here for inelastic scattering in the $\text{ND}_3(\tilde{X})+\text{Ar}$ system were recorded at higher quantum-level resolution than those for the $\text{NO}(\text{X})+\text{Ar}$ system, and that the agreement between the experimental and theoretical data is generally stronger, it was decided to subject these results to even more rigorous analysis.

In the first instance, a fitting algorithm (written originally by Eyles [110] and adapted for this thesis) was used to read the intensity around the radius of the experimental image. To this end, the image is first converted to polar coordinates, and then the intensity distribution is output as a function of the scattering angle, θ , at a resolution of 1° . The instrument function is then subtracted from this output, and the fast and slow sides of the image are averaged to remove the slow-side bias.

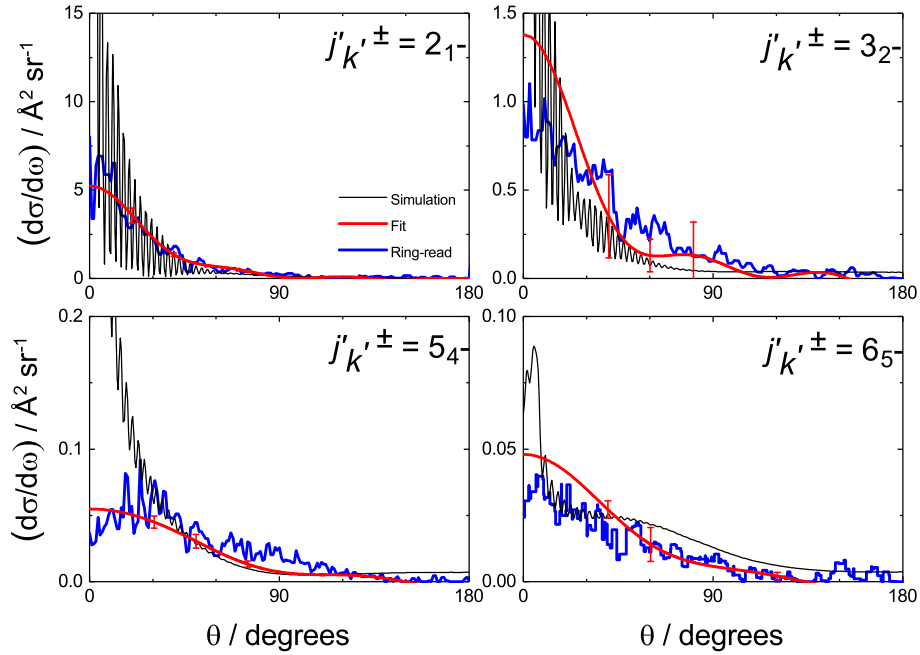


Figure 4.24: Comparison of DCSs generated from quantum-mechanical calculations, the Legendre-polynomial fitting procedures used in this work, and from a direct reading of the scattering intensity around the radius of the experimental image (with a resolution of 1°).

The results of this analysis, which are shown for a selection of states in Figure 4.24, confirm that the DCSs generated by the Legendre-polynomial fitting methods described in Chapter 2 are in generally good agreement with a simple (though crude) reading of the scattering intensity around the radius of the image. This lends weight to the idea that the fitting procedures used in this thesis give an accurate representation of experimental scattering distributions.

Following this, it was decided to pay further attention to the intensely forward-scattered region of the $\mathbf{k} - \mathbf{k}'$ distribution. For many of the images recorded (and the DCSs extracted from them), the quantum-mechanical data predict significantly more scattered intensity in the $\theta = 0 - 20^\circ$ region than is observed experimentally. One explanation for this discrepancy, apart from over-subtraction of background signal from the experimental images, is that the experimental resolution is not sufficiently high so as to resolve the intense, forward-scattered, quantum-mechanical oscillations at low θ . Instead, these dominant peaks merge with less-intense features

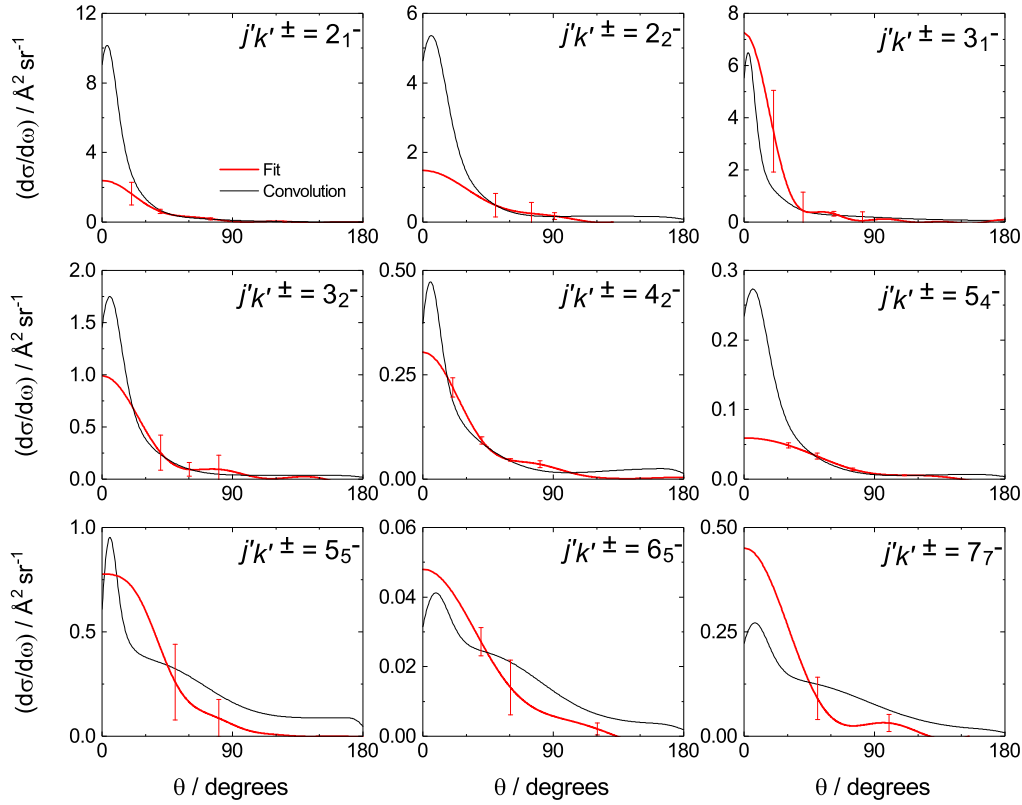


Figure 4.25: Comparison of DCSs generated from quantum-mechanical-Gaussian-convolution fitting process and from the standard Legendre-polynomial fitting procedures used in this work. Each set of DCSs has been normalised to have the same magnitude at $\theta = 45^\circ$. Note the difference in scale of the y -axes between the plots shown here and those in Figure 4.21.

at higher θ in the experimental image. For this reason, and to allow for a comparison of the experimental DCS with a more realistic theoretical simulation, the quantum-mechanical DCS was convoluted with a Gaussian distribution [178]. The FWHM of this Gaussian distribution was chosen to coincide with that of the Legendre-polynomial basis set generated using the number of Fourier moments that was appropriate for the fit in question. To achieve this, the 180° angular range of the DCS was simply divided by the number of Fourier moments used in the fit.

To carry out the quantum-mechanical-Gaussian convolution, the quantum-mechanical DCS, $\frac{d\sigma}{d\omega}$, was integrated for successive segments of a given angular-

width, p , set at $p = 0.5^\circ$, to give an integral, τ , defined as:

$$\tau(\theta) = \int_{\theta}^{\theta+p} \left(\frac{d\sigma}{d\omega} \right) d\theta, \quad (4.15)$$

Then, a normalisation Gaussian, N , centred at 0° and with a FWHM chosen as outlined above, was integrated in the range $-90^\circ \leq \theta \leq 90^\circ$, such that

$$N = \int_{-90}^{90} \frac{1}{\sqrt{2\pi}\eta} \exp \left(-\frac{1}{2} \left(\frac{\theta^2}{\eta} \right) \right) d\theta, \quad (4.16)$$

where

$$\eta = \frac{\text{FWHM}}{2\sqrt{2 \ln 2}}. \quad (4.17)$$

A normalisation factor, ξ , is then determined for each segment by dividing its area by that of the full Gaussian centred at 0° [169]:

$$\xi(\theta) = \frac{\tau(\theta)}{N}. \quad (4.18)$$

The normalisation Gaussian is subsequently centred on each incremental value of θ and multiplied by the corresponding normalisation factor, $\xi(\theta)$. The sum of these 361 Gaussian functions then gives the overall quantum-mechanical-Gaussian-convoluted DCS: [169]

$$\left(\frac{d\sigma}{d\omega} \right)_{\text{conv}} = \sum_{\substack{\theta_C=0^\circ \\ 0.5^\circ \mid \theta_C}}^{180^\circ} \xi(\theta) \frac{1}{\sqrt{2\pi}\eta} \exp \left(-\frac{1}{2} \left(\frac{\theta - \theta_C}{\eta} \right)^2 \right). \quad (4.19)$$

Figure 4.25 presents a comparison of the experimental DCSs recorded in this work and quantum-mechanical-Gaussian-convoluted DCSs. Note the difference in scale of the y -axes between the plots in Figure 4.25 and the corresponding DCSs in Figure 4.21. Although there is still discrepancy in the intensity of the forward-scattered distributions, it has been vastly reduced by the convolution, and the fitted and calculated DCSs now show much better agreement. Furthermore, the convolution process has served to make the experimental and theoretical DCSs more directly comparable by accounting for the experimental resolution.

4.11 Summary

This chapter has presented experimental and theoretical data relating to the rotationally inelastic scattering of fully quantum-state-selected $\text{ND}_3(\tilde{X}, j_k^\pm = 1_1^-)$ molecules by Ar at a collision energy of 405 cm^{-1} . The empirical and calculated data presented in this chapter agree very well with those reported in reference [160]. Both data sets confirm that the $\mathbf{k} - \mathbf{k}'$ distribution is intensely forward scattered for all the energetically states that are readily detectable by the REMPI-VMI techniques employed. Where discrepancies exist between theory and experiment, suggestions have been made to account for these, including a consideration of the effect of camera thresholding, seed ratios, and experimental resolution on the quality of resultant measurements. The data confirm that the hexapole state-selector apparatus, designed and built for this thesis, has been calibrated successfully and that it is able to facilitate the preparation of high-purity molecular-beam pulses with a single, well-defined quantum state. In addition, the experimental data reported here facilitated the development and refinement of several data-analysis techniques that will benefit future experimental work on this and similar systems.

5

2D models of non-adiabatic effects in OH(A, $v = 0$)+Rg collision dynamics

The hydroxyl radical, OH, is one of the most important oxidants that govern atmospheric chemistry in the stratosphere and lower troposphere [179]. As a highly reactive species, OH determines the lifetime of atmospheric methane [180, 181], and it also plays a key role in stratospheric ozone depletion [182]. It is, therefore, important to study the rates at which OH undergoes reactions in the atmosphere, and to understand the energy transfer that takes place when OH radicals – in both the ground and excited electronic states – collide with other gases. The resultant data can then be used to inform models for a range of atmospherically important processes [183, 184].

This chapter outlines a theoretical investigation into the dynamics of hydroxyl radicals in the first electronically excited state, OH(A), when they undergo collisions with heavy rare-gas atoms (Kr and Xe). Of particular interest in this thesis are *electronically non-adiabatic dynamics*, whereby the OH radical is seen to change electronic state following a collision with a rare-gas atom. As a result of this non-adiabatic transfer of population, the collision dynamics of OH(A)+Rg cannot be well modelled when confined to a single PES. By considering a number of PESs, and the different types of coupling between them, this thesis aims to quantify

the extent to which non-adiabatic processes affect the magnitude of a number of experimentally measured quantities for OH(A)+Kr and OH(A)+Xe.

The principal discussion in this chapter will concern the OH(A) molecule in the ground vibrational state. The angular momentum coupling in the excited electronic A state is best described by Hund's case (b), whereas that of the electronic ground state, OH(X), is best described by Hund's case (a). Details of both angular momentum coupling schemes are discussed below.

5.1 Hund's case (b): OH(A)

Like the NO(X) molecule discussed in Chapters 2 and 3, OH(A) exists as a radical species with a single, unpaired electron. However, in contrast to the ground-state NO(X) radical, the coupling of angular momenta in excited-state OH(A) is best described by Hund's case (b). Throughout this section, the reader is referred to the notation outlined in Section 2.2.

The electronic configuration of OH(A) is given by

$$1\sigma^2 2\sigma^2 3\sigma^1 1\pi^4.$$

In Hund's case (b), the spin-orbit coupling is weak, or non-existent in the case of $\Lambda = 0$. Therefore, the total electronic angular momentum is simply equal to $\mathbf{S}$, which is completely uncoupled to the nuclear axis, meaning the value of Ω is undefined.

As can be seen in Figure 5.1, $\mathbf{R}$ is coupled strongly to $\mathbf{A}$ to give $\mathbf{N}$, which, in the case of a Σ radical, means that $\mathbf{R} \equiv \mathbf{N}$. The interaction of the electron spin with the magnetic field generated by the rotation of the nuclear framework produces two spin-rotation levels by the coupling of $\mathbf{N}$ and $\mathbf{S}$. The resultant vector, $\mathbf{j}$, quantifies the total angular momentum of the system (exclusive of nuclear spin). OH(A) has a single, unpaired electron in a σ orbital, so the rotational-angular-momentum quantum number, $j = N \pm \frac{1}{2}$.

In this chapter, the two spin-rotation levels are labelled f_1 ($j = N + S$) and f_2 ($j = N - S$), and are separated by the spin-rotation coupling, $\gamma = (\mathbf{N} \cdot \mathbf{S})$, where γ takes a value of 0.2244 cm^{-1} in the ground vibrational state of OH(A)

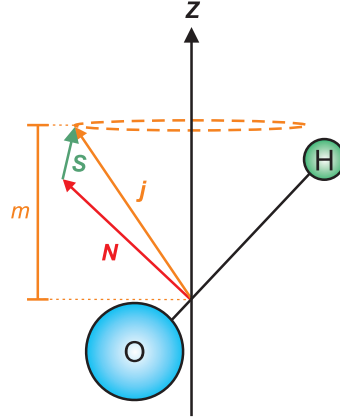


Figure 5.1: The Hund's case (b) angular momentum coupling scheme for the OH(A) molecule. The coupling of nuclear spin angular momentum is neglected throughout. See text for details.

[185]. Note that the value of this constant may be affected by second-order contributions from spin-orbit interactions (amongst others) of OH(A) with the lower-energy OH(X) state. The two spin-rotation levels have a well-defined parity with respect to inversion, given by

$$p = (-1)^N. \quad (5.1)$$

The molecular Hamiltonian for Hund's case (b) molecules can, therefore, be written as

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_{\text{rot}} + \mathcal{H}_{\text{SR}} \\ &= B\mathbf{N}^2 + \gamma(\mathbf{N} \cdot \mathbf{S}), \end{aligned} \quad (5.2)$$

and the energy of a particular spin-rotation level, $|N, j\rangle$, is given by

$$\begin{aligned} E(f_1) &= BN(N+1) + \frac{1}{2}\gamma N, \\ E(f_2) &= BN(N+1) - \frac{1}{2}\gamma(N+1), \end{aligned} \quad (5.3)$$

where $B = 17.355 \text{ cm}^{-1}$ for OH(A) in its ground vibrational state [185].

In OH(A), the coupling of the nuclear spin angular momentum, $\mathbf{I}$, to the total angular momentum excluding nuclear spin, $\mathbf{j}$, generates two hyperfine levels denoted $F = j \pm \frac{1}{2}$. In the presence of a magnetic field, each hyperfine level, F , is further split into $2F + 1$ magnetic sub-levels, with an energy splitting given by

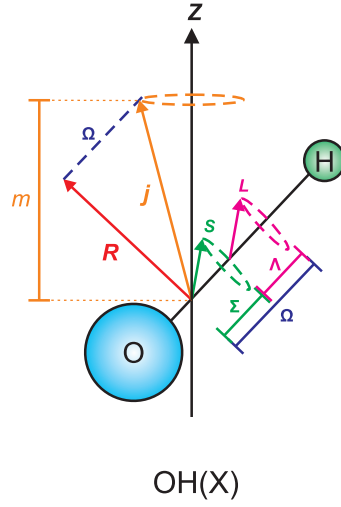


Figure 5.2: The Hund's case (a) angular momentum coupling scheme for the OH(X) molecule. The coupling of nuclear spin angular momentum is negated throughout. See text for further details.

$\Delta E = \langle \mu \cdot \mathbf{B} \rangle$, where μ is the magnetic dipole moment, and $\mathbf{B}$ is the magnetic field vector. The splitting of magnetic sub-levels is the basis of the Zeeman Quantum Beat Spectroscopy techniques [6, 7] that underpin the experimental work referenced in this chapter [26, 33].

5.2 Hund's case (a): OH(X)

The coupling of angular momenta in OH(X) is best described by the Hund's case (a) scheme outlined in Section 2.2.1. The electronic configuration of OH(X) can be written as

$$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^3.$$

Recalling Equation (2.2.1), for OH(X), $A = -139.054 \text{ cm}^{-1}$ and $B = 18.53104 \text{ cm}^{-1}$ [186]. For OH(X), the energy-ordering of rotational levels defined by each spin-orbit manifold (see Figure 2.1) is reversed compared to that in NO(X): now, the $\bar{\Omega} = 1.5$ state is around 140 cm^{-1} lower in energy than $\bar{\Omega} = 0.5$. The splitting of the OH(X) Λ -doublet is very small, at only 0.056 cm^{-1} for $j = 1.5$ in the lower $^2\Pi_{\frac{3}{2}}$ state [187].

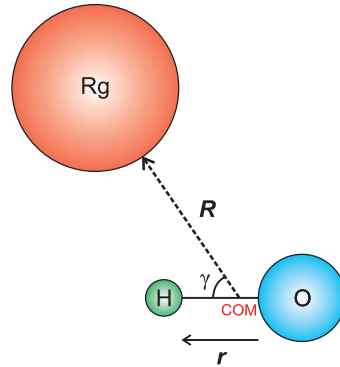


Figure 5.3: The Jacobi coordinate system (R , r , and γ) used in this thesis. ‘COM’ is the centre of mass of the OH+Rg system. See text for details.

5.3 Two-dimensional models of non-adiabatic dynamics in OH(A, $v = 0$)+Rg

This section deals with the development of theoretical frameworks that are used to model non-adiabatic effects. In all the calculations presented in this section, the OH bond length is fixed at the excited-state equilibrium value of $r_e = 1.012 \text{ \AA}$ [26, 76, 121], and so there is no consideration of the effects of vibrational motion on the collision dynamics. The PESs (which were calculated by Kłos [76–78, 188]) are a function of only two coordinates: R , the distance between the centre of mass of the OH radical and the rare-gas atom; and γ , the angle between the vector $\mathbf{R}$ and $\mathbf{r}$, the OH bond vector. Note that a value of $\gamma = 0^\circ$ corresponds to the O–H–Rg linear configuration (see Figure 5.3). The PESs used in this section are therefore referred to as ‘two-dimensional’ (2D) surfaces.

5.3.1 Two-dimensional adiabatic potential energy surfaces of OH(A)+Rg and OH(X)+Rg

As discussed in Section 2.4, the PES quantifies the potential energy of a given system as a function of the nuclear coordinates. Together with the initial conditions and kinematics, the PES is crucial to understanding the dynamics of a given diatom-atom collision. Given that the reduced masses of the OH+Kr and OH+Xe systems are very similar ($2.378 \times 10^{-26} \text{ kg}$ and $2.500 \times 10^{-26} \text{ kg}$ [189], respectively),

it can be deduced that any contrast in the dynamics of the OH+Rg systems is due to differences in their PESs.

Figure 5.4 shows the four adiabatic PESs of A' symmetry that describe the interaction of Kr and Xe with the OH(A) and OH(X) radicals, as well the mixing angle, χ , that couples the excited- and ground-state surfaces (see Section 5.3.4). In linear geometries (of $C_{\infty v}$ symmetry), the OH(A)+Rg system is a singly-degenerate Σ state and the OH(X)+Rg system is a doubly-degenerate Π state. However, any approach of the rare-gas atom in a non-linear configuration, which reduces the symmetry from $C_{\infty v}$ to C_s , will split the doubly-degenerate Π state into a component that is symmetric (A') and another that is anti-symmetric (A'') with respect to reflection in the *scattering* plane, *i.e.* that which contains the three atoms. It should be stressed that this is not the same as the notation used to describe the Λ -doublets discussed in Section 5.2, which denotes different symmetries with respect to reflection in the *rotational* plane.

In this thesis, the single adiabatic PES that describes the OH(A)+Rg system is labelled $2A'$, and the two lower states, which describe OH(X)+Rg, are denoted $1A'$ and $1A''$. All PESs for both systems were calculated at the MRCISD+Q (multi-reference configuration interaction with single and double excitation configurations) level of theory by Kłos. A multi-reference method was required to describe the PESs in regions near conical intersections: single-reference methods assume that a given PES is well described by a single Hartree-Fock calculation (that neglects electron correlation effects, and adopts the Born-Oppenheimer approximation), and so give a poor description of the wavefunction in regions of potential crossing. Notably, the +Q notation refers to the Davidson correction for size-extensivity.

Some general comments can be made about both OH(A)+Rg surfaces. The OH radical and rare-gas atom share an attractive interaction in linear configurations, forming two deep potential-energy wells that correspond to the approach of the rare gas towards either end of the hydroxyl radical. Of these, the potential-energy well corresponding to the approach of the rare gas towards the oxygen end of the

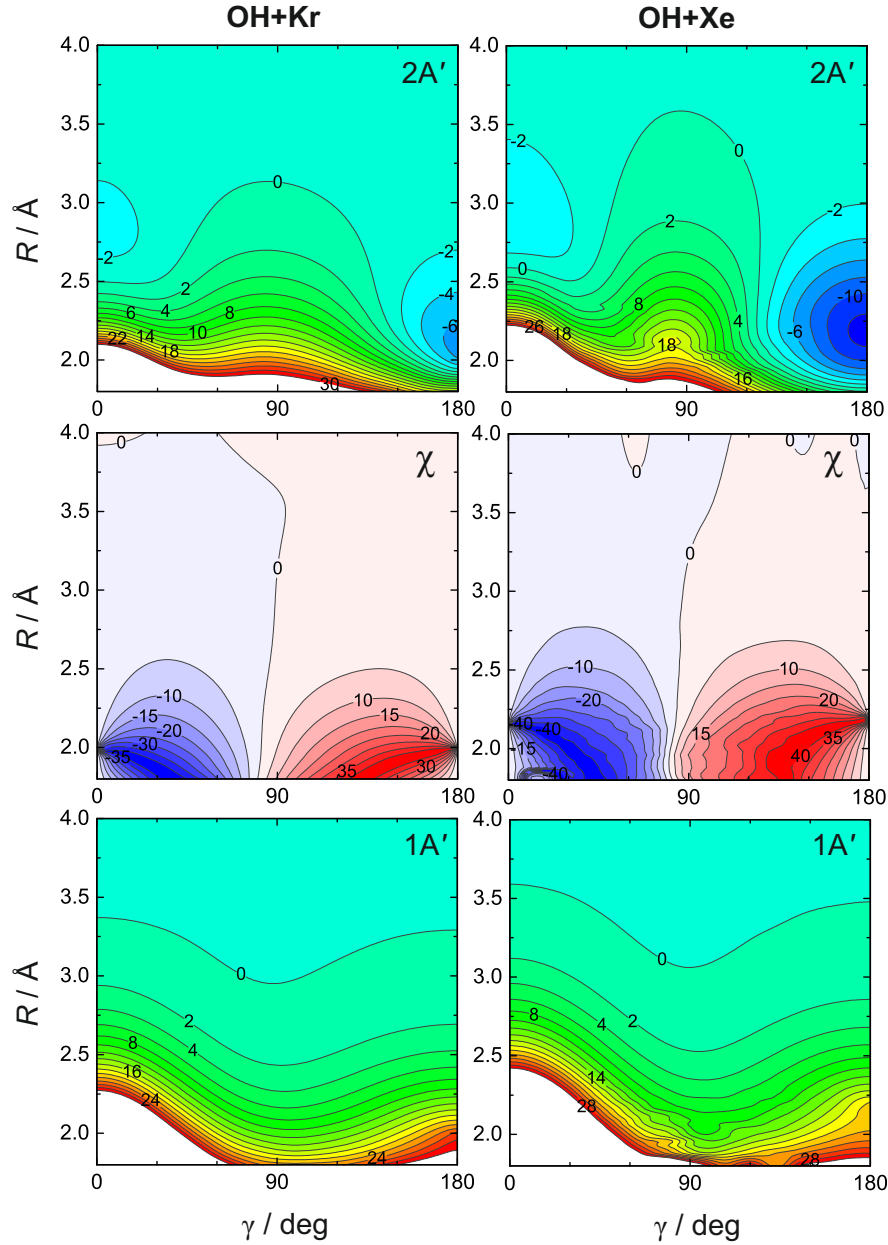


Figure 5.4: The $2A'$ and $1A'$ adiabatic PESs, and the mixing angle, χ , which couples them, for the OH+Kr [78] and OH+Xe systems [77]. The surfaces were calculated by Klos at the MRCISD+Q level. The numbers on the PES give the potential energy, in 10^3 cm^{-1} , relative to the asymptotic value for each state at large R . The numbers on the central mixing-angle plots give the value of χ in degrees – see Section 5.3.4. Note that a value of $\chi = \pm 45^\circ$ corresponds to complete mixing of the adiabatic PESs and a value of $\chi = 0^\circ$ corresponds to zero mixing.

radical is more attractive, and occurs at smaller R . These attractive regions are well separated by a strong repulsion in T-shaped geometries that extends to large R .

The major differences between the OH(A)+Kr and OH(A)+Xe surfaces – and, hence, between the dynamics they govern – are the strengths of the interactions described above. In comparison to OH(A)+Kr, the potential-energy wells are much deeper for OH(A)+Xe, and the repulsive barrier that separates them is higher, and extends to longer range. In general, the OH(A)+Xe PES can be said to be more anisotropic than that of OH(A)+Kr.

The interaction between the oxygen end of the OH radical and the rare-gas atom is relatively strong, at about twice the magnitude of the attraction between the hydrogen end and the rare gas. Indeed, for the OH(A)+Xe system, the energy of interaction between O and Xe is, rather remarkably, of the same magnitude as a moderately strong chemical bond. For example, as a point of comparison, the bond enthalpy of the I–I bond in the iodine molecule is around 12600 cm^{-1} [190], whereas the deepest point of the HO–Xe potential-energy well occurs at around -13000 cm^{-1} .

Studies by Esposti *et al.* [191] revealed that OH(A)+Ar forms a very strong van der Waals complex in the gas phase. At long-range separations, electron exchange and orbital overlap effects are negligible, and the strong interaction between OH(A) and Ar can be attributed to dispersion and induction. At short range, covalent and charge-transfer effects will contribute to the interaction energy. The strong binding in collinear geometries suggests that a weak covalent bond forms between the OH 3σ and Ar $3p_z$ orbitals, however, most of the energy will come from electron-correlation effects. In the O–H–Ar geometry, the charge-dipole and dipole-dipole interactions largely cancel, while they are additive for H–O–Ar. It is thought that similar explanations can be offered for the even stronger interaction effects seen for OH(A)+Kr and OH(A)+Xe.

5.3.2 The adiabatic representation and non-adiabatic coupling

The Born-Oppenheimer approximation states that, due to the considerable difference in their masses, it may be assumed that nuclei are stationary on the timescale of electronic motion [59]. If we consider the nuclear geometry to be defined by $\mathbf{R}$, the (slow) nuclear coordinates at a given time, t , then the total wavefunction, $\Phi_i(\mathbf{r}, \mathbf{R}, t)$, which is also a function of the (fast) electronic coordinates, $\mathbf{r}$, can be written as

$$\Phi(\mathbf{r}, \mathbf{R}, t) = \sum_i \Psi_i(\mathbf{R}, t) \phi_i(\mathbf{r}; \mathbf{R}), \quad (5.4)$$

where $\Psi_i(\mathbf{R}, t)$ and $\phi_i(\mathbf{r}; \mathbf{R})$ are the nuclear and electronic wavefunctions, respectively. The full Hamiltonian can also be separated adiabatically into its nuclear kinetic energy and electronic components:

$$\hat{\mathcal{H}}(\mathbf{r}, \mathbf{R}, t) = \hat{\mathcal{T}}_N(\mathbf{R}, t) + \hat{\mathcal{H}}_e(\mathbf{r}, \mathbf{R}). \quad (5.5)$$

Therefore, for a single nuclear geometry defined by $\mathbf{R}$, the electronic adiabatic wavefunctions outlined above, $\phi_i(\mathbf{r}; \mathbf{R})$, are the solutions of the electronic Schrödinger equation:

$$\hat{\mathcal{H}}_e \phi_i(\mathbf{r}; \mathbf{R}) = U_i(\mathbf{R}) \phi_i(\mathbf{r}; \mathbf{R}), \quad (5.6)$$

where $U_i(\mathbf{R})$ is the electronic adiabatic potential energy of the i^{th} state (in contrast to V_i , the potential energy of the i^{th} state in the diabatic representation, which is discussed later). This equation is achieved by setting the nuclear kinetic energy to zero, *i.e.* assuming that the nuclei have a fixed position. An adiabatic representation of the PES is then obtained by solving Equation (5.6) for all nuclear geometries using a diagonalised form of the potential energy (PE) matrix. In the case of OH(A/X)+Rg, Equation (5.6) can be rewritten as

$$\hat{\mathcal{H}}_e(\mathbf{r}; \mathbf{R}) \begin{pmatrix} \phi_{1A'}(\mathbf{r}; \mathbf{R}) \\ \phi_{2A'}(\mathbf{r}; \mathbf{R}) \\ \phi_{1A''}(\mathbf{r}; \mathbf{R}) \end{pmatrix} = \begin{pmatrix} U_{1A'}(\mathbf{r}; \mathbf{R}) & 0 & 0 \\ 0 & U_{2A'}(\mathbf{r}; \mathbf{R}) & 0 \\ 0 & 0 & U_{1A''}(\mathbf{r}; \mathbf{R}) \end{pmatrix} \begin{pmatrix} \phi_{1A'}(\mathbf{r}; \mathbf{R}) \\ \phi_{2A'}(\mathbf{r}; \mathbf{R}) \\ \phi_{1A''}(\mathbf{r}; \mathbf{R}) \end{pmatrix} \quad (5.7)$$

Note that the off-diagonal terms, which quantify coupling between different states, all take values of zero.

The total wavefunction, $\Phi(\mathbf{r}, \mathbf{R}, t)$, is a solution of the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial \Phi(\mathbf{r}, \mathbf{R}, t)}{\partial t} = \hat{\mathcal{H}}\Phi(\mathbf{r}, \mathbf{R}, t). \quad (5.8)$$

Multiplying through from the left by the complex conjugate of one of the set of orthonormal electronic wavefunctions, $\phi_j(\mathbf{r}; \mathbf{R})^*$, and then integrating over all the electronic coordinates, gives

$$i\hbar \frac{\partial \Psi_j}{\partial t} = (\hat{\mathcal{T}}_N + U_j)\Psi_j - \sum_i \hat{\Lambda}_{ji}\Psi_i, \quad (5.9)$$

where the coordinate dependence has been dropped from the wavefunctions and operators for the sake of clarity. The operator $\hat{\Lambda}_{ji}$ quantifies the non-adiabatic coupling between two adiabatic states, and can be expressed as

$$\hat{\Lambda}_{ji} = \delta_{ji}\hat{\mathcal{T}}_N - \langle \phi_j | \hat{\mathcal{T}}_N | \phi_i \rangle. \quad (5.10)$$

As can be seen in the second term of Equation (5.10), the kinetic-energy operator is acting on electronic wavefunctions, and so the motions of the nuclei and the electrons are coupled. Thus, non-adiabatic coupling can be said to cause a breakdown in the Born-Oppenheimer approximation.

The kinetic-energy operator, $\hat{\mathcal{T}}_N = -\frac{\hbar^2}{2\mu}\nabla^2$, can be included in Equation (5.10) to give

$$\hat{\Lambda}_{ji} = -\frac{\hbar^2}{2\mu}\delta_{ji}\nabla^2 + \frac{\hbar^2}{2\mu}\langle \phi_j | \nabla^2 | \phi_i \rangle. \quad (5.11)$$

In the limit where $i \neq j$, the first term in this equation goes to zero, and the expression for the coupling operator can be rewritten as

$$\hat{\Lambda}_{ji} = \frac{\hbar^2}{2\mu}(2\mathbf{p}_{ji}\nabla + P_{ji}). \quad (5.12)$$

in which $\mathbf{p}_{ji} = \langle \phi_j | \nabla | \phi_i \rangle$, a vector quantity relating to kinetic (nuclear momentum) non-adiabatic coupling, and $P_{ji} = \langle \phi_j | \nabla^2 | \phi_i \rangle$, the scalar second derivative, the value of which is often small enough to deem it negligible. Notably, within the Born-Oppenheimer approximation, $\hat{\Lambda}_{ji} = 0$ for $i \neq j$.

If $\mathbf{p}_{ji}$ is considered further by starting from the electronic Schrödinger equation:

$$\begin{aligned}
\hat{\mathcal{H}}_e \phi_i &= U_i \phi_i \\
\nabla(\hat{\mathcal{H}}_e \phi_i) &= \nabla(U_i \phi_i) \\
\hat{\mathcal{H}}_e \nabla \phi_i + (\nabla \hat{\mathcal{H}}_e) \phi_i &= U_i \nabla \phi_i + (\nabla U_i) \phi_i \\
\langle \phi_j | \hat{\mathcal{H}}_e \nabla \phi_i \rangle + \langle \phi_j | \nabla \hat{\mathcal{H}}_e | \phi_i \rangle &= U_i \langle \phi_j | \nabla \phi_i \rangle + \nabla U_i \delta_{ji} \\
\langle \phi_j | \hat{\mathcal{H}}_e | \nabla \phi_i \rangle + \langle \phi_j | \nabla \hat{\mathcal{H}}_e | \phi_i \rangle &= U_i \mathbf{p}_{ji} \\
\langle \nabla \phi_i | \hat{\mathcal{H}}_e | \phi_j \rangle^* + \langle \phi_j | \nabla \hat{\mathcal{H}}_e | \phi_i \rangle &= U_i \mathbf{p}_{ji} \\
U_j \langle \nabla \phi_i | \phi_j \rangle^* + \langle \phi_j | \nabla \hat{\mathcal{H}}_e | \phi_i \rangle &= U_i \mathbf{p}_{ji} \\
U_j \langle \phi_j | \nabla \phi_i \rangle + \langle \phi_j | \nabla \hat{\mathcal{H}}_e | \phi_i \rangle &= U_i \mathbf{p}_{ji} \\
U_j \mathbf{p}_{ji} + \langle \phi_j | \nabla \hat{\mathcal{H}}_e | \phi_i \rangle &= U_i \mathbf{p}_{ji}
\end{aligned} \tag{5.13}$$

and, therefore,

$$\mathbf{p}_{ji} = \frac{\langle \phi_j | \nabla \hat{\mathcal{H}}_e | \phi_i \rangle}{U_i - U_j}, \tag{5.14}$$

which implies that non-adiabatic coupling becomes infinite when two adiabatic states share a point of degeneracy.

For most systems, there will be regions of the PES where the adiabatic electronic wavefunction changes rapidly as a function of the nuclear coordinates; for example, at potential energy barriers, or regions of the PES near avoided crossings or points of degeneracy between two surfaces. If a given collision involves passing through a region of the PES where the electronic wavefunction is changing rapidly, there may not be enough time for the wavefunction to adapt sufficiently quickly with respect to the rapid nuclear motion. Thus, the system may evolve onto another PES that is a smoother continuation of the character of the initial electronic wavefunction, and a non-adiabatic transition is seen to take place.

5.3.3 The diabatic representation and the Massey parameter

As discussed previously, an adiabatic representation is achieved by solving Equation (5.6) for all states, using a diagonal potential-energy matrix in which the diagonal

elements are the adiabatic PESs and the off-diagonal elements (which couple them) are zero.

In a diabatic representation, the potential-energy matrix is no longer diagonal since it now does not obey the Born-Oppenheimer approximation. Coupling between the surfaces is achieved *via* the off-diagonal elements of the potential-energy matrix (V_{ji}), and the nuclear kinetic-energy matrix is now diagonal, *i.e.* the value of $\mathbf{p}_{ji}$ goes to zero.

The Massey parameter [192, 193] gives an indication of how a given process can be adequately described within the limits of purely diabatic and adiabatic representations. It is defined as

$$\xi = \left| \frac{\hbar \dot{\mathbf{v}} \cdot \mathbf{p}_{ji}}{U_j - U_i} \right|, \quad (5.15)$$

where $\dot{\mathbf{v}}$ is the nuclear velocity vector, and U_k is the adiabatic potential energy of the k^{th} state.

The adiabatic limit will be approached when $\xi \rightarrow 0$, *i.e.* when the nuclear velocity is small, the non-adiabatic coupling term is small, and/or the states are greatly separated in potential energy. As discussed above, the nuclei are travelling sufficiently slowly such that the electronic wavefunction has time to adapt to the changing nuclear geometry and remain in the same adiabatic state.

In contrast, the diabatic limit will be reached as $\xi \rightarrow 1$, *i.e.* when the nuclei are moving fast, are in a region of strong coupling, and/or are near a curve crossing. The rapid motion of the nuclei vastly exceeds the ability of the electrons to adapt to the new nuclear geometry, and the system may be forced to evolve onto a different PES, as outlined above.

5.3.4 Adiabatic to diabatic transformation

Adiabatic and diabatic representations of PESs can often be linked by a simple transformation. In changing from an adiabatic to a diabatic representation, the singularity of the point of degeneracy described by Equation (5.14) is lifted, since the coupling is quantified by discrete terms of the potential-energy matrix, rather than

a derivative function. Recalling Equation (5.7), and in the context of OH(A/X)+Rg coupling systems, the electronic Schrödinger equation describing an adiabatic representation of the PES can be rewritten as

$$\hat{\mathcal{H}}_e(\mathbf{r}; \mathbf{R}) \begin{pmatrix} \phi_{1A'}(\mathbf{r}; \mathbf{R}) \\ \phi_{2A'}(\mathbf{r}; \mathbf{R}) \\ \phi_{1A''}(\mathbf{r}; \mathbf{R}) \end{pmatrix} = \mathbf{A} \begin{pmatrix} \phi_{1A'}(\mathbf{r}; \mathbf{R}) \\ \phi_{2A'}(\mathbf{r}; \mathbf{R}) \\ \phi_{1A''}(\mathbf{r}; \mathbf{R}) \end{pmatrix}, \quad (5.16)$$

in which the adiabatic potential-energy matrix, $\mathbf{A}$, is

$$\begin{pmatrix} U_{1A'}(\mathbf{r}; \mathbf{R}) & 0 & 0 \\ 0 & U_{2A'}(\mathbf{r}; \mathbf{R}) & 0 \\ 0 & 0 & U_{1A''}(\mathbf{r}; \mathbf{R}) \end{pmatrix}, \quad (5.17)$$

Alternatively, in the diabatic representation (with wavefunctions φ_i), the electronic Schrödinger equation is given by

$$\hat{\mathcal{H}}_e(\mathbf{r}; \mathbf{R}) \begin{pmatrix} \varphi_{\Pi_{A'}}(\mathbf{r}; \mathbf{R}) \\ \varphi_{\Sigma_{A'}}(\mathbf{r}; \mathbf{R}) \\ \varphi_{\Pi_{A''}}(\mathbf{r}; \mathbf{R}) \end{pmatrix} = \mathbf{D} \begin{pmatrix} \varphi_{\Pi_{A'}}(\mathbf{r}; \mathbf{R}) \\ \varphi_{\Sigma_{A'}}(\mathbf{r}; \mathbf{R}) \\ \varphi_{\Pi_{A''}}(\mathbf{r}; \mathbf{R}) \end{pmatrix}, \quad (5.18)$$

in which the diabatic potential-energy matrix, $\mathbf{D}$, is

$$\begin{pmatrix} V_{\Pi_{A'}}(\mathbf{r}; \mathbf{R}) & V_{12} & 0 \\ V_{12} & V_{\Sigma_{A'}}(\mathbf{r}; \mathbf{R}) & 0 \\ 0 & 0 & V_{\Pi_{A''}}(\mathbf{r}; \mathbf{R}) \end{pmatrix}, \quad (5.19)$$

and the V_{12} elements quantify the potential-energy coupling between diabatic surfaces. At this point, it is again important to note that the $\Pi_{A'}$ and $\Pi_{A''}$ labels for the diabatic states described here do not represent the Λ -doublet levels.

If coupling is limited to being purely electrostatic in nature, states of different symmetry cannot couple. Therefore, the A'' state cannot couple to those of A' symmetry, and it can be said to be equivalent in either the adiabatic or diabatic representation, such that $\phi_{1A''} \equiv \varphi_{\Pi_{A''}}$. Conversely, the two states of A' symmetry can indeed be coupled, and so the adiabatic PESs can be related to the diabatic potentials and couplings *via* the unitary transformation

$$\begin{pmatrix} U_{1A'} & 0 & 0 \\ 0 & U_{2A'} & 0 \\ 0 & 0 & U_{1A''} \end{pmatrix} = \mathbf{C}_2 \begin{pmatrix} V_{\Pi_{A'}} & V_{\Sigma_{A'}\Pi_{A'}} & 0 \\ V_{\Sigma_{A'}\Pi_{A'}} & V_{\Sigma_{A'}} & 0 \\ 0 & 0 & V_{\Pi_{A''}} \end{pmatrix} \mathbf{C}_2^T, \quad (5.20)$$

where, as before, the coordinate dependence of the wavefunctions has been omitted for the sake of clarity, and the rotation matrix, $\mathbf{C}_2$, is expressed as

$$\mathbf{C}_2 = \begin{pmatrix} \cos \chi & \sin \chi & 0 \\ -\sin \chi & \cos \chi & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (5.21)$$

where χ is the mixing angle. A value of $\chi = \pm \frac{\pi}{4}$ corresponds to complete mixing, *i.e.* the diabatic limit, whereas a value of $\chi = 0$ corresponds to zero mixing, *i.e.* the adiabatic limit. At this point, the reader is referred back to Figure 5.4, which shows plots of the two-state mixing angle, χ , for the OH+Kr and OH+Xe systems.

In the case where states of different symmetry are allowed to couple (see Section 5.4), the transformation becomes somewhat more complicated:

$$\begin{pmatrix} U_{1A'} & 0 & 0 \\ 0 & U_{2A'} & 0 \\ 0 & 0 & U_{1A''} \end{pmatrix} = \mathbf{C}_3 \begin{pmatrix} V_{\Pi_{A'}} & V_{\Sigma_{A'}\Pi_{A'}} & V_{\Pi_{A'}\Pi_{A''}} \\ V_{\Sigma_{A'}\Pi_{A'}} & V_{\Sigma_{A'}} & V_{\Sigma_{A'}\Pi_{A''}} \\ V_{\Pi_{A'}\Pi_{A''}} & V_{\Sigma_{A'}\Pi_{A''}} & V_{\Pi_{A''}} \end{pmatrix} \mathbf{C}_3^T, \quad (5.22)$$

and the rotation matrix, $\mathbf{C}_3$, is expressed as

$$\mathbf{C}_3 = \begin{pmatrix} \cos \alpha \cos \beta - \sin \alpha \sin \omega \sin \beta & \sin \alpha \cos \omega & \cos \alpha \sin \beta + \sin \alpha \sin \omega \cos \beta \\ -\sin \alpha \cos \beta - \cos \alpha \sin \omega \sin \beta & \cos \alpha \cos \omega & -\sin \alpha \sin \beta + \cos \alpha \sin \omega \cos \beta \\ -\cos \omega \sin \beta & -\sin \omega & \cos \omega \cos \beta \end{pmatrix}, \quad (5.23)$$

where

- α is the mixing angle for states $|\Sigma_{A'}\rangle$ and $|\Pi_{A'}\rangle$,
- β is the mixing angle for states $|\Pi_{A'}\rangle$ and $|\Pi_{A''}\rangle$, and

- ω is the mixing angle for states $|\Sigma_{A'}\rangle$ and $|\Pi_{A''}\rangle$.

Notably, if β and ω are set to zero, then we revert back to the situation described by Equation (5.20), with $\alpha \equiv \chi$.

