

Development and Characterisation of a Cold Molecule Source and Ion Trap for Studying Cold Ion-Molecule Chemistry



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A thesis submitted for the degree of
Doctor of Philosophy
Trinity 2016

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A novel apparatus, combining buffer-gas cooling, electrostatic velocity selection and ion trapping, has been constructed and characterised. This apparatus is designed to investigate cold ion-molecule chemistry in the laboratory, at a variable translational and internal (rotational) temperature. This improves on previous experiments with translationally cold but rotationally hot molecule sources. The ability to vary the rotational temperature of cold molecules will allow for the experimental investigation of post-Langevin capture theories.

The properties of the cold molecular beam exiting the electrostatic quadrupole guide has been analysed thoroughly, using both mass spectrometric and spectroscopic measurements. A guided beam of mixed ammonia isotopologues (NH_3 , NH_2D , ND_2H and ND_3) is investigated and a model is developed to reconstruct the relative concentrations of each species at the guide exit. The model uses results from Monte Carlo trajectory simulations and is in excellent agreement with the experimental observables. The ability to determine and characterise a mixed molecular beam containing different isotopologues will allow for the study of astrochemically important processes such as deuterium fractionation.

The guided beam is further analysed using resonance-enhanced multi-photon ionisation (REMPI) spectroscopy. The orientation of molecules as they exit the guide and pass through regions of differing electric fields is investigated. REMPI spectra are recorded using different laser polarisations revealing a consistent difference in peak intensity for certain transitions, suggesting that the M -state distribution of the molecules is not isotropic. To confirm these results, the electric fields present in the detection region of the apparatus are modelled and state-tracking trajectory simulations performed, probing the M -state distribution of the molecules as they move through the detection setup. These simulations confirm a small retention of orientation, although the majority of orientation is lost due to adiabatic state-changing transitions as molecules pass through regions of very low electric field. Potential methods to retain a greater degree of orientation are investigated theoretically.

A linear Paul ion trap is combined with the buffer-gas cell and electrostatic guide apparatus, to facilitate the future study of ion-molecule reactions. Ca^+ Coulomb

crystals are formed in a linear Paul trap from laser-cooled Ca^+ , with bicomponent crystals formed upon the sympathetic cooling of Xe^+ ions into the crystal. A proof-of-principle charge exchange reaction between Xe^+ and ND_3 is observed by tracking the change in morphology of the Coulomb crystal. Ongoing diagnostics and technical improvements are in the process of being made to observe cold ion-molecule reactions with the new combined apparatus, which will lead to the investigation of such reactions at variable rotational temperatures. This will allow the effects of internal temperature on the rate of reaction to be determined and comparisons made with theory.

Acknowledgements

It has been an enormous pleasure and privilege for me to undertake doctoral research in the Department of Chemistry at the University of Oxford. I am honoured to thank here the extraordinary dedicated people and institutions that have facilitated and invigorated the research that has led to this thesis.

First and foremost, I would like to express my sincerest gratitude to my supervisors, Professor Timothy P. Softley and Dr. Brianna R. Heazlewood, for their excellent guidance and mentoring, for the generosity of their time and dedication and support of my research.

I would also like to thank all the members of the Softley Research Group, past and present, including Dr. Chris Rennick and Dr. Atreju Tauschinsky, whose advice and support contributed greatly to this work.

It has been a great pleasure to work along side my fellow students, who laid the foundations for this work, have assisted greatly in the development of new ideas, engaging in interesting and often fruitful discussions and contributing to the social life and camaraderie of the group. A big thanks to (in no particular order) Kathryn Twyman, Lee Harper, Laura Pollum, Jemma Gibbard, Mike Kohlhoff, Nabanita Deb, Katrin Dulitz, Jutta Toscano and Lorenzo “Alfonso” Petralia. A special mention is made to our international visiting students, Otto Schullian and Katharina Meyer, who both contributed to the group scientifically and socially.

I am also grateful to the excellent staff in the Electronics and Mechanical workshops at the Department of Chemistry, who not only fabricated the majority of the apparatus with skill and dedication but supported, developed and improved our experiments throughout the course of this project.

Last but not least, I am grateful to my family for their support and love throughout not only the past four years but my entire student career.

Chapter 3 of this doctoral thesis has been published in the following article:

E. W. Steer, K. S. Twyman, B. R. Heazlewood and T. P. Softley “Accurate determination of the relative concentrations of ammonia isotopologues in a cold, electrostatically guided molecular beam”, *Mol. Phys.*, 113, 1465 (2015).

Parts of Chapter 4 of this doctoral thesis has been submitted for publication in the following article:

E. W. Steer, L. S. Petralia, C. M. Western, B. R. Heazlewood and T. P. Softley, “Orientation of buffer-gas-cooled, electrostatically-guided ammonia molecules”, *J. Mol. Spectrosc.*, 332, 94 (2017).

I am grateful to the referees of these articles for the thorough feedback and suggestions received.

Edward Steer
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September 2016

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1

Introduction

1.1 Overview

In the previous ~ 50 years, there has been rapid progress in techniques for producing and utilising cold ($T < 10$ K) and ultracold ($T < 1$ mK) matter. Initially focused on cooling atoms, the field has expanded into cold and ultracold polyatomic molecular systems, hence paving the way for studies of cold chemistry. However, classical chemical dynamics, used to describe reactions which occur at room temperature (298 K) do not apply in the cold and ultracold regimes. Theories have been proposed in order to model chemical processes in these regimes, however there is little experimental data or evidence for these theories. The ability to study chemical processes at low temperatures will greatly improve our understanding of low-temperature chemical dynamics.

The possibility of cooling atoms down to ultracold temperatures first surfaced in the latter part of the 20th century. In 1975 Wineland and Dehmelt, and Hänsch and Schawlow [1, 2], outlined the theory of cooling atom beams with counter-propagating laser beams. This theory was not realised experimentally until 1984 when Chu *et al.* used counter-propagating lasers tuned close to a resonance of Na to slow a beam of Na atoms to 0.6 m s⁻¹ (by the relation $\frac{1}{2}mv^2 = k_{\text{B}}T$, this corresponds to a temperature of 240 μK). This work on laser cooling of atoms was regarded with such significance that it earned the 1997 Nobel Prize in Physics, awarded to Chu, Cohen-Tannoudji and Phillips. Laser cooling has since been applied to a wide variety of atoms and atomic cations¹. The alkali metals and the corresponding isoelectronic alkaline-earth metals have primarily been the focus of laser cooling due to their favourable energy level structure, although more “exotic” species such as Hg⁺ and In⁺ have been laser cooled, and many lanthanides have been suggested as potential candidates for laser cooling [5].

Despite the large impact that laser cooling continues to have on atomic physics, the technique is generally unsuitable for molecules. Laser cooling requires a closed cooling cycle, in which an electronic transition can be excited and then the ground state repopulated, generally by fluorescence. Due to the much more complex energy level landscape in molecules, arising from the rotational and vibrational degrees of freedom in molecules, such a closed cycle does not usually exist. A few experiments demonstrating laser cooling of molecules have been conducted, for example DeMille *et al.* have successfully demonstrated laser cooling for the molecule SrF [6], taking advantage of the highly diagonal Franck-Condon factors in this molecule and using the Zeeman effect to mix rotational states to minimise decay into unwanted states [7]. Additionally YO, CaH and other metal hydrides have been successfully laser cooled [6, 8, 9, 10], with BaH and LiBe proposed as candidates for laser cooling

¹Laser cooling is generally not applicable to atomic anions due to the lack of bound excited states. It has been predicted that Os⁻, and more recently, La⁻ are possible exceptions to this trend [3, 4].

[11, 12]. However, the range of molecules amenable to laser cooling is not broad enough to investigate a wide range of chemistry under cold conditions.

The first “cold” molecule reported was Cs_2 in 1998, formed from the photoassociation of laser-cooled Cs atoms. The molecule was reported to have a translational temperature of 300 μK [13]. Photoassociation is an “indirect” technique of forming a cold molecule – where the molecule is formed from pre-cooled atoms. Complementing “indirect” techniques, “direct” cooling methods were developed, which involve cooling molecules directly rather than forming them from cold atoms. Direct methods include, for example, buffer-gas cooling, Stark and Zeeman deceleration, molecular beam techniques and velocity selection. These will be introduced in more detail in Section 1.3.2.