5.3.5 Conical intersections

If we again consider the time-dependent Schrödinger equation that describes dynamics on coupled adiabatic PESs, we can rewrite Equation (5.9), in matrix form, as

$$(\hat{\mathcal{T}}_N \mathbf{I} + \mathbf{U} - \hat{\Lambda}) \Psi = i\hbar \frac{\partial \Psi}{\partial t}, \quad (5.24)$$

where $\mathbf{I}$ is the identity matrix, $\mathbf{U}$ is a diagonal matrix of adiabatic PESs, $\hat{\Lambda}$ is the non-adiabatic kinetic-energy coupling matrix, and Ψ describes the nuclear wavefunction.

If, instead, the system is modelled in the diabatic representation – which, as outlined previously, can be transformed into the adiabatic representation *via* a unitary transformation – then the Schrödinger equation can be written as

$$(\hat{\mathcal{T}}_N \mathbf{I} + \mathbf{V}) \Psi = i\hbar \frac{\partial \Psi}{\partial t}, \quad (5.25)$$

where $\mathbf{V}$ is the diabatic potential-energy matrix. The diabatic PESs are defined by the diagonal elements of the matrix, which are coupled *via* the off-diagonal potential-energy terms. The kinetic-energy matrix is diagonal and so does not couple different diabatic states.

In a two-state system, the two uncoupled, diabatic states, ϕ_1^d and ϕ_2^d , are mixed together by a coupling term to create linear combinations of the diabatic basis functions, *i.e.* the adiabatic eigenstates of the full Hamiltonian, such that

$$\phi^{ad} = c_1 \phi_1^d + c_2 \phi_2^d, \quad (5.26)$$

where c_1 and c_2 are constants. This linear combination, in conjugation with the Schrödinger equation, can be used to derive a set of secular equations:

$$\begin{pmatrix} V_{11} - E & V_{12} \\ V_{12} & V_{22} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0, \quad (5.27)$$

which will lead to a pair of solutions

$$E_{\pm} = \frac{1}{2} \left[(V_{11} + V_{22}) \pm \sqrt{(V_{11} - V_{22})^2 + 4V_{12}^2} \right]. \quad (5.28)$$

By inspection, it can be seen that, if two adiabatic potentials are to be degenerate, it must be true that $V_{11} = V_{22}$ and that $V_{12} = 0$. To satisfy both these conditions, two independent degrees of freedom for nuclear motion are needed: the *tuning* coordinate, which brings the two adiabatic states closer in energy until a point of degeneracy is reached, whilst maintaining that $V_{12} = 0$; and the *coupling* coordinate, which involves motion in a given direction such that the symmetry of the system is reduced, and $V_{12} \neq 0$. Together, the tuning and coupling coordinates define the *branching space*.

In a diatomic molecule with two diabatic states of the same symmetry, the only geometric distortion that is possible is a change in the internuclear bond length. A non-zero coupling term between the two states cannot, therefore, be reduced to zero, since the symmetry is preserved whether the bond length extends or compresses. Thus, since it is always true that $V_{12} \neq 0$, the two adiabatic states are prevented from becoming degenerate, and the adiabatic PESs cannot cross – this is the basis of the *non-crossing rule*.

If the diabatic states have different symmetries, the adiabatic states can share a crossing. However, this is no longer true if the two diabatic eigenstates are able to be mixed by a coupling term of the correct symmetry; in the present case, this coupling remains unaffected by a symmetric bond stretch, so there is no distortion-induced coupling of the adiabats.

This thesis is concerned with OH+Rg collision dynamics. This three-atom system has a total of $F = 3N - 6 = 3$ degrees of freedom meaning that, once motion along the tuning and coupling coordinates has been accounted for, there is $F - 2 = 1$ degree of freedom remaining to facilitate curve-crossings, *i.e.* there are isolated *points* of degeneracy. In more complicated systems, with more degrees of freedom – including, for example, the OH+H₂ system [105, 194–201] – there can be seams (rather than points) of intersections.

For the OH+Rg system, the tuning coordinate ($\mathbf{g}$) corresponds to the motion of the rare-gas atom towards and away from the OH radical when the three atoms share a linear geometry; the coupling coordinate ($\mathbf{h}$) describes a departure from linearity. Figure 5.5 shows cuts through the adiabatic $1A'$, $1A''$, and $2A'$ PESs for OH+Kr [76, 78, 188] and OH+Xe [77] in the near-linear ($\gamma = 175^\circ$) geometry. Also shown in the insert for the OH+Kr graph are the Σ and Π diabatic PESs [188]. The adiabatic potentials share an avoided crossing at 1.99 Å for OH+Kr, and at 2.20 Å for OH+Xe. The diabatic potentials for OH+Kr also share a curve crossing at 1.99 Å. The thermal collision energies for the experimental data quoted in this thesis are 32907 cm^{-1} for OH+Kr, and 32985 cm^{-1} for OH+Xe. The barrierless crossings of the PESs are located below these collision energies, so both systems are expected to show significant quenching to the ground state. As noted earlier, the HO(A)–Xe attractive potential-energy well is much deeper than that of HO(A)–Kr, and the conical intersection with the ground state is also located much closer to the bottom of the well in the former. In effect, conical intersections act as funnels through which there can be non-radiative transfer of population from one adiabatic state to another. It is, therefore, expected that the OH(A)+Xe system will display significantly greater non-adiabatic effects than those involving the lighter rare gases.

5.3.6 Non-adiabatic roto-electronic coupling

The coupling of adiabatic states that has been discussed so far in this thesis has been purely electrostatic in nature, facilitated by the off-diagonal elements of the potential-energy matrix within the diabatic representation. As stated previously, only states of the same symmetry are able to couple electrostatically, namely: the upper $2A'$ surface in the A $^2\Sigma^+$ state and the lower $1A'$ surface in the X $^2\Pi$ state. The second PES in the electronic ground state – of A'' symmetry, and which is degenerate with the $1A'$ PES at linearity – is deemed to be the same in both the diabatic and adiabatic representations, and is not involved in purely electrostatic coupling schemes.

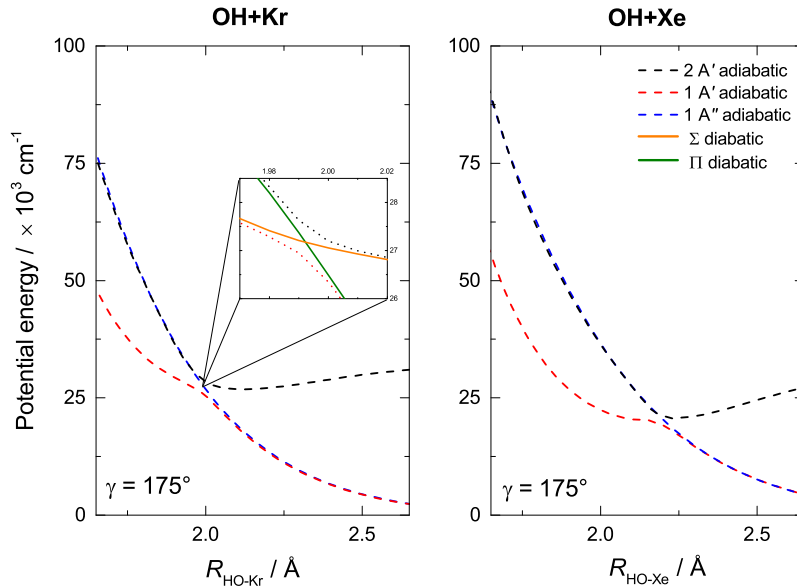


Figure 5.5: Cuts through the adiabatic $2A'$, $1A'$, and $1A''$ PESs for OH+Kr [76, 78, 188] and OH+Xe [77] in the near-linear ($\gamma = 175^\circ$) geometry. The potential energy is given relative to the asymptotic value of the OH(X)+Rg state at large R . Also shown in the insert for the OH+Kr graph are the Σ and Π diabatic PESs [188]. The adiabatic potentials share an avoided crossing at 1.99 Å for OH+Kr, and at 2.20 Å for OH+Xe. The diabatic potentials for OH+Kr also share a curve crossing at 1.99 Å. The thermal collision energies for the experimental data quoted in this thesis are 32907 cm^{-1} for OH+Kr, and 32985 cm^{-1} for OH+Xe.

Previous work published by Lehman and co-workers in reference [78] investigated OH(A)+Kr collision dynamics by using laser-induced fluorescence (LIF) experiments to measure electronic quenching cross-sections and the OH(X) product rotational-state distribution. They also modelled non-adiabatic dynamics using QCT calculations run on the two surfaces of A' symmetry that were coupled electrostatically. Though the theoretical electronic quenching cross-sections agree qualitatively with the trend in the experimental data (*i.e.* that, generally, the magnitude of the quenching cross-section decreases as the rotational quantum state of OH(A) increases), the QCT calculations were found to consistently underestimate the extent of electronic quenching. Given that the OH(X) product state distributions published in reference [78] report an almost equal population of the $1A'$ and $1A''$ states, it would appear that inclusion of coupling to the $1A''$ state is essential for a full and accurate description of OH(A/X)+Rg dynamics (see also Section

6.1.4). Neglecting this coupling may thus be responsible – at least, in part – for the consistent underestimation of quenching cross-sections seen in the theoretical models discussed therein.

Though purely electrostatic coupling cannot facilitate a transfer of population between states of different symmetry, an antisymmetric rotation of the whole triatomic OH+Rg system about an axis perpendicular to the O–H bond can make the overall symmetry of the transition totally symmetric (and, hence, allowed) since $A' \times A'' \times A'' = A'$. Transitions between A' and A'' states therefore become possible when coupling between the orbital angular momentum, ℓ , and the total angular momentum, $\mathbf{J} = \mathbf{j} + \ell$, is considered.

It is important to note that, whilst non-adiabatic electrostatic and roto-electronic couplings both violate the Born-Oppenheimer approximation, they do so in different ways. Electrostatic coupling involves a breakdown of the approximation in localised regions where there is a coupling of electronic and nuclear motions. In contrast, the Born-Oppenheimer approximation is inherently inapplicable to roto-electronic coupling regimes, since electronic motion is occurring with respect to a nuclear framework that is itself moving. For this reason, roto-electronic couplings are often cited as examples of *geometric couplings*.

This thesis considers two types of roto-electronic coupling: Renner-Teller coupling and Coriolis coupling. Renner-Teller coupling originates in the bending of a linear complex (when $\gamma = 0^\circ$ or $\gamma = 180^\circ$). At linearity, the projection of the electronic orbital angular momentum on the internuclear axis, λ , is a good quantum number, and takes values of $\pm\Lambda$. However, as the triatomic complex bends, coupling becomes possible for states with non-zero electronic orbital angular momentum. Renner-Teller coupling has been a subject of interest for many systems – most notably, in the NH_2 radical [202–204], and in the photolysis of $\text{H}_2\text{O}(\tilde{B})$ [205, 206]. Conversely, Coriolis coupling is that which mixes states of different symmetry with respect to reflection in the rotational plane. As such, it is only able to mix states with electronic-angular-momentum quantum numbers that differ by $\Delta\Lambda = \pm 1$. Coriolis coupling has also been investigated in many systems, including, but not limited to:

- electronic quenching in $\text{NH(a)}+\text{H}$ [207] and $\text{C}+\text{H}_2$ [208];
- quantum-mechanical studies of the reactive scattering of $\text{O}(^1D)+\text{H}_2$ [209];
and
- trajectory surface-hopping [204] and quantum-mechanical models [210] of $\text{N}(^2D)+\text{H}_2$.

In the specific context of the $\text{OH(A/X)}+\text{Rg}$ systems investigated in this thesis, the contributions from various types of coupling can be summarised as:

- Electrostatic coupling links the surface of A' symmetry that describes the $\text{OH(A)}+\text{Rg}$ system and that of A' symmetry that describes the $\text{OH(X)}+\text{Rg}$ system;
- Renner-Teller coupling links the two surfaces, of A' and A'' symmetry, that describe the $\text{OH(X)}+\text{Rg}$ system; and
- Coriolis coupling links the surface of A' symmetry that describes the $\text{OH(A)}+\text{Rg}$ system and that of A'' symmetry that describes the $\text{OH(X)}+\text{Rg}$ system.

Work by Perkins [33] has shown that, in terms of generating theoretical quenching cross-sections for $\text{OH(A)}+\text{Rg}$, the inclusion of Renner-Teller coupling in the surface-hopping calculations is crucial in facilitating non-adiabatic quenching. Though less important, the addition of Coriolis coupling also leads to a significant improvement in the agreement between experiment and theory. The combined model is now discussed in detail.

5.4 Non-adiabatic effects in OH(A)+Rg

5.4.1 Basis sets and mixing angles

The rotational bases used in this work are the Wigner rotational functions, $|K\rangle$, defined in reference [203] and [204],

$$\begin{aligned}\hat{J}^2|K\rangle &= J(J+1)\hbar^2|K\rangle, \\ \hat{J}_\pm|K\rangle &= \lambda_\pm^{JK}|K\pm 1\rangle, \\ \hat{J}_z|K\rangle &= K\hbar|K\rangle,\end{aligned}\tag{5.29}$$

where

$$\lambda_\pm^{JK} = \hbar[J(J+1) - K(K\pm 1)]^{\frac{1}{2}},\tag{5.30}$$

and K is the projection of $\mathbf{J}$, the total angular momentum, onto the O–H bond axis.

The diabatic electronic basis set used in this work is that of Drukker and Schatz [209]. For a diatomic molecule, these states are eigenfunctions of the electronic orbital angular momentum operator, $\hat{L}_z$, such that

$$\begin{aligned}|\pm\Lambda\rangle &= C_\pm e^{\pm i\Lambda\phi}, \\ \hat{L}_z|\pm\Lambda\rangle &= \pm\Lambda\hbar|\pm\Lambda\rangle,\end{aligned}\tag{5.31}$$

where ϕ is the electron azimuthal angle. Notably, however, the $|+1\rangle$ and $|-1\rangle$ states are not eigenfunctions of the inversion operator, the effect of which is the same as the reflection operator, $\hat{\sigma}_{xz}$, acting on a molecule lying in the triatomic plane defined by xz . Therefore, a new diabatic basis is defined as

$$\begin{aligned}|\Sigma^+\rangle &= |0\rangle, \\ |\Pi_x\rangle &= |\Lambda+\rangle = \frac{1}{\sqrt{2}}[|+1\rangle + |-1\rangle] \propto \sqrt{2}\cos\phi, \\ |\Pi_y\rangle &= |\Lambda-\rangle = \frac{-i}{\sqrt{2}}[|+1\rangle - |-1\rangle] \propto \sqrt{2}\sin\phi.\end{aligned}\tag{5.32}$$

The states can be labelled according to their inversion/reflection symmetry

$$\begin{aligned}\hat{\sigma}_{xz}|\Pi_x\rangle &= +|\Pi_x\rangle \equiv |\Pi_{A'}\rangle, \\ \hat{\sigma}_{xz}|\Pi_y\rangle &= -|\Pi_y\rangle \equiv -|\Pi_{A''}\rangle.\end{aligned}\tag{5.33}$$

And so, the new basis set becomes

$$|+1\rangle = \frac{\sqrt{2}}{2} [|\Pi_{A'}\rangle + i|\Pi_{A''}\rangle], \quad (5.34)$$

$$|0\rangle = |\Sigma^+\rangle, \quad (5.35)$$

$$|-1\rangle = \frac{\sqrt{2}}{2} [|\Pi_{A'}\rangle - i|\Pi_{A''}\rangle]. \quad (5.36)$$

The adiabatic electronic basis set, which comprises the $2A'$, $1A'$, and $1A''$ states, is linked to the diabatic basis by the mixing angle, χ , *via*

$$\begin{pmatrix} |+1\rangle \\ |0\rangle \\ |-1\rangle \end{pmatrix} = \begin{pmatrix} \frac{\cos \chi}{\sqrt{2}} & \frac{-\sin \chi}{\sqrt{2}} & \frac{i}{\sqrt{2}} \\ \sin \chi & \cos \chi & 0 \\ \frac{\cos \chi}{\sqrt{2}} & \frac{-\sin \chi}{\sqrt{2}} & \frac{-i}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} |1A'\rangle \\ |2A'\rangle \\ |1A''\rangle \end{pmatrix}, \quad (5.37)$$

and, in this basis, the electronic Hamiltonian matrix is

$$\hat{\mathcal{H}}_e \begin{pmatrix} |+1\rangle \\ |0\rangle \\ |-1\rangle \end{pmatrix} = \begin{pmatrix} D_{\text{sum}} & \frac{V_{\Sigma+\Pi_{A'}}}{\sqrt{2}} & D_{\text{diff}} \\ \frac{V_{\Sigma+\Pi_{A'}}}{\sqrt{2}} & V_{\Sigma^+} & \frac{V_{\Sigma+\Pi_{A'}}}{\sqrt{2}} \\ D_{\text{diff}} & \frac{V_{\Sigma+\Pi_{A'}}}{\sqrt{2}} & D_{\text{sum}} \end{pmatrix} \begin{pmatrix} |+1\rangle \\ |0\rangle \\ |-1\rangle \end{pmatrix}, \quad (5.38)$$

where

$$\begin{aligned} D_{\text{sum}} &= \frac{1}{2}(V_{\Pi_{A'}} + V_{\Pi_{A''}}), \\ D_{\text{diff}} &= \frac{1}{2}(V_{\Pi_{A'}} - V_{\Pi_{A''}}). \end{aligned} \quad (5.39)$$

Notably, the adiabatic and diabatic representations can be linked using a unitary transformation, as described in Section 5.3.4, as a function of the three specific mixing angles: α , β , and ω . Recalling Equation (5.22), it can be seen that

$$\begin{pmatrix} U_{1A'} & 0 & 0 \\ 0 & U_{2A'} & 0 \\ 0 & 0 & U_{1A''} \end{pmatrix} = \mathbf{C}_3 \begin{pmatrix} D_{\text{sum}} & \frac{V_{\Sigma+\Pi_{A'}}}{\sqrt{2}} & D_{\text{diff}} \\ \frac{V_{\Sigma+\Pi_{A'}}}{\sqrt{2}} & V_{\Sigma_{A'}} & \frac{V_{\Sigma+\Pi_{A'}}}{\sqrt{2}} \\ D_{\text{diff}} & \frac{V_{\Sigma+\Pi_{A'}}}{\sqrt{2}} & D_{\text{sum}} \end{pmatrix} \mathbf{C}_3^T, \quad (5.40)$$

where the rotation matrix, $\mathbf{C}_3$, is still expressed as

$$\mathbf{C}_3 = \begin{pmatrix} \cos \alpha \cos \beta - \sin \alpha \sin \omega \sin \beta & \sin \alpha \cos \omega & \cos \alpha \sin \beta + \sin \alpha \sin \omega \cos \beta \\ -\sin \alpha \cos \beta - \cos \alpha \sin \omega \sin \beta & \cos \alpha \cos \omega & -\sin \alpha \sin \beta + \cos \alpha \sin \omega \cos \beta \\ -\cos \omega \sin \beta & -\sin \omega & \cos \omega \cos \beta \end{pmatrix}. \quad (5.41)$$

Alternatively, $\mathbf{C}_3$ can be expressed as the product of three matrices, one in each rotation angle, such that

$$\mathbf{C}_3 = \begin{pmatrix} \cos \alpha & \sin \alpha & 0 \\ -\sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \omega & \sin \omega \\ 0 & -\sin \omega & \cos \omega \end{pmatrix} \begin{pmatrix} \cos \beta & 0 & \sin \beta \\ 0 & 1 & 0 \\ -\sin \beta & 0 & \cos \beta \end{pmatrix}, \quad (5.42)$$

where α represents the coupling between $|+1\rangle$ and $|0\rangle$, β mixes $|+1\rangle$ and $|-1\rangle$, and ω couples $|0\rangle$ and $|-1\rangle$. In the limit of purely electrostatic coupling, $\alpha = -\omega$ and $\beta = \frac{\pi}{4}$.

5.4.2 Matrix elements

The $\hat{L}_x$ and $\hat{L}_z$ operators in the $|\pm\Lambda\rangle$ basis are involved in both Renner-Teller and Coriolis coupling. Both operators transform as A'' with $\hat{\sigma}_{xz}$ and, in the adiabatic representation, their matrix elements are purely imaginary. The matrix elements of $\hat{L}_x$ are given by

$$\langle 0|\hat{L}_x|0\rangle = 0, \quad (5.43)$$

$$\langle \pm 1|\hat{L}_x|\mp 1\rangle = 0, \quad (5.44)$$

$$\langle \pm 1|\hat{L}_x|\pm 1\rangle = \pm i[\cos \chi \langle 1A'|\hat{L}_x|1A''\rangle - \sin \chi \langle 2A'|\hat{L}_x|1A''\rangle], \quad (5.45)$$

$$\langle 0|\hat{L}_x|\pm 1\rangle = \langle \pm 1|\hat{L}_x|0\rangle = \pm \frac{i}{\sqrt{2}}[\sin \chi \langle 1A'|\hat{L}_x|1A''\rangle + \cos \chi \langle 2A'|\hat{L}_x|1A''\rangle]. \quad (5.46)$$

where the $\hat{L}_x$ operator can be replaced by the $\hat{L}_z$ operator to yield an equivalent set of expressions.

The operators $\hat{L}_x\hat{L}_z$, $\hat{L}_z^2$, and $\hat{L}^2 (= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2)$, all transform as A' under $\hat{\sigma}_{xz}$. Their matrix elements are real in the adiabatic representation, and are given by

$$\begin{aligned} \langle 0|\hat{L}_z^2|0\rangle &= \sin^2 \chi \langle 1A'|\hat{L}_z^2|1A'\rangle + \cos^2 \chi \langle 2A'|\hat{L}_z^2|2A'\rangle \\ &\quad + \sin 2\chi \langle 1A'|\hat{L}_z^2|2A'\rangle, \end{aligned} \quad (5.47)$$

$$\begin{aligned} \langle 0|\hat{L}_z^2|\pm 1\rangle &= \langle \pm 1|\hat{L}_z^2|0\rangle = \frac{1}{\sqrt{2}} \left[\cos 2\chi \langle 1A'|\hat{L}_z^2|2A'\rangle + \frac{1}{2} \sin 2\chi (\langle 1A'|\hat{L}_z^2|1A'\rangle \right. \\ &\quad \left. - \langle 2A'|\hat{L}_z^2|2A'\rangle) \right], \end{aligned} \quad (5.48)$$

$$\begin{aligned} \langle \pm 1|\hat{L}_z^2|\pm 1\rangle &= \langle -1|\hat{L}_z^2|\mp 1\rangle = \frac{1}{2} [\cos^2 \chi \langle 1A'|\hat{L}_z^2|1A'\rangle + \sin^2 \chi \langle 2A'|\hat{L}_z^2|2A'\rangle \\ &\quad - \sin 2\chi \langle 1A'|\hat{L}_z^2|2A'\rangle \pm \langle 1A''|\hat{L}_z^2|1A''\rangle]. \end{aligned} \quad (5.49)$$

where, as before, $\hat{L}_z^2$ can be replaced by either the $\hat{L}_x\hat{L}_z$ or the $\hat{L}^2$ operator.

5.4.3 Rotational perturbations to the full Hamiltonian

The coordinate system used in this work is that of Petrongolo, which makes use of $\mathbf{r}$ -embedding, whereby the z -axis lies along the O-H bond (rather than along the $\mathbf{R}$ vector) and the Rg-O-H system lies in the xz -plane. Recall that, for this system, $\mathbf{R}$, $\mathbf{r}$, and γ are the Jacobi coordinates, where $\mathbf{r}$ is the bond vector (pointing from O to H), $\mathbf{R}$ is a vector which points from the centre of mass of the OH radical towards the Rg atom, and γ is the angle between these two vectors (such that $\gamma=0$ in the Rg-H-O linear geometry).

The full rotational Hamiltonian for a triatomic system is given by

$$\begin{aligned} \hat{\mathcal{T}}_{\text{rot}} = & \frac{B_R + b_r}{\sin^2 \gamma} (\hat{J}_z^2 + \hat{L}_z^2) + b_r \left(\hat{J}^2 - 2\hat{J}_z^2 + \hat{L}^2 - 2\hat{L}_z^2 + 2\hat{L}_x\hat{L}_z \cot \gamma - 2i\hbar\hat{L}_y \frac{\partial}{\partial \gamma} \right) \\ & + b_r \left[\hat{J}_+ \left(\hat{J}_z \cot \gamma + \hbar \frac{\partial}{\partial \gamma} + i\hat{L}_y \right) + \hat{J}_- \left(\hat{J}_z \cot \gamma - \hbar \frac{\partial}{\partial \gamma} - i\hat{L}_y \right) \right] \\ & + 2\hat{J}_z \left[b_r (\hat{L}_z - \hat{L}_x \cot \gamma) - (b_r + B_R) \frac{\hat{L}_z}{\sin^2 \gamma} \right] - \frac{b_r(\hat{J}_+ + \hat{J}_-)}{2} (\hat{L}_x + \hat{L}_z \cot \gamma), \end{aligned} \quad (5.50)$$

where

$$\begin{aligned} b_r &= \frac{1}{2\mu_{\text{OH}}r^2}, \\ B_R &= \frac{1}{2\mu_{\text{Rg-OH}}R^2}, \\ \mu_{\text{Rg-OH}} &= \frac{m_{\text{Rg}}m_{\text{OH}}}{m_{\text{Rg}} + m_{\text{OH}}}, \\ \mu_{\text{OH}} &= \frac{m_{\text{O}}m_{\text{H}}}{m_{\text{OH}}}. \end{aligned} \quad (5.51)$$

The surface-hopping *quasi*-classical trajectory calculations (see Section 5.5) carried out in this work rely on a separation of ‘fast’ and ‘slow’ coordinates such that the electrons are modelled quantum mechanically whilst the nuclei are deemed to obey classical mechanics. It is desirable to maintain the separation of electronic

and nuclear motion as far as possible, so only the terms from Equation (5.50) that are necessary for Coriolis and Renner-Teller couplings are taken as a perturbation to the electronic Hamiltonian, such that

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_e + \hat{\mathcal{H}}', \quad (5.52)$$

where the operator that comprises the perturbation terms is given by

$$\begin{aligned} \hat{\mathcal{H}}' = & b_r \hat{L}^2 + L_z^2 \left(\frac{B_R + b_r}{\sin^2 \gamma} - 2b_r \right) + 2\hat{J}_z \hat{L}_z \left(b_r - \frac{b_r + B_R}{\sin^2 \gamma} \right) - 2b_r \hat{J}_z \hat{L}_x \cot \gamma \\ & + b_r (\hat{J}_+ - \hat{J}_-) i \hat{L}_y - b_r (\hat{J}_+ - \hat{J}_-) (\hat{L}_x + \hat{L}_z \cot \gamma) + 2b_r \hat{L}_x \hat{L}_z \cot \gamma. \end{aligned} \quad (5.53)$$

In this equation, Renner-Teller terms are those in $\hat{J}_z \hat{L}_z$ and $\hat{J}_z \hat{L}_x$. Inter-symmetry Coriolis terms are those in $\hat{J}_\pm \hat{L}_x$ and $\hat{J}_\pm \hat{L}_z$.

Assuming that $K' = K \pm 1 \simeq K$ if $K \gg 1$ (which is a good approximation so long as the three atoms are not in a linear configuration), and recalling Equation (5.29), leads to the following expression:

$$\lambda_{\pm}^{JK} \simeq \lambda_0^{JK} = \hbar [J(J+1) - K^2]^{\frac{1}{2}}, \quad (5.54)$$

and, so, applying the above approximation when integrating over the rotational basis gives

$$\begin{aligned} \langle K | \hat{\mathcal{H}}' | K \rangle = & b_r \hat{L}^2 + \hat{L}_z^2 \left(\frac{b_r + B_R}{\sin^2 \gamma} - 2b_r \right) + 2b_r \hat{L}_x \hat{L}_z \cot \gamma \\ & + 2K \hbar \hat{L}_z \times \left(b_r - \frac{B_R + b_r}{\sin^2 \gamma} \right) \\ & - 2b_r K \hbar \hat{L}_x \cot \gamma - b_r \lambda_0^{JK} (\hat{L}_x + \hat{L}_z \cot \gamma). \end{aligned} \quad (5.55)$$

The resultant matrix element is then integrated over the $\{|\pm \Lambda\rangle\}$ electronic basis to give the final matrix elements, $\langle \Lambda' | \langle K' | \hat{\mathcal{H}}_e + \hat{\mathcal{H}}' | K \rangle | \Lambda \rangle$, shown in Table 5.1. In this table, the grouping of terms in $\mathcal{R}_{ij}$ and $\mathcal{C}_{ij}$ shows the different contributions from Renner-Teller and Coriolis couplings, respectively, where i and j refer to the

$\langle \Lambda' \langle K' \hat{\mathcal{H}}_e + \hat{\mathcal{H}}' K \rangle \Lambda \rangle$	$\Lambda = 1$	$\Lambda = 0$	$\Lambda = -1$
$\Lambda' = 1$	$D_{\text{sum}} + \mathcal{A}_{+1,+1} + \mathcal{R}_{+1,+1} + \mathcal{C}_{+1,+1}$	$\frac{V_{\Sigma+\Pi\Lambda'}}{\sqrt{2}} + \mathcal{A}_{+1,0} + \mathcal{R}_{+1,0} + \mathcal{C}_{+1,0}$	$D_{\text{diff}} + \mathcal{A}_{+1,-1}$
$\Lambda' = 0$	$\frac{V_{\Sigma+\Pi\Lambda'}}{\sqrt{2}} + \mathcal{A}_{+1,0} + \mathcal{R}_{+1,0} + \mathcal{C}_{+1,0}$	$V_{\Sigma} + \mathcal{A}_{0,0}$	$\frac{V_{\Sigma+\Pi\Lambda'}}{\sqrt{2}} + \mathcal{A}_{+1,0} - \mathcal{R}_{+1,0} - \mathcal{C}_{+1,0}$
$\Lambda' = -1$	$D_{\text{diff}} + \mathcal{A}_{+1,-1}$	$\frac{V_{\Sigma+\Pi\Lambda'}}{\sqrt{2}} + \mathcal{A}_{+1,0} - \mathcal{R}_{+1,0} - \mathcal{C}_{+1,0}$	$D_{\text{sum}} + \mathcal{A}_{+1,+1} - \mathcal{R}_{+1,+1} - \mathcal{C}_{+1,+1}$

Table 5.1: Final matrix elements, $\langle \Lambda' | \langle K' | \hat{\mathcal{H}}_e + \hat{\mathcal{H}}' | K \rangle | \Lambda \rangle$, for the full Hamiltonian operator, $\hat{\mathcal{H}}_e + \hat{\mathcal{H}}'$. D_{diff} and D_{sum} are defined in Equation (5.39). The groups of terms in $\mathcal{R}_{ij}$, and $\mathcal{C}_{ij}$ show the different contributions from Renner-Teller and Coriolis couplings, respectively.

$|\pm\Lambda\rangle$ basis, and can take values of $+1, 0$, or -1 . $\mathcal{A}_{ij}$, $\mathcal{R}_{ij}$, and $\mathcal{C}_{ij}$ are defined as

$$\mathcal{A}_{ij} = b_r \langle i | \hat{L}^2 | j \rangle + \left(\frac{b_r + B_R}{\sin^2 \gamma} - 2b_r \right) \langle i | \hat{L}_z^2 | j \rangle + 2b_r \cot \gamma \langle i | \hat{L}_x \hat{L}_z | j \rangle, \quad (5.56)$$

$$\mathcal{R}_{ij} = 2K\hbar \left[\left(b_r - \frac{b_r + B_R}{\sin^2 \gamma} \right) \langle i | \hat{L}_z | j \rangle - b_r \cot \gamma \langle i | \hat{L}_x | j \rangle \right], \quad (5.57)$$

$$\mathcal{C}_{ij} = -\lambda_0^{JK} b_r [\cot \gamma \langle i | \hat{L}_z | j \rangle + \langle i | \hat{L}_x | j \rangle], \quad (5.58)$$

where the relevant diabatic matrix elements are derived from the appropriate transformation of the matrix elements of these operators in the adiabatic representation (see Equations (5.43) to (5.49)). The corresponding matrix elements of the full Hamiltonian in the diabatic $|\Lambda\rangle$ basis are then used to calculate the mixing angles from

$$\alpha = \frac{1}{2} \arctan \left(\frac{2\mathcal{H}_{+1,0}}{\mathcal{H}_{+1,+1} - \mathcal{H}_{0,0}} \right), \quad (5.59)$$

$$\beta = \frac{1}{2} \arctan \left(\frac{2\mathcal{H}_{+1,-1}}{\mathcal{H}_{+1,+1} - \mathcal{H}_{-1,-1}} \right), \quad (5.60)$$

$$\omega = \frac{1}{2} \arctan \left(\frac{2\mathcal{H}_{0,-1}}{\mathcal{H}_{0,0} - \mathcal{H}_{-1,-1}} \right). \quad (5.61)$$

Figure 5.6 shows the matrix elements used in this thesis for theoretical calculations involving the OH+Kr system. The elements, which were calculated by Kłos [26, 78, 188, 211] at the CASSCF (complete active space self-consistent field) level of theory, are plotted for a single value of γ (the near-linear Kr–O–H geometry), and are grouped by the surfaces that they couple. Recall that the OH radical and the Kr atom lie in the xz -plane.

At the time of writing, only a selection of matrix elements had been calculated for the OH+Xe system [26, 211]. These elements are compared to their counterparts for OH+Kr in Figure 5.7. A comparison of the calculated elements for the two systems suggests that the remaining elements for OH+Xe could be estimated by applying a shift in R , the Rg–OH separation, to those already obtained for OH+Kr. As can be seen in the figure, elements concerning angular momentum about the

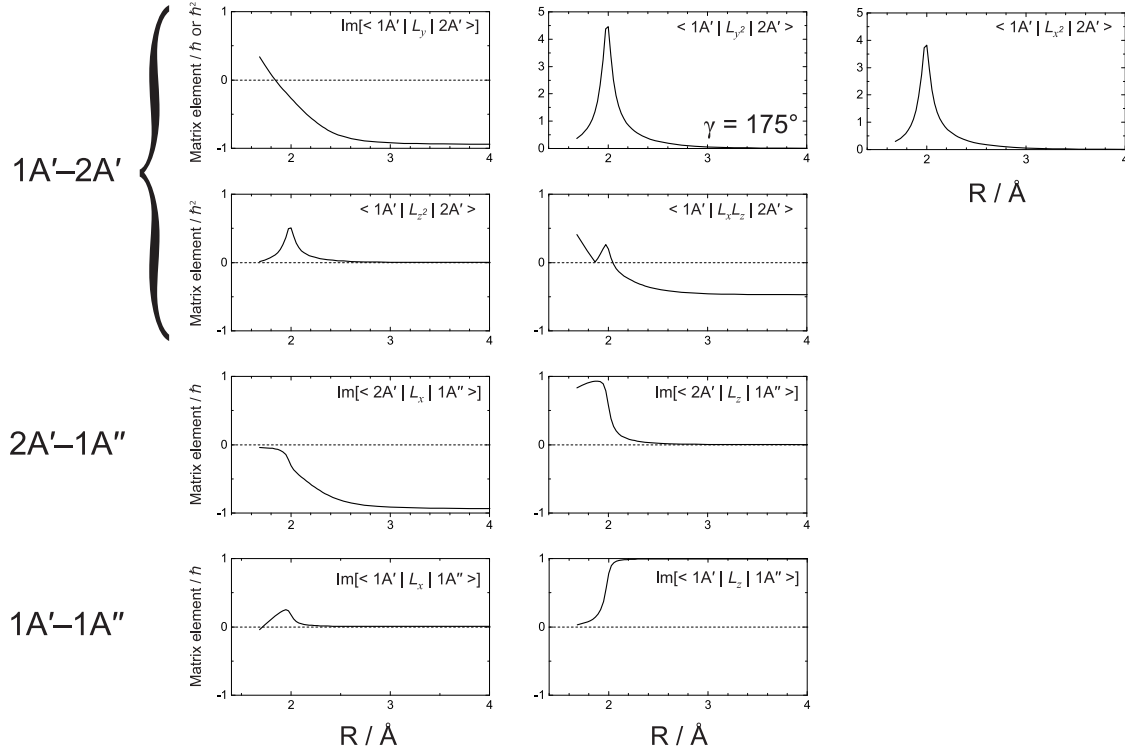


Figure 5.6: Calculated matrix elements for $\text{OH} + \text{Kr}$ in the near-linear Rg-O-H geometry ($\gamma = 175^\circ$). The label ‘Im’ indicates that the imaginary part of the matrix element is plotted. Note the difference in scale on the y-axes.

x - or y -axis are to be shifted by $+0.29 \text{ \AA}$ in R ; those concerning the z -axis are to be shifted by $+0.24 \text{ \AA}$. Notably, the shift in R applied to elements of the $\hat{L}_x \hat{L}_z$ operator was based on that of $\hat{L}_z$.

Figure 5.8 shows the adiabatic PESs used in three-state TSH QCT calculations for $\text{OH} + \text{Xe}$ along with selected off-diagonal matrix elements which couple them. The elements chosen follow an approximation made originally by Goldfield *et al.* [203] (and later adopted by Zhou *et al.* [212] and Grebenshchikov [213]) which states that $\hat{L}_x = \hat{L}_y = 0$ and that $\hat{L}^2 \simeq \hat{L}_z^2$. These approximations were applied to both the $\text{OH} + \text{Kr}$ [26] and $\text{OH} + \text{Xe}$ systems [33], however, it was found that they contributed to a consistent underestimation of the magnitude of non-adiabatic effects in these systems. As a result, the surface-hopping data presented in this thesis are the result of calculations that include all the relevant matrix elements outlined in Equations (5.56)-(5.58).

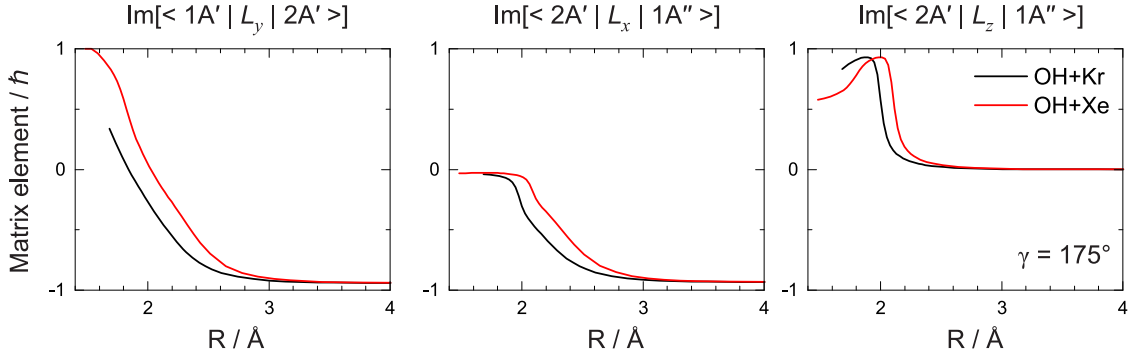


Figure 5.7: Comparison of the calculated matrix elements for OH+Kr and OH+Xe in the near-linear Rg-O-H geometry ($\gamma = 175^\circ$). Note that the label ‘Im’ indicates that the imaginary part of the matrix element is plotted. Using this plot, the radial component of the remaining matrix elements for OH+Xe are estimated by applying a shift in R of $+0.29 \text{ \AA}$ for elements along x and y , and of $+0.24 \text{ \AA}$ for those in z . Note that the latter shift is used to estimate the elements of the $\hat{L}_x \hat{L}_z$ operator.

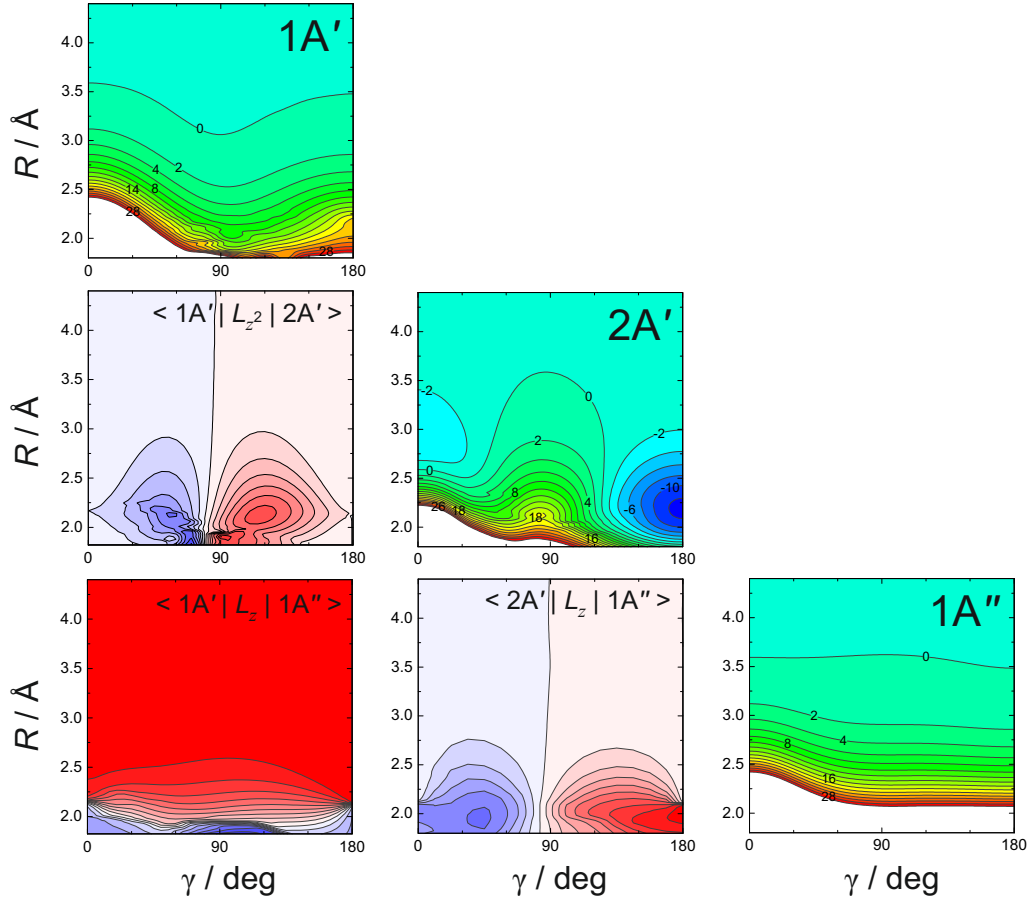


Figure 5.8: The $1A'$, $2A'$, and $1A''$ adiabatic PESs (calculated by Kłos at the MRCISD+Q level of theory [77, 188]), and a selection of non-adiabatic matrix coupling elements used in the QCT calculations carried out for the $\text{OH}+\text{Xe}$ system. The layout of the figure is intended to mimic that of Equation (5.22) in that the PESs, which lie along the diagonal, are coupled by the matrix element found at the appropriate intersecting off-diagonal element. The numbers on the PESs give the potential energy, in 10^3 cm^{-1} , relative to the asymptotic energy for each state at large R . Note that thermal energy for this system is 32985 cm^{-1} . The z -axes of the matrix-element plots are scaled arbitrarily for the sake of clarity; red suggests a positive value, and blue suggests a negative value.

5.5 *Quasi*-classical trajectory surface-hopping calculations in two- and three-state models

Quasi-classical trajectory (QCT) calculations are so named because, over the course of a single trajectory, the system is modelled both classically and (approximately) quantum mechanically. The system originates in a state that is quantised with respect to its rotational energy. In this chapter, the bond length of the OH radical, r , is fixed in all calculations, such that the molecule is restricted to its ground vibrational state, $v = 0$, and quantisation of this variable need not be considered. The decision to fix the OH bond length has been validated in many previous studies [6, 25, 26, 28, 76, 214]. At the start of the calculation, the relative-velocity vector, $\mathbf{k}$, and the Z -axis are separated by the impact parameter, b (see Figure 5.9), and the velocity of the rare-gas atom is set to coincide with the trajectory collision energy. Once initiated, the trajectory runs classically on the PES and terminates with an unquantised angular momentum. However, this momentum is then binned to the nearest discrete level, such that the trajectory both begins and ends in a quantised state. The QCT method, including the use of surface-hopping algorithms to model non-adiabatic transitions, is now discussed in detail.

A single trajectory is initiated and moves over a single PES. At its beginning, each trajectory has a specified collision energy (E_{coll}), impact parameter (b), rotational state (N), separation (R), and values of θ , ϕ , and η (see Figure 5.9). At a given time step, Δt , Hamilton's equations of classical motion are integrated numerically using a Hamming predictor-corrector method that is initialised by a fourth-order Runge-Kutta integration [215]. Simultaneously, the time-dependent Liouville equation for the density matrix, $\boldsymbol{\rho}$, is also integrated for the adiabatic state populations such that

$$i\hbar\dot{\rho}_{jk} = \sum_l [\rho_{lk}(\mathcal{H}_{jl} - i\hbar\dot{\mathbf{R}}\mathbf{d}_{jl}) - \rho_{jl}(\mathcal{H}_{lk} - i\hbar\dot{\mathbf{R}}\mathbf{d}_{lk})], \quad (5.62)$$

where $\mathcal{H}_{lk} = \langle l | \hat{\mathcal{H}}_e | k \rangle$, the matrix elements of the electronic Hamiltonian in the adiabatic representation. These correspond to the adiabatic potentials when $l = k$, and take values of zero when $l \neq k$. The non-adiabatic coupling vector is expressed as

$$\mathbf{d}_{jk} = \langle l | \nabla_{\mathbf{R}} | k \rangle, \quad (5.63)$$

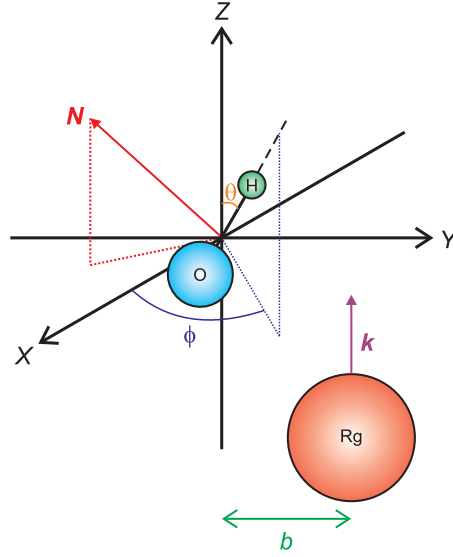


Figure 5.9: The space-fixed coordinate frame used in QCT calculations. $\mathbf{N}$ is the rotational-angular-momentum vector of the OH radical, and θ and ϕ are the polar and azimuthal angles of OH, respectively. The azimuthal angle, η , of the OH radical, which defines the rotational phase of OH, is not shown for the sake of clarity.

where $\mathbf{d}_{jk} = -\mathbf{d}_{jk}^*$, and $\mathbf{R}$ is a collective term for the positions of the nuclei. $|i\rangle = |1\rangle, |2\rangle$, and $|3\rangle$ correspond to the $1A'$, $2A'$, and $1A''$ adiabatic states, respectively. The non-adiabatic coupling matrix, $\mathbf{d}$, is given by

$$\mathbf{d} = \mathbf{C}_3 \nabla_{\mathbf{R}} \mathbf{C}_3^T, \quad (5.64)$$

which results in [216]

$$\mathbf{d}_{1,2} = \sin \omega \nabla_{\mathbf{R}} \beta - \nabla_{\mathbf{R}} \alpha, \quad (5.65)$$

$$\mathbf{d}_{1,3} = -\cos \omega \cos \alpha \nabla_{\mathbf{R}} \beta - \sin \alpha \nabla_{\mathbf{R}} \omega, \quad (5.66)$$

$$\mathbf{d}_{2,3} = \cos \omega \sin \alpha \nabla_{\mathbf{R}} \beta - \cos \alpha \nabla_{\mathbf{R}} \omega. \quad (5.67)$$

where α , β , and ω are as defined in Equations (5.59)-(5.61). From the above equations, it is important to note that setting $\beta = 0$ and $\omega = 0$ removes contributions from Renner-Teller and Coriolis couplings, respectively, and this will affect both the magnitude of the quenching cross-sections and the product rotational-state distributions of OH(X). However, in the limit where $\omega = 0$ and $\beta \neq 0$, Renner-Teller coupling can provide an indirect link that leads to transfer of population between the $2A'$ and $1A''$ surfaces.

This thesis makes use of Tully’s fewest-switches algorithm (FSA) [193] to model non-adiabatic dynamics for OH(A)+Rg. For a transition from the current state, $|k\rangle$, to a final state, $|j\rangle$, the switching probability, P_{jk} , calculated at a given time step, Δt , is given by

$$P_{jk} = -\frac{2\text{Re}(\rho_{jk}^* \dot{\mathbf{R}} \mathbf{d}_{jk}) \Delta t}{\rho_{kk}}. \quad (5.68)$$

where ρ is the density matrix for a given electronic adiabatic state population, $\mathbf{R}$ are the position vectors of the nuclei, and $\mathbf{d}$ denotes one of the non-adiabatic coupling matrices outlined above.

Note that, if its numerical value is negative, the probability is set to zero. If a random number is less than the probability, a transition occurs. The FSA computes the transition probability by minimising the number of hops that occur in a given time interval to ensure that

- no transitions occur in regions of zero coupling;
- if the integration time step is reduced, the switching probability per step is diminished by the same factor; however, there will also be proportionately more steps such that, overall, the switching probability through a finite region or a finite time is independent of step size;
- at any given time step, the probability of switching is small; and
- the FSA generates the correct statistical distribution of the resultant energy states.

Hops to higher-energy states (*i.e.* from OH(X) to OH(A)) are deemed ‘frustrated’ and are not allowed if the translational energy of the trajectory is not sufficient to overcome the potential-energy barrier. When a hop does occur, the change in potential energy is accompanied by an adjustment of the system’s linear momentum to comply with energy conservation. Importantly, a trajectory is only ever propagated on a single, adiabatic PES at any given time.

Non-adiabatic effects were investigated using both two- and three-state models. In the first instance, only electrostatic coupling between the $2A'$ and $1A'$ surfaces was considered [25, 78], before later expanding the coupling regime to include roto-electronic couplings to the $1A''$ state [26]. To date, spin-orbit coupling has been neglected in the *quasi*-classical surface-hopping code, such that non-adiabatic effects are essentially modelled as $^1\Sigma - ^1\Pi$ transitions. In the past, the lack of spin-orbit coupling has not been considered a major source of disagreement between theory and experiment [25, 26, 78, 204, 210], however, it is possible that spin-orbit coupling is a necessary component of any model that can accurately predict the magnitude of theoretical quenching cross-sections for $\text{OH}(A) + \text{Kr/Xe}$.

To quantify spin-orbit coupling, it would be necessary to consider the coupling of definite states defined by $|\Lambda\Sigma\Omega\rangle$ *via* a spherical perturbator, given by [217, 218]

$$\langle\Lambda'\Sigma'\Omega'|\hat{\mathcal{H}}_{\text{SO}}|\Lambda\Sigma\Omega\rangle = \sum_{\lambda} d_{\Omega-\Omega',0}^{\lambda}(\gamma) H_{\lambda,\Omega-\Omega'}^{\text{SO}}(R) \quad (5.69)$$

where the $\hat{L}_z\hat{S}_z$ term couples the different Π_{Ω} states, and the $\hat{L}_y\hat{S}_y$ and $\hat{L}_x\hat{S}_x$ terms couple the Σ and Π states. In $\text{OH} + \text{Rg}$ complexes with linear geometry, the $\Delta\Omega = 0$ terms are non-zero (and give rise to Λ -doublet splitting), whereas the $\Delta\Omega = \pm 2$ terms are zero. For non-linear complexes, it is possible for any of these terms to be non-zero.

5.6 Calculation details

For calculations on a single surface, the QCT methods employed in this thesis are identical to those outlined in previous works [24, 25]. The basis of this method, and the modifications needed to introduce surface-hopping capabilities, are discussed in the following subsections.

Before any further discussion of *quasi*-classical methods, however, it is important to recognise that the classical treatment of trajectories implies a number of approximations. There is no consideration of strictly quantum-mechanical phenomena, including, but not limited to: zero-point energy, tunnelling, quantum-mechanical resonances, and electron spin. However, previous studies [26, 28, 76, 78] have

shown that these factors are unlikely to play a significant role in the adiabatic dynamics of OH(A, $v = 0$)+Rg systems, and so are not anticipated to undermine the appropriateness of the QCT method.

5.6.1 Running a trajectory

Batches of 1×10^5 trajectories were run for each initial N . Within the space-fixed frame, the origin of the coordinate system is taken to be the centre of mass of the OH radical. The initial velocity of the rare-gas species lies parallel to the Z -axis, in the YZ -plane, and the distance between the Z -axis and the atom is the impact parameter, b . The value of b is sampled uniformly between 0 and $b_{\max}^2$ using the expression $b_i = \xi^{\frac{1}{2}} b_{\max}$, where b_i is the initial impact parameter, and ξ is a constant between 0 and 1. This treatment weights the sampling to high- b values, which agrees with the fact that the probability of collision between b and $b_{\max}$ is given by $2\pi b db$. The value of $b_{\max}$ is set such that the probability of a rotationally inelastic collision taking place at this impact parameter is approximately zero. The experimental data referenced in this thesis [33] were collected under thermal conditions (at 300 K). In earlier QCT calculations, the collision energy for each trajectory was fixed at 0.039 eV (or $\approx 315 \text{ cm}^{-1}$, calculated as the mean collision energy, $\frac{3}{2}kT$, at 300 K). In later calculations, and to better model experimental reality, the collision energy was sampled randomly in the range 0.001 – 0.125 eV ($\approx 8 - 1008 \text{ cm}^{-1}$), with $b_{\max}$ calculated accordingly as

$$b_{\max}(E_t) = 2.8 \times 10^{-8} [5.8 \times 10^{-8} + E_t^{-0.2}], \quad (5.70)$$

where $b_{\max}(E_t)$ is in cm and E_t is in eV.

The space-fixed, classical Hamiltonian for the system is given by the sum of the kinetic- and potential-energy contributions

$$H = \frac{1}{2\mu_{BC}} \sum_{i=1}^3 P_i^2 + \frac{1}{2\mu_{ABC}} \sum_{i=4}^6 P_i^2 + V(R, r, \gamma), \quad (5.71)$$

where A, B, and C are assigned to the rare-gas, hydrogen, and oxygen atoms, respectively, μ_x are the relevant reduced masses, and P_{1-6} are the conjugate momenta

of the Cartesian coordinates. Notably, the three coordinates/momenta (Q_i and P_i , $i = 7 - 9$) that describe the motion of the centre of mass of the system (which is a constant as a function of the motion of the system) have been neglected. The potential energy is expressed as a function of the Jacobi coordinates.

In this coordinate system, Hamilton's equations of motion are given by [219]

$$\dot{Q}_i = \frac{\partial H}{\partial P_i} = \frac{\partial T}{\partial P_i}, \quad (5.72)$$

$$\dot{P}_i = -\frac{\partial V}{\partial Q_i} = -\left(\frac{\partial V}{\partial R} \frac{\partial R}{\partial Q_i} + \frac{\partial V}{\partial r} \frac{\partial r}{\partial Q_i} + \frac{\partial V}{\partial \cos \gamma} \frac{\partial \cos \gamma}{\partial Q_i}\right). \quad (5.73)$$

At the beginning of a trajectory, when $t = 0$, the rare-gas species and the OH radical are separated by a distance, R , such that their potential energy of interaction is negligible (usually 12 Å). The polar and azimuthal angles, θ and ϕ , and η , the angle that defines the rotational plane of the diatom, are sampled randomly. The initial rotational-angular-momentum quantum number, N , is fixed, as is the magnitude and direction of the initial velocity vector, $\mathbf{k}$.

The method of Lagrange multipliers is used to force a rigid-rotor constant in the integration [24] to keep the OH internuclear separation fixed at its equilibrium value, $r_e = 1.012$ Å [121]. The time integration step was 0.05 fs, ensuring an energy conservation better than 1 in 10^5 for trajectories that do not hop, and better than 1 in 5×10^5 for those that do.

After the collision, integration of the Hamilton's equations continues until the potential energy of interaction is once again negligible. The final rotational angular momentum of OH is equated to $\hbar[N'(N' + 1)]^{\frac{1}{2}}$ and then undergoes histogram binning to the nearest integer. If the trajectory undergoes a hop, such that it ends up in a different electronic state from that in which it began, the final rotational state is influenced by the change in bond length. Equating the rotational energies of OH(A) and OH(X) gives

$$B_X N_X''(N_X'' + 1) = B_A N_A''(N_A'' + 1), \quad (5.74)$$

where B_X and B_A are the rotational constants for the X and A states, respectively. Therefore, the adjusted final rotational state after quenching from OH(A) to OH(X) can be given by

$$N_X'' = -\frac{1}{2} + \sqrt{\frac{1}{4} + \frac{N_A''^2}{x_r} + \frac{N_A''}{x_r}}. \quad (5.75)$$

5.6.2 Momentum rescaling and numerical stability

As discussed previously, whenever a given trajectory hops from a higher-energy, initial state, $|i\rangle$ to a lower-energy, final state, $|j\rangle$, the nuclear velocities must be scaled in order to conserve total energy and momentum. The linear momentum is factorised into two components, corresponding to the conjugate linear momenta of the $\mathbf{R}$ and $\mathbf{r}$ coordinates, as

$$\begin{aligned} \mathbf{p}_j &= \mathbf{p}_i - \gamma_{ij} \mathbf{d}_{ij}^r, \\ \mathbf{P}_j &= \mathbf{P}_i - \gamma_{ij} \mathbf{d}_{ij}^R, \end{aligned} \quad (5.76)$$

where $\mathbf{d}_{ij}$ is the non-adiabatic coupling vector, and the scaling factor, γ_{ij} , is determined from the need to conserve energy by

$$\gamma_{ij}^2 a_{ij} - \gamma b_{ij} - (U_i - U_j) = 0, \quad (5.77)$$

where

$$\begin{aligned} a_{ij} &= \frac{1}{2} \left[\frac{|\mathbf{d}_{ij}^r|^2}{\mu_{BC}} + \frac{|\mathbf{d}_{ij}^R|^2}{\mu_{ABC}} \right], \\ b_{ij} &= \frac{1}{2} [\mathbf{r}_i \cdot \mathbf{d}_{ij}^r + \mathbf{R}_i \cdot \mathbf{d}_{ij}^R]. \end{aligned} \quad (5.78)$$

Notably, if Equation (5.77) is insoluble, then the hop is said to be frustrated, and the velocities are reversed. Otherwise, the solution to Equation (5.77) is given by

$$\gamma_{ij} = \frac{1}{2a_{ij}} \left[b_{ij} \pm \sqrt{b_{ij}^2 + 4a_{ij}(U_i - U_j)} \right]. \quad (5.79)$$

The positive sign is used when $b_{ij} < 0$, and the negative sign is used when $b_{ij} \geq 0$.

Recalling Equations (5.56) to (5.58), it can be seen that they contain terms in $1/\sin^2 \gamma$ and $\cot \gamma$, which can lead to numerical instabilities as $\gamma \rightarrow 0$ in the near-linear Rg–H–O geometry. Instabilities may also arise when $K \rightarrow 0$, as the splitting between the $\mathcal{H}_{+1,+1}$ and $\mathcal{H}_{-1,-1}$ terms becomes negligible, and their difference appears in the denominator of Equation (5.60). In both these cases, the roto-electronic couplings outlined above should vanish. The $1A'$ and $1A''$ PESs become degenerate at linearity as the two ($\Pi_{A'}$ and $\Pi_{A''}$) components of the Π diabatic state. Notably, diabatic states of Σ and Π states cannot couple by symmetry, and, when $K = 0$, the Renner-Teller coupling should also be zero (see Equation (5.57)). Following reference [204], damping functions are applied to the mixing angle, β , to prevent unphysical behaviour; no such treatment is needed for angles α and ω :

$$\beta = \beta^*(1 - S_\gamma)(1 - S_K) \quad (5.80)$$

where β^* is the undamped mixing angle, and

$$\begin{aligned} S_\gamma &= \exp\left(-\frac{\sin^2 \gamma}{\delta_\gamma^2}\right), \\ S_K &= \exp\left(-\frac{K^2}{\delta_K^2}\right), \end{aligned} \quad (5.81)$$

and δ_γ and δ_K are set to $(0.05)^{1/2}$ and 0.25, respectively, by trial and improvement.

5.6.3 Generating theoretical cross-sections

Once a trajectory has finished, and the final angular momentum has been binned to the nearest quantum number, it is possible to extract a number of cross-sectional quantities that can then be compared to those measured experimentally. Classically, the spatial distribution of the angular-momentum vector after collision, $\mathbf{j}'$, can be related classically to the initial angular-momentum distribution, $\mathbf{j}$, by

$$P(\theta_{jj'}) = \sum_k \left(\frac{2k+1}{2}\right) a^{(k)}(j, j') P_k(\cos \theta_{jj'}), \quad (5.82)$$

where $P_k(\cos \theta_{jj'})$ are the classical Legendre polynomials and the depolarisation moments, $a^{(k)}(j, j')$, are given by

$$a^{(k)}(j, j') = \langle P_k(\cos \theta_{jj'}) \rangle. \quad (5.83)$$

These depolarisation moments are a measure of the transfer of population from the initial to the final state; odd- k moments correspond to the transfer of oriented population, and even- k moments correspond to the transfer to aligned population (see Section 2.6.3). For the empirical data reported in this thesis, which were collected using (1+1)-LIF spectroscopy, the experiment is sensitive to the $k = 1$ and $k = 2$ depolarisation moments only, which have the following classical limits:

$$-1 \leq a^{(1)} \leq 1, \quad (5.84)$$

$$-0.5 \leq a^{(2)} \leq 1. \quad (5.85)$$

$a^{(1)} = 1$ if the orientation remains unchanged over the course of the collision and $a^{(1)} = -1$ if the extent of orientation is conserved whilst the sense of rotation has been reversed. Similarly, $a^{(2)} = 1$ if the alignment of the angular-momentum distribution is unaltered by the collision and $a^{(2)} = -0.5$ if the extent of alignment is the same, however, the distribution of $\mathbf{j}'$ is perpendicular to that of $\mathbf{j}$. If $a^{(0)}(j, j') = 1$ and $a^{(k \neq 0)}(j, j') = 0$, there is absolute randomisation of the angular-momentum distribution following the collision such that the distribution of $\mathbf{j}'$ is completely isotropic to that of $\mathbf{j}$.

A link can be made between the classical and quantum-mechanical descriptions of the angular-momentum distribution by defining the tensor cross-sections, $\sigma_T^{(k)}(j, j')$, as [28, 43]

$$\sigma_T^{(k)}(j, j') = a^{(k)}(j, j') \sigma_{jj'}. \quad (5.86)$$

Specifically, these quantum-mechanical tensor cross-sections define the extent to which the original angular-momentum distribution population is transferred to the final state over the course of the collision. Thus, if $\mathcal{N}_{jj'}$ collisions from a total of $\mathcal{N}_{\text{tot}}$ result in a given $|j\rangle \rightarrow |j'\rangle$ transition, the tensor cross-section can be expressed as

$$\sigma_T^{(k)}(j, j') = \frac{\pi b_{\text{max}}^2}{\mathcal{N}_{\text{tot}}} \sum_{i=1}^{\mathcal{N}_{jj'}} P_k(\cos \theta_{jj'}^{(i)}), \quad (5.87)$$

and, according to Alexander and Davis [220, 221], as

$$\begin{aligned} \sigma_T^{(k)}(j, j') &= \frac{\pi}{k^2} \sum_{JJ'} \sum_{\ell\ell'} (2J+1)(2J'+1)(-1)^{\ell+\ell'-j-j'+2J} \\ &\times \left\{ \begin{matrix} j & j & k \\ J & J' & \ell \end{matrix} \right\} \left\{ \begin{matrix} j' & j' & k \\ J & J' & \ell' \end{matrix} \right\} T_{j'\ell'j\ell}^J T_{j'\ell'}^{J*}. \end{aligned} \quad (5.88)$$

Note that, unlike in the classical treatment, the limits of the quantum-mechanical $a^{(k)}(j, j')$ moments are j - and j' -dependent.

The experiments carried out on the OH(A)+Kr and OH(A)+Xe systems measure the loss of OH(A) polarisation that is brought about by collisions with rare-gas atoms. Indeed, since the tensor cross-section quantifies the extent to which the initial angular-momentum distribution is preserved, the theoretical collisional-depolarisation cross-section is calculated as [28, 43]

$$\begin{aligned} \sigma^{(k)}(j, j') &= \sigma_{jj'} - \sigma_T^{(k)}(j, j') \\ &= \sigma_{jj'} [1 - a^{(k)}(j, j')]. \end{aligned} \quad (5.89)$$

5.6.4 The tensor opacity formalism

Within a QCT treatment, the OH(A)+Rg systems are treated as *closed-shell*: it is assumed that the electron spin is a spectator to the collision that does not influence the observed outcome. However, it is important to recognise that the total rotational angular momentum, $\mathbf{j}$, is not equal to the nuclear rotational angular momentum, $\mathbf{N}$, since the former incorporates coupling to the electron spin, $\mathbf{S}$.

The classical tensor opacity, $P^K(N, N')$ [28, 222], is proportional to the probability that a given collision that involves a transfer of angular momentum, K , also involves a change in the nuclear rotational-angular-momentum quantum number from N to N' . The value of K can be expressed classically as

$$|\mathbf{K}|^2 = |\mathbf{N}|^2 + |\mathbf{N}'|^2 - 2|\mathbf{N}|^2|\mathbf{N}'|^2 \cos \theta_{NN'}, \quad (5.90)$$

where the notation $|\mathbf{X}|^2 = X(X+1)\hbar^2$ is used and $\theta_{NN'}$ is the angle between the vectors $\mathbf{N}$ and $\mathbf{N}'$, as shown in Figure 5.10. A modified expression for the integral

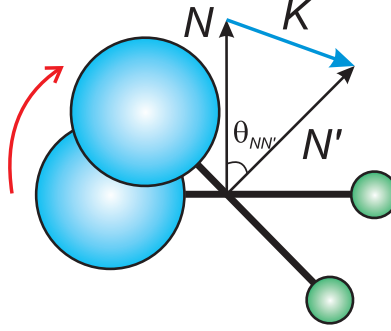


Figure 5.10: The relationship between the N , N' , and K vectors as defined by the $\theta_{NN'}$ angle.

cross-section that includes a consideration of K is then given by [28]

$$\sigma_{NN'}^{(K)} = \pi b_{\max}^2 \frac{\mathcal{N}(K; N, N')}{\mathcal{N}_{\text{tot}}}, \quad (5.91)$$

where $\mathcal{N}(K; N, N')$ is the number of trajectories (of the total, $\mathcal{N}_{\text{tot}}$) with specific K , N , and N' quantum numbers. It is then possible to calculate a value of $P^K(N, N')$ from closed-shell, dynamical calculations – such as those reported in this work – using the equation [28]

$$P^K(N, N') = \frac{k_i^2}{\pi} [N] \sigma_{NN'}^{(K)}, \quad (5.92)$$

where $k_i = p/\hbar$ (the wavevector number).

Extension of the above theory to a *quasi-open-shell* treatment is achieved by coupling N to S quantum mechanically, using the following expression for $\sigma_{jj'}$ in the energy-sudden (spin-independent) limit [28, 222–224]:

$$\sigma_{jj'} = \frac{\pi}{k_i^2} (2j' + 1) \sum_K \left\{ \begin{matrix} N & N' & K \\ j' & j & S \end{matrix} \right\}^2 P^K(N, N'), \quad (5.93)$$

where $j = N \pm S$ is the initial and $j' = N' \pm S$ the final spin-rotation level and $\{\cdots\}$ is a $6j$ symbol that accounts for the coupling of the three angular momenta. Thus, it can be seen that the expression for $\sigma_{jj'}$ can be factorised into two contributing parts: all the dynamical information about an OH(A)+Rg collision is contained within the tensor opacity function; the remaining terms in Equation (5.93) comprise the geometric contribution to the open-shell cross-section.

The summation of the $\sigma_{jj'}$ cross-sections for collisions originating in the $f_1 = N + S$ and $f_2 = N - S$ levels of a given N (excluding the elastic collision, for which $j = j'$) will give a value for open-shell σ_{RET} . Once $\sigma_{jj'}$ has been determined, it is possible to extract values of $a^{(k)}(j, j')$ using [28]

$$a^{(k)}(j, j') = (-1)^{k-j-j'} [j]^{\frac{1}{2}} [j']^{\frac{1}{2}} \frac{\sum_K (-1)^K \left\{ \begin{matrix} j & j & k \\ j' & j' & K \end{matrix} \right\} \left\{ \begin{matrix} N & N' & K \\ j' & j & S \end{matrix} \right\}^2 P^K(N, N')}{\sum_K \left\{ \begin{matrix} N & N' & K \\ j' & j & S \end{matrix} \right\}^2 P^K(N, N')}, \quad (5.94)$$

where the notation $[x] = \sqrt{2x+1}$ has been used and the various parameters are as previously defined. Thus, it has been shown that it is possible to obtain the open-shell polarisation moments, $a^{(k)}(j, j')$, from a closed-shell calculation of the tensor opacities which, in turn, can be used to calculate j' -resolved depolarisation cross-sections, $\sigma_{jj'}^{(k)}$, using Equation (5.89).

5.7 Summary

This chapter has provided a detailed outline of the development of novel, 2D trajectory surface-hopping *quasi*-classical trajectory (TSH QCT) algorithms that are employed in this thesis to investigate the non-adiabatic collision dynamics of the OH(A, $v = 0$)+Kr and OH(A, $v = 0$)+Xe systems. The most complete models used in this work incorporate all three PESs that are needed to describe OH(A/X)+Rg systems, as well as the full range of electrostatic and roto-electronic couplings between them, for the first time. The theoretical data generated by these models are subjected to rigorous comparison with experimental cross-sections in the subsequent chapter.

6

2D models of OH(A, $v = 0$)+Rg: comparing experiment and theory

This chapter presents a detailed comparison of experimental and theoretical data relating to electronically and rotationally inelastic collisions of OH(A, $v = 0$) with Kr and Xe. Data are reported for a number of processes, namely: non-adiabatic electronic quenching, rotational energy transfer (RET), and the collisional depolarisation (total and elastic) of angular momentum. Particular emphasis is placed on quantifying the competitive relationship between adiabatic and non-adiabatic processes in the collision dynamics of these relatively simple gas-phase systems.

The experimental data referenced here have been published previously [25, 26, 33, 76, 78, 225, 226], and the focus of this thesis is, therefore, to compare these results with new theoretical data from the extended trajectory-surface-hopping, *quasi*-classical trajectory (TSH QCT) model described in Chapter 5.

Data are presented concurrently for both the OH(A)+Kr and OH(A)+Xe systems. Although the collision dynamics of both show similar behavioural trends with increasing rotational excitation of OH(A), the results also reveal that non-adiabatic effects play a much more significant role in the OH(A)+Xe system than in that of OH(A)+Kr. The theoretical data are generated from various models, and clearly demonstrate the improved agreement between experiment and theory

as the treatment of non-adiabatic effects becomes increasingly sophisticated. It can be seen that, whilst the most complete TSH QCT model presented in this work has achieved near-quantitative agreement between experiment and theory for the OH(A)+Kr system, there remains a considerable level of disagreement for OH(A)+Xe. The nature and origin of the observed discrepancies, and suggestions for how they may be resolved, are discussed at the end of this chapter.

6.1 Electronic quenching

Though largely unimportant in the OH(A)+He and OH(A)+Ar systems [6, 7, 225, 227, 228], non-adiabatic electronic quenching effects have been shown to play a fundamental role in the collision dynamics of the OH(A)+Kr and OH(A)+Xe systems [25, 26, 33, 226]. This phenomenon, which competes directly with single-state, adiabatic processes such as RET and angular-momentum depolarisation, has been observed in experimental data reported previously. Therefore, it is essential to develop theoretical models that are able to generate cross-sectional quantities for non-adiabatic quenching if they are to accurately predict experimental outcomes. Earlier work on the OH(A)+Kr and OH(A)+Xe systems has also shown that single-surface, adiabatic calculations consistently overestimate cross-sectional values for RET and the depolarisation of angular momentum because they fail to take non-adiabatic loss of OH(A, j) into account. The emphasis of this section is on demonstrating the improved agreement as the non-adiabatic model is expanded and refined.

In experiments described in references [25, 26, 33, 76, 78, 225, 226], rate constants were collected for the electronic quenching of selected OH(A, j) states with Kr or Xe at thermal collision energy (300 K), and were then converted to thermal flux-averaged cross-sections. Notably, the experimental data reported here are consistent with those reported by Hemming *et al.* [225], and show no significant difference between quenching from f_1 or f_2 levels within experimental error.

6.1.1 $OH(A) + Kr$

Figure 6.1 presents a comparison between experimental and theoretical quenching cross-sections, σ_Q , for the $OH(A) + Kr$ system. The theoretical data shown were generated using three different models that are summarised as:

1. Two-state model, run at a fixed collision energy of 0.039 eV, that considered only purely electrostatic coupling in $OH(A) + Kr$ [25];
2. Three-state model, run at a fixed collision energy of 0.039 eV, that included electrostatic coupling and the $\langle 2A' | \hat{L}_x | 1A'' \rangle$ and $\langle 1A' | \hat{L}_x | 1A'' \rangle$ calculated roto-electronic coupling matrix elements for $OH(A) + Kr$ [26, 33];
3. Three-state model, run at variable collision energies in the range 0.005 – 0.125 eV, that included electrostatic coupling and all the calculated roto-electronic coupling matrix elements for $OH(A) + Kr$.

The numerical labels assigned to each model are referenced throughout this section.

Generally, the magnitude of the experimental quenching cross-section is seen to fall with increasing rotational excitation of $OH(A)$. Classically, it can be said that, as the rotational angular momentum of the $OH(A)$ radical increases, it becomes progressively more difficult for the Kr atom to reach the conical intersection on the excited-state PES that facilitates transfer of population to the ground $OH(X)$ electronic state. For $OH(A) + Kr$, the quenching cross-section is largest for $N = 0$ and falls to zero by $N = 10$.

As can be seen in Figure 6.1, there has been a gradual improvement in the agreement between experimental and theoretical quenching cross-sections for $OH(A) + Kr$ as the models developed. A comparison between Models 1 and 2 reveals the most significant modification to the TSH QCT code: the addition of the $OH(X) + Kr$ $1A''$ PES and a number of associated coupling matrix elements. These modifications made the agreement between experiment and theory largely quantitative for many of the N measured. However, at $N \geq 6$, the theoretical data underestimate the extent of experimentally observed quenching, and the converse is

true for $N = 0$. Here, the theoretical data were found to overestimate the magnitude of the experimental quenching cross-section by a considerable margin.

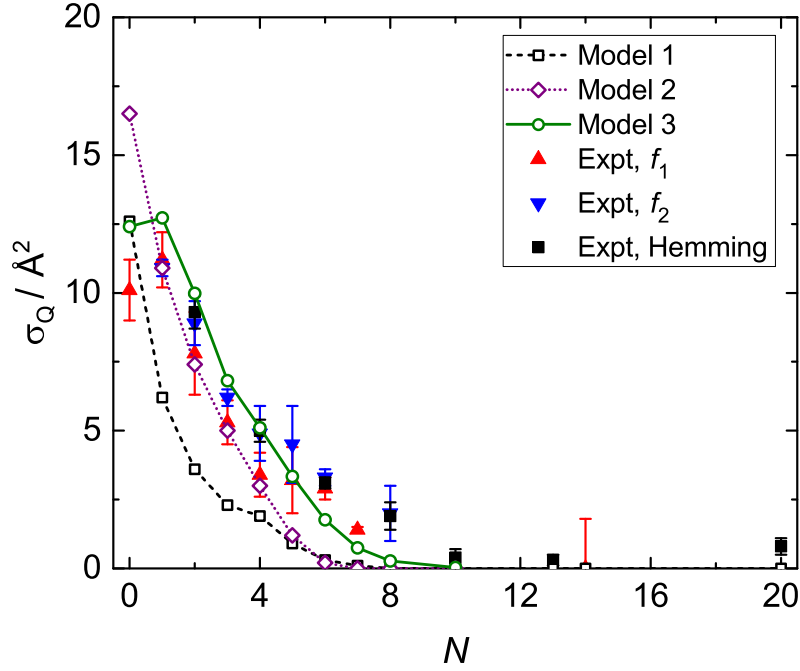


Figure 6.1: Comparison of experimental [25, 26, 33, 226] and theoretical quenching cross-sections, σ_Q , for the OH(A)+Kr system. Upward-pointing, red triangles denote f_1 spin-rotation levels and downward-pointing, blue triangles denote f_2 spin-rotation levels. Experimental data collected by Hemming *et al.* are shown as black squares, since they did not specify the spin-rotation level of their data in reference [225]. The scatter points connected by lines refer to theoretical quenching cross-sections generated from three different TSH QCT models. See text for details.

For Model 3, the inclusion of the remaining, calculated matrix elements for OH(A)+Kr and the use of a Boltzmann distribution of collision energies (rather than a single, fixed value) led to an increase in the quenching cross-section by around 7%. In this case, the theoretical cross-sections for $N \leq 4$ are significantly larger than the corresponding experimental values and, as before, the calculated data for $N \geq 6$ remain relatively small in magnitude. The relative increases in the magnitude of σ_Q on progressing from Model 2 to 3 confirms that the use of the variable-collision-energy algorithm led to a significant growth in the magnitude of the electronic quenching cross-section. This may have important consequences for the OH(A)+Xe system, as discussed in the subsequent section.

One further, important feature of Model 3 is that the magnitude of the quenching cross-section for the $N = 0$ state is reduced to close to that of the two-state model, and is thus found to be in better agreement with the experimental data point. The origin of this change lies in an alternative, semi-classical treatment of the OH(A) angular momentum, whereby $|\mathbf{N}| = (N + \frac{1}{2})\hbar$ (rather than $|\mathbf{N}| = [N(N + 1)]^{\frac{1}{2}}\hbar$), and the Maslov index takes a value of 0.5. In principle, the former, Bohr-Sommerfeld quantisation is also suitable for an open-shell molecule such as OH(A) and, for the $N = 0$ state, this results in the radical possessing non-zero rotational angular momentum prior to collision. In this instance, such a treatment also results in better agreement between theory and experiment. To that end, it is recommended that future work consider a similar treatment of higher OH(A) rotational states so that the data are self-consistent.

Figure 6.2 shows a comparison of σ_Q cross-sections obtained from Models 2 and 3 and those obtained from a subset of Model-3 calculations where the $\langle 1A' | \hat{L}_{x^2} | 2A' \rangle$, $\langle 1A' | \hat{L}_{y^2} | 2A' \rangle$, $\langle 1A' | \hat{L}_z^2 | 2A' \rangle$, and $\langle 1A' | \hat{L}_x \hat{L}_z | 2A' \rangle$ elements were removed for a selection of N . For all the rotational states sampled, there is a noted increase in the magnitude of σ_Q on progressing from Model 2 to the version of Model 3 in which the above elements have been omitted. The subsequent addition of these elements to form the complete version of Model 3 does little to increase the size of the quenching cross-section and, indeed, for $N = 2$ and $N = 4$, the magnitude of σ_Q actually decreases. This somewhat surprising observation is discussed in more detail in Section 6.1.3.

In summary, the most complete model of the non-adiabatic collision dynamics of the OH(A)+Kr system – which makes use of all three PESs and the full range of electrostatic and roto-electronic couplings between them – manages to successfully account for 93% of the quenching observed experimentally. However, although the agreement between experiment and theory is very good and, indeed, quantitative for $N \leq 5$, it can be said that the overall trends in the magnitude of quenching cross-sections with increasing N are still somewhat different for experiment and theory for the OH(A)+Kr system. To that end, Section 6.1.3 will consider further

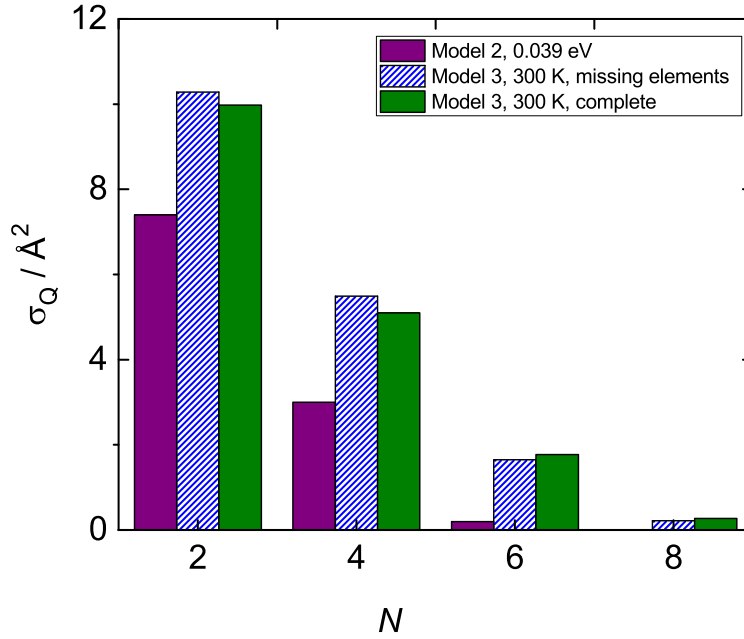


Figure 6.2: Comparison of theoretical quenching cross-sections, σ_Q , for the OH(A)+Kr system. The data were obtained from fixed-energy and variable-energy TSH QCT calculations run using Models 2 and 3, as well as a subset of Model-3 calculations in which a selection of coupling matrix elements was omitted. See text for details.

analysis of the data shown here to assess the relative importance of and possible issues with different aspects of the models discussed here.

6.1.2 OH(A)+Xe

Figure 6.3 presents a comparison of experimental [25, 26, 33, 226] and theoretical quenching cross-sections for the OH(A)+Xe system. The theoretical data shown were generated using three further models that can be summarised as:

4. Two-state model, run at a fixed collision energy of 0.039 eV, that considered only purely electrostatic coupling for OH(A)+Xe [33, 226];
5. Three-state model, run at a fixed collision energy of 0.039 eV, that included electrostatic coupling and the $\langle 2A' | \hat{L}_x | 1A'' \rangle$ calculated roto-electronic coupling matrix element for OH(A)+Xe [33];

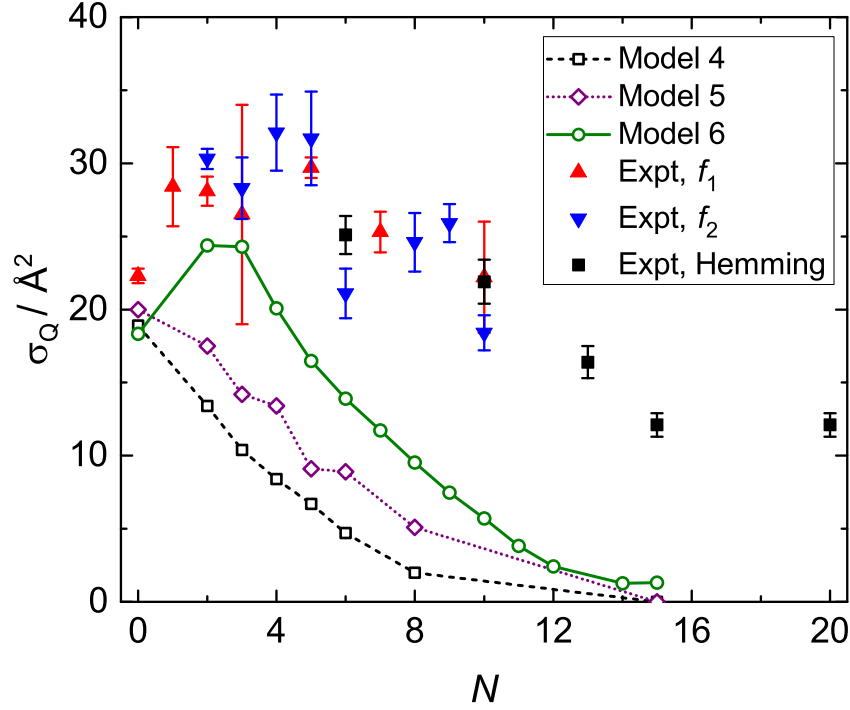


Figure 6.3: Comparison of experimental [25, 26, 33, 226] and theoretical quenching cross-sections, σ_Q , for the $\text{OH}(A)+\text{Xe}$ system. Upward-pointing, red triangles denote f_1 spin-rotation levels and downward-pointing, blue triangles denote f_2 spin-rotation levels. Experimental data collected by Hemming *et al.* are shown as black squares, since they did not specify the spin-rotation level of their data in reference [225]. The scatter points connected by lines refer to theoretical quenching cross-sections generated from three different TSH QCT models. See text for details.

6. Three-state model, run at variable collision energies in the range 0.005 – 0.125 eV, that included electrostatic coupling, all the calculated roto-electronic coupling matrix elements for $\text{OH}(A)+\text{Xe}$, as well as those roto-electronic coupling matrix elements that were estimated by applying a shift in R to the corresponding $\text{OH}(A)+\text{Kr}$ elements.

The reader should note that models for the $\text{OH}(A)+\text{Xe}$ system are outlined separately here because they are similar, though not identical, to those of $\text{OH}(A)+\text{Kr}$.

As for $\text{OH}(A)+\text{Kr}$, the magnitude of σ_Q for $\text{OH}(A)+\text{Xe}$ is seen to fall as N increases. However, in contrast to $\text{OH}(A)+\text{Kr}$, the experimental cross-sections for $\text{OH}(A)+\text{Xe}$ are seen to peak at $N = 4$, and quenching is still significant at

the highest values of N . Thus, it appears that OH(A)+Xe collisions are at least able to sample part of the H-O(A)-Xe potential-energy well for all N recorded, owing to a greater force of attraction and a more accessible conical intersection. As such, the considerable anisotropy of the OH(A)+Xe PES is not washed out by the rotation of the OH(A) molecule in the same way that it is for lighter rare-gas systems. The larger quenching cross-sections recorded for OH(A)+Xe relative to lighter rare-gas systems can also be explained by the location of the conical intersection on the PES. For the OH(A)+He, OH(A)+Ne, and OH(A)+Ar systems [33, 188], the conical intersection is located at a collision energy much higher than that available from a thermal distribution of kinetic energies at 300 K. For OH(A)+Kr, the intersection is found near the beginning of the repulsive wall and, for OH(A)+Xe, the crossing is at the bottom of the H-O(A)-Xe well, meaning the route to quenching is energetically accessible.

To demonstrate this observation, Figure 6.4 shows the location of non-adiabatic hops on the excited $2A'$ adiabatic PES of OH(A)+Xe for a total of 4×10^3 trajectories that originated in the $N = 2$ rotational state. The plot demonstrates that most of the hops between the excited- and ground-state PESs take place in the H-O(A)-Xe potential-energy well, where the PESs are most strongly coupled. This finding, which has also been confirmed in work carried out by Perkins on OH(A)+Kr [33], has important consequences for OH(A)+Rg systems, since electronic quenching will thus compete directly with other inelastic processes that occur predominantly in the highly attractive region of the $2A'$ PES.

Further consideration of Figure 6.3 reveals that there is a significant increase in the magnitude of the theoretical cross-sections on going from Model 4 to Model 5, *i.e.* adding in the $1A''$ PES. There was also a significant increase in the magnitude of the quenching cross-section on introducing a variable-collision-energy algorithm and adding the remaining, estimated matrix elements, as shown in the comparison of data from Models 5 and 6. Figure 6.5 presents the magnitudes of σ_Q for Models 5 and 6, along with those from subsets of calculations run using modified versions of these models. The introduction of a variable-collision-energy algorithm to the

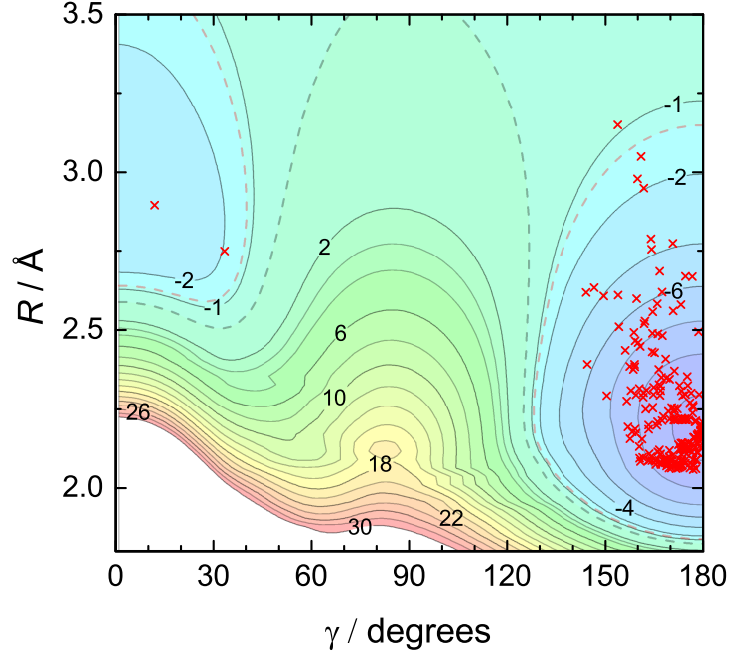


Figure 6.4: Location of surface hops on the $\text{OH}(A)+\text{Xe } 2A'$ adiabatic PES [77] for quenched trajectories that originated in the $N = 2$ rotational quantum level. The green, dotted line indicates a potential energy of 0 cm^{-1} ; the red, dotted line denotes a potential energy of -1200 cm^{-1} (that which delimits the potential-energy wells; see Section 6.2.2). The numbers that label the black contours give the potential energy in 10^3 cm^{-1} . A total of 4×10^3 trajectories were run, of which 218 underwent surface-hopping.

code for Model 5 led to a significant increase in the quenching cross-section and, for all the N shown here, accounts for most of the difference in the results from Models 5 and 6 (see the excitation functions and discussion thereof in Section 6.1.4). Subsequent addition of the calculated $\langle 1A' | \hat{L}_x | 1A'' \rangle$ element for $\text{OH}(A)+\text{Xe}$ and the full range of estimated $\text{OH}(A)+\text{Kr}$ elements led to a further, more modest increase in the magnitude of σ_Q . As a check, a subset of Model-6 calculations were also run in which the calculated and estimated coupling matrix elements were multiplied by a factor of two to exaggerate the non-adiabatic effects observed – see Figure 6.6. The resultant data from these calculations also showed a notable increase in the quenching cross-section for the N shown in Figure 6.5, as would be expected.