When laser cooling is applied to atomic cations, the ions are typically confined using an ion trap. Ion traps spatially confine charged particles (ions) using time-varying electric fields, creating an effective potential minimum (or *pseudopotential*) in a localised region of space. Localisation of ions is required for laser cooling as each ion must undergo a large number (*ca* 10^6) of cooling cycles in a short period of time, in order to be cooled effectively. Recently, ion traps have found utility in cold chemistry experiments [14] in order to increase interaction time between reactants, to accumulate density of reactants and to observe “slow” processes in the laboratory. The linear Paul ion trap, perhaps the most commonly used ion trap, is employed in this work. The development of the linear Paul ion trap was regarded with such significance that H. G. Dehmelt and W. Paul were awarded the 1989 Nobel Prize in Physics for development of this technique [15]. Further information on ion trapping can be found in Chapter 5. Cold physics and chemistry experiments have utilised many different forms of trap, including ion traps, magnetic traps, hybrid traps (a combination of an overlapping ion trap and an atomic trap, usually a Paul trap and magneto-optical trap – often used to study the interactions between a Bose-

Einstein condensate of ultracold atoms and trapped cold ions) [16], optical traps and magneto-optical traps. Recent experimental developments in ion trap design include toroidal traps [17] and surface-electrode ion traps (“trap on a chip”) [18]. One interest in cold molecules arises from the long de Broglie wavelengths exhibited at these temperatures. The de Broglie wavelength is defined as $\lambda = h/p$, where λ is the de Broglie wavelength, h is Planck’s constant and p is the momentum of the molecule, which is related to its translational temperature. While generally very small at ambient temperatures (298 K), the de Broglie wavelength becomes comparable to, or larger than, the typical range of intermolecular interactions at cold temperatures. For example, the de Broglie wavelength of ND₃ is 35.4 pm at 298 K, but increases to 194 pm at 10 K and 19.4 nm at 1 mK, which is comparable to the intermolecular spacings at which chemical interactions occur. Chemical bonds typically have lengths between 100 pm and 300 pm and long range intermolecular interactions are on the order of 5 nm [19]. It is therefore clear that the wave-like properties of molecules become increasingly important in the cold and ultracold regimes. The objective of this work is to investigate chemical reactions, specifically ion-molecule chemistry, at cold temperatures and explore the importance of such effects on chemical behaviour.

1.2 (Ultra)cold reaction dynamics

The potential reaction pathways for few-atom systems can often be depicted using a simplified potential energy surface. In one valley are the reactants, and in the other valley are the products. These two valleys are separated by an activation barrier, E_a , along the reaction coordinate. In such cases, the reaction rate constant,

k , is given, to first approximation, by the Arrhenius equation:

$$k = Ae^{-E_a/RT} \quad (1.1)$$

where A is a reaction-dependent scaling factor and R is the molar gas constant. Arrhenius-type reactions proceed *via* a transition state, a highly reactive intermediate which lies at the highest energy point on the reaction coordinate. Various transition state theories have been developed to predict the reaction rate constants for such reactions. More information on transition state theory can be found in references [20, 21].

Equation 1.1 would suggest that the rate of chemical reactions at cold and ultracold temperatures to be negligible. However, some reactions (termed “barrierless”) remain fast even at low temperatures, due to their lack of an activation barrier. Barrierless reactions include some radical-radical, radical-neutral and ion-neutral processes, reactions involving excited (Rydberg) states and some unimolecular decompositions and atom-molecule reactions [22]. These barrierless reactions are thought to dominate the chemistry in naturally cold environments, such as those that occur at high altitudes in the Earth’s atmosphere and in the interstellar medium. Molecules have translational, rotational, vibrational, electronic and in some cases, nuclear or electronic spin degrees of freedom. At room temperature, a very large number of translational and internal (primarily rotational) energy levels are populated. Rate constants and reaction parameters obtained at room temperature are an average over all of these states. At cold temperatures, only a few energy levels are populated (in some cases, only the ground state), allowing the quantum state distribution to be established and rate constants extracted with minimal (or no) averaging over quantum states. Long-range intermolecular forces are often very important in cold chemical reactions, where weak interactions such as van der Waals’ forces can guide reactants along reactive channels and pre-organise

reactants, enabling the formation of intermediates or transition states. Such effects are seen in the $\text{Cl} + \text{HD}$ reaction [23]. Quantum mechanical calculations of the reactive potential energy surface, ignoring van der Waals’ forces, predict an equal ratio of HCl and DCl products; however, explicitly including the van der Waals’ forces gives a preference for DCl , a result that is confirmed by crossed-beam experiments [24]. Many of these weak interactions are quantum state dependent. Hence the observation of cold, state-selected reactions can elucidate previously hidden features on the intermolecular potential energy surface which lead to new reaction pathways that are undetectable in “hot” systems, where there is a degree of thermal averaging over quantum states.

Typically, rate constants for barrierless reactions can be predicted using the Langevin model [25]. The Langevin model states that the rate constant for a reaction between an ion and a neutral molecule is given by [26]:

$$k = 2\pi\sqrt{\frac{q^2\alpha}{\mu}} \quad (1.2)$$

where α is the polarisability of the molecular reactant, q is the charge of the ion and μ is the reduced mass of the reacting pair. From Equation 1.2, it can be seen that k does not depend upon the chemical identity or quantum state of the reactants, and is temperature independent. Hence, it would be expected for barrierless reactions that the rate constant would be independent of the reaction conditions (such as temperature). Further refinements to the Langevin model added molecule- and state-dependent terms to better predict rate constants for fast, barrierless reactions [27], leading to the development of post-Langevin theories [28].

A simple method for considering barrierless reactions is to assume the reaction takes place on an isotropic potential energy surface. Although barrierless reactions do not have a thermal activation energy, E_a , such reactions can have a centrifugal barrier

arising from the orbital angular momentum of the colliding reactants. A typical intermolecular potential, $V_{\text{eff}}(r)$ in this instance, is given in Equation 1.3 [29]:

$$V_{\text{eff}}(r) = \frac{b^2 E_{\text{coll}}}{r^2} - \frac{C_s}{r^s} \quad (1.3)$$

where E_{coll} is the collisional energy, r is the distance between reactants, s is dependent on the type of interaction being considered (s takes a value of 4 for an ion-dipole interaction, and 6 in the case of only van der Waals' forces present), C_s is an orientation dependent parameter and b is the impact parameter, defined as the distance of closest approach of the reactants in the absence of intermolecular forces (see Figure 1.1), and is defined as:

$$b = \frac{l}{\mu v_{\text{rel}}} \quad (1.4)$$

where l is the orbital angular momentum, μ is the reduced mass and v_{rel} the relative velocity of the reactants. b is related to the reaction cross section σ , in the case the particles can be modelled as hard spheres, by the relation:

$$\sigma = 2\pi \int_0^{b_{\text{max}}} P(b) b \, db \quad (1.5)$$

where $P(b)$ is the *opacity function*, which gives the impact-parameter-dependent probability of a reaction occurring for a given collision. The cross section is linked to the reaction rate constant by:

$$k(T) = \int_0^\infty v_{\text{rel}} \sigma f(v_{\text{rel}}) \, dv_{\text{rel}} \quad (1.6)$$

where $f(v_{\text{rel}})$ is the velocity distribution in the sample.

From Equation 1.4, it can be seen that for a given impact parameter (b), if v_{rel} is smaller (indicative of cold temperatures) then l is smaller as a result, the

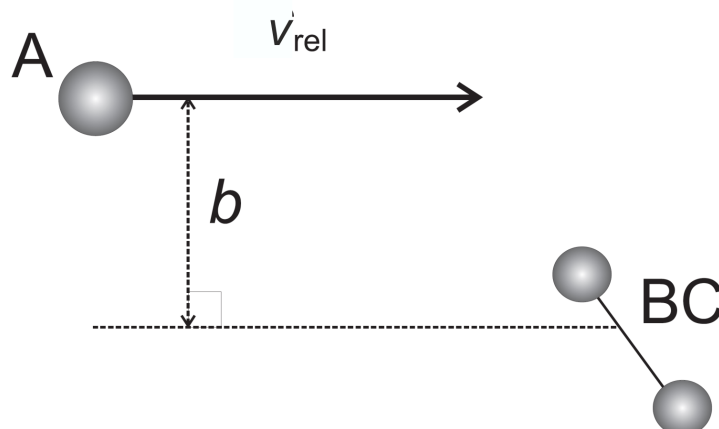


Figure 1.1: Schematic showing the impact parameter b for the collision between reactants A and BC. A range of b values are obtained under experimental conditions.

centrifugal barrier is reduced and the probability of a reactive collision is increased. The use of an effective intermolecular potential, such as the example given in Equation 1.3, is useful in considering the dynamics of ion-molecule reactions as only the motion along the one-dimensional reaction coordinate needs to be considered *i.e.* it removes any angular dependence on the potential. This simplifies the problem allowing for more efficient calculation of a theoretical rate constant.

The majority of post-Langevin theories (often termed “capture theories”) include the Langevin assumption that if the centrifugal barrier is surmountable, the probability of a reaction occurring is unity, hence ignoring the internal state of the molecules [28, 30]. More advanced quantum-capture theories, such as rotationally-adiabatic quantum capture theory [31], developed by D. Clary, have been introduced to account for the fewer internal quantum states populated in cold molecules. These theories consider the rotational motion of molecules by calculating radial potential energy curves for the relevant rotational (J) states of the reactants, and hence predict a temperature- and quantum-state dependence [32]. These theories show significant deviations from the Langevin model in the cold temperature regime [28]. Rotationally-adiabatic capture theory predicts further enhancements in k

at temperatures $T < 20$ K, which are due to the ability of reactants to “lock-in” to a favourable conformation before collision. An example of the rotational state dependence on k as a function of T for an ion-molecule reaction in the low-temperature regime is shown in Figure 1.2. These theories, proposed by Clary, are semi-classical in nature. More recently, quantum mechanical capture theories have been developed and proposed (such as adiabatic channel capture theory and quantum capture theory [33, 34]) which have been successfully deployed to predict the behaviour of low-temperature chemical reactions (such as $\text{Li} + \text{CaH} \rightarrow \text{LiH} + \text{Ca}$ at 1 K [35]) and Penning ionisation reactions in the ultracold regime [36].