As noted previously, the $\text{OH}(A)+\text{Xe}$ experimental data are unique amongst the $\text{OH}(A)+\text{Rg}$ systems investigated in that electronic quenching is seen to extend to the full range of N measured. The data published in reference [25] give values of

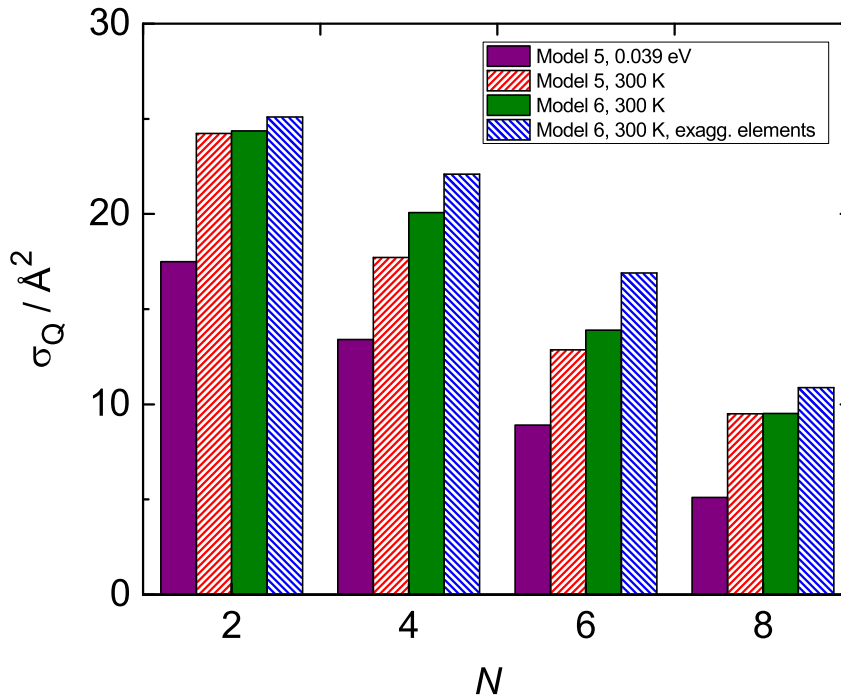


Figure 6.5: Comparison of theoretical quenching cross-sections, σ_Q , for the OH(A)+Xe system. The data were obtained from fixed-energy and variable-energy TSH QCT calculations run using Models 5 and 6, as well as those from subsets of modified Model-5 and Model-6 calculations. See text for details.

σ_Q up to, and including, $N = 10$, and Hemming reported values as high as $N = 20$ in reference [225], with $\sigma_Q > 10 \text{ \AA}^2$ for all rotational states. In contrast, for all the theoretical models employed, the magnitude of the quenching cross-section falls gradually with N , becoming negligible at around $N = 8$ for Model 4, and at $N = 13$ for Models 5 and 6. The fact that the experimental data plateau at a non-zero value of σ_Q , whereas the various theoretical models all predict a vanishing magnitude at high N , further suggests that there are inherent issues with how well currently available PESs are able to model non-adiabatic transitions.

6.1.3 Further discussion

A consideration of Figure 6.7, which shows the proportion of experimentally observed quenching that is recovered by different theoretical models, confirms that, whilst there is now near-quantitative agreement for many of the rotational states recorded

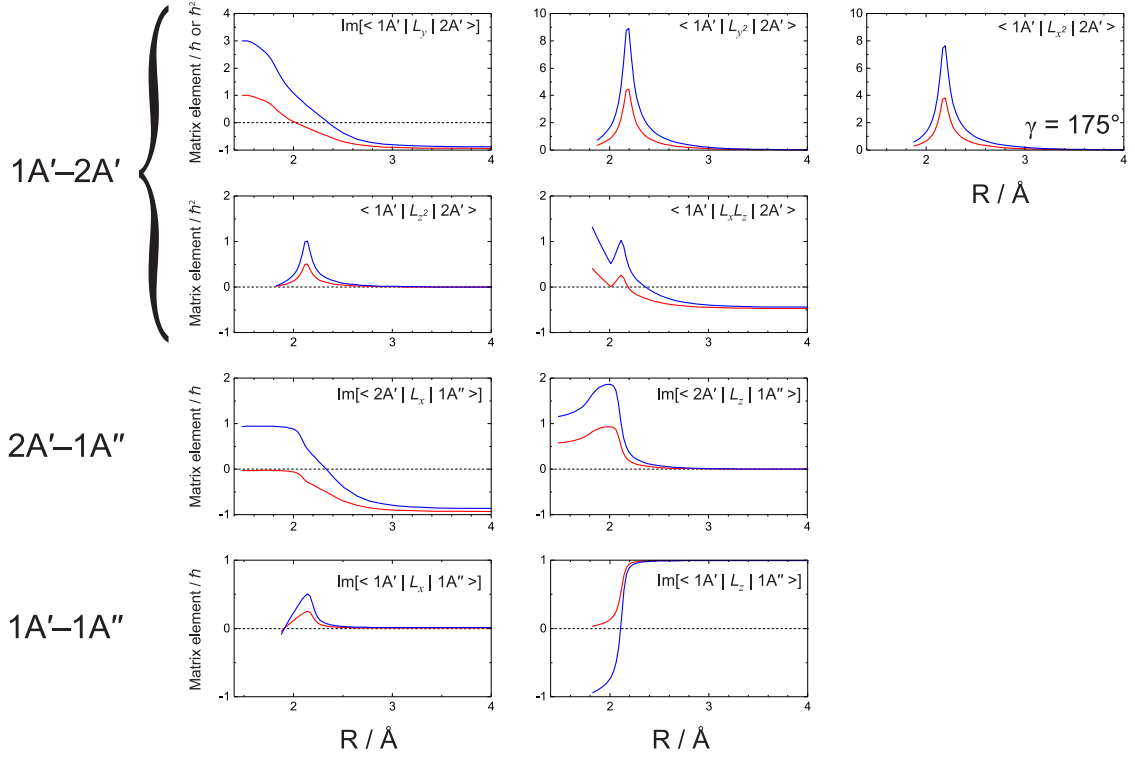


Figure 6.6: Calculated and estimated matrix elements for OH+Xe in the near-linear Rg–O–H geometry ($\gamma = 175^\circ$). The label ‘Im’ indicates that the imaginary part of the matrix element is plotted. Note the difference in scale on the y -axes. The majority of the elements for OH+Xe in red are generated by applying the relevant shifts in R to the corresponding element for OH+Kr. The elements in blue are the result of multiplying the red matrix elements by a factor of two.

for the OH(A)+Kr system, the most complete theoretical models continue to underestimate the full magnitude of the quenching cross-section for OH(A)+Xe. What is more, the previous discussion has revealed that, for both systems, the trends in the experimental and theoretical data differ slightly at low and high N . This is particularly true for OH(A)+Xe, where the theoretical results fail to predict a non-zero limit for σ_Q as N increases.

At first glance, a particularly surprising result of the calculations described above has been that the addition of the $\langle 1A' | \hat{L}_{x^2} | 2A' \rangle$, $\langle 1A' | \hat{L}_{y^2} | 2A' \rangle$, $\langle 1A' | \hat{L}_{z^2} | 2A' \rangle$, and $\langle 1A' | \hat{L}_x \hat{L}_z | 2A' \rangle$ matrix elements failed to significantly increase the magnitude of the calculated quenching cross-sections for the OH(A)+Kr system. The upper panel of Figure 6.8 presents cross-sectional plots of the $2A'$ and $1A'$ PESs for the OH+Kr system, along with a selection of the matrix elements that couple them. It

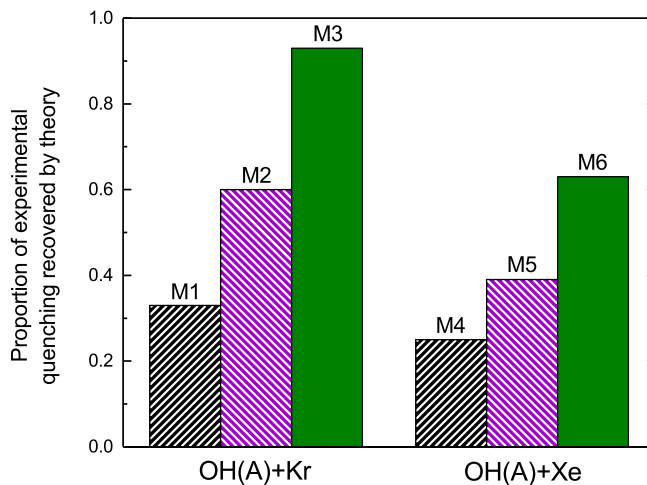


Figure 6.7: Proportion of experimentally observed quenching that is recovered by various theoretical models for the OH(A)+Kr and OH(A)+Xe systems. The trapezium rule is used to calculate the area under the line that links the theoretical cross-sections for a given model, which is then expressed as a fraction of the graphical area under the line that links the experimental data over a given range of N .

can be seen clearly that the peak in the magnitudes of the different coupling matrix elements for OH+Kr coincides with the conical intersection of the corresponding $2A'$ and $1A'$ PESs. Thus, it should be expected that the inclusion of greater numbers of elements, particularly those with the largest magnitudes, should lead to a corresponding increase in the quenching cross-section.

It may be the case that the majority of non-adiabatic transitions between the upper and lower surfaces of A' symmetry have already been accounted for by purely electrostatic coupling. Thus, on addition of those roto-electronic coupling matrix elements that also link the two surfaces of A' symmetry, there is little change in the magnitude of the resultant quenching cross-section. Indeed, though this was not necessarily a problem for the OH(A)+Kr system, for which the agreement was already near-quantitative without these additional matrix elements, it had previously been hoped that there would be an improvement in the agreement between experiment and theory for OH(A)+Xe.

The previous discussion outlined that, since only a few coupling matrix elements for OH+Xe had actually been calculated at the time of writing, it was decided

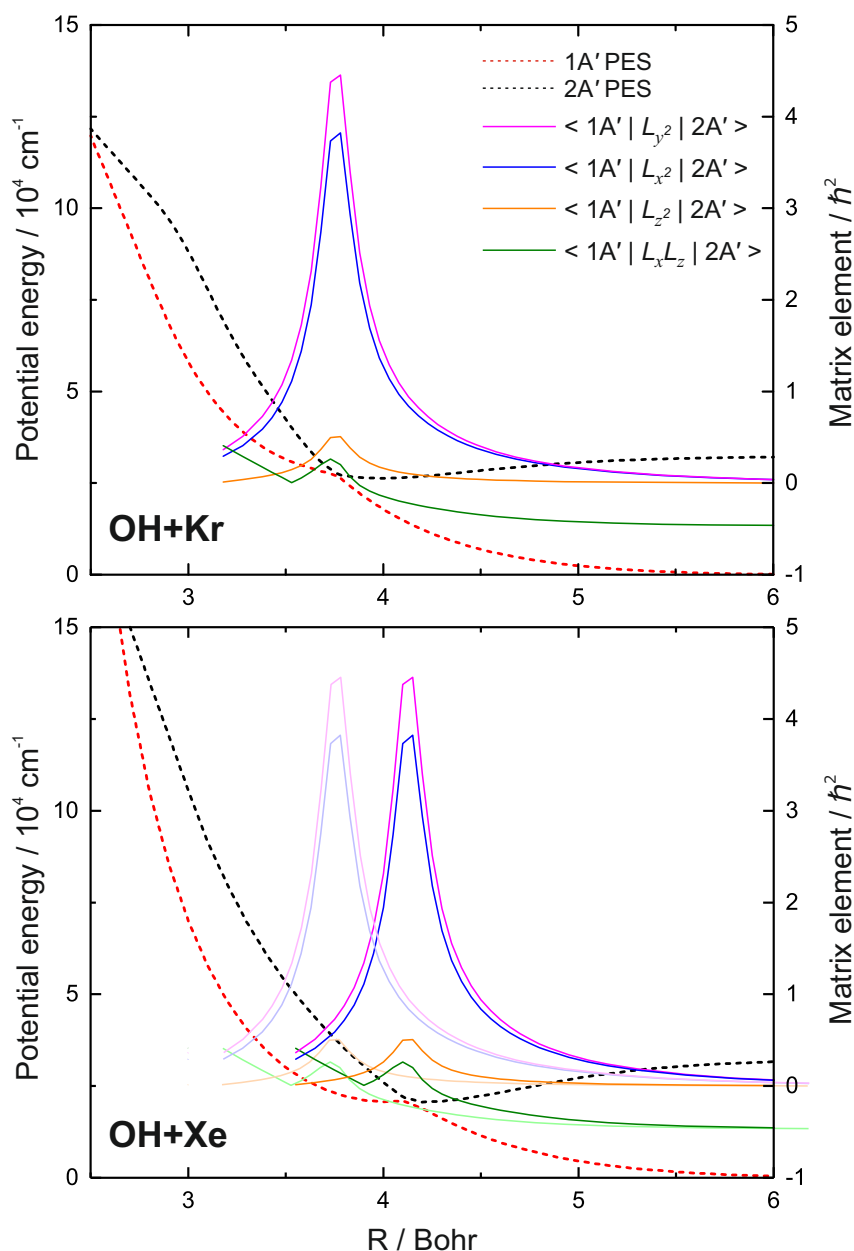


Figure 6.8: Upper panel: Comparison of the 2A' and 1A' PESs, and a selection of matrix elements that couple them, for the OH+Kr system. The plot clearly shows that the peak in magnitude of the coupling matrix elements largely coincides with the location of the conical intersection (in terms of R) between the PESs. Lower panel: Comparison of the 2A' and 1A' PESs, and a selection of matrix elements that couple them, for the OH+Xe system. The matrix elements shown in bold colour are the result of taking the faintly-coloured elements (for OH+Kr) and shifting them in R . See text for details.

to estimate the remaining elements by shifting those of OH+Kr in terms of R to generate the full range of elements needed in Model 6. The shifts were chosen specifically so that the peak (with respect to R) of the matrix elements would sit directly on the conical intersection, as shown in the lower panel of Figure 6.8. These shifts, when applied to all the estimated matrix elements that comprise Model 6, were found to produce only a modest increase in the magnitude of calculated quenching cross-sections. The reasons for the lack of a significant increase in σ_Q on inclusion of the exaggerated matrix elements are, as yet, not well understood.

One explanation could potentially lie in the different levels of theory at which the bases of the OH+Xe PESs and OH+Kr coupling matrix elements were calculated. The OH+Kr PESs and associated coupling matrix elements were all calculated at the the MRCISD+Q level of theory using a CASSCF/aVTZ-DK (complete active space self-consistent field/augmented valence triple zeta Douglas-Kroll-Hess Hamiltonian) basis. In contrast, although the OH+Xe PESs and coupling matrix elements were also generated at the MRCISD+Q level of theory, a CASSCF/aVQZ-PP (augmented valence quadruple zeta with *pseudo*-potentials for heavy atoms) basis set was used. It is, therefore, possible that the OH+Kr coupling matrix elements, which were calculated using a less rigorous theoretical treatment, are not able to successfully facilitate coupling between the higher-level OH+Xe potentials. For this reason, it is recommended that a focus of future theoretical work should be to calculate and implement a full set of coupling matrix elements for the OH+Xe at the same (CASSCF/aVQZ-PP) level of theory as the PESs.

6.1.4 Post-quenching product-state distributions

It is important to determine the extent to which TSH QCT calculations are able to predict the relative populations of the Λ -doublet levels within the OH(X) electronic state following quenching from OH(A) [78]. However, as noted in Chapter 5, the $1A'$ and $1A''$ PESs are not the same as the $\Pi_{A'}$ and $\Pi_{A''}$ Λ -doublet levels.

As a reminder, the symmetry labels of the PESs refer to reflection in the body-fixed three-atom plane, whereas the Λ -doublet symmetry labels describe reflection in the plane of OH rotation.

In reference [229], Jambrina *et al.* outlined a method by which the PES on which a given trajectory terminates can be linked to the Λ -doublet it populates. The flux between the two concurrent PESs in the $OH(X)+Rg$ electronic ground state implies that, following quenching:

$$\sigma_{N''}(\Pi_{A'}) = W_{A'}\sigma_{N''}(A') + (1 - W_{A''})\sigma_{N''}(A''), \quad (6.1)$$

$$\sigma_{N''}(\Pi_{A''}) = (1 - W_{A'})\sigma_{N''}(A') + W_{A''}\sigma_{N''}(A''), \quad (6.2)$$

where $\sigma_{N''}(\Pi_{A'})$ and $\sigma_{N''}(\Pi_{A''})$ are the rotational-state-resolved cross-sections for quenching into each of the ground-state Λ -doublets; $\sigma_{N''}(A')$ and $\sigma_{N''}(A'')$ are the rotational-state-resolved cross-sections for quenching onto each of the ground-state PESs; and $W_{A'}$ and $W_{A''}$ are the correction factors that are used to obtain the Λ -doublet populations from a given terminal-PES distribution. Note that, in this section: N is the initial rotational state in $OH(A)$ and N'' is the final rotational state in $OH(X)$. The correction factors are trivial to calculate *via* [229]

$$W_{A'} \approx 1 - \left[\frac{2}{3}a_0^{(2)}(N'') + \frac{1}{3} \right]^{\frac{1}{2}}, \quad (6.3)$$

where the polarisation moments $-a_0^{(2)}(N'')$, the second Legendre moment, in cosine, of the angle between the $\mathbf{N}''$ and $\mathbf{k}'$ vectors – have been calculated on the $1A'$ PES. An equivalent expression for $W_{A''}$ is generated when using polarisation moments calculated on the $1A''$ PES. As such, it can be seen that the stereodynamics of the $OH(X)$ product can be used to directly relate the population of a given Λ -doublet to the PES onto which quenching took place. Classically, $a_0^{(2)}(N'')$ can take values in the range $[-0.5, 1]$. Values close to -0.5 indicate that $\mathbf{N}''$ is perpendicular to $\mathbf{k}'$, whereas values close to 1 indicate that $\mathbf{N}''$ is parallel to $\mathbf{k}'$. As such, for $a_0^{(2)}(N'') \approx -0.5$, the correction factor tends to 1 and products on the $1A'$ PES also populate the $\Pi_{A'}$ Λ -doublet; for $a_0^{(2)}(N'') \approx 1$, the correction factor tends

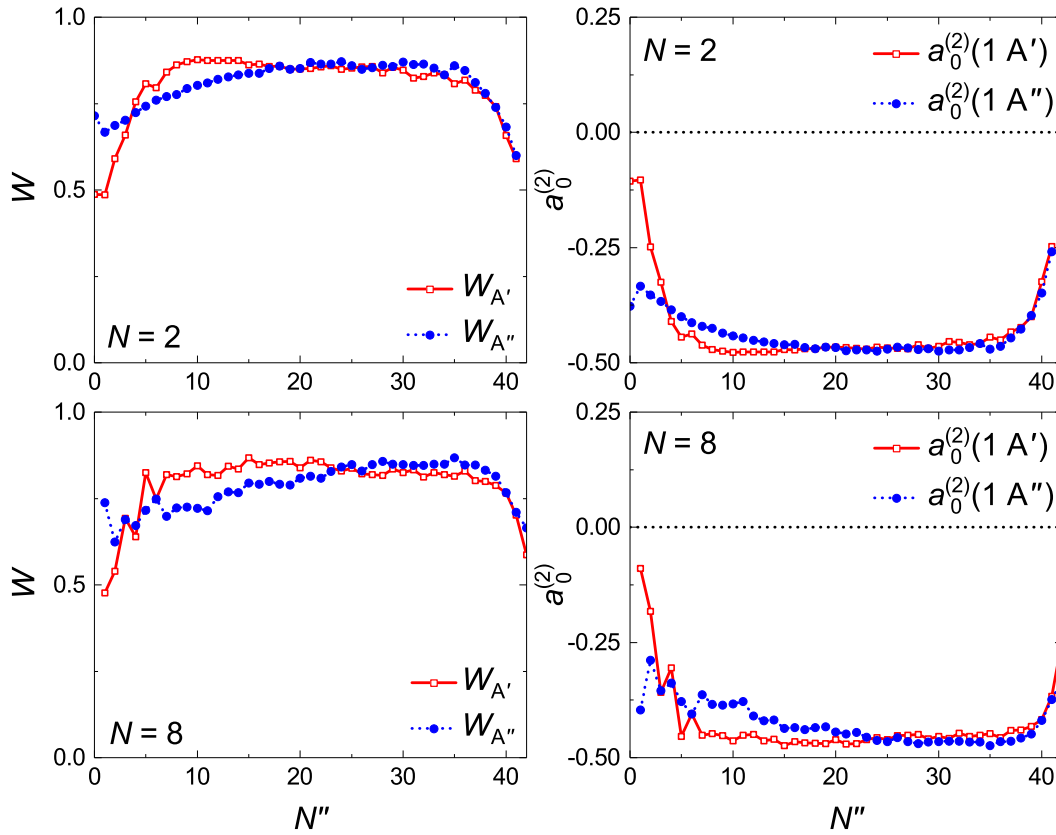


Figure 6.9: Left panel: correction factors that relate the ground-state PES on which a quenched OH(A)+Xe trajectory terminates to the Λ -doublet level it populates. Right panel: polarisation parameters for quenched trajectories that terminate on each of the ground-state OH(X)+Xe PESs.

to 0 and products on the $1A'$ PES populate the $\Pi_{A''}$ Λ -doublet. An equivalent relationship can also be established for the $1A''$ PES.

Figure 6.9 shows the correction factors and polarisation moments for two sets of Model-6 OH(A)+Xe calculations that began in the $N = 2$ and $N = 8$ rotational states of OH(A) and terminated in a range of N'' states in OH(X). For almost all final N'' states, the value of $a_0^{(2)}(N'')$ is close to -0.5, indicating that $\mathbf{N}''$ is strongly polarised perpendicular to $\mathbf{k}'$. As a consequence, the corresponding correction factors take values close to 1 on both surfaces.

Figure 6.10 shows the effect of inserting the calculated correction factors into Equations (6.1) and (6.2). It can be seen clearly that, because the values of W are uniformly close to 1, there is a very strong correlation between the terminal-PES

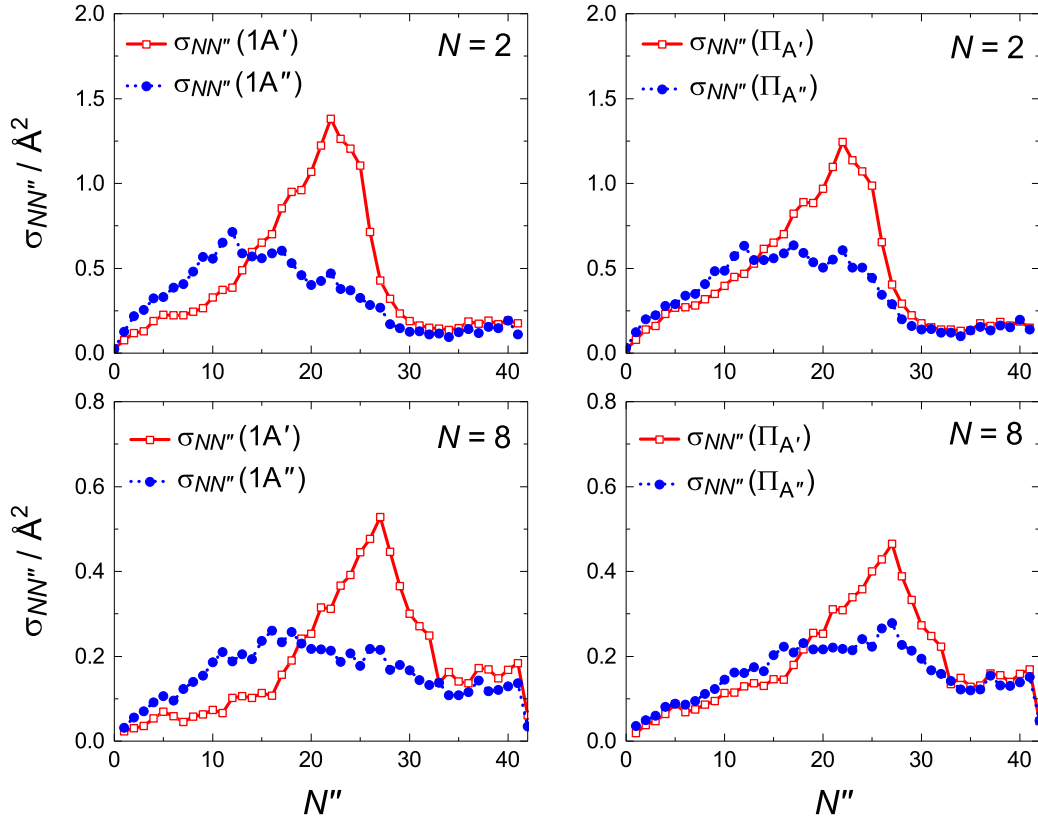


Figure 6.10: Left panel: Product rotational-state distributions for quenched $OH(A)+Xe$ trajectories that began in the $N = 2$ and $N = 8$ initial rotational states of $OH(A)$ and terminated on each of the ground-state PESs in $OH(X)+Xe$. Right panel: product rotational-state distributions for quenched $OH(A)+Xe$ trajectories that began in the $N = 2$ and $N = 8$ initial rotational states of $OH(A)$ and terminated in each of the ground-state Λ -doublets of $OH(X)$.

and terminal- Λ -doublet product rotational-state distributions. Similar behaviour is seen for the full range of initial N states for both the $OH(A)+Kr$ and $OH(A)+Xe$ systems. Thus, it can be inferred that, for the $OH(A)+Rg$ systems investigated in this work, the rotational plane of the OH radical coincides strongly with the $O-H-Rg$ triatomic plane (at least in the quenching exit channel). Such behaviour presents a stark contrast to that observed for the $O(^3P)+D_2$ system in reference [229], which shows significant transfer of population from the A'' PES to the $\Pi_{A'}$ Λ -doublet.

Although not measured experimentally in the work reported here, the TSH QCT calculations performed in this thesis allow for a determination of the $OH(X)$ product rotational-state distribution following quenching of $OH(A)$ by Rg . To that end, it is

also helpful to determine a quantitative measure of preferential Λ -doublet population by calculating the *degree of electron alignment* (DEA), which is defined as

$$\text{DEA} = \frac{\sigma_{N''}(\Pi_{A'}) - \sigma_{N''}(\Pi_{A''})}{\sigma_{N''}(\Pi_{A'}) + \sigma_{N''}(\Pi_{A''})}. \quad (6.4)$$

As such, positive values of the DEA (that range between 0 and +1) imply a preference for population of the $\Pi_{A'}$ Λ -doublet and the $1A'$ PES; negative values (that range between 0 and -1) imply a preference for population of the $\Pi_{A''}$ Λ -doublet and the $1A''$ PES.

Figure 6.11 shows the OH(X) product rotational-state distributions of OH(A)+Xe trajectories that originated in designated excited-state OH(A, N) levels before quenching to a distribution of ground-state OH(X, N'') levels and terminating in either of the Λ -doublet levels. The figure shows the rotational-state-resolved cross-sections for specific OH(X, N'') $\leftarrow$ OH(A, N) transitions, $\sigma_{N''}$, as well as the DEA. These variable-collision-energy (300 K) calculations were run using three-surface TSH QCT algorithms that incorporated all possible electrostatic and roto-electronic couplings (Model 6).

In general, the OH(X) product rotational-state distribution following quenching in OH(A)+Xe is found to be vibrationally cold (the vast majority of collisions terminate in $v'' = 0$) and rotationally hot, reflecting the strong torques experienced by the OH molecules on passage through the conical intersection. Summing the cross-sections for quenching into the $\Pi_{A'}$ and $\Pi_{A''}$ Λ -doublets would produce a bimodal distribution of intensity with respect to the N'' population. Indeed, such behaviour has been reported experimentally for a number of OH(A) collision systems [230], including, for example: Kr [78], H₂ and D₂ [194–196], N₂ [231], and O₂ [232]. For CO₂ [232], the distribution is significantly colder, and this may be a consequence of the collision partners forming a long-lived complex. It can also be said that, in general, the rotational-state distribution in the $\Pi_{A''}$ Λ -doublet is markedly broader than that in $\Pi_{A'}$. This is likely due to the fact that the $\Pi_{A''}$ Λ -doublet is populated exclusively by roto-electronic coupling mechanisms, whereas the $\Pi_{A'}$ Λ -doublet is also populated by electrostatic coupling to give a sharp peak at medium N'' [33].

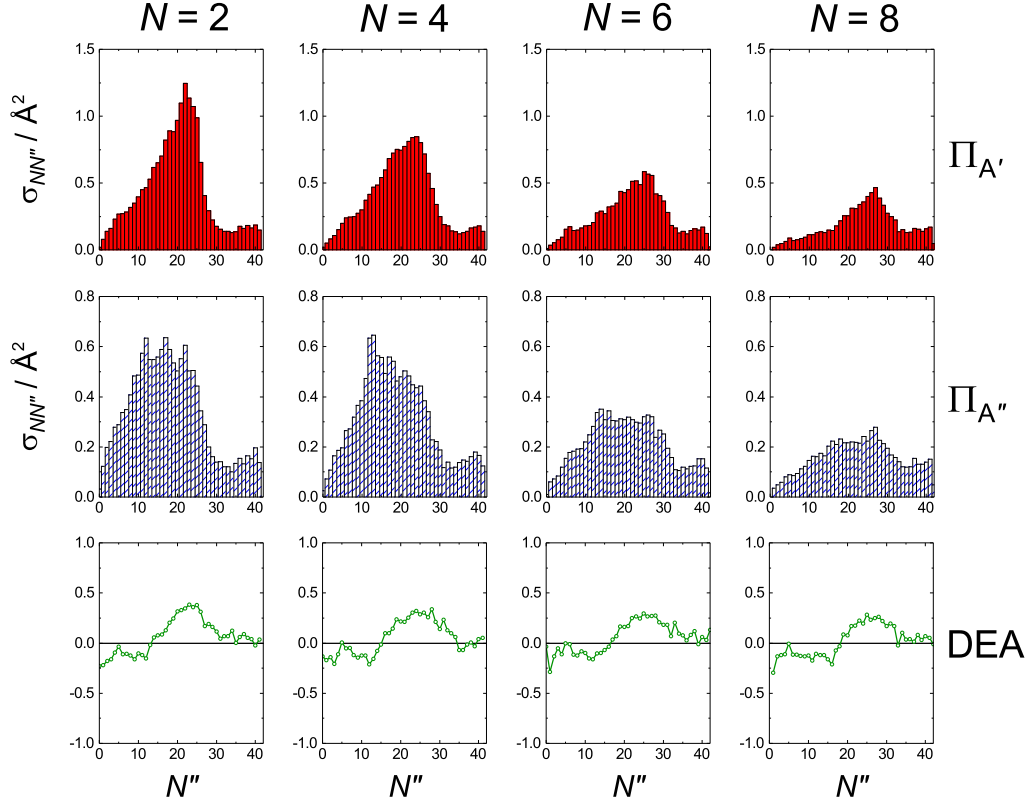


Figure 6.11: Upper and middle panels: Theoretical rotational-state-resolved cross-sections, $\sigma_{NN''}$, for the non-adiabatic transfer of population from $\text{OH}(A, N) + \text{Xe}$ to $\text{OH}(X, N'') + \text{Xe}$. The cross-sections are further resolved in the terminal Λ -doublet ($\Pi_{A'}$ or $\Pi_{A''}$). These data were generated from variable-collision-energy (300 K) TSH QCT calculations run using three-surface TSH QCT algorithms that incorporated all possible electrostatic and roto-electronic couplings (Model 6). Note the difference in scale of the y -axes in the upper and middle panels. Lower panel: DEA for $\text{OH}(X, N'') \leftarrow \text{OH}(A, N)$ transitions.

The integral cross-section falls as N increases, reflecting the trend shown by the non-adiabatic quenching data discussed earlier. It can also be seen that, as N increases, the mean value of the ground-state rotational quantum number becomes larger, since collisions need to become increasingly head-on in nature if they are to bring about a change in the magnitude of N . This trend is seen for both the $\Pi_{A'}$ and $\Pi_{A''}$ Λ -doublets. Moreover, for all the N sampled, trajectories that terminate in the $\Pi_{A'}$ Λ -doublet also tend to show greater rotational excitation – however, the difference between the two Λ -doublets decreases as N becomes larger. To illustrate these observations more clearly, the plot on the left of Figure

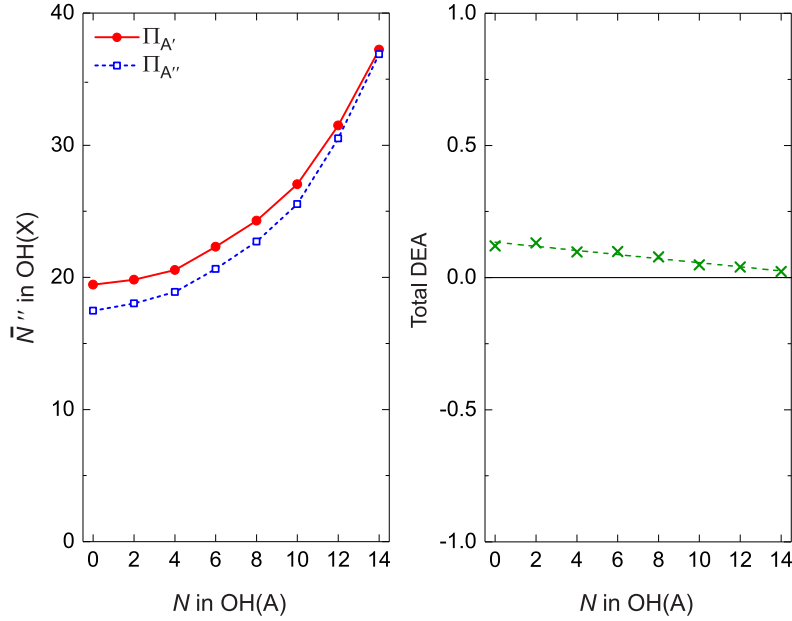


Figure 6.12: Left panel: Mean value of N'' for trajectories that originated in a range of OH(A, N) levels and terminated in each of the two Λ -doublet levels of OH(X). Right panel: Total DEA, summed over all final N'' , for OH(X, N'') $\leftarrow$ OH(A, N) trajectories that originated in a selection of rotational levels across the full range of N sampled in this work. A line of best fit has been added to guide the eye.

6.12 shows the mean value of the final rotational quantum level, $\bar{N}''$, resolved in the terminal ground-state PES, for OH(A)+Xe trajectories that began in the full range of N sampled in this work.

The lower panel of Figure 6.11 shows the DEA calculated from Equation (6.4). A consideration of the data shown reveals that, for all initial N , the $\Pi_{A''}$ Λ -doublet is preferentially populated by collisions that terminate in $N'' \leq 15$; conversely, the $\Pi_{A'}$ Λ -doublet is preferentially populated by collisions that end in $N'' \geq 15$. Recalling Equations (5.57) and (5.58), it can be shown that the strength of both Coriolis and Renner-Teller roto-electronic coupling is dependent on K , the projection of the total-angular-momentum vector, $\mathbf{J}$, onto the OH internuclear axis. The strength of Coriolis coupling, which populates the $\Pi_{A''}$ Λ -doublet exclusively during quenching, is proportional to K^2 . In contrast, the strength of Renner-Teller coupling, which can facilitate the transfer of population between the nearly-degenerate $\Pi_{A'}$ and $\Pi_{A''}$ Λ -doublets, is proportional to K . Since $\mathbf{J} = \mathbf{j} + \mathbf{\ell}$, it follows that the strength of roto-electronic coupling should also vary as a function of the impact

parameter, b , since this will affect the magnitude of the orbital-angular-momentum vector, ℓ . Thus, collisions at high impact parameter, with larger orbital angular momenta, are particularly likely to induce energy transfers that are facilitated by Coriolis coupling. As such, the $\Pi_{A''}$ Λ -doublet (coincident with the $1A''$ PES) is populated most efficiently by collisions at high b . Since these collisions are more glancing-blow in nature, and require the Xe atom to deviate less from its original trajectory, they induce less torque on the OH radical and result in colder OH(X) product rotational-state distributions than transitions that terminate in $\Pi_{A'}$. This rationalisation is further confirmed by the data relating to the mean value of N'' that are shown in Figure 6.12, which report consistently colder distributions of N'' in the $\Pi_{A''}$ Λ -doublet for all N . Of course, it is also important to remember that electrostatic coupling, the strength of which does not depend on K , populates the $\Pi_{A'}$ Λ -doublet exclusively, and this has a resultant impact on both the product rotational-state distribution and the DEA.

To investigate the trend in DEA further, the plot on the right of Figure 6.12 shows the total DEA, summed over all final N'' , for OH(A) + Xe trajectories that originated in the full range of N sampled in this work. In general, there is very little preference for one Λ -doublet to be populated over another, however, if anything, there does exist a slight propensity for $\Pi_{A'}$ that decreases as N becomes larger. In the first instance, it is important to recognise that, since there is no strong preference for either terminal Λ -doublet (or PES), it is essential to include all three PESs in any model that will accurately describe the collision dynamics of OH(A)+Xe.

To further probe the observed dependence of total DEA on N , Figure 6.13 shows opacity functions, resolved in the terminal PES, that were calculated from Model-6 calculations for OH(A)+Xe in which the OH(A) radical began in the $N = 4$ and $N = 8$ rotational levels. The opacity functions confirm the trends outlined by the product rotational-state distributions and total DEA shown earlier: as N increases, the magnitude of the quenching cross-section falls, and the proportion of trajectories that terminate in the $\Pi_{A''}$ Λ -doublet (coincident with the $1A''$ PES) increases, even though the $1A'$ PES (coincident with the $\Pi_{A'}$ Λ -doublet)

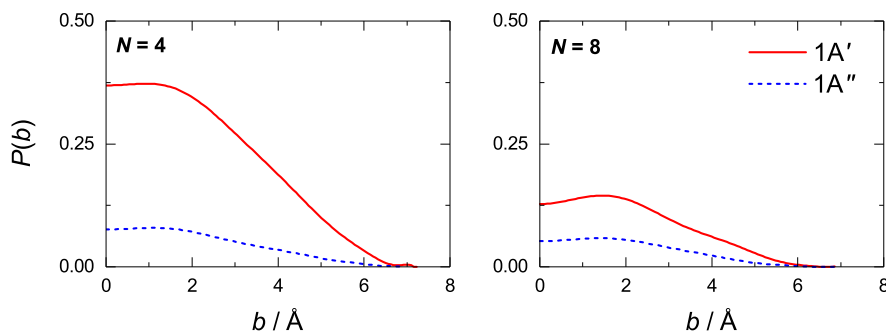


Figure 6.13: Opacity functions, $P(b)$, resolved in the terminal PES, that were calculated from Model-6 calculations for OH(A)+Xe in which the OH(A) radical began in the $N = 4$ and $N = 8$ rotational levels.

remains dominant. Interestingly, although the magnitude of the opacity function for trajectories that terminate in the $\Pi_{A'}$ Λ -doublet falls considerably at higher N , this is not the case for the $\Pi_{A''}$ Λ -doublet, for which the magnitude of $P(b)$ is notably similar for both N shown.

To rationalise these observations, it is important to consider the relative strengths of different types of coupling at low and high N . The Model-4 quenching data shown in Figure 6.3 demonstrated that the magnitude of the cross-section for non-adiabatic transitions that are facilitated by electrostatic coupling falls considerably as N increases: the relatively fast rotation of OH at high N diminishes the anisotropy of the OH(A)+Xe PES, meaning trajectories are less likely to sample the attractive H-O(A)–Xe potential-energy well where the conical intersection with the ground-state is located. Thus, at high N , there are fewer trajectories that are liable to undergo quenching to the ground state. However, as N increases, so too will the magnitude of the OH total-angular-momentum vector, $\mathbf{j}$, and, by extension, the magnitude of the total-angular-momentum vector for the triatomic system, $\mathbf{J}$. As noted earlier, this will predominantly favour Coriolis coupling (the strength of which has a K^2 -dependence), rather than Renner-Teller coupling (the strength of which has a K -dependence) or electrostatic coupling (which does not depend on K). As such, those trajectories that do enter the H-O(A)–Xe well are increasingly likely to quench to the $1A''$ PES as N increases. Therefore, since the relative influence of electrostatic and Renner-Teller coupling on the product rotational-state distribution

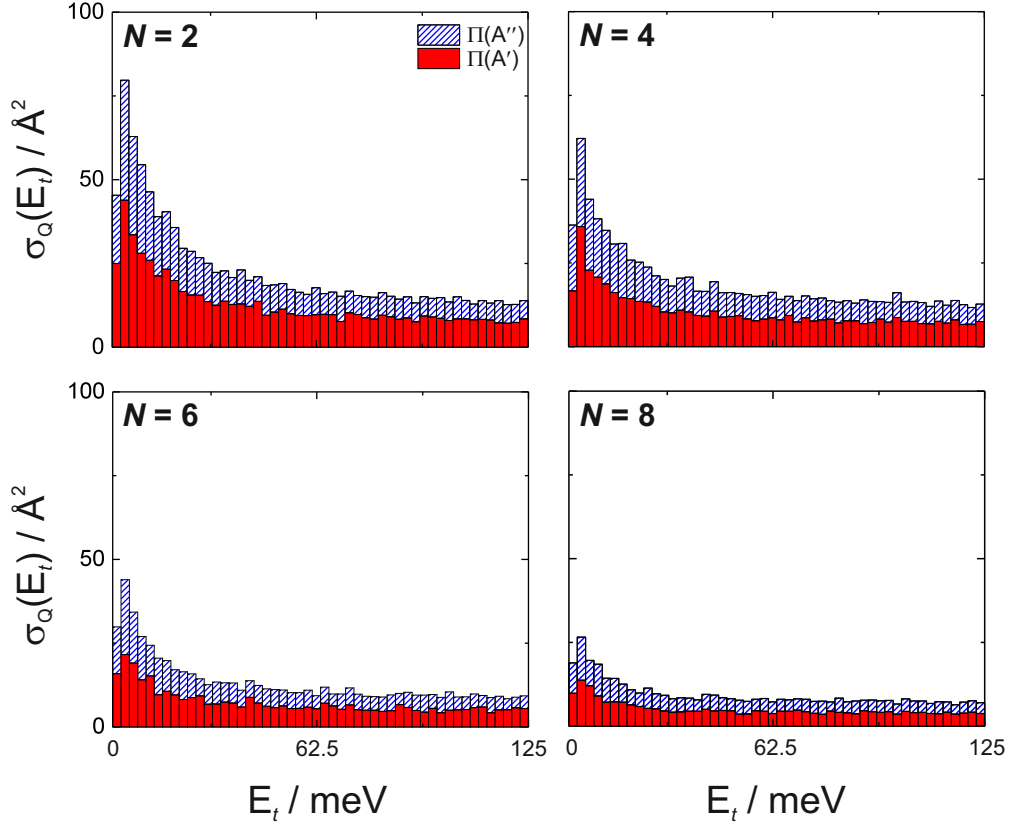


Figure 6.14: Excitation functions – plots of $\sigma_Q(E_t)$ vs. E_t – for non-adiabatic quenching for batches of $OH(A) + Xe$ trajectories that began in various N . The histogram bins have been split into contributions from trajectories that terminated in each of the $OH(X)$ Λ -doublets. The calculations from which the excitation functions were extracted were run using Model 6.

falls off more quickly with rotational excitation than that of Coriolis coupling, there is an increase in the proportion of trajectories that terminate in the $\Pi_{A''}$ Λ -doublet, and this produces a lower total DEA at high N . Of course, to understand the observed trends more fully, it would be helpful to compare product rotational-state distributions and the DEA from batches of trajectories run using various models in which different combinations of couplings were included. This has been carried out previously for the $N = 0$ level in $OH(A) + Kr$ system [26, 33], and it is recommended that future theoretical work should aim to do the same for $OH(A) + Xe$.

Figure 6.14 presents excitation functions – histogram plots of $\sigma_Q(E_t)$ vs. E_t – for non-adiabatic quenching for batches of trajectories that began in a selection of rotational quantum states of the $OH(A) + Xe$ system. The data shown were generated

from Model-6 calculations. First and foremost, the data clearly demonstrate the importance of using the variable-collision-energy algorithms described earlier in this chapter when modelling non-adiabatic effects in the OH(A)+Xe system. The plots show that the magnitude of the cross-sections remains high over the full range of collision energies sampled (0.005 – 0.125 eV) and, as such, using fixed-energy algorithms in which all trajectories are assigned a collision energy of 0.039 eV risks undermining the extent of quenching considerably. As such, it is also not surprising that the data reported in Figure 6.5 showed such a significant difference in the magnitude of the quenching cross-sections extracted from Model-5 calculations that were run using both fixed- and variable-collision-energy algorithms.

In agreement with the data reported in Figure 6.12, resolving the excitation functions suggests that the proportion of trajectories that terminate in the $\Pi_{A''}$ Λ -doublet decreases slightly as N increases. As such, it can also be said that the excitation functions infer that low-collision-energy trajectories are, by extension, more likely to terminate in the $\Pi_{A''}$ Λ -doublet than their high-energy counterparts. This observation lends further support to the earlier statement that high- b trajectories, which do not require high collision energies to come about, are more likely to populate the $\Pi_{A''}$ Λ -doublet.

6.2 Rotational energy transfer

Experimental RET cross-sections were measured previously [25, 26, 33, 226] by using a monochromator to resolve the fluorescent emission from a particular OH(A, j) state both in the absence and presence of a rare-gas quencher (as outlined in, for example, references [6–8, 25, 33]). The loss of population from a particular j state is measured as a function of the rare-gas concentration and a *pseudo*-first-order rate constant is extracted for the loss of excited-state population: $k_p = k_0 + k_1[\text{Rg}]$, where k_0 is the inverse of the fluorescence lifetime (τ_0), k_1 is the rate constant for the collisional loss of population, and $[\text{Rg}]$ is the rare-gas concentration. If the fluorescent emission is unresolved in j , then k_1 corresponds to the rate constant for quenching; for rotationally resolved fluorescence, k_1 is the sum of both the quenching

and the RET rate constants. Thus, it is possible to determine rate constants for both quenching and RET and convert them to absolute cross-sections. Notably, the RET process described here involves all collisions for which $N' \neq N$, as well as those for which $N' = N; j' \neq j$ – so-called ‘purely spin-rotation-level-changing’ collisions. See references [6–8, 25, 33] for further details.

6.2.1 RET: experimental data

By comparing Figures 6.15 and 6.16, it can be seen that the magnitude of σ_{RET} is smaller for the $OH(A)+Kr$ system than for $OH(A)+Xe$. Since the reduced masses of these two triatomic systems are relatively similar, any difference in the observed dynamics can largely be attributed to differences in the PESs rather than any kinematic effect. It has been shown (see Figure 5.4) that the $OH(A)+Xe$ system has a much more anisotropic PES than $OH(A)+Kr$. In the former, the deeply attractive potential-energy wells in the near-linear $H-O(A)-Xe$ and $O-H(A)-Xe$ geometries exert strong torques on the OH radical, and often lead to a transfer of rotational energy to/from $OH(A)$ over the course of a collision. It is also of crucial importance that the extent to which the attractive potential extends in R is significantly greater for $OH(A)+Xe$ than for $OH(A)+Kr$. Thus, even trajectories with relatively large impact parameters are liable to sample the attractive regions of the $OH(A)+Xe$ PES, leading to an increase in the RET cross-section.

However, further comparison of σ_{RET} for the $OH(A)+Kr$ and $OH(A)+Xe$ systems also reveals that the two sets of data share more similar magnitudes than is seen for electronic quenching. This is likely due to the fact that, even though there is a stronger propensity to undergo RET in the $OH(A)+Xe$ system, electronic quenching also competes more effectively with adiabatic energy transfer than it does in $OH(A)+Kr$. In both cases, a gradual decrease in the magnitude of σ_{RET} at higher N is anticipated, owing to the fact that the separation between adjacent rotational levels increases with N . This is seen clearly in the experimental data for $OH(A)+Kr$. In contrast, the longer-range, more attractive PES for $OH(A)+Xe$ results in relatively constant magnitudes for σ_{RET} across the range of N sampled.

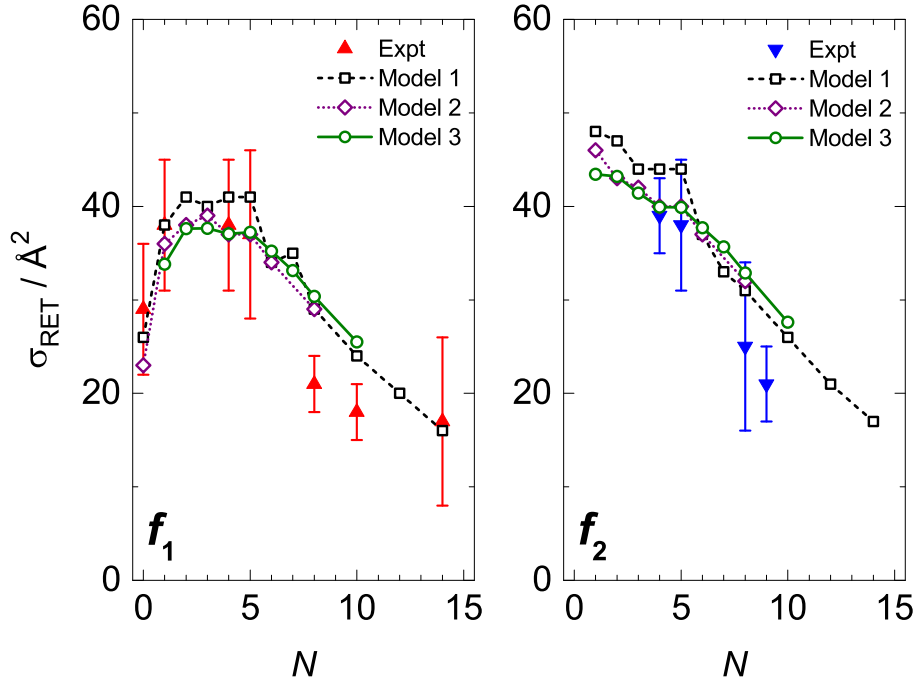


Figure 6.15: Comparison of experimental [25, 26, 33, 226] and theoretical RET cross-sections, σ_{RET} , for the OH(A)+Kr system. Upward-pointing, red triangles denote f_1 spin-rotation levels and downward-pointing, blue triangles denote f_2 spin-rotation levels. The scatter points connected by lines refer to theoretical RET cross-sections generated from TSH QCT Models 1-3. See text for details.

6.2.2 RET: comparison with theory

Figure 6.15 presents a comparison of experimental [25, 26, 33, 226] σ_{RET} cross-sections for the OH(A)+Kr system with those calculated using Models 1-3 [25, 26, 33, 226]. Note that, for the more complete theoretical models, data are only included for $N \leq 10$, since electronic quenching is negligible for higher rotational states.

For the OH(A)+Kr system, there is near-quantitative agreement between experiment and QCT TSH theory for virtually all the values of N sampled. The agreement is especially good for $N \leq 5$. The development of the QCT TSH code has not led to a significant change in the magnitude of σ_{RET} , in accordance with the relatively modest changes seen in the magnitude of σ_{Q} whilst gradually improving the accuracy of the models for OH(A)+Kr.

In comparison, the agreement between experiment and theory is considerably

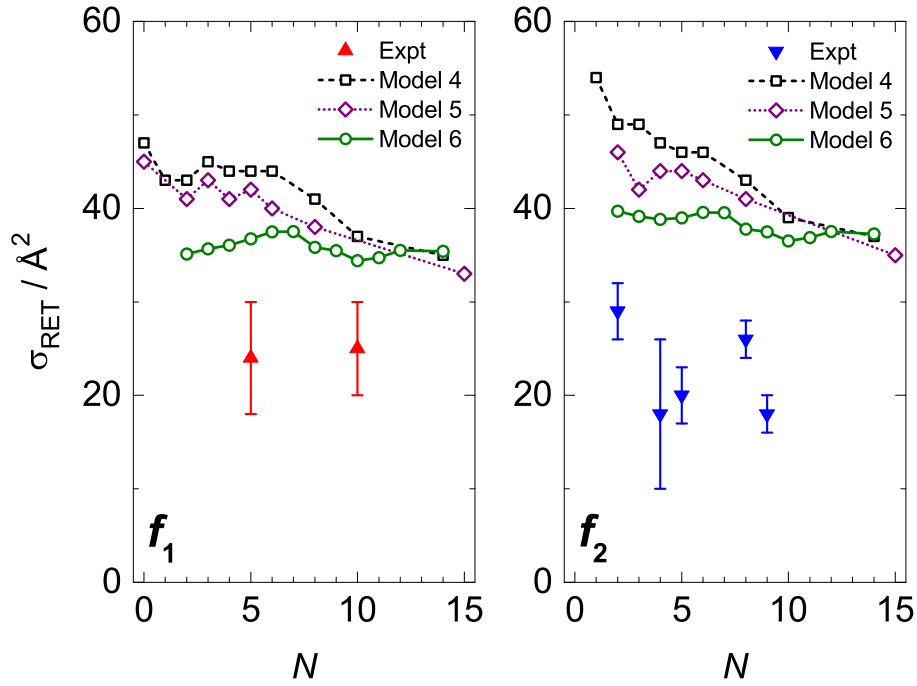


Figure 6.16: Comparison of experimental [25, 26, 33, 226] and theoretical RET cross-sections, σ_{RET} , for the $\text{OH}(\text{A})+\text{Xe}$ system. Upward-pointing, red triangles denote f_1 spin-rotation levels and downward-pointing, blue triangles denote f_2 spin-rotation levels. The scatter points connected by lines refer to theoretical RET cross-sections generated from TSH QCT Models 4-6. See text for details.

poorer for the $\text{OH}(\text{A})+\text{Xe}$ system: the QCT TSH calculations continue to overestimate the magnitude of the experimental RET cross-section, though there has been a significant improvement in agreement between the two with employment of the more sophisticated theoretical treatments [33, 226]. Figure 6.16 shows a comparison of $\text{OH}(\text{A})+\text{Xe}$ experimental data with those generated by Models 4-6. In Section 6.1.2, it was reported that even the most complete model of the $\text{OH}(\text{A})+\text{Xe}$ system fails to reproduce all of the experimental quenching, meaning the theoretical RET data points are not lowered enough by competitive non-adiabatic collisions to agree well with experiment.

Figure 6.17 presents a comparison of four different data sets for both the $\text{OH}(\text{A})+\text{Kr}$ and $\text{OH}(\text{A})+\text{Xe}$ systems: experimentally determined total-removal cross-sections, which correspond to the sum of quenching and RET cross-sections [25, 33, 226]; RET cross-sections from fixed-energy, adiabatic QCT calculations run on

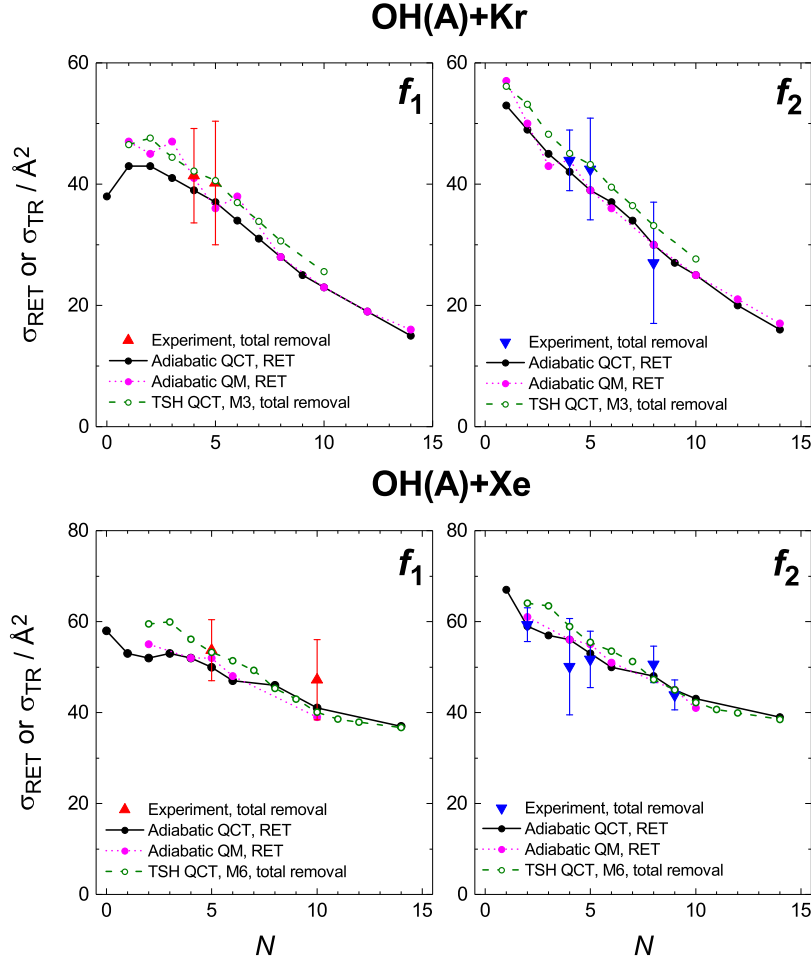


Figure 6.17: Comparison of: experimental total-removal cross-sections, which correspond to the sum of quenching and RET cross-sections [25, 33, 226]; RET cross-sections from fixed-energy, adiabatic QCT calculations run on the upper OH(A)+Kr and OH(A)+Xe $2A'$ PESs with $E_{\text{coll}} = 0.039$ eV [25, 33, 226]; total-removal cross-sections from Model-3 and Model-6 TSH QCT calculations run at 300 K; and RET cross-sections from fixed-energy, adiabatic quantum-mechanical calculations run on the upper OH(A)+Kr and OH(A)+Xe $2A'$ PESs with $E_{\text{coll}} = 0.039$ eV [226].

the upper OH(A)+Kr and OH(A)+Xe $2A'$ PESs with $E_{\text{coll}} = 0.039$ eV [25, 33, 226]; total-removal cross-sections from Model-3 and Model-6 TSH QCT calculations run at 300 K; and RET cross-sections from fixed-energy, adiabatic quantum-mechanical calculations run on the upper OH(A)+Kr and OH(A)+Xe $2A'$ PESs with $E_{\text{coll}} = 0.039$ eV [226]. In the first instance, the figure confirms the excellent agreement between the data generated from both adiabatic and non-adiabatic QCT calculations

and those from a more rigorous quantum-mechanical treatment. This validates the use of a *quasi*-classical treatment for the systems investigated in this thesis.

The figure also highlights that experimental total-removal cross-sections are in excellent, fully quantitative agreement with adiabatic and non-adiabatic theoretical RET data, for which there is no consideration of electronic quenching. Thus, it can be said that, in any TSH QCT models that attempt to model non-adiabatic dynamics, it is the accuracy with which quenching is treated that determines the level of agreement between experiment and theory. Since non-adiabatic transitions and inelastic energy transfer take place in the same regions of the PES (see below), any TSH algorithms that underestimate the extent of quenching will necessarily generate RET data that overestimate the magnitude of corresponding experimental quantities.

To investigate the trend shown in the magnitude of RET cross-sections with respect to N , and to elucidate the competitive interaction between adiabatic and non-adiabatic dynamics, a set of calculations was run that output the time spent by rotationally inelastic trajectories in the H-O(A)–Xe potential-energy well, where the conical intersection with the electronic-ground-state PES is found [226]. To this end, the potential-energy well was defined as any region of the OH(A)+Xe PES for which the potential energy, V , has a value of $V \leq -1200 \text{ cm}^{-1}$ and $\gamma > 90^\circ$. The angular restriction ensures that any time spent in the well generated in the O-H(A)–Xe geometry – which, as demonstrated in Figure 6.4, does not facilitate electronic quenching – does not count towards the ‘time in well’ discussed below.

Figure 6.18 shows the time spent in the H-O(A)–Xe well by trajectories originating in the $N = 2, 10$, and 20 rotational quantum levels. Notably, the proportion of inelastic trajectories that enter the well increases with N : since it is more difficult to bring about a change in $|\mathbf{N}|$ in higher rotational states, such a process requires trajectories that sample the most attractive regions of the PES. Furthermore, a consideration of the variation in time-in-well reveals that, for low N , there is a unimodal peak at relatively high time-in-well; for medium values of N , there is a bimodal distribution; and, for high N , the distribution once again becomes unimodal, however, the peak occurs at much lower time-in-well than for low N .

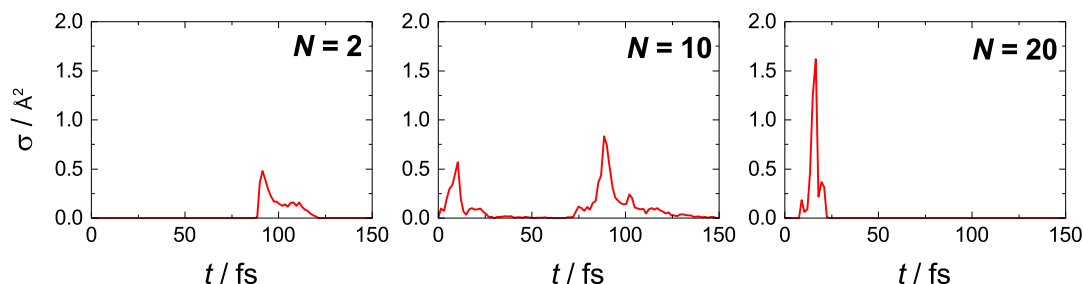


Figure 6.18: Integral cross-sections *vs.* time-in-well for rotationally inelastic trajectories that originated in $N = 2, 10$ or 20 . The H-O(A)–Xe well is defined as a region of the OH(A)+Xe PES in which $V \leq -1200 \text{ cm}^{-1}$ and $\gamma > 90^\circ$.

Following this, a number of individual classical trajectories were projected onto the OH(A)+Xe PES, for various N , to elucidate the contrasting behaviours shown in the time-in-well analysis. These projections are reported in Figure 6.19. At low N , the repulsive region in the T-shaped geometry directs trajectories to the bottom of the H-O(A)–Xe well, where they spend a relatively long period of time before exiting again. This gives a single peak with a high time-in-well (105 fs). For medium values of N , the peak at higher time-in-well (76 fs) corresponds to trajectories that sample the full depth of the H-O(A)–Xe well. However, it is important to note that the time-in-well is generally less than that experienced at low N by virtue of the higher rotational energy of the system. The inner peak at lower time-in-well (34 fs) corresponds to trajectories that merely sample the well edge and leave soon after entering. At high N , when the OH(A) radical is rotating very fast, the rate of change of γ is sufficiently great such that the trajectory cannot be directed into either the H-O(A)–Xe or the O-H(A)–Xe well exclusively. Equally, the trajectory is unable to access the deepest part of the H-O(A)–Xe well without also having to surmount the repulsive barrier generated in the T-shaped geometry. As a result, the trajectories tend to only sample the outer regions of the potential-energy well, and spend relatively little time there, giving a unimodal distribution at low time-in-well.

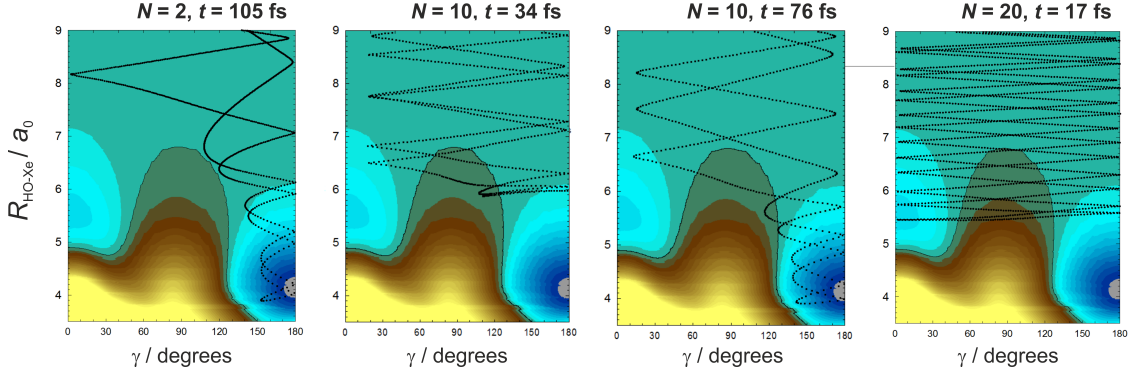


Figure 6.19: Pictorial projections of individual trajectories that began in a selection of N onto the $OH(A)+Xe$ PES. Each of the four panels corresponds to a single peak in Figure 6.18. The time, t , is the cumulative time spent in the $H-O(A)-Xe$ well, a region of the PES defined by $V \leq -1200 \text{ cm}^{-1}$ and $\gamma > 90^\circ$.

6.3 Depolarisation of angular momentum

Much like for RET, collisions that bring about the depolarisation of the angular-momentum distribution of the $OH(A)$ radical are most likely to occur in the potential-energy wells generated in the $O-H(A)-Rg$ and $H-O(A)-Rg$ geometries. This section first considers the *total* depolarisation of angular momentum: that is, the sum of the rotationally elastic and rotationally inelastic contributions to the depolarisation cross-sections, and then considers the trends shown in the j -resolved *elastic* cross-sections. These are defined as [110]:

$$\text{Total: } \sigma^{(k)} = \sum_{j'} \sigma_{jj'} \left(1 - a^{(k)}(j, j')\right), \quad (6.5)$$

$$\text{Elastic: } \sigma_{\text{el}}^{(k)} = \sigma_{jj'} \left(1 - a^{(k)}(j, j')\right), \quad j = j' \quad (6.6)$$

where $k = 1$ and $k = 2$ for disorientation and disalignment, respectively.

6.3.1 Total depolarisation: experimental data

Figures 6.20 and 6.21 compare experimental total depolarisation cross-sections [25, 26, 33, 226] with those from QCT TSH calculations run using Models 1-6. Note that the f_2 spin-rotation level does not exist for $N = 0$ and that there is no data point for disalignment of the $j = 0.5$ level. Both total disorientation and total disalignment data are presented for $OH(A)+Kr$. For the $OH(A)+Xe$

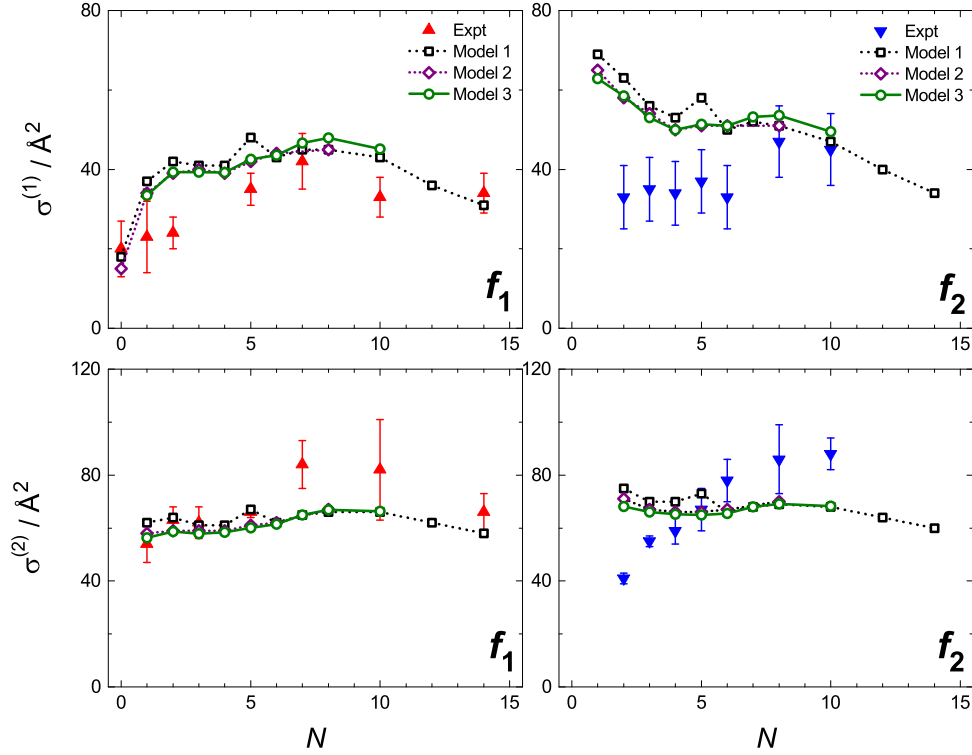


Figure 6.20: Comparison of experimental [25, 26, 33, 226] and theoretical total disorientation cross-sections, $\sigma^{(1)}$, and total disalignment cross-sections, $\sigma^{(2)}$, for the OH(A)+Kr system. Upward-pointing, red triangles denote f_1 spin-rotation levels and downward-pointing, blue triangles denote f_2 spin-rotation levels. The scatter points connected by lines refer to theoretical RET cross-sections generated from TSH QCT Models 1-3. Note the difference in scale of the y -axes. See text for details.

system, only disalignment cross-sections were determined experimentally, so no disorientation data are presented for this system.

Some general comments can be made about the trends shown by the total disorientation and total disalignment data for both rare-gas systems. Unlike for RET, there is a significant difference in the magnitude of the depolarisation cross-sections for OH(A)+Kr and OH(A)+Xe, and in the trend they exhibit with respect to rotational-level excitation. In general, the depolarisation cross-section is uniformly larger for the f_2 level since, for a given j , N will be higher for the f_2 spin-rotation level. Thus, a collision that is sufficient to bring about a change at higher N will also likely be depolarising. It is also the case that the difference in the cross-sections for the f_1 and f_2 levels becomes less noticeable as N increases and S makes a proportionally

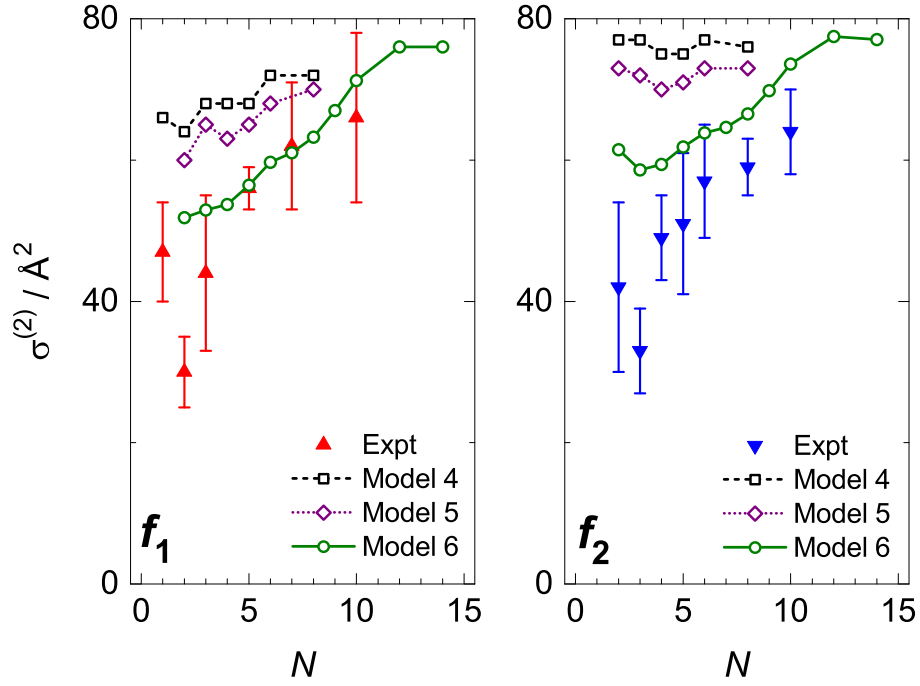


Figure 6.21: Comparison of experimental [25, 26, 33, 226] and theoretical total disalignment cross-sections, $\sigma^{(2)}$, for the $\text{OH}(A)+\text{Xe}$ system. Upward-pointing, red triangles denote f_1 spin-rotation levels and downward-pointing, blue triangles denote f_2 spin-rotation levels. The scatter points connected by lines refer to theoretical RET cross-sections generated from TSH QCT Models 4-6. See text for details.

lower contribution to the total spin-rotational-angular-momentum number, j .

Indeed, it is important to bear in mind that the magnitudes of experimentally determined depolarisation cross-sections are exaggerated by *dephasing*, a phenomenon that originates in that fact that, on going from $j \rightarrow j'$, there is a change in the g -value of the spin-rotation level. Thus, the angular-momentum distributions before and after the collisions precess at slightly different rates, leading to destructive interference and reducing the intensity of the recorded fluorescence decay in much the same way as depolarisation does. However, detailed simulations have revealed that dephasing contributes less than 10% to the total cross-section [33, 112], and so it is not considered further in this thesis.

The general trend shown by the experimental data is that the magnitude of the total disorientation and total disalignment cross-sections increases with rotational excitation. For the $\text{OH}(A)+\text{Kr}$ system, the trend appears to level off at higher

N , though this is not the case for OH(A)+Xe. Indeed, the behaviour of heaviest rare-gas system contrasts sharply with that exhibited by lighter rare-gas collision partners (such as OH(A)+He [7]) for which the magnitude of $\sigma^{(k)}$ is seen to fall with increasing N . In these systems, the increasing rotational angular momentum of the OH(A) radical leads to an averaging out of the PES such that it appears markedly less anisotropic. As a result, collisions in which there is sufficient transfer of angular momentum to bring about a change in the magnitude and/or direction of $\mathbf{N}$ occur less frequently as N increases.

6.3.2 Total depolarisation: comparison with theory

The use of TSH QCT models succeeds in reducing the magnitude of the theoretical depolarisation cross-sections beyond that predicted by adiabatic calculations [25, 26, 33, 226], however, the decrease is generally not sufficient to bring the theoretical data into agreement with experimental values. As with RET, the underestimation of non-adiabatic effects in the TSH QCT code means that the theoretical calculations over-predict the extent of depolarisation by suppressing the number of trajectories that undergo competitive quenching. The agreement between experiment and theory is thus seen to improve at higher N as the magnitude of the quenching cross-section falls.

The TSH QCT calculations for the OH(A)+Xe system show a marked improvement in their agreement with theory as the models become increasingly sophisticated. Indeed, for Model 6, there is quantitative agreement between the experimental and theoretical disalignment cross-sections for many of the N reported in Figure 6.21. This suggests that, as quenching has been modelled with increasing accuracy, the magnitude of the total depolarisation cross-sections has fallen accordingly. However, although the underestimation of quenching is believed to cause the majority of the observed discrepancy between experiment and theory for OH(A)+Xe, this cannot be the case for OH(A)+Kr. For this system, the TSH QCT quenching cross-sections agree almost quantitatively with those measured experimentally, and yet there remains a considerable level of disagreement between experiment and

N	T / fs	Modal time(s)-in-well / fs
2	404.48	90
10	94.47	10, 90
20	48.34	15

Table 6.1: Comparison of the rotational time period, T , of an $\text{OH}(\text{A})$ radical in a selection of rotational quantum levels, defined by N , and the approximate modal time(s)-in-well for trajectories that begin in the same rotational quantum levels. The rotational time periods have been calculated using a rotational constant of $B = 17.355 \text{ cm}^{-1}$ for the $\text{OH}(\text{A})$ radical.

theory for the depolarisation cross-sections. It is possible that these issues arise from inadequacies or inaccuracies in the PESs and the couplings between them. This will be discussed further in Section 6.4.

Table 6.1 presents a comparison of the modal time(s) that a given $\text{OH}(\text{A}) + \text{Xe}$ trajectory spends in the $\text{H-O}(\text{A})\text{-Xe}$ potential-energy well and the rotational time period, T , of the $\text{OH}(\text{A})$ radical at that particular N . The data reveal that the magnitude of the depolarisation cross-section is virtually independent of the time-in-well. In many systems, such as the $\text{S}(^1D) + \text{H}_2$ insertion reaction [233], *following collisions* – those in which the collision partners form a rotational complex that survives for several rotational periods – are those that most often result in the depolarisation of angular momentum. For the $\text{OH}(\text{A}) + \text{Xe}$ trajectories shown in Figures 6.18 and 6.19, and included in Table 6.1, $N = 10$ is the only rotational quantum level for which T is of a comparable magnitude to the time-in-well. For $N = 2$, the rotational time period of the rotational quantum level is much greater than the modal time-in-well. This is also true for the $N = 20$ rotational quantum level, however, the difference between the rotational time period and the modal time-in-well is reduced here. Nonetheless, in both cases, the depolarisation of angular momentum remains a very efficient process, and this notable behaviour (supported by the experimental results) is attributed to the highly anisotropic nature of the $\text{OH}(\text{A}) + \text{Xe}$ PES.

6.3.3 Elastic depolarisation: experimental data

As outlined at the beginning of this section, the use of a monochromator allows fluorescent radiation to be resolved into a single j' spin-rotation level, meaning it is possible to obtain experimental cross-sections for *elastic* depolarisation, *i.e.* that which comes about during collisions for which $j' = j$. Since these resolved cross-sections can also be extracted from the TSH QCT calculations, it is then possible to ascertain whether the disagreement between experiment and theory for the total depolarisation cross-sections can be attributed wholly or in-part to either rotationally elastic or rotationally inelastic collisions. By extension, calculating j -resolved cross-sections allows for a clearer characterisation of the interaction of quenching and depolarisation, since non-adiabatic effects are known to compete most effectively with inelastic collisions, and occur in different regions of the PES to elastic trajectories.

Figures 6.22 and 6.23 present a comparison between experimental elastic depolarisation cross-sections for the OH(A)+Kr and OH(A)+Xe systems and those generated from QCT TSH Models 1-6 [25, 26, 33, 226]. As before, both elastic disorientation and elastic disalignment data are reported for OH(A)+Kr, however, only elastic disalignment cross-sections are presented for OH(A)+Xe.

Within experimental error, the magnitude of the elastic disalignment cross-sections is constant as a function of increasing rotational excitation. This behaviour is also seen for the OH(A)+Ar system [6, 7, 227], and is assigned to the highly anisotropic nature of the OH(A)+Kr and OH(A)+Xe PESs. Rotational excitation, even at relatively high N , will not succeed in completely averaging out the anisotropy of the PES, and inelastic RET is achievable at all the N sampled in this work. The slight reduction in elastic depolarisation cross-section at low N is attributed to the fact that a higher proportion of collisions are rotationally inelastic in nature for trajectories that originate in low-energy rotational states.

6.3.4 Elastic depolarisation: comparison with theory

A comparison of experimental [25, 26, 33, 226] and QCT TSH cross-sections for elastic depolarisation reveals that, in general, the two share good agreement,

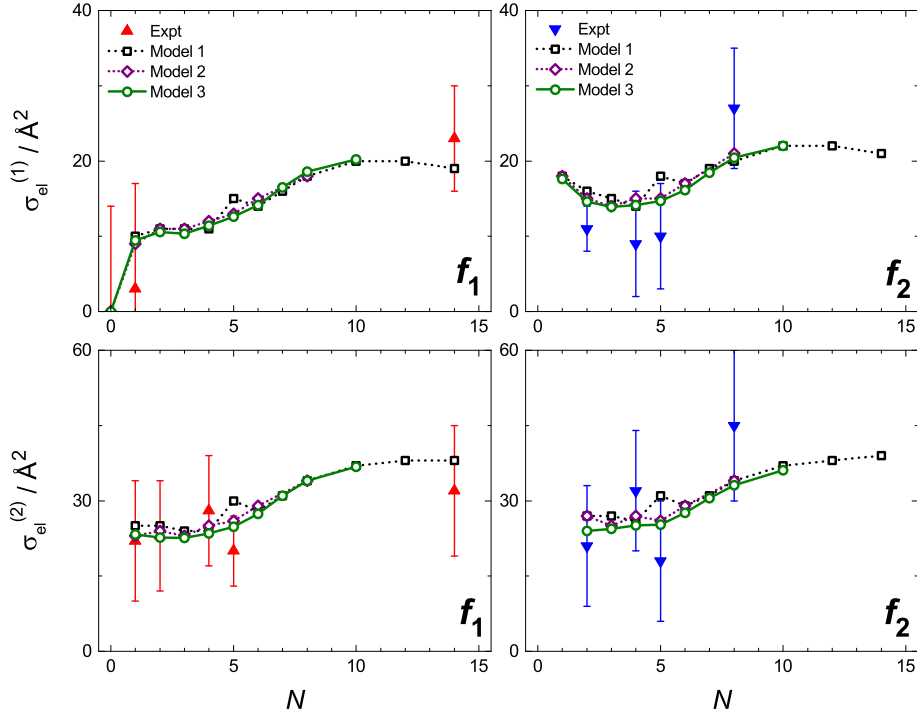


Figure 6.22: Comparison of experimental [25, 26, 33, 226] and theoretical elastic disorientation cross-sections, $\sigma_{el}^{(1)}$, and elastic disalignment cross-sections, $\sigma_{el}^{(2)}$, for the $OH(A)+Kr$ system. Upward-pointing, red triangles denote f_1 spin-rotation levels and downward-pointing, blue triangles denote f_2 spin-rotation levels. The scatter points connected by lines refer to theoretical elastic depolarisation cross-sections generated from TSH QCT Models 1-3. Note the difference in scale of the y -axes. See text for details.

especially for the $OH(A)+Kr$ system. It can thus be inferred that, in contrast to the trends shown by the RET and total depolarisation data, elastic depolarisation is relatively unaffected by electronic quenching. This is principally a result of the fact that the two processes are thought to occur in very different regions of the PES, with elastic depolarisation occurring at larger impact parameters and away from the $H-O(A)-Rg$ potential-energy well, where the majority of quenching takes place. The trends established by the data shown in Figures 6.20-6.23 thus confirm that the disagreement between the experimental and theoretical total depolarisation cross-sections can likely be attributed to poor modelling of the competitive interaction between inelastic depolarising collisions and those that undergo quenching.

A consideration of the closed-shell opacity functions for RET, elastic disalign-

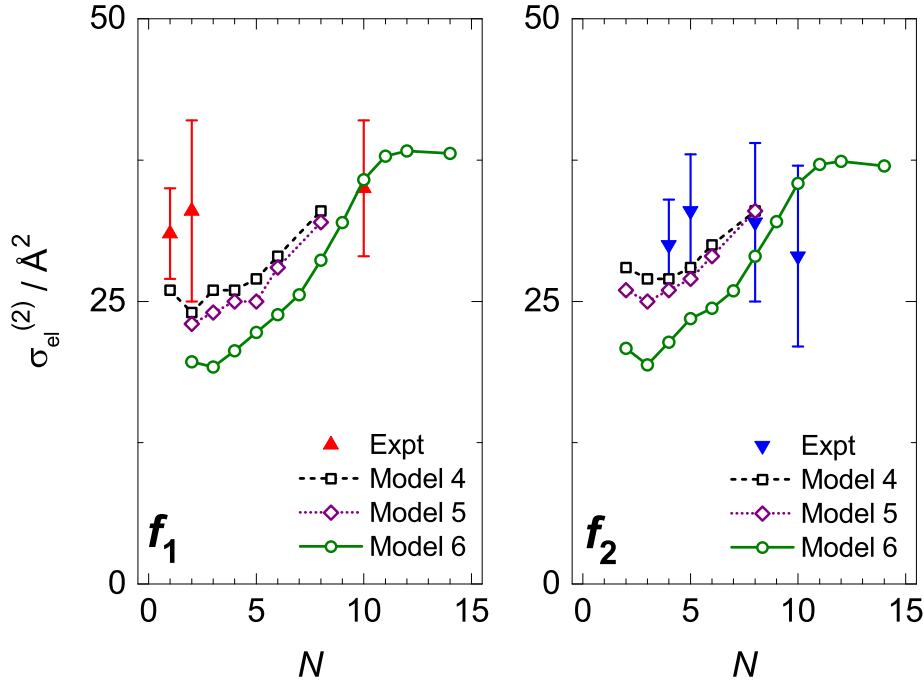


Figure 6.23: Comparison of experimental [25, 26, 33, 226] and theoretical elastic disalignment cross-sections, $\sigma_{\text{el}}^{(2)}$, for the OH(A)+Xe system. Upward-pointing, red triangles denote f_1 spin-rotation levels and downward-pointing, blue triangles denote f_2 spin-rotation levels. The scatter points connected by lines refer to theoretical elastic disalignment cross-sections generated from TSH QCT Models 4-6. See text for details.

ment, and quenching can help elucidate the interaction of these three dynamical processes. The opacity function, $P(b)$, expresses the probability that a particular type of collision event will take place as a function of impact parameter, b . Since the opacity function for elastic collisions does not converge in b , it is necessary to define the opacity function for elastic disalignment as [110]

$$P^{(2)}(b) = P(b) \left[1 - a^{(2)}(N, N') \right], \quad (6.7)$$

where $P(b)$ is the closed-shell opacity function and $a^{(2)}(N, N')$ is the $k = 2$ Legendre moment for closed-shell elastic ($N = N'$) disalignment, both as a function of b [110].

In Figure 6.24, it can be seen that, for both systems, the range of impact parameters that is able to bring about elastic disalignment is considerably greater than that which can effect inelastic RET or electronic quenching. The latter two processes involve larger changes in energy and so require trajectories with

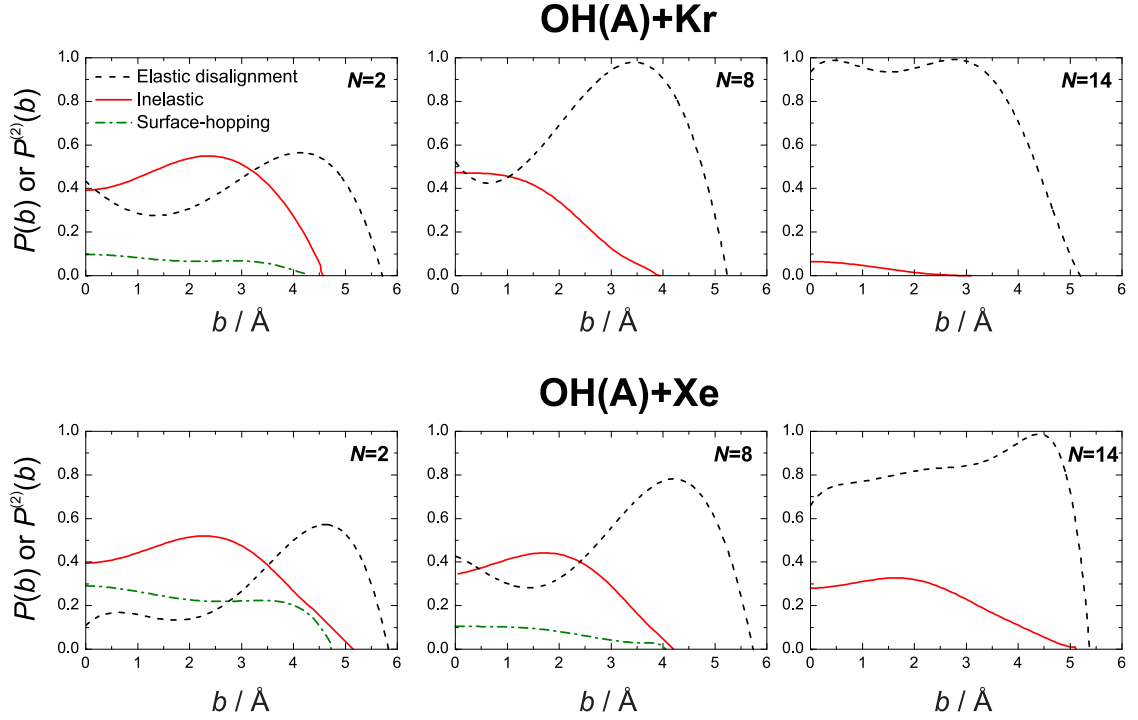


Figure 6.24: Closed-shell opacity functions, $P(b)$ and $P^{(2)}(b)$, for elastic disalignment, inelastic, and surface-hopping trajectories that originate in the $N = 2$, $N = 8$, and $N = 14$ rotational levels of the $OH(A)+Kr$ and $OH(A)+Xe$ systems. Note that surface-hopping opacity functions are only included for those rotational levels that have quenching cross-sections of non-negligible magnitude. See text for details.

smaller impact parameters that sample the most anisotropic regions of the PES, where the conical intersection is also located. It can also be seen that the peak in the elastic disalignment opacity function occurs at higher b than those for RET or electronic quenching, since the proportion of collisions that are elastic in nature increases in regions of the PES where inelastic/quenching collisions are energetically inaccessible. Furthermore, with increasing N , the magnitude of the quenching and RET opacity functions is seen to decrease, whereas that for elastic disalignment increases, in agreement with the cross-sections reported in the figures shown previously. A consideration of these opacity functions further confirms that it is the accuracy with which the competition between electronic quenching and adiabatic processes is modelled that fundamentally determines the quality of the agreement between experiment and theory.