However, due to the technical challenges of performing cold, state-selected reactions in the laboratory, minimal experimental work has been conducted to verify these theories. Preliminary investigations into reactions of atomic ions with small polar molecules such as HCl, H₂S and SO₂ have been conducted using the CRESU (*Cinétique de Réaction en Ecoulement Supersonique Uniforme* - Reaction Kinetics in Uniform Supersonic Flow) method (outlined in Section 1.2.1) and show good agreement with post-Langevin theory [37] (an example is given in Figure 1.3). However, the limited range of temperatures accessible in the laboratory has restricted the ability to record a full range of experimental data to confirm these theories. Hence, the ability to perform controlled, cold ion-molecule experiments in the laboratory will act as a test for post-Langevin theories and greatly improve our understanding of this area of chemistry.

1.2.1 Applications of Cold Chemistry

Cold molecules have many (potential) applications across different branches of physics and chemistry. In chemistry, one of the key applications is in high resolution spectroscopy and precision measurements. For example, resolving small energy differences between different isomers or enantiomers [39, 40], and investigating

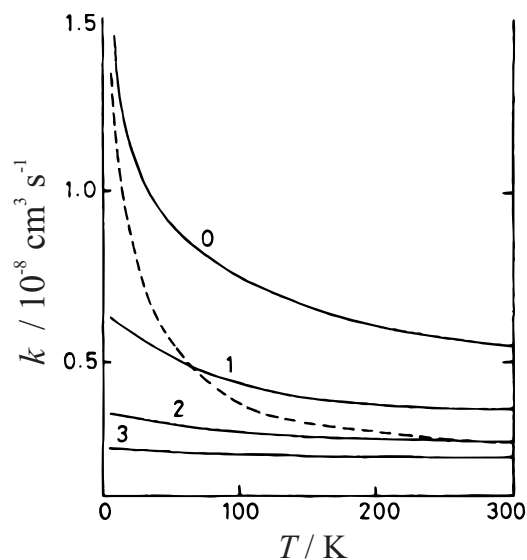


Figure 1.2: Dependence of k with T in the $\text{N}^+ + \text{NH}_3$ reaction, for rotational levels $J = 0-3$, as calculated from rotationally-adiabatic capture theory. The solid curves represent the rate constant for a given J and the dotted line gives k for a Boltzmann distribution of rotational states. Reproduced from [31] with permission from The Royal Society of Chemistry.

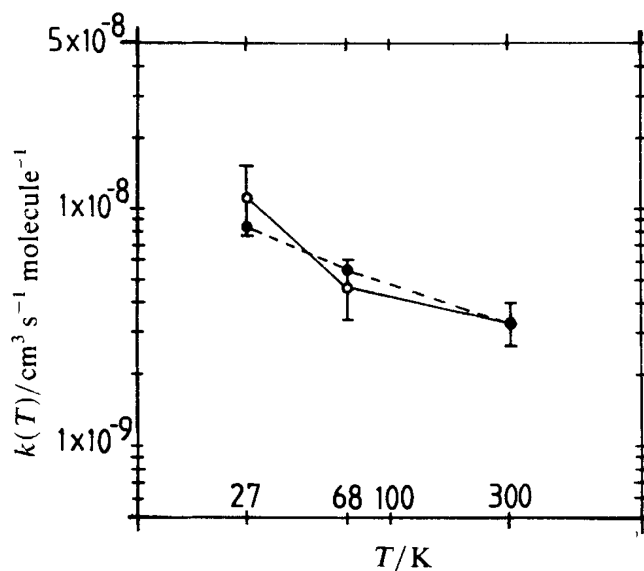


Figure 1.3: Comparison of rate constants obtained by experiment (CRESU) and rotationally-adiabatic capture theory for the $\text{He}^+ + \text{HCl}$ reaction. The dotted lines and solid points are obtained from theory, and the circles and solid line are from experimental measurements. Reproduced from [38] with permission from The Royal Society of Chemistry.

the dynamics of exotic transient species such as DyCl^+ [41]. Such measurements are made possible in cold molecular sources due to the longer interaction times with the probe radiation and hence the greater degree of averaging that can be achieved. Long interaction times also allow weakly allowed transitions to be observed due to the narrower linewidths achievable (this arising as a consequence of the Heisenberg uncertainty principle). Cold molecules allow for other more “fundamental” spectroscopic experiments, such as resolving weakly-allowed spectroscopic transitions [42], probing the potential for time-variation of the fundamental constants [43, 44], the electric dipole moment of the electron [45] and the theory of parity violation in chiral molecules [46]. For example, the group of S. Willitsch have used cold, trapped N_2^+ ions (sympathetically cooled by laser-cooled Ca^+ ions) to resolve weak dipole-forbidden transitions. Such transitions were resolved due to the longer interaction times available with the laser radiation (on the order of minutes) in localised environments such as ion traps [47], hence the enhanced sensitivity. Another novel experiment is in the group of J. Doyle, who are investigating cryogenic buffer-gas-cooled ThO as a probe for the electric dipole moment of the electron, exploiting the large internal electric field in ThO (104 GV cm^{-1} in the metastable $^3\Delta$ electronic state [48]) to enhance sensitivity. Further information on these measurements can be found in reference [45].

Other applications for trapped ions have included high-precision sensors for electromagnetic fields, mass spectrometry and metrology [49]. An example of trapped ions being employed as a sensor can be found in the experiments of I. Baumgard *et al.*, who employ a trapped $^{171}\text{Yb}^+$ ion to sense weak magnetic fields, with a sensitivity $\sim 4 \text{ pT Hz}^{1/2}$, greater than that of many existing crystal-based methods [50]. Ion traps are frequently utilised in mass spectrometers, particularly in the biosciences, to enhance the mass resolution, and allow for “tandem” experiments in which several experiments or measurements are conducted sequentially [51].

Trapped ions have been suggested as potential “qubits” as part of a quantum computer [52]. For example, the group of W. Hensinger at the University of Sussex have developed arrays of microfabricated ion traps on a 2D SiO₂ substrate, in which Yb⁺ ions are trapped and can be shuttled around the substrate [53], allowing different traps to be used for computation and information storage, as well as providing scalability [54]. Research at Oxford Physics by D. Lucas *et al.* is investigating the use of ⁴³Ca⁺ ions (cooled to 1.25 μ K) as qubits – in these experiments, a small magnetic field (10 mT) is applied and a laser pulse is used to entangle the Zeeman sublevels of the ion and hence change the information stored in the “bit” [55].

Low temperature chemistry has particular relevance to astrochemistry; temperatures in the interstellar medium range from 30 K in dense molecular clouds to 2.7 K, the temperature of the cosmic microwave background. Temperatures as low as 1 K have been observed in the centre of the Boomerang Nebula, where CO molecules absorb microwave photons and adiabatic expansion of the cloud results in a lower overall temperature [56]. Around 10% of the total matter of the universe is found in interstellar clouds formed of dust and gases. Molecules were first detected in these clouds in 1937 by rotational (microwave) spectroscopic measurements [57]. Since then, in excess of 190 molecules and molecular ions have been detected in the interstellar medium, including isotopologues of these species [58].

A particular phenomenon of interest in astrochemistry is deuterium fractionation, where the cosmic abundance of deuterated molecules is greater than what would be expected from the natural abundance of deuterium in the interstellar medium. This suggests that the mechanism for forming such molecules favours the deuterated product. Deuterium fractionation has been observed in cold chemistry reactions in the laboratory, where the reaction of laser-cooled Mg⁺ ($3p\ ^2P_{3/2}$) with HD favoured the production of MgD⁺ over MgH⁺ [59]. The ratio of MgD⁺ to MgH⁺ observed was 5:1, whereas statistically it would be expected to be 1:1. A previous

(hot) ion beam experiment investigated the reactions of singly charged metal ions (M^+) with HD and found two competing mechanisms – one which favoured MD^+ formation and the other MH^+ [60, 61]. Models have been developed to predict the possible pathways of chemical reactions in the interstellar medium, however to enhance and understand these models fully, experimental branching ratios and rate constants at low temperatures are required [62]. Traditionally, data on astrochemical processes has been obtained by performing an equivalent reaction over a range of typical laboratory temperatures (the lowest temperature often being that of liquid N_2 : 77 K) and extrapolating back to interstellar temperatures. However, due to the different scaling laws predicted under (ultra)cold conditions, as alluded to in Section 1.2, this can lead to an uncertainty in the low temperature rate constant of several orders of magnitude.