Ultimately, it is rather surprising that the total depolarisation cross-sections

and, even more so, the elastic depolarisation cross-sections for both the OH(A)+Kr and OH(A)+Xe systems show such good agreement between experiment and theory. Given that this is not the case for quenching and RET, it can be inferred that the depolarisation of angular momentum takes place in different regions of the PES, away from the potential-energy wells that govern non-adiabatic and rotationally inelastic collisions. Thus, the accuracy with which electronic quenching is modelled has little effect on theoretical depolarisation cross-sections, which show invariably good agreement with experimental data. This is demonstrated particularly well by the total and elastic depolarisation data for OH(A)+Kr: the difference in the magnitudes of the depolarisation cross-sections generated by Models 1-3 is significantly less than that seen for quenching and RET. For the OH(A)+Xe system, the PES of which has much deeper potential-energy wells and extends to larger R , quenching and depolarisation are seen to interact more strongly and, as a result, there is a greater difference in the magnitudes of the theoretical total and elastic depolarisation cross-sections generated by Models 4-6.

6.4 Possible sources of error in current TSH QCT models

The data reported in this chapter have highlighted that, at present, there is still an unsatisfactory level of disagreement between experimental and TSH QCT data. Despite a number of major modifications to increase the completeness and accuracy of the *quasi*-classical models being used, the theoretical treatments currently available are unable to account fully for the experimentally observed collision dynamics of the OH(A)+Kr and OH(A)+Xe systems. A number of factors are believed to be responsible for the continued discrepancy between theory and experiment, and each of these is now discussed in turn.

As noted previously, spin-orbit coupling has been ignored in the different *quasi*-classical surface-hopping codes used to date, meaning that non-adiabatic effects are essentially modelled as $^1\Sigma - ^1\Pi$ transitions. In the past, the lack of spin-orbit coupling has not been considered a major source of disagreement between theory and

experiment [25, 26, 78, 204, 210]. However, it is possible that spin-orbit coupling is a necessary component of any model that can accurately predict the magnitude of theoretical quenching cross-sections for $\text{OH}(\text{A}) + \text{Kr/Xe}$. Spin-orbit coupling originates in the interaction of the magnetic moment of an electron (associated with its spin) with the magnetic field generated by its orbital motion. Non-adiabatic transitions in bimolecular collisions can then be mediated by spin-orbit coupling when either a reactant or a product has non-zero electronic orbital and spin angular momenta. This is certainly true for collisions that involve $\text{OH}(\text{A})$, an open-shell radical [41]. Indeed, recently, a combined experimental and theoretical study of the $\text{O}({}^1D) + \text{Xe}$ system by Garofalo *et al.* [234, 235] has successfully incorporated spin-orbit coupling into quantum-mechanical calculations for comparison with empirical DCSs. Since (for atoms) spin-orbit coupling has a Z^4 dependence, where Z is the effective nuclear charge, it is entirely possible that neglecting spin-orbit coupling is not appropriate for the heavier rare-gas systems investigated in this thesis. It is, therefore, recommended that future theoretical work investigate the effect of spin-orbit coupling on $\text{OH}(\text{A}) + \text{Kr/Xe}$ dynamics.

Section 5.6.1 described how the method of Lagrange multipliers [24] is used to force a rigid-rotor approximation, such that the bond length of the $\text{OH}(\text{A})$ radical is assumed to remain fixed at its equilibrium value over the course of a trajectory. Though this approximation has worked well in terms of predicting the dynamics observed when $\text{OH}(\text{A})$ collides with lighter rare gases, it is possible that this is not the case for $\text{OH}(\text{A}) + \text{Kr/Xe}$.

Work by Perkins [33] involved investigating both rotationally and vibrationally inelastic collisions of the $\text{OH}(\text{A}, v = 1) + \text{Kr}$ collision system. The aims of these experiments were: to quantify the vibrational energy process (VET) taking place, to assess whether vibronic coupling would affect the rate of electronic quenching, and, by extension, to study the resultant impact of vibrational excitation on the adiabatic processes with which quenching competes directly. Indeed, the introduction of vibrational excitation will add an r -dependence to the PES that describes the system and, as a consequence, could allow the *quasi*-classical trajectories to access

regions of the PES where non-adiabatic couplings are either enhanced or diminished. Although the conclusions drawn from Perkins' work [33] suggest that including a single quantum of vibrational energy does significantly increase the magnitude of σ_Q , it does not amplify the range of N over which quenching is observed. It is, therefore, possible that allowing for vibrational excitation in the OH(A)+Rg calculations could improve the agreement between experiment and theory at low N . However, it may not recover the lack of quenching currently predicted by theory at high N , where the disparity is largest. Novel QCT models, which consider the effect of the vibrational degree of freedom on the observed collision dynamics, are discussed in detail in Chapter 7.

As noted previously, although the adiabatic PESs and coupling matrix elements used in the TSH QCT models presented in this chapter were all calculated at the MRCISD+Q level of theory, the data for OH+Kr were generated using a CASSCF/aVTZ-DK basis and those for OH+Xe used a CASSCF/aVQZ-PP basis [236]. At the *ab initio* level, calculations at the CASSCF level can be used to perform single-point surface hops. A limited number of orbitals is selected to define the active space, which are then optimised (along with the corresponding expansion coefficients), to yield the CASSCF wavefunction. As such, the CASSCF wavefunction is able to account for the *static* interaction energy arising from electron-correlation effects and give a reasonably accurate description of electronic dynamics at conical intersections. However, the CASSCF method is largely unable to properly predict *dynamic* correlation effects that may prove important in OH+Rg systems where the nature of these effects can change rapidly with electronic state. Though the use of a larger active set does improve the outcome, this solution is often impeded by vastly increased computational demands and costs [236]. It is possible that the levels of theory used to generate the surfaces and elements for the calculations reported here are not sufficiently rigorous and/or compatible to accurately reproduce experimental observations, and it is recommended that future work should aim to address this uncertainty.

6.5 Summary

This chapter has outlined the results of a rigorous theoretical investigation into the dynamics of hydroxyl radicals in the first electronically excited state, $\text{OH}(\text{A})$, when they undergo collisions with heavy rare-gas atoms (Kr and Xe). Electronic quenching dynamics, and their competitive interaction with rotationally inelastic, electronically adiabatic processes have been the primary focus of this chapter. To this end, a range of 2D *quasi*-classical trajectory surface-hopping calculations have provided an informative insight into the dynamics that underpin $\text{OH}(\text{A}, v = 0) + \text{Rg}$ collisions.

For many of the dynamical quantities that describe the $\text{OH}(\text{A}, v = 0) + \text{Kr}$ system, quantitative agreement between experiment and theory has been achieved for the first time. For the $\text{OH}(\text{A}, v = 0) + \text{Xe}$ system, theory continues to underestimate the extent of electronic quenching observed experimentally, and this impacts negatively on the resultant agreement between experiment and theory for the adiabatic processes with which quenching is seen to compete. A number of suggestions that may explain the persistent discrepancies for the $\text{OH}(\text{A}, v = 0) + \text{Xe}$ system have also been outlined in detail. It is, therefore, hoped that the conclusions drawn from this chapter will inform future theoretical work on the $\text{OH}(\text{A}, v = 0) + \text{Rg}$ systems.

7

Developing 3D models of OH(A, $v = 0/1$)+Kr collision dynamics

All the *ab initio* calculations that have been reported previously in this thesis were run with the OH bond length fixed at its equilibrium value in the A electronic state: 1.012 Å. It was noted in the preceding chapter that, even though the most complete 2D QCT model of OH(A, $v = 0$)+Kr successfully recovers 93% of experimentally observed quenching, there is significant disagreement between experiment and theory for the data relating to the total depolarisation of angular momentum. It can thus be inferred that, regardless of how well the current QCT algorithms are able to predict non-adiabatic dynamics in the OH(A)+Kr system, there remain issues with how adiabatic processes (such as the depolarisation of angular momentum) are modelled on the excited-state OH(A)+Kr PES.

It is possible that the use of the rigid-rotor approximation for the OH(A) radical is at least partly responsible for the disagreement between experiment and theory. To that end, this chapter considers the effect of introducing an additional degree of freedom into the QCT models described previously by allowing the OH bond length, r , to vary prior to (and, in later models, over the course of) a given trajectory. The development of these theoretical models, which will consider the effect of vibrational excitation on rotationally inelastic collisions of OH(A)+Kr for the first

time, are intended to complement experimental data already collected by Perkins [33]. The work presented here was carried out in collaboration with Dr Pablo Jambrina at Universidad Complutense de Madrid.

It is thought that the introduction of a quantum of vibrational energy into the current QCT models of the OH(A)+Kr system could potentially influence the outcome of calculations in two main ways: firstly, through vibronic coupling and, secondly, from the *r*-dependence of the PES(s). The work presented in the previous chapter outlined how the inclusion of roto-electronic coupling in current TSH QCT models has led to almost quantitative agreement between experiment and theory for a number of dynamical processes in the OH(A, *v* = 0)+Kr system. It is, therefore, possible that vibronic coupling may be responsible for the enhanced cross-sections observed experimentally for inelastic processes in OH(A, *v* = 1)+Kr dynamics. It could also be the case that changes in *r* allow trajectories to access regions of the PES where coupling to the grounds state is enhanced or diminished. If this is the case, the magnitude of the electronic quenching cross-section will vary accordingly, as will the cross-sections of other inelastic processes with which non-adiabatic effects have been shown to compete. This chapter will focus on improving our understanding of the *r*-dimension of the PESs.

7.1 *r*-dependent adiabatic PES

Figure 7.1 shows contour plots of 3D MRCISD+Q 2A' and 1A' PESs for the OH+Ar [237] and OH+Kr [238] systems where the angle, γ , between the OH bond vector, $\mathbf{r}$, and the vector between the centre-of-mass of the OH radical and Rg, $\mathbf{R}$, has been fixed at $\gamma = 175^\circ$. The plots on the right of the figure show the same PESs over a much smaller range of *r*. The dashed, white lines on the figures on the right delimit r_e for isolated OH(A) as well as the equilibrium values of *r* in the *v* = 0 and *v* = 1 vibrational levels. The relevant bond lengths were obtained using the vibrational-state-dependent rotational constants, B_v , quoted in Huber and Herzberg [115], with

$$B_v = \frac{h}{8\pi^2 c I_v}, \quad (7.1)$$

where I_v is the vibrational-state-dependent moment of inertia and the other constants have their usual meaning.

For both systems, the depth of the near-linear H-O(A)–Rg potential-energy well is seen to decrease with increasing r , emphasising that, as the OH radical becomes vibrationally excited, the conical intersection with the ground-state $1A'$ surface will occur closer to the bottom of the H-O(A)–Rg well. A consideration of the $1A'$ surface shown for the OH(X)+Kr system reveals that there is very little variation in the ground-state surface with r . This agrees with the semi-empirical surfaces for OH(X)+Kr reported by Sumiyoshi and co-workers in reference [239]. Thus, any dynamical effects that result from vibrational excitation can largely be attributed to changes in the excited-state $2A'$ surface.

Figure 7.2 shows slices through the 3D OH(A)+Ar and OH(A)+Kr PESs at $\gamma = 175^\circ$ for various values of r . As in Figure 7.1, the plots presented here clearly show that the H-O(A)–Rg potential-energy well becomes shallower as the OH bond length increases with vibrational excitation. This may facilitate an increased rate of electronic quenching by shifting the conical intersection between the excited-state and ground-state PESs to a more energetically accessible position. From a comparison of the plots for OH(A)+Ar and OH(A)+Kr, it is clear that: the H-O(A)–Kr well is consistently deeper than that of H-O(A)–Ar for the three values of r sampled, and that the effect of changing r is somewhat less significant for the well depth of H-O(A)–Kr than it is for that of H-O(A)–Ar.

It can be seen in Figures 7.1 and 7.2 that the effect of changing r over the course of a trajectory will have an impact on the dynamics of both the OH(A)+Ar and OH(A)+Kr systems. It is also true that an enhancement in electronically and/or rotationally inelastic cross-sections may be brought about by the increase in the capacity for vibronic coupling on increasing r . At the time of writing, vibronic coupling matrix elements were not available for the newly generated surfaces, and so they are not considered further in this thesis. It is recommended that future theoretical work should focus on including this coupling in the TSH code.

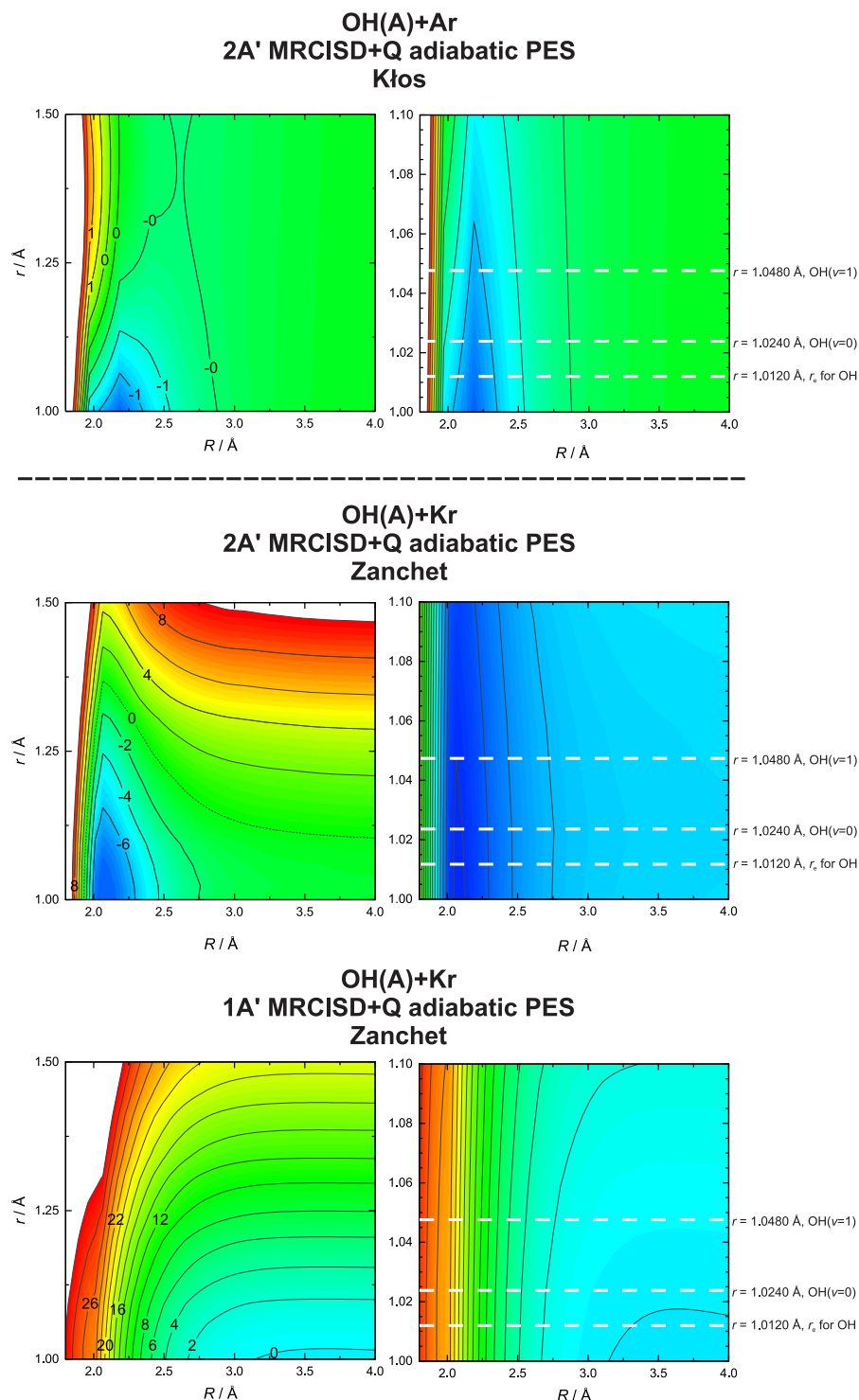


Figure 7.1: Comparison of MRCISD+Q adiabatic PESs for the OH(A)+Ar [237] and OH(A)+Kr [238] systems as a function of r and R in the near-linear H-O(A)–Rg geometry ($\gamma = 175^\circ$). The values on the surfaces give the potential energy in 10^3 cm^{-1} . Note the difference in colour scales of the Ar and Kr contour plots. Upper and middle panels: The excited-state 2A' PESs for OH(A)+Ar and OH(A)+Kr. For both systems, the depth of the H-O(A)–Rg potential-energy well is seen to decrease with increasing r . Lower panel: The 1A' PES for the OH(X)+Kr system. The plot shows that the variation in potential energy with r is much less pronounced in the electronic ground state of OH than in the first excited state.

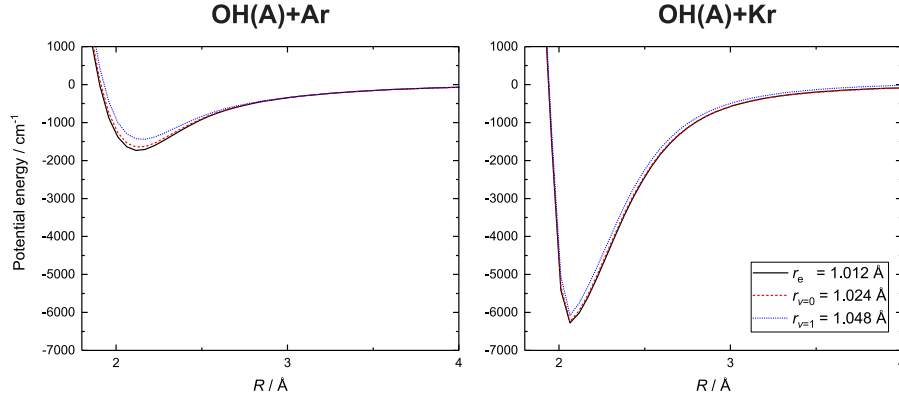
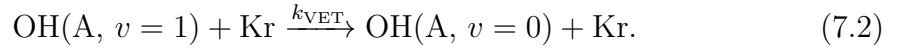


Figure 7.2: Cross-sectional slices through the 3D OH(A)+Ar and OH(A)+Kr $2A'$ PESs at $\gamma = 175^\circ$ for various values of r .

7.2 Theoretical results: rotational energy transfer

The experiments reported in reference [33] measured three different dynamical processes in the OH(A, $v = 1$)+Kr system: quenching, RET, and vibrational energy transfer (VET), where the latter can be summarised as



This work revealed that, over the range of rotational states investigated by Perkins ($N = 0 - 7$), the magnitude of the VET cross-section is small (around $\sigma = 0.5 \text{ \AA}^2$) and generally constant within experimental error. In comparison to the quenching and RET cross-sections, those for VET may be deemed to have near-negligible magnitude; indeed, at low N , σ_{Q} and σ_{RET} are nearly two orders of magnitude larger than σ_{VET} . As such, electronic quenching and RET are seen to dominate the inelastic collision dynamics of OH(A, $v = 1$)+Kr.

It has also been confirmed by others that the magnitude of σ_{VET} is largely independent of both the nature of the monatomic collision partner and the rotational state of the OH radical in OH(A, $v = 1$)+Rg systems [240–242]. The negligible degree of VET in these systems can be explained by considering the timescale of the translational and vibrational motions involved. If a molecule that is vibrating on a femtosecond timescale is to convert its vibrational energy into the translational

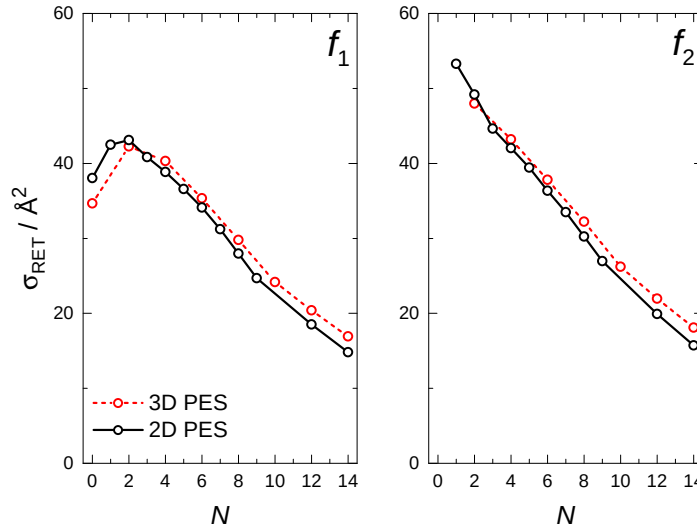


Figure 7.3: RET cross-sections generated from batches of adiabatic, fixed- r QCT calculations run on the 2D and 3D PESs for the OH(A)+Kr system with fixed values of $E_{\text{coll}} = 0.039$ eV and $r = 1.012$ Å. Data are shown for both the f_1 ($j = N + S$) and f_2 ($j = N - S$) manifolds.

energy of a monatomic collision partner, the collision between the two species must also take place on a femtosecond timescale [41, 243]. Data reported in reference [226] have confirmed that the OH(A)+Kr collisions investigated in this thesis occur over a period of nanoseconds and, therefore, they fail to generate the energy-sudden conditions necessary for efficient VET. In contrast, effective VET (with cross-sections of the same order of magnitude as σ_Q , if not larger) has been reported in collisions between OH(A, $v = 1$) and diatomic molecules such as O₂ [242, 244], N₂ [240, 242, 244], H₂ [240, 241], and D₂ [240, 241]. For these systems, the rotational and vibrational degrees of freedom of the diatomic collision partner are able to undergo femtosecond-scale energy transfer and so facilitate VET from OH(A, $v = 1$).

In this section, RET cross-sections from calculations run on the new 3D OH(A)+Kr PES are presented and, where possible, these are compared both with those run on the 2D surface and with experimental data [33]. By examining the effect of increasing r on the magnitude of cross-sections for RET, it is possible to better understand the r -dimension of the PES and its influence on rotationally inelastic OH(A)+Kr dynamics.

In the first instance, it was necessary to probe the agreement between theoretical data from adiabatic QCT calculations run under identical conditions using the 2D OH(A)+Kr PES of Kłos and the 3D OH(A)+Kr PES of Zanchet. Figure 7.3 shows a comparison of open-shell RET cross-sections from calculations run on both surfaces at a fixed collision energy of 0.039 eV and with $r = 1.012 \text{ \AA}$ (r_e in the OH(A) state) for a range of N . As can be seen in the data for both the f_1 and f_2 manifolds, the agreement between the two sets of theoretical results is very good, though it is worth noting that the points shown were generated from running 1×10^5 trajectories on the 2D surface and 5×10^3 trajectories on the 3D surface. Error bars are not included for the sake of clarity. Based on the good agreement between the two sets of data, it was decided to run calculations at larger, fixed values of r on the 3D surface to probe the effect of vibrational excitation on the system's dynamics.

7.2.1 Fixed- r QCT calculations on 3D PES

Before considering variable- r algorithms, it is helpful to model OH(A, v)+Kr dynamics on a set of vibrationally averaged PESs, where the value of r is fixed at that corresponding to the appropriate vibrational state and does not change over the course of a given trajectory. Figure 7.4 shows RET cross-sections generated from adiabatic QCT calculations run on the 3D PES for OH(A)+Kr at various, fixed values of r :

- $r = 1.012 \text{ \AA}$, r_e in isolated OH(A);
- $r = 1.024 \text{ \AA}$, the equilibrium value of r for $v = 0$; and
- $r = 1.048 \text{ \AA}$, the equilibrium value of r for $v = 1$.

The data show the effect of vibrational excitation on the probability that a given collision will be rotationally inelastic in nature. As such, it can be seen clearly that, as the OH bond lengthens, the magnitude of σ_{RET} increases.

As for the adiabatic calculations run the 2D surface previously, it is not possible to achieve quantitative agreement between theory and experiment when cross-sections

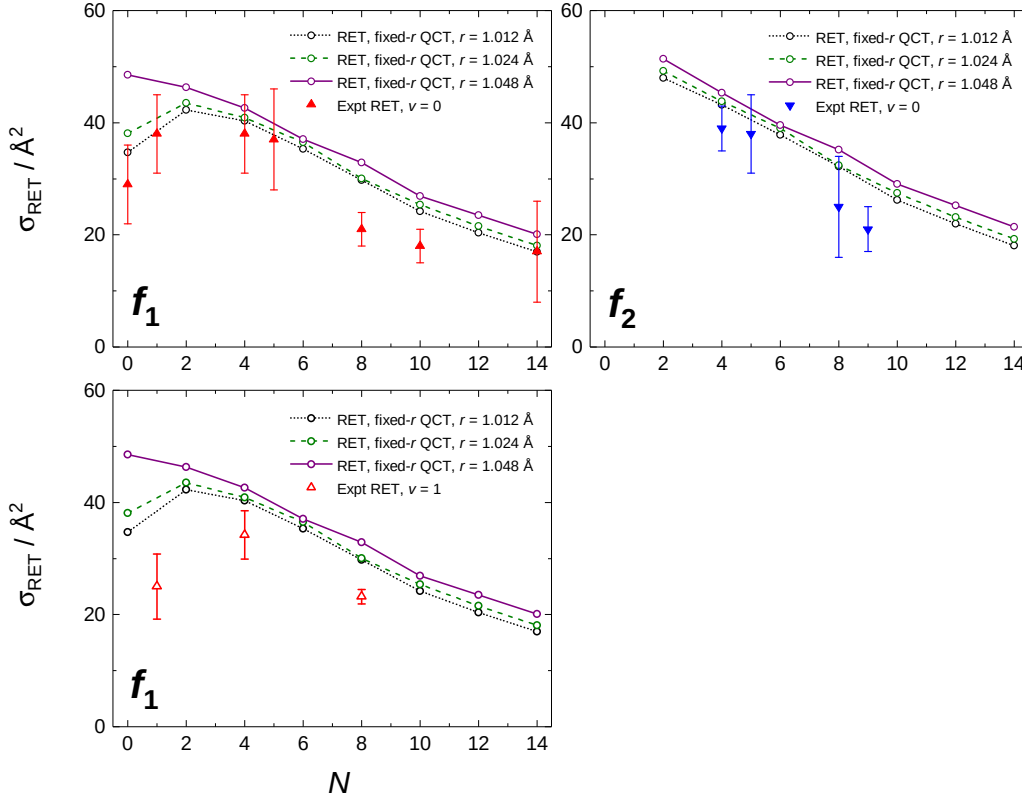


Figure 7.4: Upper panels: Comparison of experimental RET cross-sections for the $\text{OH}(A, v=0) + \text{Kr}$ system with those generated from batches fixed- r adiabatic QCT calculations at $E_{\text{coll}} = 0.039$ eV. Data are shown for both the f_1 ($j = N + S$) and f_2 ($j = N - S$) manifolds. Lower panels: Comparison of experimental RET cross-sections for the $\text{OH}(A, v=1) + \text{Kr}$ system with those generated from batches of fixed- r adiabatic QCT calculations at $E_{\text{coll}} = 0.039$ eV. Data are only shown for the f_1 ($j = N + S$) manifold since f_2 data ($j = N - S$) were not recorded.

for RET alone are compared directly. Indeed, as before, failing to include non-adiabatic surface-hopping in the QCT code means that the calculated RET data from the 3D surface consistently overestimate those measured experimentally. However, as shown in Figure 7.5, the theoretical adiabatic RET data are generally in better agreement with experimental ‘total-removal’ cross-sections, *i.e.* those generated by summing the cross-sections for quenching and RET to quantify the total depletion of population from any given $\text{OH}(A, v, j, f_i)$ state. Note that, in this instance, the total-removal cross-sections did not include VET, since the magnitude for this process is negligible [33]. The agreement shown here emphasises that the discord

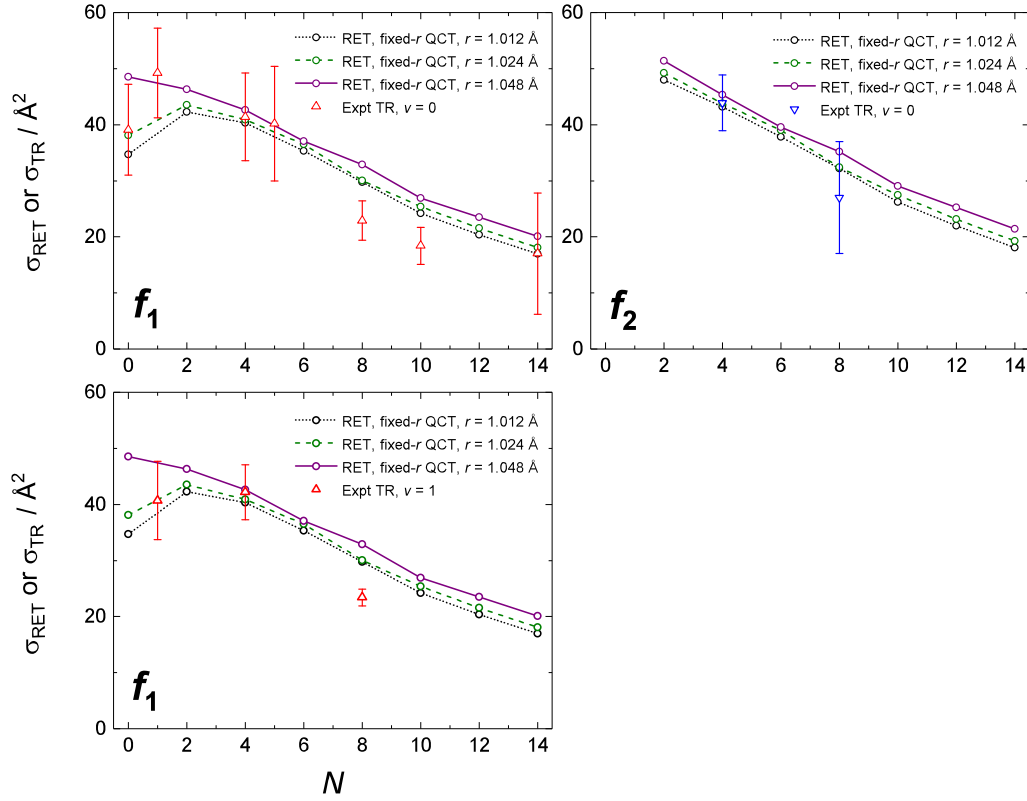


Figure 7.5: Upper panels: Comparison of experimental total-removal cross-sections for the $\text{OH}(\text{A}, v=0) + \text{Kr}$ system with theoretical RET cross-sections generated from batches fixed- r adiabatic QCT calculations at $E_{\text{coll}} = 0.039 \text{ eV}$. Data are shown for both the f_1 ($j = N + S$) and f_2 ($j = N - S$) manifolds. Lower panels: Comparison of experimental total-removal cross-sections for the $\text{OH}(\text{A}, v=1) + \text{Kr}$ system with theoretical RET cross-sections generated from batches of fixed- r adiabatic QCT calculations at $E_{\text{coll}} = 0.039 \text{ eV}$. Data are only shown for the f_1 ($j = N + S$) manifold since f_2 data ($j = N - S$) were not recorded.

between the experimental and theoretical RET cross-sections reported is most likely due to the lack of surface-hopping in the adiabatic QCT model of $\text{OH}(\text{A}) + \text{Kr}$.

7.2.2 Variable- r QCT calculations on 3D PES

Figure 7.6 presents the first sets of RET cross-sections generated from adiabatic QCT calculations, run on Zanchet's 3D $\text{OH}(\text{A}) + \text{Kr}$ surface, during which the value of r was allowed to vary over the course of the collision [245]. At the start of each trajectory, the initial value of r , r_i , was set for the appropriate vibrational level; it was then allowed to vary as the trajectory was propagated over the PES. As such,

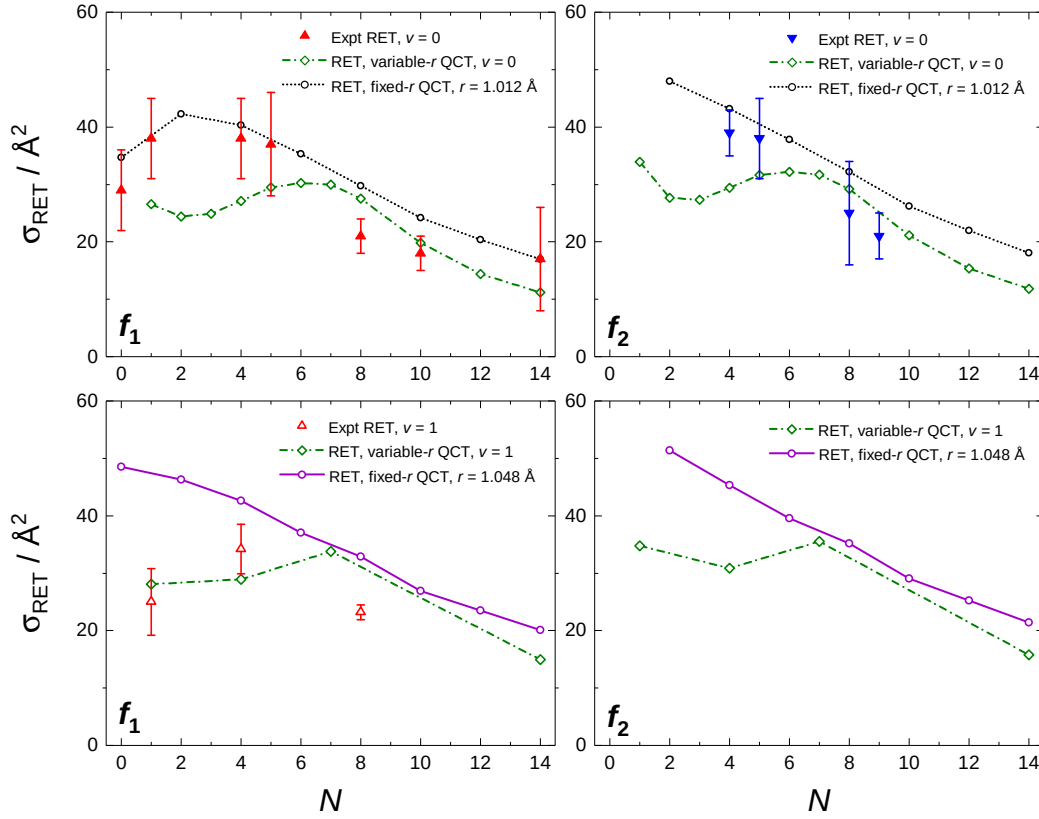


Figure 7.6: Upper panels: Comparison of experimental RET cross-sections with those generated from batches of variable- r and fixed- r (with $r = 1.012 \text{ \AA}$) adiabatic QCT calculations for the $\text{OH}(\text{A}, v = 0) + \text{Kr}$ system at $E_{\text{coll}} = 0.039 \text{ eV}$. Data are shown for both the f_1 ($j = N + S$) and f_2 ($j = N - S$) manifolds. Lower panels: Comparison of experimental RET cross-sections with those generated from batches of variable- r and fixed- r (with $r = 1.048 \text{ \AA}$) adiabatic QCT calculations for the $\text{OH}(\text{A}, v = 1) + \text{Kr}$ system at $E_{\text{coll}} = 0.039 \text{ eV}$. Experimental data are only shown for the f_1 ($j = N + S$) manifold since f_2 data ($j = N - S$) were not recorded.

these calculations constitute the first set of variable- r trajectories that were used to model the r -dependence of inelastic processes in both the $\text{OH}(\text{A}, v = 0) + \text{Kr}$ and $\text{OH}(\text{A}, v = 1) + \text{Kr}$ systems.

In Figure 7.6, the theoretical RET data are compared to experimental RET cross-sections that were measured in the $v = 0$ and $v = 1$ vibrational states, and also to fixed- r calculations in which the bond length was set at $r = 1.012 \text{ \AA}$ and $r = 1.048 \text{ \AA}$, respectively, over the course of the entire trajectory. In addition, Figure 7.7 shows a comparison of experimental total-removal cross-sections with

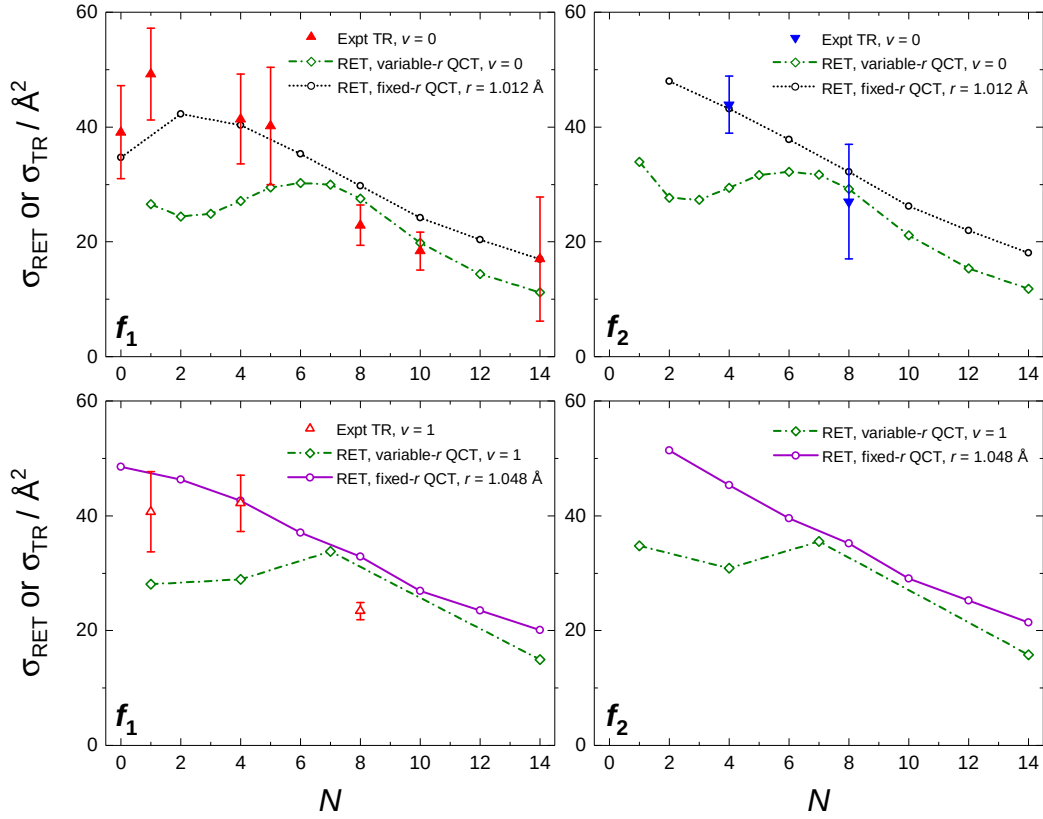


Figure 7.7: Upper panels: Comparison of experimental total-removal cross-sections with those generated from batches of variable- r and fixed- r (with $r = 1.012 \text{ \AA}$) adiabatic QCT calculations for the $\text{OH}(\text{A}, v = 0) + \text{Kr}$ system at $E_{\text{coll}} = 0.039 \text{ eV}$. Data are shown for both the f_1 ($j = N + S$) and f_2 ($j = N - S$) manifolds. Lower panels: Comparison of experimental total-removal cross-sections with those generated from batches of variable- r and fixed- r (with $r = 1.048 \text{ \AA}$) adiabatic QCT calculations for the $\text{OH}(\text{A}, v = 1) + \text{Kr}$ system at $E_{\text{coll}} = 0.039 \text{ eV}$. Experimental data are only shown for the f_1 ($j = N + S$) manifold since f_2 data ($j = N - S$) were not recorded.

the same theoretical RET data that are reported in Figure 7.6.

From the theoretical data, it can be seen that there is a significant decrease in the magnitude of σ_{RET} for all N when r is allowed to vary over the course of a trajectory in variable- r calculations. Moreover, the trend shown by these data with respect to rotational excitation in $\text{OH}(\text{A}, v = 1)$ is also different: for the fixed- r calculations, there is a gradual decrease in the magnitude of σ_{RET} with increasing N ; in contrast, the variable- r cross-sections are seen to peak at $N = 6 - 7$, and fall off slightly at both lower and higher N .

Interestingly, the variable- r RET data lie almost within the error bars of the $v = 1$ experimental RET data shown in Figure 7.6. In contrast, the variable- r calculations consistently underestimate experimentally observed RET in $v = 0$, especially at low N . In terms of the comparison of experimental total-removal cross-sections with variable- r theoretical RET data, the agreement is generally poorer: for both the $v = 0$ and $v = 1$ states, the variable- r calculations fail to reproduce the full magnitude of the experimental total-removal cross-section, particularly at low N . As discussed previously, it would be expected that adiabatic RET cross-sections should show the best agreement with experimental total-removal cross-sections, since the former do not account for the quenching that is observed experimentally in both the $\text{OH}(\text{A}, v = 0) + \text{Kr}$ and $\text{OH}(\text{A}, v = 1) + \text{Kr}$ systems. As such, it is somewhat surprising that the variable- r calculations show slightly better agreement with experimental RET cross-sections than with experimental total-removal data.

It is possible that there are inherent issues with how well these *quasi*-classical calculations are able to model the vibrational degree of freedom in $\text{OH}(\text{A})$. As noted previously, the quantum of vibrational energy with which the OH radical begins can leak out into other (rotational) degrees of freedom during the classical regime of the trajectory and give rise to unphysical RET that violates the requirement for vibrational zero-point energy. To that end, it may prove helpful to develop a semi-classical treatment of this system in which, for example, vibration and rotation are treated quantum mechanically and translation is treated classically [246–250].

Previously, and independently, Bowman and coworkers [251] and Miller and coworkers [252] outlined a method by which to include a zero-point energy constraint in QCT calculations: the sign of the momentum vector is changed when the energy of any vibrational mode approaches the zero-point energy. Though this method did prevent energy from going below the zero-point energy, the instantaneous change in momentum (equivalent to an impulse of infinite magnitude) was found to be too abrupt, and led to noise in the classical correlation functions. Alternatively, Xie and Bowman suggest turning off coupling to a particular vibrational mode if the energy

drops below the zero-point energy [253]. Indeed, it would certainly prove interesting to investigate the application of such treatments to the OH(A, $v = 1$)+Kr system.

In general, it should also be stressed that the effect of vibration on the magnitude of the experimental RET cross-sections reported in reference [33] is minimal: indeed, the cross-sectional values reported for the $v = 1$ state lie within the margins of error of those recorded for $v = 0$. It is, of course, also important to bear in mind that, since only three data points were measured experimentally for RET in ($v = 1$, f_1), and no data were recorded at all for the ($v = 1$, f_2) manifold, it is difficult to properly assess the extent of agreement between experiment and theory for vibrationally excited OH(A). Thus, it can be said that RET may not be the most useful metric with which to try to understand the impact of vibrational excitation; instead, the 3D code must be expanded to include vibrationally dependent non-adiabatic coupling. To that end, it is recommended that future work should aim to develop a set of variable- r TSH QCT algorithms to generate theoretical quenching cross-sections that can undergo rigorous comparison with experimental data.

7.3 Summary

This chapter has reported a novel investigation into the role played by the vibrational degree of freedom of the OH radical on rotationally inelastic collisions in the OH(A, $v = 1$) + Kr system. In the first instance, a set of newly calculated, variable- r PESs [238] for OH(A)+Kr and OH(X)+Kr are presented and discussed. The excited-state surface was also compared to a previously calculated, 3D surface for OH(A)+Ar [237].

Following this, a comparison was drawn between experimental RET and total-removal data collected by Perkins [33] and novel adiabatic calculations that were run on the newly calculated OH(A)+Kr surface. Firstly, RET cross-sections from calculations that were run on the 2D surface of Kłos were compared to the results of a set of fixed- r ($r = 1.012$ Å) calculations on the 3D surface of Zanchet to confirm that the two were in good agreement. Secondly, RET and total-removal experimental cross-sections were compared to data drawn from adiabatic calculations in which

the OH bond length was fixed at several different values to reflect the change in r on vibrational excitation. It was found that increasing the OH bond length led to modest increases in the magnitude of σ_{RET} and that the calculated data generally lay within experimental error for both RET and total-removal data.

Finally, experimental data relating to both RET and total removal in the $\text{OH}(\text{A}, v = 0) + \text{Kr}$ and $\text{OH}(\text{A}, v = 1) + \text{Kr}$ systems were compared to the first results of novel, variable- r calculations in which the bond length of OH was allowed to vary over the course of the trajectory. However, as the experimental data for RET from $v = 1$ are relatively sparse, it is recommended that future work should aim to devise a set of variable- r TSH QCT algorithms to generate theoretical data that can be compared to the more extensive set of $v = 1$ experimental quenching cross-sections reported in reference [33].