CRESU is a technique developed in 1984 for performing cold reactions ($T < 80$ K) in a uniform flow [63, 64]. This technique can be used to study neutral-neutral collisions, or alternatively ion-neutral collisions (by intersecting the beam with an electron gun). The CRESU technique has seen extensive use in studying reactions of astrochemical significance in the laboratory, due to the low temperatures than can be obtained (as low as 6 K [65]) and high densities ($10^{16} - 10^{18} \text{ cm}^{-3}$ [66]). However, due to the high laboratory frame velocity of the gas in a CRESU experiment, only fast reactions (typically $k > 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) can be studied. Also, the Laval nozzle used in CRESU has a larger aperture compared to the pulsed valve used in a supersonic expansion [67], and additionally produces a continuous molecular beam, resulting in high gas consumption (typically $\sim 50 \text{ dm}^3 \text{ min}^{-1}$, with 1% of the total gas being the reactants [68]) and the need for large pumping capacity to maintain high-vacuum conditions. While later amendments addressed some of these limitations (for example, operating in pulsed mode to reduce gas consumption [69]), few reactions can be easily studied at $T < 20$ K, and extension to temperatures

below 1 K is probably not achievable.

1.3 Methods to produce cold molecules

Methods to form cold and ultracold molecules can be grouped into two categories: “direct” methods, in which molecules themselves are cooled to low temperatures, and “indirect” methods, in which a molecule is formed *in situ* from cold atoms. In this section an overview of these methods will be presented.

1.3.1 Indirect methods

1.3.1.1 Photoassociation

Photoassociation involves the formation of a molecule from two ultracold atoms. The atoms absorb a photon (γ) during a collision, promoting the pair of atoms (whose orbitals are sufficiently overlapped during the collision) to an excited molecular electronic state (the forward reaction in Equation 1.7). This excited molecule either dissociates (the reverse reaction), or emits a photon, decaying to a bound ground (or lower in energy) electronic state of the newly formed molecule (Equation 1.8).



This method has been used to form molecules such as LiCs and Cs₂ in their vibrational ground state from laser cooled atoms [70, 71]. In a typical photoassociation experiment, laser cooled atoms are held in a magneto-optical trap (MOT) and the photoassociation process is driven by a narrowband continuous wave laser [72]. This can produce ultracold molecules ($T < 1$ mK), however the probability of forming a

ground state molecule is small (most photoassociated molecules dissociate from the excited state) and it is challenging to accumulate a significant density of molecules. A comprehensive discussion of the formation of molecules by photoassociation can be found in references [73, 74].

1.3.1.2 Magneto-association

Magneto-association is similar to photoassociation, in that a molecule is formed *in situ* from ultracold atoms (these ultracold atoms are usually produced by laser cooling). Feshbach resonances occur when a pair of atoms in a non-bound state have potential energy identical to that of a bound (molecular) state on an excited potential energy curve. For paramagnetic species, an external magnetic field will affect the potential energy of the species. By tuning the external magnetic field, B , such that the potential energy of the atoms passes through the resonance, an adiabatic crossing between the dissociated and associated (molecular dimer) potential energy curves can occur, hence it is possible to drive the formation of ultracold molecules.

The ability to form ultracold molecules from photo- and magneto-association has lead to several studies on alkali metal dimers. The reactive collisions of these dimers have been studied *e.g.* inelastic collisions of homoatomic systems such as $\text{Rb} + \text{Rb}_2$ [75], $\text{Cs} + \text{Cs}_2$ [76] and $\text{Na} + \text{Na}_2$ [77], in addition to similar processes in heteroatomic systems such as $\text{K/Rb} + \text{KRb}$, $\text{Cs} + \text{LiCs}$ and association of Cs_2 to form Cs_3 and Cs_4 [78, 79]. These experiments represent some of the lowest temperature reactions observed to date; in the case of $\text{KRb} + \text{K/Rb/KRb}$, temperatures as low as 250 nK have been observed [80, 81]. It is noted that these photo- and magneto-associated molecules are generally formed in an internally excited state, in order to reach the ground state optical pumping methods such as stimulated Raman adiabatic passage (STIRAP) are used. The work on KRb was extended further, using external electric fields to control the stereodynamics of the reaction

between two KRb molecules trapped in an optical array. The reaction rate was reduced by two orders of magnitude by suppressing “head-to-tail” collisions, where the dipoles are oriented [82]. This is a demonstration of the use of ultracold atoms and molecules to gain a greater degree of control over chemical processes. However, photo- and magneto-association is only applicable to a small subset of diatomic molecules, primarily those of alkali metals, with favourable resonances.

1.3.1.3 Photostop

Photostop is a method designed to produce cold atoms (or molecules) from a molecular precursor, by the careful selection of the photodissociation laser wavelength, such that the molecular fragments have a well defined centre-of-mass and lab-frame velocity. In a photostop experiment, the molecular precursor to the species of interest is seeded in an inert gas and introduced into a region of high vacuum *via* a supersonic expansion. A laser beam is tuned to a dissociative transition of the molecule, resulting in its fragmentation. When molecules are dissociated into fragments, the fragments recoil relative to the centre-of-mass frame. The lab frame velocity is given by the resultant vector of this recoil and the centre-of-mass frame velocity of the fragment. The photolysis energy and beam velocity can be selected such that this resultant vector is significantly less than the initial beam velocity (*i.e.* deceleration has occurred) or even zero *i.e.* the selected fragments are stationary in the lab frame. This method has been employed by J. Lam and C. Rennick using Br₂ molecules to produce stationary Br atoms [83]. A Newton (vector) diagram of the deceleration process is given in Figure 1.4. Here, the photostop apparatus was combined with a mechanical chopper to tune the beam pulse duration and a magnetic trap to accumulate Br atom density [84], with a view to utilising the accumulated stationary Br atoms to perform chemical experiments *e.g.* by leaking a reactive species into the chamber or *via* a further supersonic expansion. In the

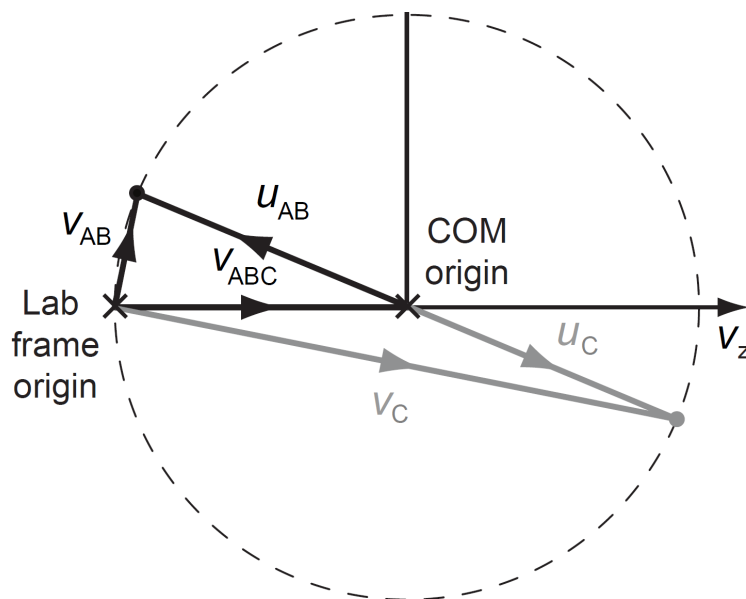


Figure 1.4: Newton diagram showing the principles of the photostop method. u refers to centre-of-mass frame velocities and v refers to lab-frame velocities. If u_{AB} is equal and opposite to v_{ABC} , then $v_{AB} = 0$. The grey lines show a theoretical acceleration of particles using this method. Reproduced from [89].

current setup, shown in Figure 1.5, REMPI spectroscopy and velocity map imaging has been employed to confirm the presence, and position of, Br atoms in the trap. Production of stationary I atoms (from ICl) [85] and O atoms (from NO_2) [88] by photostop has also been demonstrated. The technique has been extended to molecules with the production of cold NO molecules (also from NO_2) with a temperature of 1.6 K [86, 87]. A disadvantage of the photostop method is that a molecular precursor species that can be seeded in a molecular beam and easily dissociated into the target atom or molecule is required. Also, the combination of the photostop technique and a magnetic trap yielded fairly low densities – on the order of 10^7 cm^{-3} , which will limit the potential for performing chemical reactions.