8

Conclusions and future outlook

This chapter summarises the main conclusions drawn from the experimental and theoretical work reported in this thesis, and highlights a number of suggestions for future lines of investigation.

8.1 Conclusions

The primary aims of this thesis were two-fold. Firstly, the major experimental goal was to commission, characterise, and optimise a crossed-molecular beam machine, including a hexapole state-selector apparatus, that could be used to investigate the fully quantum-state-resolved, rotationally inelastic collisions of simple molecules with rare-gas partners. Secondly, a principal aim of this work was to continue the development of novel, trajectory surface-hopping, *quasi*-classical trajectory algorithms that probed non-adiabatic effects in the electronically and rotationally inelastic collisions of the $\text{OH}(\text{A}, v = 0) + \text{Kr}$ and $\text{OH}(\text{A}, v = 0) + \text{Xe}$ systems. In addition, this thesis also reported provisional, theoretical rotational energy transfer cross-sections that were calculated on a novel, variable- r PES for the $\text{OH}(\text{A}) + \text{Kr}$ system. In these calculations, the bond length of the OH radical was allowed to vary over the course of the trajectory, allowing for an investigation into the r -dependence of the PES for the first time.

Chapter 3 of this thesis reported experimental and theoretical data relating to the rotationally inelastic scattering of $\text{NO}(\text{X})+\text{Ar}$ at three different collision energies: 469 cm^{-1} , 1480 cm^{-1} , and 2210 cm^{-1} . This non-reactive collision system, which has been studied extensively in other work [15, 21, 22, 35, 38, 79–96], was chosen to calibrate and characterise a newly commissioned CMB machine. To that end, the data collected at 469 cm^{-1} and 1480 cm^{-1} , which came about from the first scattering experiments to be conducted on this apparatus, were used to: maximise the overlap of the molecular beams and probe lasers in time and space, refine the ion-optics, detector, and camera settings necessary for decent velocity-map imaging, and determine the numerous input parameters for the analysis programs that were used to generate fitted images and experimental DCSs. The empirical data collected were subjected to rigorous comparison with quantum-mechanical calculations and were generally found to be in good agreement with theory in that the calculations successfully reproduced the number, angular distribution, and relative intensity of the peaks in the fitted DCSs (within the limit of current experimental resolution).

Following this, an extensive set of experimental images (which included scattering into the full range of energetically accessible rotational states for spin-orbit-conserving and spin-orbit-changing collisions) were collected at a collision energy of 2210 cm^{-1} . This energy is considerably higher than any other reported in the literature and, as such, provided a unique opportunity to study high-energy dynamics of the $\text{NO}(\text{X})+\text{Ar}$ system by probing the repulsive region of the PES. Fully quantum-mechanical calculations were found to reproduce the trends shown in the empirical data relatively well. Detailed consideration was given to the various input parameters for both the simulation and fitting procedures used in this work in an attempt to account for currently observed discrepancies at low and high θ in the DCSs. To that end, it is recommended that future work continue to refine and optimise the instrument function used in the simulation and fitting algorithms in order to model experimental reality more accurately.

Chapter 4 of this thesis presented a combined experimental and theoretical study of the rotationally inelastic scattering of $\text{ND}_3(\tilde{\text{X}}) + \text{Ar}$ at a collision energy of

405 cm^{-1} . These experiments were the first to involve the use of a newly commissioned hexapole state-selector apparatus, which required meticulous calibration to ensure that the voltages applied to the hexapole rods generated a high-density gas pulse of optimal rotational-state purity. The experimental images that were recorded were subjected to rigorous analysis and interpretation, including, but not limited to: a direct comparison with experimental data collected previously at a similar collision energy [160], an assessment of the agreement between the experimental data and fully quantum-mechanical calculations [46, 160], and a number of additional, in-depth analyses that aimed to confirm the accuracy of the fitting algorithms used elsewhere in this work. Ultimately, the experimental data showed good agreement with those collected previously and with the output of quantum-mechanical calculations, in that each data set confirms that the $\mathbf{k} - \mathbf{k}'$ distribution is intensely forward-scattered for all the states that are readily detectable by REMPI-VMI techniques.

Chapters 5 and 6 outlined the continued development of novel theoretical treatments of non-adiabatic effects in the $\text{OH}(\text{A}, v = 0) + \text{Kr}$ and $\text{OH}(\text{A}, v = 0) + \text{Xe}$ systems. In this work, currently available 2D, three-state, TSH QCT algorithms [25, 26, 33, 226] were expanded to include the full range of electrostatic and roto-electronic couplings for the $\text{OH}(\text{A}, v = 0) + \text{Kr}$ system. Combined with the use of variable-collision-energy (rather than fixed-energy) algorithms, the most complete QCT model of $\text{OH}(\text{A}, v = 0) + \text{Kr}$ has produced near-quantitative agreement between experiment and theory for a range of dynamical processes. Indeed, calculated cross-sections for electronic quenching recovered 93% of the non-adiabaticity observed experimentally. Moreover, QCT cross-sections for rotational energy transfer and the depolarisation of the angular momentum of the OH radical have shown decent agreement with experiment. An estimation of the matrix elements that have not yet been calculated for the $\text{OH}(\text{A}, v = 0) + \text{Xe}$ system, along with the use of variable-collision-energy algorithms, led to a considerable improvement in the agreement between calculated and empirical data (such that the most complete model is able to recover 63% of experimentally observed quenching). However, theoretical calculations continue to underestimate the magnitude of the

non-adiabatic effects observed in the empirical data and it is recommended that future work should seek to resolve this discrepancy.

Chapter 7 of this thesis expanded on the QCT models discussed in earlier chapters by probing the r -dependence of the $\text{OH}(\text{A}) + \text{Kr}$ and $\text{OH}(\text{X}) + \text{Kr}$ PESs for the first time. The theoretical data complemented previous experimental work by Perkins on quenching and RET in the $\text{OH}(\text{A}, v = 1) + \text{Kr}$ system [33]. In the first instance, a number of calculations were run on vibrationally averaged surfaces in which the bond length of the OH radical was fixed at various values that corresponded to different vibrational quantum states [238]. The data generated from these calculations were shown to be in good agreement with experimental RET cross-sections and, in many cases, in quantitative agreement with experimental total-removal cross-sections. Following this, variable- r calculations were run on the new PES for the first time [245]. The resultant agreement between these data and those measured experimentally was found to be generally poorer than that for the fixed- r data. As such, it is recommended that future work aim to consider how to best avoid unphysical energy transfers (such as those which violate the vibrational zero-point energy requirement of OH) during the classical regime of the trajectories. It is also hoped that future studies will further probe the accuracy of the new PESs by developing a set of variable- r TSH QCT algorithms. The theoretical data generated from these models can then be compared to the more extensive set of $v = 1$ experimental quenching cross-sections reported in reference [33].

8.2 Future outlook

The experimental and theoretical work presented in this thesis naturally lend themselves to continual development, refinement, and expansion. The experimental investigations described herein have resulted in a newly commissioned CMB machine that is capable of imaging the products of the rotationally inelastic scattering of fully quantum-state-selected molecules by atomic collision partners. To that end, complementary theoretical simulations of the various apparatus have been developed

and rigorously optimised, such that experimental data can be accurately and reliably simulated from quantum-mechanical or *quasi*-classical calculations.

The theoretical methods devised in this work are also amenable to a wide range of applications, some of which may prove complementary to current and future experimental investigations. To that end, a number of suggestions are outlined in the text that follows.

8.2.1 Experiment

- **Characterisation of the quenched products of $\text{OH}(\text{A})+\text{X}$ – where X is, for example, a rare gas or H_2 – using REMPI [187, 254–257] and VMI.** In the case where $\text{X} = \text{Kr}$ or Xe , the resultant data could be compared to the calculated $\text{OH}(\text{X})$ product rotational-state distributions reported in Chapter 6 and elsewhere [26, 78]. Data for the $\text{OH}(\text{A})+\text{H}_2$ system would also provide a welcome extension to recent studies of angular-momentum depolarisation carried out by Seamons [105, 258].
- **Imaging the products from the $\text{OH}(\text{A})+\text{H}_2$ reaction using REMPI detection of H_2O and Rydberg tagging of H atoms [194–201].** It may also prove particularly interesting to employ coincidence techniques [259, 260] to probe correlations between pairs of reaction products.
- **Determination of the $k - k'$ vector correlation (DCS) for the rotationally and vibrationally inelastic scattering of $\text{OH}(\text{A})+\text{Kr}$ and $\text{OH}(\text{A})+\text{Xe}$.** Such experiments, which could make use of a novel REMPI scheme for detection of $\text{OH}(\text{A})$ (see Appendix A), would provide a natural extension of previous studies referenced in this work [25, 26, 33, 226] and would complement the extensive theoretical investigation of non-adiabatic effects described in Chapters 5-7.
- **Investigation of the inelastic scattering of bond-oriented, hexapole-state-selected polar molecules by rare-gas atoms.** In an extension of the experimental work presented in this thesis, strongly polar molecules,

such as ammonia and methyl iodide, could be hexapole-state-selected and then oriented in space prior to collision with rare-gas atoms. If, in addition, polarised laser light is used for product REMPI detection, the full four-vector $(\mathbf{r} - \mathbf{k} - \mathbf{k}' - \mathbf{j}')$ correlation for the collision system can be measured experimentally [35, 81, 261–268].

8.2.2 Theory

- **Fully quantum-mechanical calculations for non-adiabatic transitions in the OH(A)+Kr and OH(A)+Xe systems.** Though computationally demanding and costly, there are recent examples of quenching studies that employ three-state TSH quantum-mechanical calculations [33, 269]. The development of fully quantum-mechanical non-adiabatic models would certainly provide an interesting extension of the *quasi*-classical treatments discussed in this work.
- **Application of the TSH QCT models described in Chapters 5-7 to atmospherically important systems that also display significant non-adiabatic dynamics.** A potential candidate system is found in $\text{O}(^1D) + \text{H}_2$ [270, 271]).
- **Development of the variable- r QCT calculations described in Chapter 7 to include surface-hopping capabilities.** This would allow for a more complete comparison of theory with the experimental data reported in reference [33]. A semi-classical approach may also be pertinent to these studies to avoid unphysical energy transfers into and out of the vibrational degree of freedom of OH [246–250].
- **Extension of the current 2D and 3D QCT algorithms to investigate diatom + diatom scattering.** Many systems, such as OH(A)+H₂, provide new and exciting challenges since both collision partners can gain or lose angular momentum over the course of a trajectory [196, 201, 272–277]. Careful attention must, therefore, be paid to the binning methods used in QCT

calculations [105] and to the conservation of vibrational zero-point energies in variable- r calculations. Of course, in addition to electronic quenching, thought would also need to be given to how to account for the reactive channel that accounts for 80% of the products emerging in the ground-state OH(X)+H₂ PES [195, 199].

Appendices



Towards a new experiment: CMB studies of OH(A)+Rg systems

Chapters 5-7 of this thesis outlined the development of *quasi*-classical trajectory algorithms that model non-adiabatic dynamics in OH(A, $v = 0/1$)+Kr/Xe collisions. The experimental data to which the theoretical calculations were compared were taken from LIF-ZQBS experiments and, as such, they offer absolute cross-sections for scalar processes such as electronic quenching and RET, as well as for the two-vector correlation between the initial ($\mathbf{j}$) and final ($\mathbf{j}'$) angular momentum vectors of the OH radical.

A key aim of building the new, compact, CMB machine described in this thesis is to further our understanding of non-adiabatic dynamics in OH(A) systems. To this end, it is anticipated that the newly commissioned apparatus will be used to investigate the $\mathbf{k} - \mathbf{k}'$ correlation in the OH(A)+Kr/Xe systems. To our knowledge, no previous work has been published on the DCSs that result from the inelastic scattering of OH(A) radicals and much of the work in this thesis has been driven by a desire to build a machine capable of realising these experiments in the near future. To achieve this, a source of OH radicals and a suitable product-detection scheme are required – both of which are now discussed in detail.

A.1 Pulsed-discharge source of OH radicals

Because of their short lifetimes and high reactivity, OH radicals must be generated *in situ*. Common methods to achieve this include

1. the photolysis of parent molecules such as hydrogen peroxide [6, 7, 278], and nitric acid [25, 26, 78, 230, 279, 280],
2. radiofrequency discharge [281],
3. chemical reactions [282], and
4. direct current (DC) discharge [187, 255–257, 283, 284].

There are notable issues with using photolysis or chemical reactions to generate OH, which include the premature decomposition of parent molecules and the formation of unwanted (and often corrosive) by-products. Of the discharge sources, the DC method is the simplest and most cost-effective.

To that end, a pulsed-discharge source of OH radicals was designed and built in-house, largely on a model published in reference [285], with elemental contributions from reference [187] and reference [286]. Directly in front of the molecular-beam-valve face-plate are mounted four discs, shown in Figure A.1: two stainless steel electrodes, and two insulating spaces (made from MACOR®). The spacers and metallic discs are mounted alternately and encased in a MACOR® housing to isolate the conducting plates from each other and the metallic face-plate.

The spacer and electrode closest to the valve nozzle each have a central hole of diameter 2 mm and the pair further away from the face-plate both have holes of diameter 4 mm. The larger diameter of the downstream discs is intended to accommodate the increase in beam width that comes about as a result of the supersonic expansion.

As noted in Chapter 3, the primary-molecular-beam valve used in this thesis produces a gas pulse with a full-width half-maximum (FWHM) of $\sim 150 \mu\text{s}$. After the valve opens, a pulsed voltage of around -1.5 kV is applied to the downstream

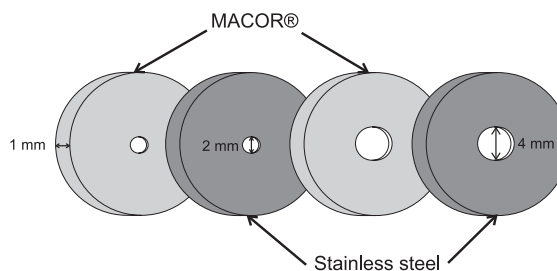


Figure A.1: Diagram showing the four discs that constitute the pulsed-discharge source of OH radicals. The discs are mounted in front of the primary-molecular-beam-valve face-plate, from left to right in the order they are shown. A negative voltage is applied to the stainless-steel electrode on the right; the electrode on the left is grounded. The pair of electrodes is separated by insulating spacers.

electrode for a period of tens of microseconds. The electrons then discharge to the upstream electrode (which is grounded) and, in the process, some are used to dissociate one of the O–H bonds in the water molecules present in the gas mixture. Notably, the direction in which the discharge electrons are accelerated counterpropagates that of the molecular beam, since this produces a more stable discharge [285].

Whilst the discharge is in operation, 3 A of DC are passed through a tungsten filament that is held in position just below the molecular-beam valve. The presence of the filament acts to further stabilise the resultant discharge at short pulse durations. In doing so, it reduces the voltage that is needed to generate a sufficient population of OH radicals, meaning the nascent beam is also rotationally colder. As discussed in reference [285], the discharge pulse duration is intentionally much shorter than that of the molecular-beam valve. Reducing the time during which the discharge is supplied causes a further decrease in the rotational temperature of the beam. As the aim of these experiments is to investigate the rotationally inelastic scattering of low- j OH radicals, it is crucially important to generate the coldest beam possible.

At the time of writing, the newly built pulsed-discharge source is being incorporated into the experimental apparatus, and it is hoped that experiments relating to the inelastic scattering of OH(X) and OH(A) will begin shortly.

Chapter 4 described the design, implementation, and characterisation of a hexapole-state selector to generate and isolate polar molecules in a specific quantum

state. If similar scattering experiments are to be carried out on hydroxyl radicals in the first-excited electronic state – whereby a primary beam of OH(A) radicals undergoes collision with a secondary beam of heavy rare-gas atoms – a method is required by which to populate a single quantum state in the OH(A) molecule and, furthermore, a state-selective technique is needed to detect post-collision OH(A). A number of potential detection schemes are now discussed in turn.

A.2 Novel REMPI detection scheme for OH(A)

The combined use of a pulsed-discharge source and hexapole state-selector allows for the preparation of a significant population of OH(X, $v = 0$, $j = 1.5$, $^2\Pi_{\frac{3}{2}}$, f) radicals [187, 254–257, 287]. From this starting point, a number of options are now outlined for the quantum-state-selective preparation and detection of OH(A, v , j , f_i) radicals. Figure A.2, which has been adapted from references [288] and [289], shows the potential-energy curves for the OH radical in various electronic states, all of which are discussed in the sections that follow. As an aside, although the detection of OH(X) *via* the D state is well-documented [187, 254–257, 287], no consideration is given to the D state as a viable resonant intermediate for the REMPI detection of OH(A), since the required $D^2\Sigma^+ \leftarrow A^2\Sigma^+$ transition is symmetry-forbidden.

A.2.1 (1+1) REMPI detection of OH(X $^2\Pi$) *via* the OH(A $^2\Sigma^+$) state

This method, published in reference [280] and reproduced in Figure A.3, is primarily used as a (1 + 1') REMPI scheme for the detection of ground-state OH(X) radicals *via* the A electronic state. The OH(X) radicals absorb a single photon from a tunable laser at around 282 nm to access a specific OH(A, $v = 1$, j , f_i) quantum state, and then a single photon at 118 nm is used to ionise from OH(A). Photoionisation from OH(A) initially accesses the OH⁺(A $^3\Pi\ 3d$) Rydberg state, which then undergoes Auger decay [290, 291] to the ground, cationic OH⁺(X $^3\Sigma^-$) state. Importantly, the energy from the VUV photon is sufficient to reach the OH⁺(A $^3\Pi\ 3d$) state from OH(A, $v = 1$), however, there is not enough energy available to access this state from

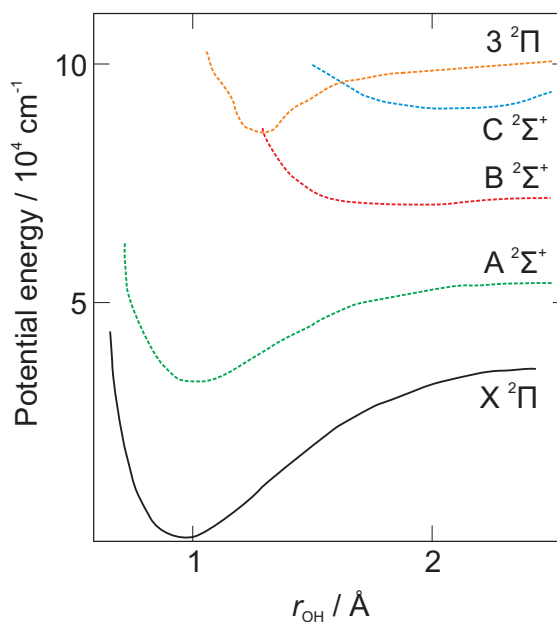


Figure A.2: Potential energy surfaces, adapted from those reported in references [288] and [289], for various electronic states of the OH radical.

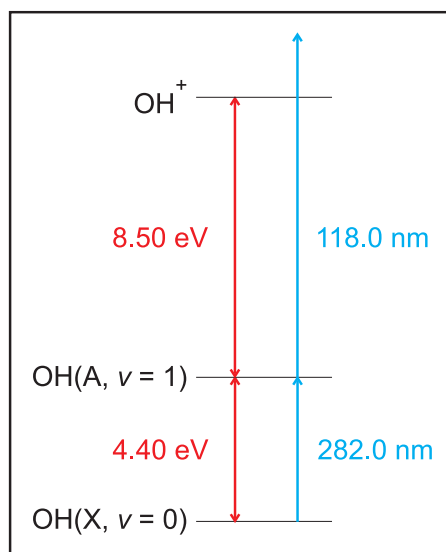


Figure A.3: Established detection scheme for the $\text{OH}(A, v = 1)$ radical based on direct ionisation from $\text{OH}(A, v = 1)$ [280]. The numbers and arrows in red indicate the energy separation of successive states; those in blue show the suggested energies of the photons used to achieve the desired transition.

$\text{OH}(A, v = 0)$. Thus, this method would be suitable for investigating the inelastic scattering of vibrationally excited $\text{OH}(A)$, and could potentially complement the experimental and theoretical data already discussed in Chapter 7.

In the method published in reference [280], 282 nm light is generated by frequency

doubling the output of an Nd:YAG-pumped tunable dye laser. After a 20-ns delay, a fixed-frequency 118 nm laser beam, counterpropagating to the initial UV pump beam, is used to ionise the OH(A) radicals. 118 nm light is generated by frequency tripling the third harmonic of an Nd:YAG laser in a phase-matched 1:10 Xe/Ar gas mixture. The 355 nm output of the Nd:YAG laser is focused with a quartz lens into a stainless steel cell, and a magnesium fluoride lens is then used to selectively focus the VUV beam into the centre of a free-jet expansion of OH radicals. Beames *et al.* report that OH(A, $v = 1$, $j = 8.5$, f_1) is the highest rovibrational state that can be detected using this method. It is also noted that the relative intensities of OH(A, $v = 1$) $\leftarrow$ OH(X, $v = 0$) transitions detected by (1 + 1') REMPI are different to those observed in LIF experiments.

It would be possible to carry out CMB experiments on OH(A, $v = 1$) + Kr/Xe dynamics and detect the scattered OH(A) products using the method outlined above by increasing the time delay between the 282 nm and 118 nm lasers. In previous LIF-ZQBS experiments on OH(A)+Kr dynamics, conducted by Chadwick *et al.* [25, 33], fluorescence signal was recorded from 200 – 300 ns after the pump laser was fired. The initial delay was to avoid the effect of scattered light on the fluorescence intensity observed; the fluorescence signal after 300 ns was ignored so that the data were not influenced by secondary inelastic collisions. In future CMB experiments on this system, where the effects of scattered laser light are unimportant, it may be possible to use a 100-ns delay between firing the 282 nm and 118 nm lasers to allow enough time to observe the results of primary scattering events before ionisation takes place.

A.2.2 (1+1) REMPI detection of OH(A $^2\Sigma^+$) *via* the OH(B $^2\Sigma^+$) state

This section presents a possible alternative to the direct ionisation of OH(A) outlined above. Note that, in this and subsequent sections, the energies of the various electronic states are those reported by Herzberg [115]. A significant population of

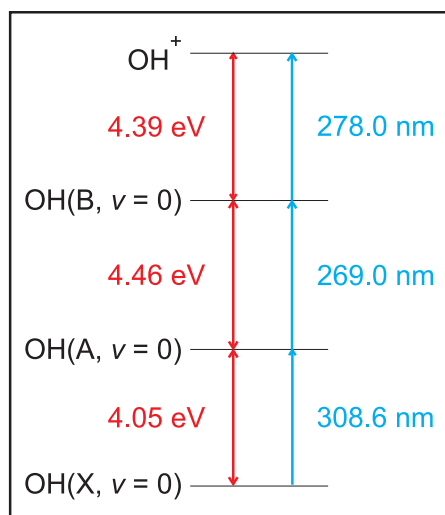


Figure A.4: Potential REMPI detection scheme for the $\text{OH}(A, v=0)$ radical that utilises $\text{OH}(B)$ as a resonant, intermediate. The numbers and arrows in red indicate the energy separation of successive states; those in blue show the suggested energies of the photons used to achieve the desired transition.

the desired $\text{OH}(A, v, j, f_i)$ state is first prepared from a beam of hexapole-state-selected $\text{OH}(X, {}^2\Pi_{3/2}, v=0, j=1.5, f)$ radicals. The desired $\text{OH}(A) A \leftarrow X$ transition can be achieved using the frequency-doubled 308 nm output of a tunable dye laser pumped by the second harmonic of an Nd:YAG laser at 532 nm and containing Rhodamine 6G dye in methanol.

After around 100 ns, during which time the nascent $\text{OH}(A)$ radicals are free to undergo collisions with Kr or Xe atoms, it is suggested that the $\text{OH}(A)$ molecules are detected using one-colour (1+1) REMPI, *via* the B state, at around 269 nm, as shown in Figure A.4. This wavelength can be produced by frequency doubling the output of a dye laser pumped by an Nd:YAG laser at 532 nm and containing Rhodamine 575 dye.

The Frank-Condon factors for various $\text{OH}(A, v') \leftarrow \text{OH}(B, v)$ transitions were reported by Bergeman *et al.* [288], and are reproduced in Table A.1. In general, transitions from the $\text{OH}(B, v=0)$ state show the strongest overlap with low $\text{OH}(A, v')$ states, and are uniformly high for $v' \leq 4$. In contrast, the most favourable overlap factors for the $\text{OH}(B, v=1)$ state are seen for transitions to higher $\text{OH}(A, v')$ states.

OH(A)	v'									
	0	1	2	3	4	5	6	7	8	9
OH(B, $v = 0$)	5.27	–	6.74	8.96	7.53	4.17	1.53	3.49	3.78	6.21
OH(B, $v = 1$)	1.21	6.09	1.29	1.50	1.04	4.28	9.21	5.37	5.16	6.27

Table A.1: Frank-Condon factors, reported by Bergeman *et al.* [288], for selected OH(A, v') $\leftarrow$ OH(B, v) transitions.

Bergeman *et al.* report lifetimes of 2 μ s for the OH(B, $v' = 0$) state, and 3 μ s for the OH(B, $v' = 1$) state, which are more than sufficient for them to act as resonant intermediates for REMPI detection. Notably, the lifetime of the B state was found to be three times larger than that of OH(A). This is unsurprising, given that the B state consists of a weakly bound hydrogen atom attached to an O(1S) atom, for which radiative decay to form H(3P) and H(1D) is highly forbidden at the atomic limit [288]. Bergeman *et al.* also note that OH(B) is unlikely to be affected by predissociation. However, it should be borne in mind that the potential-energy curve for the B state is much shallower than that of the A and X states, and there is a considerable risk that population of the B state will ultimately lead to molecular photodissociation.

A.2.3 (1+1) REMPI detection of OH(A $^2\Sigma^+$) *via* the OH(C $^2\Sigma^+$) state

As before, a significant population of radicals in the desired OH(A, v, j, f_i) state is first prepared from a beam of hexapole-state-selected OH(X, $^2\Pi_{3/2}$, $v = 0$, $j = 1.5$, f) radicals. However, in this instance, the suggested detection method is REMPI, *via* the OH(C) state, using a (2+1) scheme at 358.3 nm, as illustrated in Figure A.5. Photons at this wavelength can be generated by pumping a dye laser containing LDS 698 dye in methanol with the third-harmonic output of an Nd:YAG laser.

The Frank-Condon factors for given OH(A, v') $\leftarrow$ OH(C, v) transitions, as reported by Bergeman *et al.* [288], are shown in Table A.2. In contrast to the trend shown by the OH(A, v') $\leftarrow$ OH(B, v) data, it appears as though the

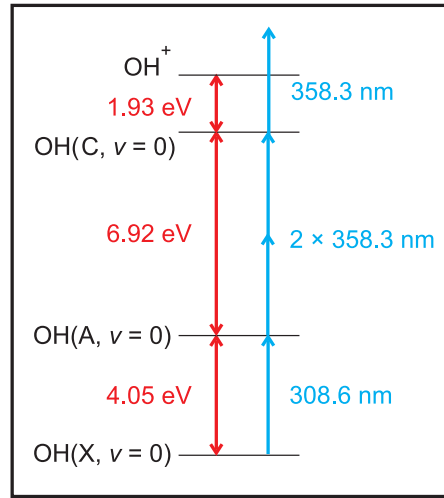


Figure A.5: Potential REMPI detection scheme for the OH(A, $v=0$) radical that utilises the OH(C) state as a resonant intermediate. The numbers and arrows in red indicate the energy separation of successive states; those in blue show the suggested energies of the photons used to achieve the desired transition.

OH(A)	v'									
	0	1	2	3	4	5	6	7	8	9
OH(C, $v=0$)	5.37	3.97	1.45	3.49	6.33	9.21	1.09	9.44	4.47	3.83
OH(C, $v=1$)	1.28	7.91	2.34	4.38	5.75	5.52	3.72	1.37	7.90	3.09

Table A.2: Frank-Condon factors, reported by Bergeman *et al.* [288], for selected OH(A, v') $\leftarrow$ OH(C, v) transitions.

strongest overlap is seen for transitions between OH(C, $v=0$) and intermediate/high OH(A, v') states, and between OH(C, $v=1$) and low/intermediate OH(A, v') states.

Table A.3 reports lifetimes, in ns, for the OH(C, $v'=0$) and OH(C, $v'=1$) states. In general, the lifetimes published by Bergeman *et al.* [288], Quickenden *et al.* [292], and Smith *et al.* [293] are in good agreement. Notably, a much shorter lifetime for the A $\leftarrow$ C transition (of around 2 ns) is reported by Smith *et al.* in the 1700 – 1950 Å region, however, this is not inconsistent with the assignment of at least part of these bands to X $\leftarrow$ C transitions. In contrast, Remy [294] reports a significantly higher lifetime of around 80 ns. They also quote an instrumental decay time of 15 ns, meaning that, in any case, the transitions observed by Bergeman *et al.*, Quickenden *et al.*, and Smith *et al.* would have been prevented from being

	OH(C, v') lifetime / ns	
	$v' = 0$	$v' = 1$
Bergeman <i>et al.</i> [288]	4.2 ± 0.8	3.5 ± 0.8
Quickenden <i>et al.</i> [292]	3.9 ± 0.5	3.7 ± 0.6
Smith <i>et al.</i> [293]	5.9 ± 1.2	6.1 ± 1.2
Remy [294]	80.0 ± 5.2	–

Table A.3: Lifetimes for the OH(C, $v' = 0$) and OH(C, $v' = 1$) states.

recorded. Interestingly, in the experiments conducted by Remy, as in those proposed in this thesis, the OH radicals are generated by passing a pulsed discharge through water vapour, and Remy subsequently attributes the longer lifetime of OH(C) to the presence of molecular hydrogen in the gas mixture.

Smith *et al.* [293] also note a lack of predissociation in the OH(C, $v' = 1$) state, since crossings with repulsive potential-energy curves are situated well above that for $v' = 1$, and no appreciable kinetic isotope effect is seen in the comparison of data for OH and OD. This claim is supported by Bergeman *et al.* [288]. Notably, although Easson and Pryce [295] assert that the C state is crossed by many repulsive potentials that would facilitate efficient predissociation, none of these are energetically accessible in the first-excited vibrational state. However, whilst low-pressure sources only show transitions from OH(C, $v' = 1$), higher gas pressures allow the measurement of transitions from OH(C, $v' = 3$) [289], and so the effects of predissociation may become more noticeable here. In any case, Smith *et al.* report that absorption into the C state will ultimately result in photodissociation. This is compounded by the fact that lifetimes for the A $\leftarrow$ C region showed effects of blending and cascading. Moreover, the A state is also predissociated for all rotational levels of the vibrational states of the electronic transitions lying in the region observed in reference [293], which, together with the other factors discussed in this section, makes it an unfavourable candidate for OH(A) REMPI detection.

A.2.4 (2+1) and (3+1) REMPI detection of OH(A $^2\Sigma^+$) *via* the OH(3 $^2\Pi$) state

(3+1) REMPI detection of OH(X), *via* the OH(3 $^2\Pi$) state, has already been reported in reference [296], and is based on the absorption of four photons at 293 nm, generated by frequency doubling the output of an XeCl excimer-pumped dye laser. This section focuses on possible REMPI schemes (shown in Figure A.6) for the detection of OH(A) *via* the same resonant, intermediate state; these include:

- one-colour (2+1) detection at 286.8 nm, produced by frequency doubling the output of a dye laser pumped by the third harmonic of an Nd:YAG laser and containing Rhodamine 6G dye in methanol;
- one-colour (3+1) detection at 430 nm, produced by frequency doubling the output of a dye laser pumped by the third harmonic of an Nd:YAG laser and containing Coumarin 440 dye in methanol.

Although quantitative values of the Frank-Condon factors for the overlap of the A and 3 $^2\Pi$ states were not found in the literature, based on the comparable shapes of the OH(X) and OH(A) potential-energy curves in Figure A.2, it can be assumed that the relative overlap of the X and A states with the 3 $^2\Pi$ state is similar. Thus, since REMPI detection of OH(X) *via* the 3 $^2\Pi$ state is viable, it may be assumed that the same can be said for OH(A) in terms of the overlap of the initial- and resonant-state wavefunctions.

A.2.5 Summary

The preceding sections outlined a number of proposals for REMPI schemes that could be used for the detection of OH(A) radicals in CMB experiments that also employ a newly commissioned pulsed-discharge source of OH radicals. The suggested methods include a modification to a scheme used previously in reference [280], as well as several novel procedures that would involve REMPI detection of OH(A) *via* the B, C, or 3 $^2\Pi$ states for the first time.

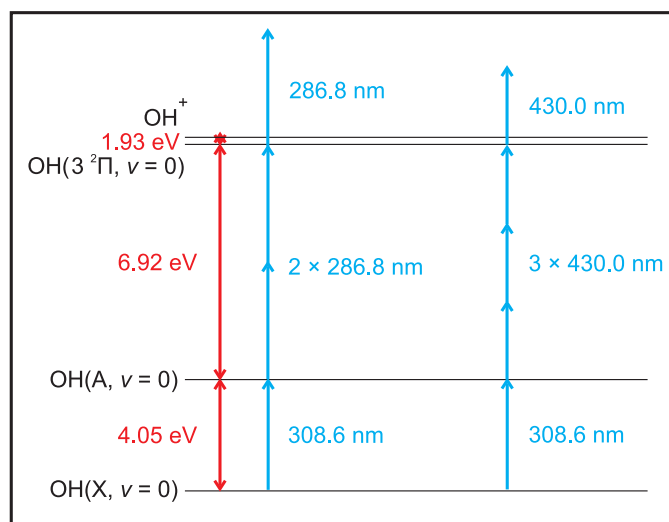


Figure A.6: Potential REMPI detection scheme for the OH(A, $v = 0$) radical that utilises OH(3 $^2\Pi$) as a resonant, intermediate. The numbers and arrows in red indicate the energy separation of successive states; those in blue show the suggested energies of the photons used to achieve the desired transition.

REMPI detection *via* the C state is deemed to be the least favourable, owing to: poor Frank-Condon overlap factors, a relatively short lifetime in the C state, and a tendency for excitation to the C state to lead to photodissociation. A scheme that involves excitation *via* the B state may prove more successful. The Frank-Condon factors for B – A transitions are considerably more favourable than those for C – A, and the B state has a significantly longer lifetime (some 2 – 3 μs). The B state is also not believed to be affected by predissociation, and B – A transitions are favoured by a smaller energy gap than for C – A.

The 3 $^2\Pi$ state is also a viable option as a resonant intermediate in the detection of OH(A). A (3+1) scheme for the ionisation of OH(X) that proceeds *via* the 3 $^2\Pi$ state is already available [296] and, based on the potential-energy curves shown in Figure A.2, there should also be favourable Frank-Condon overlap between the A and 3 $^2\Pi$ states. One notable drawback of this scheme is that the suggested wavelengths require the absorption of either three or four photons. Multi-photon absorption demands considerably more laser power, owing to the fact that the cross-section for absorption is appreciably lower. As such, it is possible that this smaller absorption cross-section will counteract any benefit of having better Frank-Condon

overlap than for B – A transitions.

In summary, it is recommended that REMPI detection of OH(A) could be attempted either by modification of the method described in reference [280], or *via* novel schemes that utilise the B or 3 $^2\Pi$ states as resonant intermediates. The relative efficiency of the latter two schemes will depend largely on molecular-beam densities and ionising laser power.

B

Examples of input files for algorithms
that simulate experimental images

B.1 $NO(X)+Ar$

B.1.1 File name: inp.dat

```

S_FIT --- Self-Assembled Input File
--- SYSTEM SPECIFICATION ---
15.50d0      RJP - Value of j prime
1.0          OINIT - 1: f, 1/2, 2: f, 3/2, 3: e 1/2, 4: e 3/2
1.0          OFINL - same as above, but for final state
F           QFLAG - Generate Q-branch simulations
T           BRANCH this should be "T" for pure branches
--- BASIS SET CONTROL ---
300000000    NTRAJ - Number of ***TRIAL*** trajectories
16           NORDERL - Number of legendre moments (max 48)
F           oFLAG - T/F orientation
0.0050       xdet - laser position in x
-0.0010      ydet - laser position in y
0.000040     dtlaser - make the laser fire later
3.0          fwhmblur - make the image blurrier
4.7          PIX2V - pixel to velocity conversion factor
T            simulate only
T            onlyfitdcs
T            onlyfitpddcs
--- I/O CONTROL ---
F F          blur grid/newton triangle - Print these output
T F          T/F - Output to file / use unfomatted IO (faster)
F           Reblur - apply a different blurring
--- FITTING CONTROL ---
3           iiter - Main loop iterations?
600        nume_itr - Child genes?

```

```

8 12 0 12 0
0 0 0 0 0
T
1
45
45
0.0
360.0
1.0d0 1.0d0
1.0d0
T
0.0d0
1.0d0
— EOF —

usecoe — How much sugar?
morder — How much spice?
interactivity — ask questions about what to do
renorm — scale the image
norderf — number of fourier moments
nring — number of consecutive rings
ang_start — the beginning of the angular range
ang_end — the end of the angular range
branchf — Mixed branch contributions
branchr — branching ratio (use if branch=F)
dflag — Normalised difference
satur — laser saturating transition fraction
lambda — Error function scaling

```

B.1.2 File name: parameters.f90

MODULE PARAMETERS

```

implicit none

character(len=30),parameter :: build='mccruden_070617_0742'

integer, parameter :: dp=kind(0.0d0)
integer, parameter :: sp=kind(0.0)

! Essential elements and parameters
integer, parameter :: img_size = 300

integer, parameter :: maxdim = 320
integer, parameter :: mgene = 4000
integer, parameter :: maxord = 20
integer, parameter :: maxcoe = 50
integer, parameter :: maxvar = 100

! System specification
real(dp), parameter :: Rg_mass = 40.0_dp * 1.66053886d-27
real(dp), parameter :: NO_mass = 30.0_dp * 1.66053886d-27
real(sp), parameter :: ROTCONST = 3.359e-23_sp
real(dp), parameter :: rot_oxygen = 2.855866e-23_dp
real(sp), parameter :: SpinO = 2.445e-21_sp
real(sp), parameter :: V_NO = 1654.5_sp
real(sp), parameter :: V_Rg = 589.3_sp

real(dp), parameter :: mu = ( Rg_mass * NO_mass ) / ( Rg_mass + NO_mass )

```

```

real(dp), parameter :: half_mu = mu * 0.5_dp
real(dp), parameter :: two_mu = mu * 2.0_dp
real(dp), parameter :: twoOmu = 2.0_dp / mu
real(dp), parameter :: inv_mNOmRg = 1.0_dp / (Rg_mass+NO_mass)
real(dp), parameter :: mass_const = (Rg_mass/(NO_mass + Rg_mass))

! Collision parameters based upon expeimmental geometry
real(sp), parameter :: dist_NO = 0.055_dp
real(sp), parameter :: dist_Rg = - 0.06_dp
real(sp), parameter :: vlablim = 1.0_dp
real(sp), parameter :: zdet = 0.0_dp

! Timings
real(dp), parameter :: t_NO = dist_NO / V_NO
real(dp), parameter :: t_Rg = -dist_Rg / V_Rg
real(dp), parameter :: dtNORg = t_NO - t_Rg

! Beam profiles - Rare gas beam
real(sp), parameter :: fwhm_Rg_V = 60.0_sp
real(sp), parameter :: fwhm_Rg_t = 0.00005_sp
real(sp), parameter :: fwhm_Rg_w = 0.006_sp
real(sp), parameter :: fwmh_Rg_ang = 0.04_sp

real(sp), parameter :: ALS2 = fwhm_Rg_V/2.0_dp/0.83255461115769775_sp
real(sp), parameter :: V2_min = V_Rg - 2.00_sp * ALS2
real(sp), parameter :: V2_max = V_Rg + 2.55_sp * ALS2
real(sp), parameter :: s_Rg_t = 4.0_sp* 0.693147180559945309_sp/ (fwhm_Rg_t*fwhm_Rg_t)

real(sp), parameter :: invALS2 = 1.0_sp/ als2

```

```

! Beam profiles - NO gas beam
real(sp), parameter :: fwhm_NO_V = 165.4_sp
real(sp), parameter :: fwhm_NO_t = 0.00018_sp
real(sp), parameter :: fwhm_NO_w = 0.0055_sp
real(sp), parameter :: fwhm_NO_ang = 0.0_sp

real(sp), parameter :: ALS1 = fwhm_NO_V/2.0_dp/0.83255461115769775_sp
real(sp), parameter :: V1_min = V_NO - 2.00_sp * ALS1
real(sp), parameter :: V1_max = V_NO + 2.55_sp * ALS1

real(sp), parameter :: invALS1 = 1.0_sp/ als1
real(sp), parameter :: gas_width = fwhm_Rg_w * fwhm_NO_w

! Detection volume parameterization
real(dp), parameter :: fwhm_226 = 0.0015_dp
real(dp), parameter :: fwhm_308 = 0.003_dp

real(dp), parameter :: s_308 = 4.0_dp*0.693147180559945309_dp / (fwhm_308*fwhm_308)
real(dp), parameter :: s_226 = 4.0_dp*0.693147180559945309_dp / (fwhm_226*fwhm_226)

! Geometric quantities
real(dp), parameter :: pi = 3.14159265358979323_dp
real(dp), parameter :: dtheta = 2.0_dp * pi / 180.0_dp
real(dp), parameter :: two_pi = 2.00_dp* pi
real(dp), parameter :: hpi = 0.50_dp* pi
real(dp), parameter :: tpiot = 3.0_dp* pi / 2.0_dp
real(dp), parameter :: tpiof = 3.0_dp* pi / 4.0_dp
real(dp), parameter :: qpi = 0.25_dp* pi
real(dp), parameter :: hpimtwo_pi = hpi - two_pi
real(dp), parameter :: invpi180 = 180.0_dp/ pi
real(dp), parameter :: three_pi = 3.00_dp* pi

```



```

real(dp), parameter :: sqrt2 = 1.4142135623730950_dp
real(dp), parameter :: invsqrt2 = 0.5_dp * sqrt2
real(dp), parameter :: sqrt3 = 1.7320508_dp
real(dp), parameter :: invsqrt3 = 1.0_dp / sqrt3
real(dp), parameter :: athird = 1.0_dp / 3.0_dp

! Squish Parameters
real(dp), parameter :: stretch = 1.0_dp
real(dp), parameter :: rtheta= 90.0_dp * pi / 180.0_dp

! Monte Carlo parameters
real(sp), parameter :: tfwhmnoangpdiv360 = fwmh_NO_ang*2.0_dp*pi/360.0_sp
real(sp), parameter :: tfwhmRgangpdiv360 = fwmh_Rg_ang*2.0_dp*pi/360.0_sp
real(sp), parameter :: invsqrt2als1 = ALS1 * invsqrt2
real(sp), parameter :: invsqrt2als2 = ALS2 * invsqrt2

! Blur quantities
real(sp), parameter :: Tolc_Blur = 0.05_sp
real(sp), parameter :: B_weight = 0.00_sp
real(sp), parameter :: st_dev_splat = 1.0_sp

! Data parameters
integer, parameter :: num_states = 19
integer, parameter :: maxdim1 = maxdim+1
integer, parameter :: maxdim20 = maxdim*20
integer, parameter :: maxdimdim = (maxdim*2+1)*(maxdim*2+1)
integer, parameter :: maxdimdimimg = maxdimdim*3
integer, parameter :: img_elements = 1+(img_size*2)
integer, parameter :: img_elements_2d = (1+(img_size*2))*(1+(img_size*2))
integer, parameter :: img_elements_3d = (1+(img_size*2))*(1+(img_size*2))*(1+(img_size*2))
integer, parameter :: proimg_elements = (1+(img_size*2))*(1+(img_size*2))*(1+(img_size*2))

```

```

integer, parameter :: fnomdim = (2*maxord+1)*(maxord+1)*(maxord*5+1)
integer, parameter :: basdim = (2*img_size+1)*(2*img_size+1)*(maxord+1)

! Variable definitions
end module parameters

module variables

use parameters

implicit none

real(dp) dcs_test(-maxdim:maxdim, -maxdim:maxdim)
CHARACTER(len=1) akey
CHARACTER(len=10) output(2)
CHARACTER(len=13) output2(2)
CHARACTER(len=18) flmask
CHARACTER(len=18) flocoe
CHARACTER(len=18) flout
CHARACTER(len=21) flpddc
CHARACTER(len=22) string(0:1)
CHARACTER(len=3) thresh
CHARACTER(len=24) image_name(3)
CHARACTER(len=27) format_basis
CHARACTER(len=3) format_len
CHARACTER(len=3) command_here
CHARACTER(len=30) command
CHARACTER(len=105) command2
INTEGER(4) iretw
INTEGER(4) SIGUSR1
INTEGER :: failcount1 = 0