1.3.2 Direct Methods

Direct cooling methods yield cold ensembles of molecular species from molecules already existing in a bound state, rather than forming the molecular species *in*

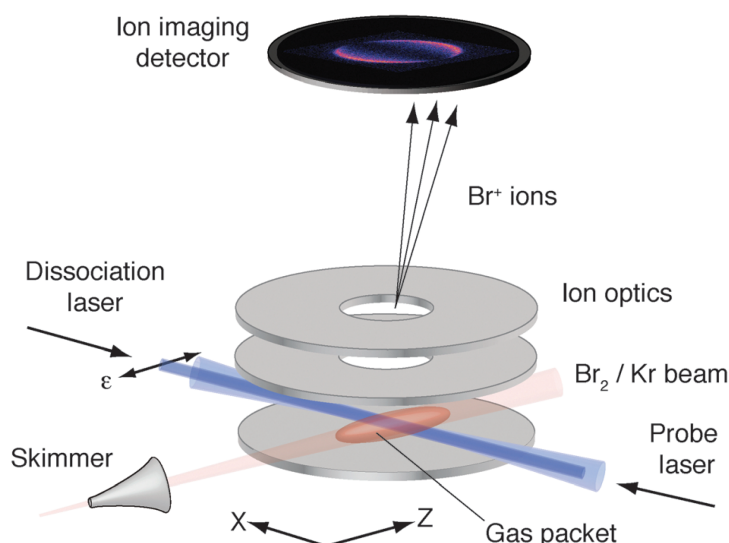


Figure 1.5: Schematic of the Oxford photostop experiment. Br_2 atoms are dissociated by a tunable dye laser. Br atoms accumulate in the magnetic trap and after a set delay, a further laser resonantly ionises the Br atoms which are detected by the imaging setup. Reproduced from [83] with permission from The Royal Society of Chemistry

situ from cold atoms. Traditionally, molecules are cooled in the laboratory using supersonic expansions, where gaseous species (usually seeded in a non-reactive carrier gas) are expanded from a high pressure reservoir into a vacuum. While this gives high densities ($\sim 10^{13} \text{ cm}^{-3}$) and low translational temperatures in the centre-of-mass frame (typically $\sim 1 \text{ K}$), these beams have very high laboratory-frame velocities. Many direct methods involve reducing the lab-frame velocity of a supersonic molecular beam.

To improve upon the basic supersonic expansion, mechanical methods involving a non-stationary molecular beam source have been used to produce molecular beams with a low lab-frame velocity. This technique involves mounting a pulsed valve to a rotating plane. The velocity of the rotor cancels the molecular beam velocity, giving a low beam velocity in the lab frame. The advantage of this technique is that it can be applied to any species which is gaseous under ambient conditions and has been employed to produce slow beams of the noble gases, O_2 , Cl_2 , NO_2 , NH_3 and SF_6 with velocities as low as 35 m s^{-1} [90]. However, the molecules have a broad velocity

distribution and are typically not quantum state selected, thus limiting the usefulness of the technique for studying chemical reactions under cold, controlled conditions.

1.3.2.1 Deceleration

Stark deceleration, as the name implies, utilises the Stark effect to decelerate a packet of molecules. The Stark effect describes the perturbation in the energy levels of a polar species when it is subjected to an external electric field. Depending on the quantum state, this effect results in either an increase or a decrease in potential energy with increasing applied electric field. Such states are labelled low-field seeking states (LFS) or high-field seeking states (HFS), respectively. An energy level diagram for ND₃, a molecule often utilised in Stark deceleration, showing the HFS and LFS states is given in Figure 1.6. The mathematical formulation of the Stark effect is described in more detail in Sections 2.3 and 4.5.1. Stark deceleration was pioneered by the group of G. Meijer in 1999 and was initially demonstrated using CO molecules [91]. The technique is now utilised in many different laboratories, including our group [30], and has been applied to a wide array of neutral polar molecules such as NH₃, ND₃, CO, SO₂ *etc.*, small organics including formaldehyde and benzonitrile [92], as well as radical species such as OH [93], NO [98] and NH [99]. The van der Meerakker group (Radboud University Nijmegen) have been at the forefront of utilising Stark deceleration to investigate the chemistry and underlying quantum mechanics of collisions in cold molecular beams. Experiments include investigating the reactions of OH radicals with *ortho*- and *para*-H₂ [94] and O₂ and H₂ [95], as well as imaging resonances in cold inelastic radical-atom collisions, such as those between NO and He [96] and OH and Xe [97].

Stark decelerators consist of many pairs of electrodes to which high voltages are applied, creating an applied electric field across the electrode array. The experimental design of a Stark decelerator is shown in Figure 1.7. Packets of molecules from a

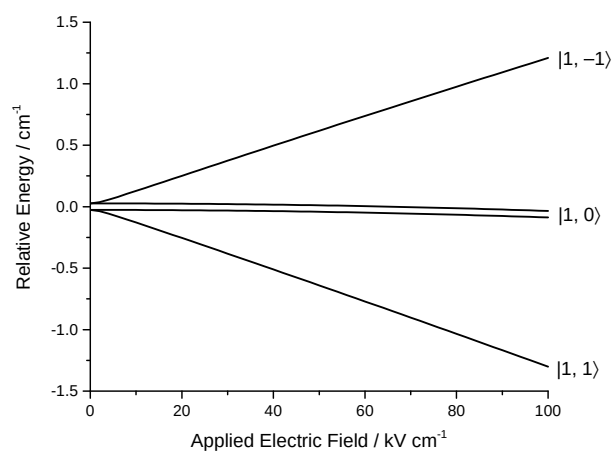


Figure 1.6: Energy level diagram showing the effect of applied electric field on the levels of ND_3 , due to the Stark effect. States are labelled $|J, MK\rangle$.

supersonic molecular beam pass through these electrodes, to which high voltages are applied sequentially. Polar molecules interact with this inhomogeneous electric field and molecules in LFS states are progressively decelerated. When a molecule in a LFS state approaches a pair of electrodes with high voltages applied, the molecule experiences a potential energy maximum, which has the effect of converting the kinetic energy of the molecule to potential energy. If the electrodes are held at static voltage, the molecule would regain the kinetic energy when it passes beyond the maximum of the potential energy curve. However, a switching sequence is timed such that when a packet of molecules has lost a selected amount of kinetic energy, the voltages are switched and high voltages are applied to the next pair of electrodes, hence creating another potential energy maximum. A schematic of the operation of a Stark decelerator is given in Figure 1.8.

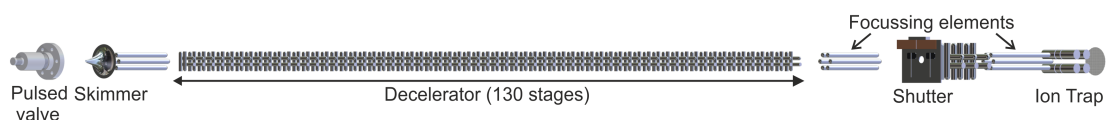


Figure 1.7: Schematic of the Oxford Stark Decelerator. Molecules, seeded in a noble gas, enter via a pulsed valve and are decelerated by applying voltages to the 131 electrodes in the decelerator. A fast shutter removes undecelerated components and focussing elements direct the decelerated beam into the ion trap. Adapted from [30].

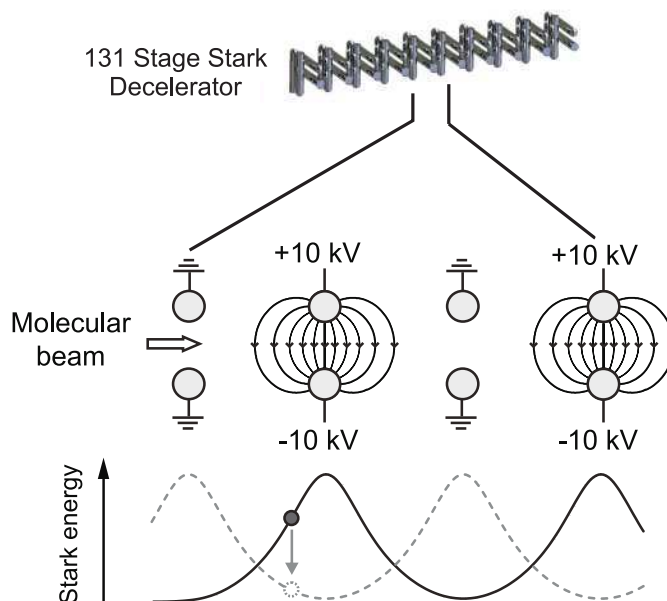


Figure 1.8: Diagram showing the operation of the Oxford Stark decelerator. Voltages of ± 10 kV are applied to individual electrode pairs in sequence, which creates a potential maximum (solid line on Stark energy plot). When the molecules have reached a selected point between the electrode pairs, the voltages are switched and a small amount of molecular kinetic energy is converted to potential energy. The molecules then encounter another potential maximum on the next electrode pair (dotted line). Figure adapted from [100].

Stark deceleration is quantum state selective – molecules at the end of the deceleration sequence are typically in a single quantum state. Stark decelerators have been used in high resolution spectroscopy, taking advantage of the increased interaction time between molecules in a slow moving beam and electromagnetic radiation. One example of this is the elucidation of the hyperfine structure of $^{15}\text{ND}_3$ [101] using a Stark-decelerated molecular beam, obtaining spectral linewidths as narrow as 1 kHz. Stark decelerators have been combined with ion traps, as in the Oxford experiment (see Figure 1.7 and references [30, 102]), to investigate ion-neutral reactions.