```

```

INTEGER :: failcount2 = 0
INTEGER :: failcount3 = 0
INTEGER :: failcount4 = 0
INTEGER Blur_limit
INTEGER cut_START
INTEGER cut_END
INTEGER NT_err
INTEGER NX
INTEGER NY
INTEGER n
INTEGER maxdcord
INTEGER N_gauss
INTEGER NxNxp
INTEGER NyNyp
INTEGER TARRY(3)
INTEGER coeind(0:maxdim)
INTEGER counter
INTEGER endhere
INTEGER err_pddcs
INTEGER err_write
INTEGER expr_img_max
INTEGER i,ii,j,k
INTEGER i_here
INTEGER iiter
INTEGER jjter
INTEGER iiterg
INTEGER img
INTEGER img_end
INTEGER img_start
INTEGER inp_err
INTEGER iseed

```

```

INTEGER nring
INTEGER internalcount
INTEGER itest(mgene)
INTEGER jj
INTEGER j_here
INTEGER last
INTEGER mfit
INTEGER m
INTEGER morder_int(0:4)
INTEGER ncol
INTEGER ndim
INTEGER nl
INTEGER nume_iter
INTEGER norderf
INTEGER norderl
INTEGER nr,nt
INTEGER nrow
INTEGER nsum
INTEGER num_fitmoments
INTEGER numcoe(0:4)
INTEGER nxp
INTEGER nyp,mmom
INTEGER p,q,s,t,l
INTEGER perc
INTEGER r_here
INTEGER readerr
INTEGER scounter
INTEGER skip
INTEGER start_time
INTEGER start_time_temp
INTEGER TPS

```

```

INTEGER theta_here
INTEGER torder_here(0:9)
INTEGER torderl
INTEGER unit_here
INTEGER usecoe(0:4)
INTEGER(kind=8) nto100
INTEGER(kind=8) nto
INTEGER(kind=8) ntraj
LOGICAL BRANCH
LOGICAL NT_wanted
LOGICAL Qflag
LOGICAL blur_grid_wanted
LOGICAL complag
real(dp) dflag
integer morder(0:4)
LOGICAL interactivity
LOGICAL oFlag
LOGICAL onlybasis
LOGICAL onlyfitdcs
LOGICAL onlyfitpddcs
LOGICAL outflag
LOGICAL posdef_flag
LOGICAL reblur
LOGICAL sim
LOGICAL sflag
LOGICAL triggerretry
real(dp) rxtemp, rytemp
real(dp) y_temp
real(dp) :: dxno = 0.0_dp
real(dp) :: dyno = 0.0_dp
real(dp) :: dzno = 0.0_dp

```

```

real(dp) :: vcollsum = 0.0_dp
real(dp) A20V, A20H, A22H, A22V, oH, oV
real(dp) Centre(1:18)
real(dp) Dep_fact1
real(dp) Dep_fact2
real(dp) ER
real(dp) EROTF
real(dp) junk
real(dp) EROTI
real(dp) EROTD
real(dp) EROTDd
real(dp) EXP_weight(-maxord:maxord,2)
real(dp) Fmoment_expr(-maxord:maxord,0:180,2)
real(dp) HCOE_Sim1
real(dp) HCOE_Sim2
real(dp) Intensity_H
real(dp) Intensity_V
real(dp) KHI_Ver
real(dp) epartner
real(dp) Khi_rot
real(dp) NOdist(3)
real(dp) RJP
real(dp) Radial_blur
real(dp) RkpNO(3)
real(dp) ThetaHigh
real(sp) V_Rg_p
real(dp) Vec_HOR_X(3)
real(dp) Vec_HOR_Y(3)
real(dp) Vec_HOR_Z(3)
real(dp) Vec_NOXHOR(3)
real(dp) Vec_NOYHOR(3)

```

```

real(dp) Vec_NOZHOR(3)
real(dp) Vector_226_Det(3)
real(dp) Vector_226_X(3)
real(dp) Vector_226_Y(3)
real(dp) Vector_226_Z(3)
real(dp) Vector_226sp(3)
real(dp) YColl(3)
real(dp) YColl_NO(3)
real(dp) ZColl(3)
real(dp) ZZETan(3)
real(dp) a11_res_H
real(dp) a11_res_V
real(dp) a20_res_H
real(dp) a20_res_V
real(dp) a21_res_H
real(dp) a21_res_V
real(dp) a22_res_H
real(dp) a22_res_V
real(dp) alpha
real(dp) aux_v1(3)
real(dp) aux_v2(3)
real(dp) aux_v3(3)
real(dp) beta
real(dp) branch_val
real(dp) branchf(2)
real(dp) branchr
real(dp) fsim(0:maxdim,-maxord:maxord)
real(dp) branchw
real(dp) chilim
real(dp) chiold
real(dp) chisq(-1:maxord)

```

```

real(dp) chol_mat(maxord*2+1,maxord*2+1)
real(dp) coe(0:maxord)
real(dp) coeff(0:maxord)
real(dp) coeffbest(0:maxord)
real(dp) coeffbestin(0:maxord)
real(dp) coefflim(0:maxord,2)
real(dp) coefin(4,0:maxord)
real(dp) coefit(0:maxord)
real(dp) coenew(0:maxord)
real(dp) coevec(0:maxord,0:maxord)
real(dp) cos_2phi
real(dp) cos_2psi
real(dp) cos_oangle
real(dp) cos_phi
real(dp) cos_theta
real(dp) cos_theta0
real(dp) cos_thetacom
real(dp) cvec(0:maxord+5)
real(dp) d226
real(dp) d308
real(sp) dZ
real(dp) denom(-img_size:img_size,-img_size:img_size)
real(dp) der
real(dp) dtRg
real(sp) dtno
real(sp) dwRgx
real(sp) dwnoy
real(dp) evrel
real(dp) evrelp
real(dp) exp_sqr(-maxord:maxord,2)
real(dp) exp_sum(0:3)

```



```

real(dp) fbasis(0:maxdim,0:maxord,-maxord:maxord)
real(dp) fctvec(0:maxord*10)
real(dp) fexp1(0:maxdim,-maxord:maxord)
real(dp) fexp2(0:maxdim,-maxord:maxord)
real(dp) fexp3(0:maxdim,-maxord:maxord)
real(dp) fit
real(dp) fitness(mgene)
real(dp) flcoe(18)
real(dp) fmoment(-maxord:maxord,0:maxord,0:maxord*5)
real(dp) gene(100,mgene)
real(dp) hand
real(dp) hcoe1
real(dp) hcoe2
real(sp) no_ang_p
real(dp) oAngle
real(dp) oldfit(mgene)
real(dp) p226det
real(dp) p308det
real(dp) part
real(dp) phi_rot
real(dp) phicom
real(dp) pithetas
real(dp) pixtov
real(dp) pixmaxh
real(dp) pixmaxv
real(dp) proba11h
real(dp) proba11v
real(dp) proba20h
real(dp) proba20v
real(dp) proba21h
real(dp) proba21v

```

```

real(dp) proba22h
real(dp) proba22v
real(dp) probdcs_hor
real(dp) probdcs_ver
real(dp) probdet
real(dp) probhordcs
real(dp) probtot11
real(dp) probtot20
real(dp) probtot21
real(dp) probtot22
real(dp) probverdcs
real(dp) proj226
real(dp) proj308
real(dp) r
real(sp) rg_ang_p
real(sp) rg_ang_t
real(dp) rknox
real(dp) rknoy
real(dp) rknoz
real(dp) rkpnx
real(dp) rkpny
real(dp) rkpnoz
real(dp) rmodk
real(dp) rmodkp
real(dp) rx
real(dp) ry
real(dp) rz
real(dp) sblur
real(dp) sigma(1:18)
real(dp) sim_img(-maxdim:maxdim,-maxdim:maxdim)
real(dp) sim_img_r(-maxdim:maxdim,-maxdim:maxdim)

```

```

real(dp) sin_2phi
real(dp) sin_2psi
real(dp) sin_2theta
real(dp) sin_NOangt
real(dp) sin_oangle
real(dp) sin_phi
real(dp) sin_rg_ang_t
real(dp) sin_theta
real(dp) sin_theta0
real(dp) sin_thetacom
real(dp) space
real(dp) summon
real(dp) sumfit
real(dp) t_nodtl
real(dp) tcoll
real(dp) temprknox
real(dp), allocatable :: temppolimh(:, :)
real(dp), allocatable :: temppolimv(:, :)
real(dp) temprkpnoy
real(dp) theta0
real(dp) theta0_fit
real(dp) theta226
real(dp) theta308
real(dp) theta_rot
real(dp) thetacom
real(dp) thetalow
real(dp) thetasave
real(dp) thetaswap
real(dp) unit_vec(maxord*2+1, maxord*2+1)
real(sp) v1_peak
real(sp) v2_peak

```

```

real(dp) vRgxp
real(dp) vRgyp
real(dp) vRgzp
real(dp) vcoll
real(dp) vcomx
real(dp) vcomy
real(dp) vcomz
real(dp) vector_308_det(3)
real(dp) vlabx
real(sp) sobdtheta
real(sp) sob
real(dp) vlaby
real(dp) vlabz
real(dp) vnoxp
real(dp) vnoyp
real(dp) vnozp
real(dp) vrelnono(3)
real(dp) vrelx
real(dp) vrely
real(dp) vrelz
real(sp) ang_end
real(sp) ang_start
real(sp) AKQVEC(10)
real(dp) BasHit(-img_size:img_size,-img_size:img_size)
real(dp) BasHitt(-img_size:img_size,-img_size:img_size)
real(sp) BasHittsp(-img_size:img_size,-img_size:img_size)
real(dp) BasHit_temp(-img_size:img_size,-img_size:img_size)
real(sp) FACTJ
real(sp) OFINL
real(sp) OINIT
real(sp) PDDCS(0:999,20)

```

```

real(sp) V_NO_p
real(sp) V_NO_psq
real(sp) V_rg_psq
real(dp) als1sqrt2
real(dp) als2sqrt2
real(dp) angthe
real(sp) angvec(3602)
real(dp) anorm1
real(dp) anorm2
real(dp) bas1lh(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas1lv(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas20h(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas20v(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas21h(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas21v(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas22h(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas22v(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) basdcsh(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) basdcsv(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas1lht(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas1lvt(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas20ht(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas20vt(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas21ht(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas21vt(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas22ht(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas22vt(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) basis(-img_size:img_size,-img_size:img_size,0:maxord*9)
real(dp) blur_const
real(dp) dang
real(dp) dcs_fit1(-1000:1000,maxord)

```

```

real(dp) dcs_fit2(-1000:1000,maxord)
real(dp) dcs_fit3(-1000:1000,maxord)
real(dp) dcs_fit4(-1000:1000,maxord)
real(dp) dtlaser
real(dp) expr_img(-maxdim:maxdim,-maxdim:maxdim,3)
real(dp) expr_img_temp(-maxdim:maxdim,-maxdim:maxdim,3)
real(dp) expr_img_here1(-maxdim:maxdim,-maxdim:maxdim)
real(dp) expr_img_here2(-maxdim:maxdim,-maxdim:maxdim)
real(dp) expr_img_here3(-maxdim:maxdim,-maxdim:maxdim)
real(dp) expr_img_here1_pddcs(-img_size:img_size,-img_size:img_size)
real(dp) expr_img_here2_pddcs(-img_size:img_size,-img_size:img_size)
real(dp) expr_img_here3_pddcs(-img_size:img_size,-img_size:img_size)
real(dp) expr_img_here4(-maxdim:maxdim,-maxdim:maxdim)
real(dp) factor
real(sp) fwhmblur
real(sp) h_here
real(sp) v_here
real(dp) high_limit_NO
real(dp) high_limit_Rg
real(dp) hitmat(-img_size:img_size,-img_size:img_size)
real(dp) inv_dang
real(dp) inv_pixtov
real(dp) invsqrt3factj
real(dp) jfact1
real(dp) jfactlinv
real(dp) jfact2
real(dp) jfact2inv
real(dp) lambda
real(sp) low_limit_NO
real(sp) low_limit_Rg
real(dp) modvrel

```

```

real(dp) nl_val
real(sp) no_ang_t
real(dp) norm_diff
real(dp) olbaba(-maxord:maxord,-maxord:maxord,-maxord:maxord)
real(dp) olexba(-maxord:maxord,-maxord:maxord)
real(dp) olexex(-maxord:maxord)
real(sp) pang
real(sp) peak1
real(sp) peak2
real(dp) polimh(-img_size:img_size,-img_size:img_size)
real(dp) polimht(-img_size:img_size,-img_size:img_size)
real(sp) polimhtsp(-img_size:img_size,-img_size:img_size)
real(dp) polimh_b(-img_size:img_size,-img_size:img_size)
real(dp) polimv(-img_size:img_size,-img_size:img_size)
real(dp) polimvt(-img_size:img_size,-img_size:img_size)
real(sp) polimvtsp(-img_size:img_size,-img_size:img_size)
real(dp) polimv_b(-img_size:img_size,-img_size:img_size)
real(dp) proimg(-img_size:img_size,-img_size:img_size,0:maxord*9)
real(sp) random_gauss1
real(sp) random_gauss2
real(sp) random_gauss3
real(sp) random_gauss4
real(sp) random_gauss5
real(sp) random_gauss6
real(sp) random_gauss7
real(sp) random_gauss8
real(sp) random_gauss11
real(sp) random_gauss12
real(sp) random_gauss13
real(sp) random_gauss14
real(sp) random_gauss15

```

```

real(sp) random_gauss16
real(dp) real_nr
real(dp) real_nr_dtheta
real(dp) renorm
real(sp) rn1
real(sp) rn2
real(dp) satur
real(dp) savetheta
real(dp) scafax
real(dp) scafay
real(dp) scaling
real(sp) sob1
real(sp) sob2
real(sp) sob2_param1
real(sp) sob2_param2
real(sp) sob3
real(sp) sob4
real(sp) sob4_param1
real(sp) sob4_param2
real(dp) sqrtrip_const
real(dp) sum_here
real(dp) temp_image_h(-img_size:img_size,-img_size:img_size,3)
real(dp) theta
real(dp) theta_deg
real(dp) theta_nt(0:180)
real(dp) thetamax
real(dp) thetamin
real(dp) thetap
real(dp) thetaxy
real(dp) vl_av
real(sp) vl_peakx2

```



```

real(dp) v2_av
real(sp) v2_peakx2
real(dp) v_NOx2
real(dp) v_Rgx2
real(sp) weightblur(-img_size:img_size,-img_size:img_size)
real(sp) weivec(-maxord:maxord)
real(dp) x,y,z
real(dp) xt(2001)
real(dp) xdet
real(dp) y1
real(dp) y2
real(dp) ydet
real(dp) zmax_here(0:maxdim)

integer counter_hist(0:180)

! Zero arrays – makes binary huge (but fast)!
DATA weightblur / img_elements_2d * 0.0_dp /
DATA polimv / img_elements_2d * 0.0_dp /
DATA polimh_b / img_elements_2d * 0.0_dp /
DATA polimv_b / img_elements_2d * 0.0_dp /
DATA fmoment / fmomdim * 0.0_dp /
DATA BasHit / img_elements_2d * 0.0_dp /
DATA BasHitt / img_elements_2d * 0.0_dp /
DATA BasHittsp / img_elements_2d * 0.0_dp /
DATA BasHit_temp / img_elements_2d * 0.0_dp /
DATA proimg / proimg_elements * 0.0_dp /
DATA basis / proimg_elements * 0.0_dp /
DATA PDDCS / 20000 * 0.0_sp /
DATA angvec / 3602 * 0.0_sp /
DATA sigma / 18 * 0.0_dp /

```

```

DATA AKQVEC / 10 * 0.0_sp /
DATA zmax_here / maxdim1 * 0.0_dp /
! DATA exp_sqr / 202 * 0.0_dp /
DATA exp_sum / 4 * 0.0_dp /
! DATA exp_weight / 202 * 0.0_dp /
DATA expr_img / maxdimimg * 0.0_dp /
DATA expr_img_here1 / maxdim * 0.0_dp /
DATA expr_img_here2 / maxdim * 0.0_dp /
DATA expr_img_here3 / maxdim * 0.0_dp /
DATA denom / img_elements_2d * 0.0_dp /
DATA counter_hist / 181 * 0 /
DATA usecoe / 5 * 0 /
DATA numcoe / 5 * 0 /
DATA bas11h / basdim * 0.0_dp /
DATA bas11v / basdim * 0.0_dp /
DATA bas20h / basdim * 0.0_dp /
DATA bas20v / basdim * 0.0_dp /
DATA bas21h / basdim * 0.0_dp /
DATA bas21v / basdim * 0.0_dp /
DATA bas22h / basdim * 0.0_dp /
DATA bas22v / basdim * 0.0_dp /
DATA basdcsh / basdim * 0.0_dp /
DATA basdcsv / basdim * 0.0_dp /
DATA bas11ht / basdim * 0.0_dp /
DATA bas11vt / basdim * 0.0_dp /
DATA bas20ht / basdim * 0.0_dp /
DATA bas20vt / basdim * 0.0_dp /
DATA bas21ht / basdim * 0.0_dp /
DATA bas21vt / basdim * 0.0_dp /
DATA bas22ht / basdim * 0.0_dp /
DATA bas22vt / basdim * 0.0_dp /

```

```

DATA  polimht      / img_elements_2d * 0.0_dp /
DATA  polimhtsp    / img_elements_2d * 0.0_sp /
DATA  polimvt      / img_elements_2d * 0.0_dp /
DATA  polimvtsp    / img_elements_2d * 0.0_sp /

```

```

END MODULE variables

```

B.2 $ND_3(\tilde{X})+Ar$

B.2.1 File name: inp.dat

```

S_FIT --- Self-Assembled Input File
--- SYSTEM SPECIFICATION ---
  2.0d0    RJP - Value of j prime
  1.0      KINIT -
  1.0      KFINL -
  F        QFLAG - Generate Q-branch simulations
  T        BRANCH this should be "T" for pure branches
--- BASIS SET CONTROL ---
  300000000 NTRAJ - Number of ***TRIAL*** trajectories
  18        NORDERL - Number of legendre moments (max 48)
  F         oFLAG - T/F orientation
            xdet - laser position in x
            ydet - laser position in y
            dtlaser - make the laser fire later
            fwhmblur - make the image blurrier
            PIX2V - pixel to velocity conversion factor
            simulate only
            onlyfitdcs
            onlyfitpddcs
--- I/O CONTROL ---
  F T      blur grid/newton triangle - Print these output
  T F      T/F - Output to file / use unfomatted IO (faster)
  F        Reblur - apply a different blurring
--- FITTING CONTROL ---
  3         iiter - Main loop iterations?
  600      nume_itr - Child genes?

```

```

8 12 0 12 0
0 0 0 0 0
T
1.01
24
32
0.0
360.0
1.0d0 1.0d0
1.0d0
T
0.0d0
1.0d0
— EOF —

usecoe — How much sugar?
morder — How much spice?
interactivity — ask questions about what to do
renorm — scale the image
norderf — number of fourier moments
nring — number of consecutive rings
ang_start — the beginning of the angular range
ang_end — the end of the angular range
branchf — Mixed branch contributions
branchr — branching ratio (use if branch=F)
dflag — Normalised difference
satur — laser saturating transition fraction
lambda — Error function scaling

```

B.2.2 File name: parameters.f90

MODULE PARAMETERS

```

implicit none

character(len=30),parameter :: build='lady4637_090217_1425'

integer, parameter :: dp=kind(0.0d0)
integer, parameter :: sp=kind(0.0)

! Essential elements and parameters
integer, parameter :: img_size = 150

integer, parameter :: maxdim = 320
integer, parameter :: mgene = 4000
integer, parameter :: maxord = 50
integer, parameter :: maxcoe = 50
integer, parameter :: maxvar = 100

! System specification
real(dp), parameter :: Rg_mass = 40.0_dp * 1.66053886d-27
real(dp), parameter :: NO_mass = 20.0_dp * 1.66053886d-27
real(sp), parameter :: ROTCONST = 1.536e-22_sp
real(sp), parameter :: CROTCONST = 6.207e-23_sp
real(dp), parameter :: rot_oxygen = 2.855866e-23_dp
real(sp), parameter :: SpinO = 2.445e-21_sp
real(sp), parameter :: V_NO = 614.4_sp
real(sp), parameter :: V_Rg = 589.3_sp

```

```

real(dp), parameter :: mu = ( Rg_mass * NO_mass ) / ( Rg_mass + NO_mass )
real(dp), parameter :: half_mu = mu * 0.5_dp
real(dp), parameter :: two_mu = mu * 2.0_dp
real(dp), parameter :: twoOmu = 2.0_dp / mu
real(dp), parameter :: inv_mNOmRg = 1.0_dp / (Rg_mass+NO_mass)
real(dp), parameter :: mass_const = (Rg_mass/(NO_mass + Rg_mass))

! Collision parameters based upon expeimgental geometry
real(sp), parameter :: dist_NO = 0.29_dp
real(sp), parameter :: dist_Rg = 0.077_dp
real(sp), parameter :: vlablim = 1.0_dp
real(sp), parameter :: zdet = 0.0_dp

! Timings
real(dp), parameter :: t_NO = dist_NO / V_NO
real(dp), parameter :: t_Rg = -dist_Rg / V_Rg
real(dp), parameter :: dtNORg = t_NO - t_Rg

! Beam profiles - Rare gas beam
real(sp), parameter :: fwhm_Rg_V = 60.0_sp
real(sp), parameter :: fwhm_Rg_t = 0.00005_sp
real(sp), parameter :: fwhm_Rg_w = 0.0035_sp
real(sp), parameter :: fwmh_Rg_ang = 1.50_sp

real(sp), parameter :: ALS2 = fwhm_Rg_V/2.0_dp/0.83255461115769775_sp
real(sp), parameter :: V2_min = V_Rg - 2.00_sp * ALS2
real(sp), parameter :: V2_max = V_Rg + 2.55_sp * ALS2
real(sp), parameter :: s_Rg_t = 4.0_sp* 0.693147180559945309_sp/ (fwhm_Rg_t*fwhm_Rg_t)

real(sp), parameter :: invALS2 = 1.0_sp/ als2

```

```

! Beam profiles - NO gas beam
real(sp), parameter :: fwhm_NO_V = 290.0_sp
real(sp), parameter :: fwhm_NO_t = 0.00018_sp
real(sp), parameter :: fwhm_NO_w = 0.0035_sp
real(sp), parameter :: fwhm_NO_ang = 1.50_sp

real(sp), parameter :: ALS1 = fwhm_NO_V/2.0_dp/0.83255461115769775_sp
real(sp), parameter :: V1_min = V_NO - 2.00_sp * ALS1
real(sp), parameter :: V1_max = V_NO + 2.55_sp * ALS1

real(sp), parameter :: invALS1 = 1.0_sp/ als1
real(sp), parameter :: gas_width = fwhm_Rg_w * fwhm_NO_w

! Detection volume parameterization
real(dp), parameter :: fwhm_226 = 0.0015_dp
real(dp), parameter :: fwhm_308 = 0.003_dp

real(dp), parameter :: s_308 = 4.0_dp*0.693147180559945309_dp / (fwhm_308*fwhm_308)
real(dp), parameter :: s_226 = 4.0_dp*0.693147180559945309_dp / (fwhm_226*fwhm_226)

! Geometric quantities
real(dp), parameter :: pi = 3.14159265358979323_dp
real(dp), parameter :: dtheta = 2.0_dp * pi / 180.0_dp
real(dp), parameter :: two_pi = 2.00_dp* pi
real(dp), parameter :: hpi = 0.50_dp* pi
real(dp), parameter :: tpiot = 3.0_dp* pi / 2.0_dp
real(dp), parameter :: tpiof = 3.0_dp* pi / 4.0_dp
real(dp), parameter :: qpi = 0.25_dp* pi
real(dp), parameter :: hpi2two_pi = hpi - two_pi
real(dp), parameter :: invpi180 = 180.0_dp/ pi

```



```

real(dp), parameter :: three_pi = 3.00_dp * pi
real(dp), parameter :: sqrt2 = 1.4142135623730950_dp
real(dp), parameter :: invsqrt2 = 0.5_dp * sqrt2
real(dp), parameter :: sqrt3 = 1.7320508_dp
real(dp), parameter :: invsqrt3 = 1.0_dp / sqrt3
real(dp), parameter :: athird = 1.0_dp / 3.0_dp

! Squish Parameters
real(dp), parameter :: rstretch = 1.00_dp
real(dp), parameter :: rtheta = 90.0_dp * pi / 180.0_dp

! Monte Carlo parameters
real(sp), parameter :: tfwhmnoangpdiv360 = fwmh_NO_ang*2.0_dp*pi/360.0_sp
real(sp), parameter :: tfwhmRgangpdiv360 = fwmh_Rg_ang*2.0_dp*pi/360.0_sp
real(sp), parameter :: invsqrt2als1 = ALS1 * invsqrt2
real(sp), parameter :: invsqrt2als2 = ALS2 * invsqrt2

! Blur quantities
real(sp), parameter :: Tolc_Blur = 0.05_sp
real(sp), parameter :: B_weight = 0.00_sp
real(sp), parameter :: st_dev_splat = 1.0_sp

! Data parameters
integer, parameter :: num_states = 19
integer, parameter :: maxdimp1 = maxdim+1
integer, parameter :: maxdim20 = maxdim*20
integer, parameter :: maxdimdim = (maxdim*2+1)*(maxdim*2+1)
integer, parameter :: maxdimdimimg = maxdimdim*3
integer, parameter :: img_elements = 1+(img_size*2)
integer, parameter :: img_elements_2d = (1+(img_size*2))*(1+(img_size*2))
integer, parameter :: img_elements_3d = (1+(img_size*2))*(1+(img_size*2))

```

```

integer, parameter :: proimg_elements = (1+(img_size*2))*(1+(img_size*2))*(maxord*9+1)
integer, parameter :: fmdim = (2*maxord+1)*(maxord+1)*(maxord*5+1)
integer, parameter :: basdim = (2*img_size+1)*(2*img_size+1)*(maxord+1)

! Variable definitions
end module parameters

module variables

use parameters

implicit none

real(dp) dcs_test(-maxdim:maxdim, -maxdim:maxdim)
CHARACTER(len=1) akey
CHARACTER(len=10) output(2)
CHARACTER(len=13) output2(2)
CHARACTER(len=18) flmask
CHARACTER(len=18) flocoe
CHARACTER(len=18) flout
CHARACTER(len=21) flpddc
CHARACTER(len=22) string(0:1)
CHARACTER(len=3) thresh
CHARACTER(len=24) image_name(3)
CHARACTER(len=27) format_basis
CHARACTER(len=3) format_len
CHARACTER(len=3) command_here
CHARACTER(len=30) command
CHARACTER(len=105) command2
INTEGER(4) iretw
INTEGER(4) SIGUSR1

```

```

INTEGER :: failcount1 = 0
INTEGER :: failcount2 = 0
INTEGER :: failcount3 = 0
INTEGER :: failcount4 = 0
INTEGER Blur_limit
INTEGER cut_START
INTEGER cut_END
INTEGER NT_err
INTEGER NX
INTEGER NY
INTEGER n
INTEGER maxdcord
INTEGER N_gauss
INTEGER NxNxp
INTEGER NyNyp
INTEGER TARRY(3)
INTEGER coeind(0:maxdim)
INTEGER counter
INTEGER endhere
INTEGER err_pddcs
INTEGER err_write
INTEGER expr_img_max
INTEGER i,ii,j,k
INTEGER i_here
INTEGER iiter
INTEGER jjter
INTEGER iiterg
INTEGER img
INTEGER img_end
INTEGER img_start
INTEGER inp_err

```

```

INTEGER iseed
INTEGER nring
INTEGER internalcount
INTEGER itest (mgene)
INTEGER jj
INTEGER j_here
INTEGER last
INTEGER mfit
INTEGER m
INTEGER morder_int (0:4)
INTEGER ncol
INTEGER ndim
INTEGER nl
INTEGER nume_iter
INTEGER norderf
INTEGER norderl
INTEGER nr , nt
INTEGER nrow
INTEGER nsum
INTEGER num_fitmoments
INTEGER numcoe (0:4)
INTEGER nxp
INTEGER nyp , nmom
INTEGER p , q , s , t , l
INTEGER perc
INTEGER r_here
INTEGER readerr
INTEGER scounter
INTEGER skip
INTEGER start_time
INTEGER start_time_temp

```

```

INTEGER TPS
INTEGER theta_here
INTEGER torder_here(0:9)
INTEGER torderl
INTEGER unit_here
INTEGER usecoe(0:4)
INTEGER(kind=8) nto100
INTEGER(kind=8) nto
INTEGER(kind=8) ntraj
LOGICAL BRANCH
LOGICAL NT_wanted
LOGICAL Qflag
LOGICAL blur_grid_wanted
LOGICAL complag
real(dp) dflag
integer morder(0:4)
LOGICAL interactivity
LOGICAL oFlag
LOGICAL onlybasis
LOGICAL onlyfitdcs
LOGICAL onlyfitpddcs
LOGICAL outflag
LOGICAL posdef_flag
LOGICAL reblur
LOGICAL sim
LOGICAL sflag
LOGICAL triggerretry
real(dp) rxtemp, rytemp
real(dp) y_temp
real(dp) :: dxno = 0.0_dp
real(dp) :: dyno = 0.0_dp

```

```

real(dp) :: dzno = 0.0_dp
real(dp) :: vcollsum = 0.0_dp
real(dp) A20V, A20H, A22H, A22V, oH, oV
real(dp) Centre(1:18)
real(dp) Dep_fact1
real(dp) Dep_fact2
real(dp) ER
real(dp) EROTF
real(dp) junk
real(dp) EROTI
real(dp) EROTD
real(dp) EROTDd
real(dp) EXP_weight(-maxord:maxord,2)
real(dp) Fmoment_expr(-maxord:maxord,0:180,2)
real(dp) HCOE_Sim1
real(dp) HCOE_Sim2
real(dp) Intensity_H
real(dp) Intensity_V
real(dp) KHI_Ver
real(dp) epartner
real(dp) Khi_rot
real(dp) NOdist(3)
real(dp) RJP
real(dp) Radial_blur
real(dp) RkpNO(3)
real(dp) ThetaHigh
real(sp) V_Rg_p
real(dp) Vec_HOR_X(3)
real(dp) Vec_HOR_Y(3)
real(dp) Vec_HOR_Z(3)
real(dp) Vec_NOXHOR(3)

```

```

real(dp) Vec_NOYHOR(3)
real(dp) Vec_NOZHOR(3)
real(dp) Vector_226_Det(3)
real(dp) Vector_226_X(3)
real(dp) Vector_226_Y(3)
real(dp) Vector_226_Z(3)
real(dp) Vector_226sp(3)
real(dp) YColl(3)
real(dp) YColl_NO(3)
real(dp) ZColl(3)
real(dp) ZZETan(3)
real(dp) a11_res_H
real(dp) a11_res_V
real(dp) a20_res_H
real(dp) a20_res_V
real(dp) a21_res_H
real(dp) a21_res_V
real(dp) a22_res_H
real(dp) a22_res_V
real(dp) alpha
real(dp) aux_v1(3)
real(dp) aux_v2(3)
real(dp) aux_v3(3)
real(dp) beta
real(dp) branch_val
real(dp) branchf(2)
real(dp) branchr
real(dp) fsim(0:maxdim,-maxord:maxord)
real(dp) branchw
real(dp) chilim
real(dp) chield

```

```

real(dp) chisq(-1:maxord)
real(dp) chol_mat(maxord*2+1,maxord*2+1)
real(dp) coe(0:maxord)
real(dp) coeff(0:maxord)
real(dp) coeffbest(0:maxord)
real(dp) coeffbestin(0:maxord)
real(dp) coefflim(0:maxord,2)
real(dp) coefin(4,0:maxord)
real(dp) coefit(0:maxord)
real(dp) coenew(0:maxord)
real(dp) coevec(0:maxord,0:maxord)
real(dp) cos_2phi
real(dp) cos_2psi
real(dp) cos_oangle
real(dp) cos_phi
real(dp) cos_theta
real(dp) cos_theta0
real(dp) cos_thetacom
real(dp) cvec(0:maxord+5)
real(dp) d226
real(dp) d308
real(sp) dZ
real(dp) denom(-img_size:img_size,-img_size:img_size)
real(dp) der
real(dp) dtRg
real(sp) dtno
real(sp) dwRgx
real(sp) dwnoy
real(dp) evrel
real(dp) evrelp
real(dp) exp_sqr(-maxord:maxord,2)

```



```

real(dp) exp_sum(0:3)
real(dp) fbasis(0:maxdim,0:maxord,-maxord:maxord)
real(dp) fctvec(0:maxord*10)
real(dp) fexp1(0:maxdim,-maxord:maxord)
real(dp) fexp2(0:maxdim,-maxord:maxord)
real(dp) fexp3(0:maxdim,-maxord:maxord)
real(dp) fit
real(dp) fitness(mgene)
real(dp) flcoe(18)
real(dp) fmoment(-maxord:maxord,0:maxord,0:maxord*5)
real(dp) gene(100,mgene)
real(dp) hand
real(dp) hcoe1
real(dp) hcoe2
real(sp) no_ang_p
real(dp) oAngle
real(dp) oldfit(mgene)
real(dp) p226det
real(dp) p308det
real(dp) part
real(dp) phi_rot
real(dp) phicom
real(dp) pithetas
real(dp) pixtov
real(dp) pixmaxh
real(dp) pixmaxv
real(dp) proba11h
real(dp) proba11v
real(dp) proba20h
real(dp) proba20v
real(dp) proba21h

```

```

real(dp) proba21v
real(dp) proba22h
real(dp) proba22v
real(dp) probdcs_hor
real(dp) probdcs_ver
real(dp) probdet
real(dp) probhordcs
real(dp) probtot11
real(dp) probtot20
real(dp) probtot21
real(dp) probtot22
real(dp) probverdcs
real(dp) proj226
real(dp) proj308
real(dp) r
real(sp) rg_ang_p
real(sp) rg_ang_t
real(dp) rknox
real(dp) rknoy
real(dp) rknoz
real(dp) rkpnox
real(dp) rkpnoy
real(dp) rkpnz
real(dp) rmodk
real(dp) rmodkp
real(dp) rx
real(dp) ry
real(dp) rz
real(dp) sblur
real(dp) sigma(1:18)
real(dp) sim_img(-maxdim:maxdim,-maxdim:maxdim)

```

```

real(dp) sim_img_r(-maxdim:maxdim,-maxdim:maxdim)
real(dp) sin_2phi
real(dp) sin_2psi
real(dp) sin_2theta
real(dp) sin_NOangt
real(dp) sin_oangle
real(dp) sin_phi
real(dp) sin_rg_ang_t
real(dp) sin_theta
real(dp) sin_theta0
real(dp) sin_thetacom
real(dp) space
real(dp) summom
real(dp) sumfit
real(dp) t_nodtl
real(dp) tcoll
real(dp) temprknox
real(dp), allocatable :: temppolimh(:, :)
real(dp), allocatable :: temppolimv(:, :)
real(dp) temprkpnoy
real(dp) theta0
real(dp) theta0_fit
real(dp) theta226
real(dp) theta308
real(dp) theta_rot
real(dp) thetacom
real(dp) thetalow
real(dp) thetasave
real(dp) thetaswap
real(dp) unit_vec(maxord*2+1,maxord*2+1)
real(sp) vl_peak

```

```

real(sp) v2_peak
real(dp) vRgxp
real(dp) vRgyp
real(dp) vRgzp
real(dp) vcoll
real(dp) vcomx
real(dp) vcomy
real(dp) vcomz
real(dp) vector_308_det(3)
real(dp) vlabx
real(sp) sobdtheta
real(sp) sob
real(dp) vlaby
real(dp) vlabz
real(dp) vnoxp
real(dp) vnoyp
real(dp) vnozp
real(dp) vrelnono(3)
real(dp) vrelx
real(dp) vrely
real(dp) vrelz
real(sp) ang_end
real(sp) ang_start
real(sp) AKQVEC(10)
real(dp) BasHit(-img_size:img_size,-img_size:img_size)
real(dp) BasHitt(-img_size:img_size,-img_size:img_size)
real(sp) BasHittsp(-img_size:img_size,-img_size:img_size)
real(dp) BasHit_temp(-img_size:img_size,-img_size:img_size)
real(sp) FACTJ
real(sp) OFINL
real(sp) OINIT

```

```

real(sp) PDDCS(0:999,20)
real(sp) V_NO_p
real(sp) V_NO_psq
real(sp) V_rg_psq
real(dp) als1sqrt2
real(dp) als2sqrt2
real(dp) angthe
real(sp) angvec(3602)
real(dp) anorm1
real(dp) anorm2
real(dp) bas1lh(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas1lv(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas20h(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas20v(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas21h(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas21v(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas22h(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas22v(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) basdcsh(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) basdcsv(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas1lht(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas1lvt(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas20ht(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas20vt(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas21ht(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas21vt(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas22ht(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) bas22vt(-img_size:img_size,-img_size:img_size,0:maxord)
real(dp) basis(-img_size:img_size,-img_size:img_size,0:maxord*9)
real(dp) blur_const
real(dp) dang

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real(dp) dcs_fit1(-1000:1000,maxord)
real(dp) dcs_fit2(-1000:1000,maxord)
real(dp) dcs_fit3(-1000:1000,maxord)
real(dp) dcs_fit4(-1000:1000,maxord)
real(dp) dtlaser
real(dp) expr_img(-maxdim:maxdim,-maxdim:maxdim,3)
real(dp) expr_img_temp(-maxdim:maxdim,-maxdim:maxdim,3)
real(dp) expr_img_here1(-maxdim:maxdim,-maxdim:maxdim)
real(dp) expr_img_here2(-maxdim:maxdim,-maxdim:maxdim)
real(dp) expr_img_here3(-maxdim:maxdim,-maxdim:maxdim)
real(dp) expr_img_here1_pddcs(-img_size:img_size,-img_size:img_size)
real(dp) expr_img_here2_pddcs(-img_size:img_size,-img_size:img_size)
real(dp) expr_img_here3_pddcs(-img_size:img_size,-img_size:img_size)
real(dp) expr_img_here4(-maxdim:maxdim,-maxdim:maxdim)
real(dp) factor
real(sp) fwhmblur
real(sp) h_here
real(sp) v_here
real(dp) high_limit_NO
real(dp) high_limit_Rg
real(dp) hitmat(-img_size:img_size,-img_size:img_size)
real(dp) inv_dang
real(dp) inv_pixtov
real(dp) invsqrt3factj
real(dp) jfact1
real(dp) jfact1inv
real(dp) jfact2
real(dp) jfact2inv
real(dp) lambda
real(sp) low_limit_NO
real(sp) low_limit_Rg

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real(dp) modvrel
real(dp) nl_val
real(sp) no_ang_t
real(dp) norm_diff
real(dp) olbaba(-maxord:maxord,-maxord:maxord,-maxord:maxord)
real(dp) olexba(-maxord:maxord,-maxord:maxord)
real(dp) olexex(-maxord:maxord)
real(sp) pang
real(sp) peak1
real(sp) peak2
real(dp) polimh(-img_size:img_size,-img_size:img_size)
real(dp) polimht(-img_size:img_size,-img_size:img_size)
real(sp) polimhtsp(-img_size:img_size,-img_size:img_size)
real(dp) polimh_b(-img_size:img_size,-img_size:img_size)
real(dp) polimv(-img_size:img_size,-img_size:img_size)
real(dp) polimvt(-img_size:img_size,-img_size:img_size)
real(sp) polimvtsp(-img_size:img_size,-img_size:img_size)
real(dp) polimv_b(-img_size:img_size,-img_size:img_size)
real(dp) proimg(-img_size:img_size,-img_size:img_size,0:maxord*9)
real(sp) random_gauss1
real(sp) random_gauss2
real(sp) random_gauss3
real(sp) random_gauss4
real(sp) random_gauss5
real(sp) random_gauss6
real(sp) random_gauss7
real(sp) random_gauss8
real(sp) random_gauss11
real(sp) random_gauss12
real(sp) random_gauss13
real(sp) random_gauss14

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```

real(sp) random_gauss15
real(sp) random_gauss16
real(dp) real_nr
real(dp) real_nr_dtheta
real(dp) renorm
real(sp) rn1
real(sp) rn2
real(dp) satur
real(dp) savetheta
real(dp) scafax
real(dp) scafay
real(dp) scaling
real(sp) sob1
real(sp) sob2
real(sp) sob2_param1
real(sp) sob2_param2
real(sp) sob3
real(sp) sob4
real(sp) sob4_param1
real(sp) sob4_param2
real(dp) sqrttrjp_const
real(dp) sum_here
real(dp) temp_image_h(-img_size:img_size,-img_size:img_size,3)
real(dp) theta
real(dp) theta_deg
real(dp) theta_nt(0:180)
real(dp) thetamax
real(dp) thetamin
real(dp) thetap
real(dp) thetaxy
real(dp) vl_av

```



```

real(sp) v1_peakx2
real(dp) v2_av
real(sp) v2_peakx2
real(dp) v_NOx2
real(dp) v_Rgx2
real(sp) weightblur(-img_size:img_size,-img_size:img_size)
real(sp) weivec(-maxord:maxord)
real(dp) x,y,z
real(dp) xt(2001)
real(dp) xdet
real(dp) y1
real(dp) y2
real(dp) ydet
real(dp) zmax_here(0:maxdim)

integer counter_hist(0:180)

! Zero arrays - makes binary huge (but fast)!
DATA weightblur / img_elements_2d * 0.0_dp /
DATA polimv / img_elements_2d * 0.0_dp /
DATA polimh_b / img_elements_2d * 0.0_dp /
DATA polimv_b / img_elements_2d * 0.0_dp /
DATA fmoment / fmomdim * 0.0_dp /
DATA BasHit / img_elements_2d * 0.0_dp /
DATA BasHitt / img_elements_2d * 0.0_dp /
DATA BasHittsp / img_elements_2d * 0.0_dp /
DATA BasHit_temp / img_elements_2d * 0.0_dp /
DATA proimg / proimg_elements * 0.0_dp /
DATA basis / proimg_elements * 0.0_dp /
DATA PDDCS / 20000 * 0.0_sp /
DATA angvec / 3602 * 0.0_sp /

```

DATA sigma	/ 18 * 0.0_dp	/
DATA AKQVEC	/ 10 * 0.0_sp	/
DATA zmax_here	/ maxdim1 * 0.0_dp	/
DATA exp_sqr	/ 202 * 0.0_dp	/
DATA exp_sum	/ 4 * 0.0_dp	/
DATA exp_weight	/ 202 * 0.0_dp	/
DATA expr_img	/ maxdimimg * 0.0_dp	/
DATA expr_img_here1	/ maxdimdim * 0.0_dp	/
DATA expr_img_here2	/ maxdimdim * 0.0_dp	/
DATA expr_img_here3	/ maxdimdim * 0.0_dp	/
DATA denom	/ img_elements_2d * 0.0_dp	/
DATA counter_hist	/ 181 * 0	/
DATA usecoe	/ 5 * 0	/
DATA numcoe	/ 5 * 0	/
DATA bas11h	/ basdim * 0.0_dp	/
DATA bas11v	/ basdim * 0.0_dp	/
DATA bas20h	/ basdim * 0.0_dp	/
DATA bas20v	/ basdim * 0.0_dp	/
DATA bas21h	/ basdim * 0.0_dp	/
DATA bas21v	/ basdim * 0.0_dp	/
DATA bas22h	/ basdim * 0.0_dp	/
DATA bas22v	/ basdim * 0.0_dp	/
DATA basdcsh	/ basdim * 0.0_dp	/
DATA basdcsv	/ basdim * 0.0_dp	/
DATA bas11ht	/ basdim * 0.0_dp	/
DATA bas11vt	/ basdim * 0.0_dp	/
DATA bas20ht	/ basdim * 0.0_dp	/
DATA bas20vt	/ basdim * 0.0_dp	/
DATA bas21ht	/ basdim * 0.0_dp	/
DATA bas21vt	/ basdim * 0.0_dp	/
DATA bas22ht	/ basdim * 0.0_dp	/

```

DATA bas22vt
DATA polimht
DATA polimhtsp
DATA polimvt
DATA polimvtsp
/ basdim * 0.0_dp
/ img_elements_2d * 0.0_dp
/ img_elements_2d * 0.0_sp
/ img_elements_2d * 0.0_dp
/ img_elements_2d * 0.0_sp

```

```

END MODULE variables

```


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