Following on from the success of Stark deceleration, Zeeman deceleration was developed [103], based on similar principles as Stark deceleration but using magnetic, rather than electric, fields. This expanded the range of species that could be decelerated to include paramagnetic species. Species that have been successfully decelerated

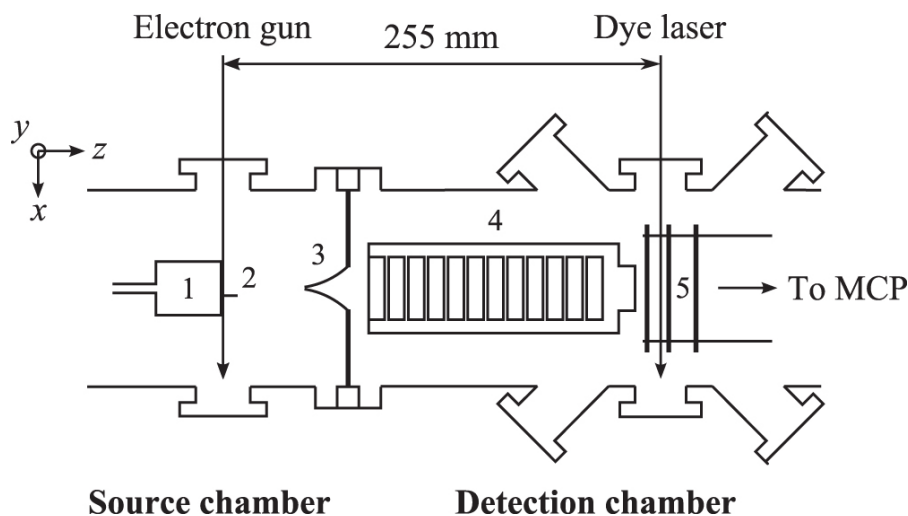


Figure 1.9: Outline of the Oxford Zeeman decelerator. The components are labelled as: 1) Pulsed valve. 2) Capillary tube. 3) Skimmer. 4) Zeeman decelerator (coils). 5) Time-of-Flight mass spectrometer (for detection). Figure adapted from [109].

using a Zeeman decelerator include H and D atoms [103], metastable $\text{Ne}(^3P)$ [104] and $\text{N}(^2D)$ [105] atoms, CH_3 radicals [106] and O_2 molecules [107]. Similar to Stark decelerators, Zeeman decelerators have a series of coils (electromagnets) which are pulsed sequentially to produce a moving potential energy maximum for molecules travelling through the decelerator. A typically Zeeman decelerator design is given in Figure 1.9. Recent developments have utilised genetic algorithms to optimise the pulse sequence to improve density and the degree of deceleration [108].

Another direct cooling technique is optical deceleration, where an intense optical field is used to manipulate molecules. This technique can be applied to a wide range of neutral species – in contrast to Stark and Zeeman deceleration, which can only be applied to polar molecules and paramagnetic species, respectively. Often, in an optical deceleration experiment, two counter-propagating laser beams are used. The interference pattern of these lasers form an optical lattice, with each lattice site representing a potential minimum [110]. The laser frequency is adjusted such that the lattice sites move at the same velocity as the molecular beam. Deceleration is achieved by reducing the velocity of the lattice. This method has been used to cool I_2 and C_6H_6 to $T = 1$ K at a density of 10^{12} cm^{-3} [111].

However, optical deceleration requires very intense laser pulses ($> 10^{12} \text{ W cm}^{-2}$) and highly stable tunable laser systems, which can present technical challenges. Furthermore, depending on the molecule being decelerated, the laser field may excite low lying electronic transitions. Finally, as only a small portion of the initial ensemble is decelerated, the technique requires a large initial volume of molecules, hence this technique has not been fully exploited to date.

1.3.2.2 Velocity Selection

Velocity selection, while not strictly a method of “cooling” (as it does not increase phase-space density), can be employed to produce cold molecular beams. A gas sample at equilibrium with a temperature T exhibits a Maxwell-Boltzmann distribution of velocities, as given in Equation 1.9:

$$f(v) = \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} 4\pi v^2 e^{-mv^2/k_B T} \quad (1.9)$$

At any temperature, there is a portion of molecules in the Maxwell-Boltzmann distribution with a low velocity *i.e.* which are translationally “cold”. Velocity selection preferentially selects the cold portion of the distribution. A bent guide is used in velocity selection, with electric or magnetic fields applied to the guide electrodes. This creates a shallow potential well in the centre of the guide. Molecules with a velocity below a certain threshold (dependent on the field strength in the guide and the radius of curvature, see Equation 2.2) can not escape the potential well and are guided around the bend. Fast molecules have sufficient kinetic energy to “overshoot” the bend as they are not confined by the potential. Electrostatic velocity selection is used in the experiments detailed later in this thesis and the technique is described in Section 2.3 in greater detail.

A recent experimental development in the area of velocity selection is the “centrifuge

decelerator”, combining the mechanical method described above with electrostatic velocity selection in order to produce cold (~ 1 K) continuous molecular beams from a liquid nitrogen-cooled (77 K) source [112]. This setup involves a circular quadrupole guide, which velocity selects molecules from the source, and a rotating quadrupolar guide. Molecules in the static guide transfer across to the rotating guide and as it rotates the molecules convert their kinetic energy into centrifugal potential energy $E_{\text{pot}} = \frac{1}{2}m(\omega r)^2$, where m is the mass of the molecule, ω is the angular velocity of the quadrupole and r is the distance from the axis of rotation. The experiment is typically operated with $\omega = 50$ Hz and was used to decelerate a beam of CF_3H from 200 m s^{-1} to 15 m s^{-1} [113].

1.3.2.3 Cryogenic and Additional Methods

Buffer-gas cooling is a versatile technique for cooling atoms and molecules through inelastic collisions with a cryogenic gas, typically He or Ne. In contrast to electrostatic velocity selection, buffer-gas cooling (when applied to molecules) gives a translationally and internally cold ensemble. In buffer-gas cooling, atoms or molecules are admitted to a cell *via* a capillary, or alternatively can be formed in the cell by laser ablation of a solid target. The cell contains a high density of buffer gas and is cryogenically cooled using techniques such as liquid He pulsed-tube refrigeration, which keeps the cell at ~ 4 K. An aperture in the cell allows a molecular beam to “escape” from the buffer-gas cell. The size of this aperture determines the Reynolds number of the molecular beam, which in turn determines the properties of the beam (effusive, hydrodynamic, supersonic). In the case of supersonic beams, the molecules can be internally cooled to temperatures below 4 K [114] (at the expense of a faster lab-frame velocity of the molecules). Provided the molecules being cooled have undergone enough collisions with the buffer gas to reach thermal equilibrium, the molecules will exhibit a low-temperature Boltzmann distribution of quantum

states, replicating the internal energy distribution of molecules in naturally cold environments. Buffer-gas cooling has been used in some experiments in combination with electrostatic velocity selection to increase the number of molecules in the low velocity portion of the Maxwell-Boltzmann distribution, and hence increase the density of molecules reaching the end of the guide. Buffer-gas cooling has also been used in combination with ion traps, as an alternative to laser cooling, to cool trapped ions. The reaction of CH_3^+ and C_2H_2^+ with H_2 has been studied at $T = 10$ K using a buffer-gas cooled 22-pole ion trap [115].

To broaden the scope of molecules that can be cooled to milliKelvin temperatures or lower while avoiding the use of high densities of cryogenic buffer gases in a trap environment, which can result in collisional losses from the trap, the method of Sisyphus cooling has been developed by the group of G. Rempe. This approach allows the cooling of molecules directly, without requiring a closed laser cooling cycle. Molecules are confined in a microelectrode RF trap (400 μm electrode width), with both low and high-field regions. An IR laser is used to stimulate a vibrational transition in the molecule, with RF fields applied to perturb the energy of the individual rovibrational levels by mixing low and high field seeking states, such that molecules lose kinetic energy when returning to the ground state (similar to Stark deceleration). Cooling occurs over many cycles and the process is likened to the Greek myth in which Sisyphus was condemned to eternally push a heavy rock up a steep hill, hence the name Sisyphus cooling. This method has been successfully demonstrated for CH_3F , with molecules cooled from 390 mK to 29 mK [116]. In practice, due to the minor temperature reduction resulting from Sisyphus cooling ($\Delta T = -361$ mK for CH_3F), it would need to be used in conjunction with other methods to cool molecules from room temperature to $T < 1$ K. Sisyphus cooling is only applicable to polar molecules and requires long-lived excited rotational states for the process to take place [117].

An additional method employed to cool molecular species is He nano-droplets. These are small assemblies (droplets) of ultracold He atoms containing the molecular species of interest, which is cooled to a similar temperature as the surrounding cryogenic He. This technique involves a supersonic expansion of He into vacuum from a high pressure source (~ 45 bar), which cools the He to ~ 5 K. Evaporation leaves residual He with a temperature in the mK regime. This ultracold He is typically passed through a vapour pickup cell, which incorporates the molecular species into the droplet. Due to the very low temperatures of the nano-droplets, this technique has found applications in studying highly reactive species and intermediates, facilitating the recording of high-resolution spectroscopic measurements on such species [118]. The use of He nano-droplets in chemistry, and in spectroscopy, has been the subject of several reviews [119, 120, 121].

The technique of merged beams allows for the study of chemical reactions at low relative collision energies, E_{coll} . This technique involves combining two molecular beams (generally formed by supersonic expansion). The collisional energy between the molecules in the two combined beams is given by [122]:

$$\begin{aligned} E_{\text{coll}} &= \frac{\mu}{2} v_{\text{rel}}^2 \\ &= \frac{\mu}{2} (\vec{v}_1 - \vec{v}_2)^2 \\ &= \frac{\mu}{2} (|\vec{v}_1|^2 + |\vec{v}_2|^2 - 2 |\vec{v}_1| |\vec{v}_2| \cos \theta) \end{aligned} \tag{1.10}$$

where μ is the reduced mass of the colliding pair and θ is the angle between the velocity vectors of the two beams. Merged beam experiments have been used to experimentally observe partial wave resonances in bimolecular gas-phase reactions such as $\text{CO}_2 + \textit{para}\text{-H}_2$ [123] and $\text{O}_2 + \text{H}_2$ [124], with $E_{\text{coll}} < 3.85 \text{ cm}^{-1}$. These measurements yielded enhanced sensitivity of features on the reactive potential energy surface, such as low J partial wave resonances, which are typically obscured by thermal averaging when the reactions are observed at room temperature

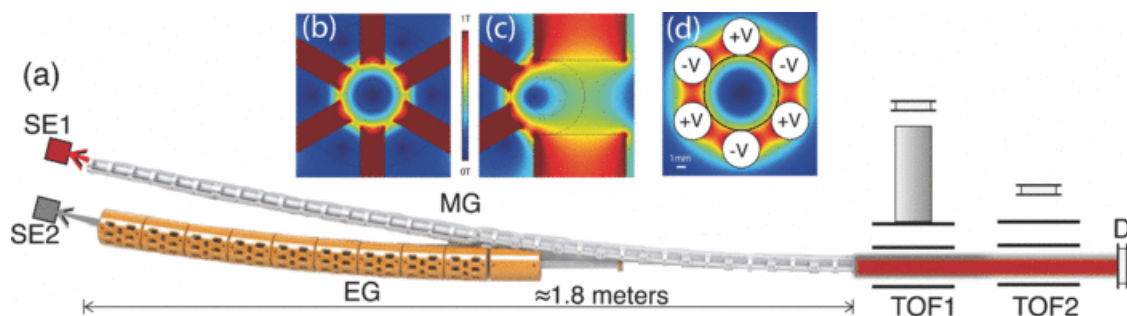


Figure 1.10: Schematic of the merged beam experiment in the group of A. Osterwalder. SE1 and SE2 are supersonic expansions. MG, EG and TOF n are the magnetic guide, electrostatic guide and the n^{th} Wiley-McLaren type time-of-flight mass spectrometer, respectively. Inset b) gives the magnetic fields in the first portion of the guide (before merging), c) the magnetic fields after merging, and d) the electric fields in the guide EG. Reproduced from [126]. Copyright 2014 AIP Publishing LLP <http://dx.doi.org/10.1063/1.4883517>.

As shown by Equation 1.10, E_{coll} is minimised when $\theta = 0^\circ$. This has been made possible by using electromagnetic guides to combine two molecular beams at an angle of 0° . Such experiments have been conducted in the groups of A. Osterwalder and E. Narevicius. A diagram of a typical 0° angle merged-beam experiment is shown in Figure 1.10, and these experiments can achieve collision energies as low as 8 μeV (0.065 cm^{-1}). Such merged beam experiments, as shown in Figure 1.10, have been used to investigate resonances in Penning ionisation processes between metastable $\text{He}(^2S)$ and H_2 [125], and $\text{Ne}(^3P)$ with ND_3 , NH_3 [126] and CH_3F [127]. While merged beam methods have shown great utility in studying neutral-neutral and metastable-neutral reactions, conducting ion-molecule reactions which such a setup would pose technical challenges. An ionisation setup, such as a thermionic emission filament, would be required in one beam before merging. However, guiding ions in a molecular beam is likely to result in charge exchange reactions with other molecules or background gas and hence the ions are unlikely to be long-lived enough to travel the distances required in such a setup.

1.4 Scope of this thesis

This thesis is concerned with the development and implementation of a new experimental apparatus, incorporating a combination of direct techniques: buffer-gas cooling and electrostatic velocity selection to produce a continuous beam of translationally and internally cold molecules. Chapter 2 introduces the experimental apparatus and the properties of the cold molecule source, including design considerations, modifications made at a later date and characterisation studies. Chapter 3 presents a model developed to ascertain the relative concentrations of ammonia isotopologues in a cold molecular beam from the mass spectrometry signature of the beam. Chapter 4 investigates the orientation of ammonia molecules as they emerge from the quadrupole guide into the detection chamber.

This source of cold molecules is combined with an ion trap, in which laser- or sympathetically-cooled cationic atomic or molecular species are spatially confined. The combination of the buffer-gas cell and guide with the ion trap is detailed later in Chapters 2 and 5. The goal of this project is to develop and characterise an experimental apparatus for the investigation of cold ion-molecule chemistry. In particular this apparatus will allow investigations with rotationally cold neutral molecules, which has not been possible in previous experiments. This will enable us to observe ion-molecule reactions under conditions comparable to natural cold environments such as the interstellar medium. Chapter 6 concludes this work and gives future prospects for both the experimental apparatus and the field in general.

2

Experimental design and characterisation

The apparatus used in the experiments described in this thesis consists of a cryogenic buffer gas cell combined with an electrostatic quadrupole velocity selecting guide. These are both *direct* cooling techniques - they act on a sample of molecules directly to produce a cold sample, rather than the *in situ* formation of cold molecules from cold atoms.

The buffer-gas cell and electrostatic guide components were designed and constructed by K. Twyman and M. Bell [100, 128], based on an earlier design from the group of G. Rempe [129, 130]. During my project, this setup (which acts as a continuous source of translationally and internally cold molecules) is combined with a linear Paul ion trap. The ion trap component was initially designed and characterised as a stand-alone experiment by L. Pollum [142]. The physical combination of these two distinct components – the buffer gas cell-electrostatic guide source and the ion

trap – was undertaken by myself. Modifications to facilitate this combination and improve robustness (*e. g.* modifying the guide length - see Section 2.3, design of an open Faraday cup - see Section 2.7, and new insulator - see Figure 2.9) were also carried out by myself. Characterisation of the cold molecule source and the determination of optimal parameters (see Section 2.6) was undertaken jointly by myself and K. Twyman. Experiments conducted in the latter parts of this thesis utilised the “completed” combined setup *i.e.* buffer gas cell, electrostatic guide and ion trap. An overview of the combined experiment is shown in Figure 2.1.

The aim of this experiment is to perform, and observe, the dynamics of cold ion-neutral reactions. This experiment aims to broaden the scope of previous studies in this field [131] by performing reactions using internally cold species, whereas previous experiments utilised a translationally cold yet internally hot neutral source. Such studies are of significance in astrochemistry [62, 132], where the temperatures achievable in my experiments are observed naturally, and the internal state distribution of the species is in equilibrium with the environment.

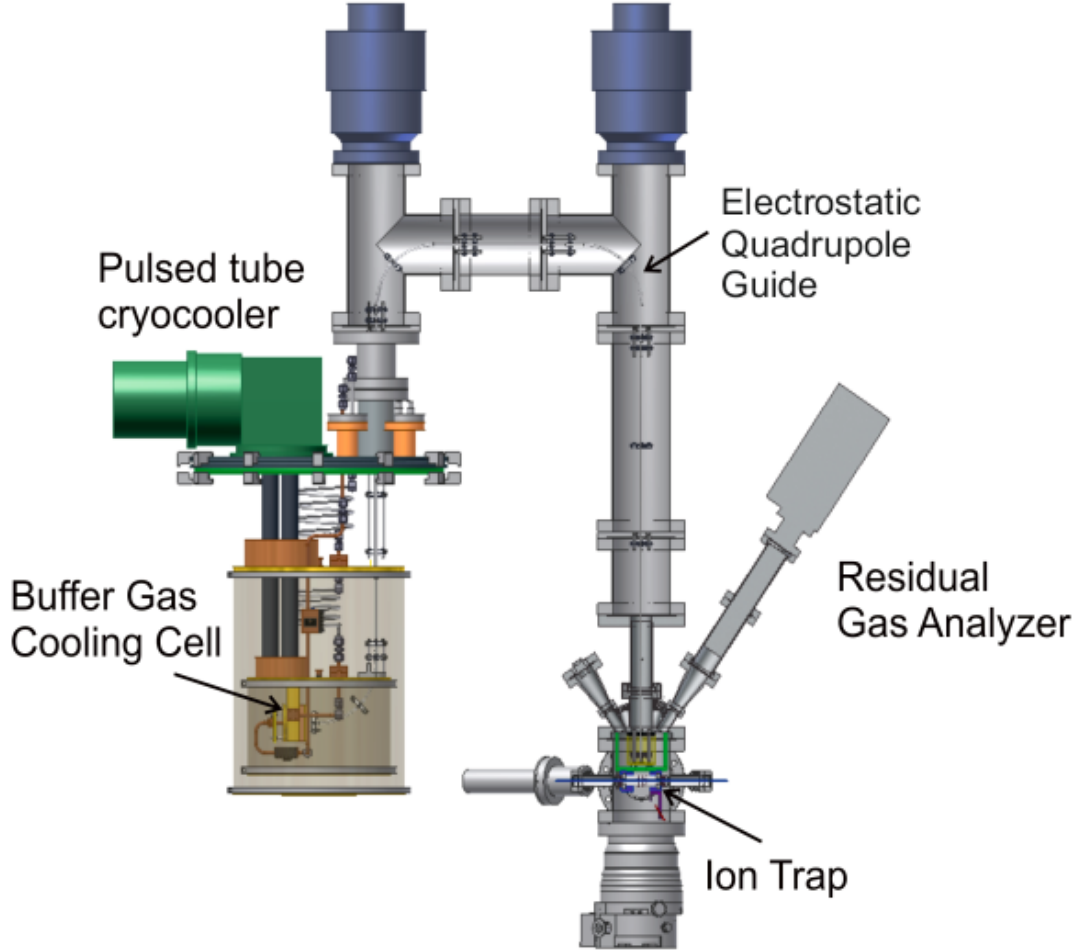


Figure 2.1: Overview of the experimental setup, showing a 6 K cryostat on the left side containing a buffer gas cell and a 2.1 m long electrostatic quadrupole guide with three 90° bends for velocity selection, leading to a linear Paul ion trap, shown in the bottom right of the figure.

2.1 The buffer gas cell

The experimental setup, shown in Figure 2.1, is composed of several individual vacuum chambers sealed together using conflat (CF) flanges; most of the chambers have an inner diameter of 100 mm (DN 100 CF flanges), with a much larger chamber (400 mm diameter) being used for the cryostat containing the buffer gas cell and

smaller diameter chambers (DN 35 CF) at the join between the guide and ion trap. The experiment is pumped by turbomolecular pumps, backed by rotary vane or scroll pumps, maintaining high-vacuum conditions throughout.

Traditionally, beams of cold molecules have been produced in the laboratory using supersonic expansions, where a high pressure reservoir of molecules seeded in an inert gas such as Ar are released into a high vacuum chamber using a pulsed valve. The expansion of the gas into the vacuum facilitates elastic and inelastic collisions with the seed gas which cools the molecules translationally (in the centre of mass frame) and internally. The final temperature of a supersonic expansion is given by Equation 2.1 [256]:

$$T = T_0 \left(1 + \frac{\gamma - 1}{2} M^2 \right)^{-1} \quad (2.1)$$

where $\gamma = C_p/C_v$, the ratios of the heat capacity at constant pressure and volume, T_0 and T are the temperatures of the gas before and after the expansion and M is the Mach number, the ratio of the supersonic beam velocity to the local speed of sound. Temperatures of 1 K in the centre of mass frame are routinely obtainable in supersonic expansions [133]. However, supersonic expansions have a high laboratory-frame velocity and often a low density of the molecule of interest. The flow conditions within a supersonic expansion are not uniform throughout the beam and hence the beam is not in thermodynamic equilibrium (*i.e.* can not be described by a Maxwell-Boltzmann distribution). Molecular beams formed from buffer-gas cooled molecules overcome these limitations, resulting in molecular beams with a low lab frame velocity and, in some pressure regimes, a relatively high flux. In a buffer gas cell, a cryogenic inert gas (often He) is used. The molecules to be cooled enter the cell and undergo Brownian motion through the cell; collisions

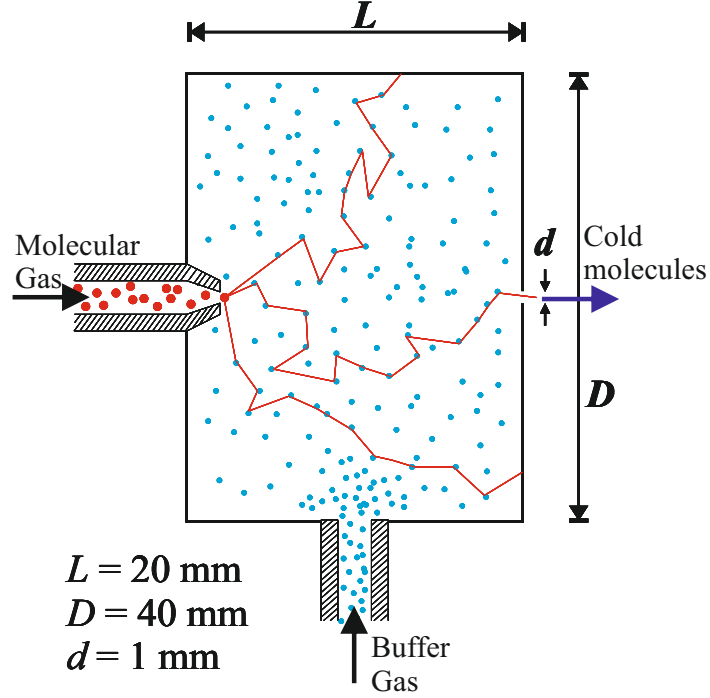


Figure 2.2: Schematic of a buffer gas cell. Hot molecules (red) thermalise with the cryogenic buffer gas (blue) and exit via a small aperture, shown on the right.

with the cryogenic buffer gas result in energy transfer, cooling the molecules (see figure 2.2). A small aperture in the cell allows molecules to escape into the vacuum chamber, resulting in a continuous effusive source of cold molecules. A relatively low density of buffer gas is required to thermalise a gas to cryogenic temperatures. For the molecules used in these experiments, the value of the vibrational partition function $q_{\text{vib}} \approx 1$ at room temperature, vibrational cooling is less of a concern in the experiment, however other work shows efficient vibrational cooling in buffer gas cells [134].

2.2 Injection of molecules into the buffer gas cell

The injection of the molecule of interest into the buffer gas cell can be something of a technical challenge. The main methods to do this are laser ablation of a solid

target, or capillary filling [135]. Typically, a balance needs to be struck between a high enough density of molecules in the cell to obtain a decent flux out of the cell, and a low enough density such that molecule-buffer gas collisions dominate the dynamics of the cell (as molecule-molecule collisions will not provide effective cooling and in some cases could result in the formation of dimers, clusters *etc.*). Generally a mole fraction of *ca.* 1% is loaded into the cell.

2.2.1 Capillary Filling

Capillary filling is, from a technical point of view, the easiest method of introducing molecules into a buffer gas cell. In this method, molecules enter the buffer gas cell through a capillary or gas line. However, this method is limited to those species that are gases (or have high vapour pressure) at ambient temperatures. To implement this method, the molecular gas line must be thermally disconnected from the buffer gas cell to avoid it reaching cryogenic temperatures. If the molecular gas line reaches a temperature below the freezing point of the molecular gas, molecular ices can form in the line, hindering the flow rate.

To overcome the issue of low vapour pressures of some substances at typical gas-line temperatures (200 - 300 K), experiments utilising ovens to heat a sample to increase its vapour pressure have been used [136]. However this requires a multi-stage design to isolate the cryogenic cell from the oven.

In this experiment, capillary filling of the buffer gas cell is used. Capillary filling provides a constant, reasonably dense influx of molecular gas and therefore produces a stable, steady state environment in the cell and continuous effusion of cold molecules from the buffer-gas cell. The design of the interface between the molecular gas line and the buffer gas cell is discussed in Section 2.4

2.2.2 Laser Ablation

The other commonly used method of loading a buffer-gas cell is laser ablation of a solid sample. In this method, a solid “target” is placed in the buffer gas cell, generally a metal such as Yb [137] or a crystalline substance such as YO, PbO, CaF, ThO *etc.* [8, 45, 138, 139, 140]. A high powered pulsed laser beam (generally a Nd:YAG laser) is used to ablate the “target”, releasing atoms or molecules into the gas phase within in the buffer-gas cell. As in the capillary filling technique, these atoms/molecules collide with the cryogenic buffer gas, resulting in thermalisation.

While laser ablation can be used to cool relatively unstable species (as the molecular gas is produced *in situ* in the cell) and high fluxes can be produced with high energy lasers, ablative methods tend to lead to unstable molecular beams. The quantity of substance released into the cell with each laser pulse depends upon several properties including laser power, beam size and ablation surface topography, hence, it is difficult to obtain a reproducible amount of substance ablated per laser pulse. Also, after an incident laser pulse, the local surface temperature of the ablation target can be on the order of 1000 K. This creates large temperature gradients across the cell and non-equilibrium conditions, which results in instabilities and a poorly defined temperature of the resulting molecular beam. A discussion of the thermalisation process of ablation loaded molecules can be found in [141].

2.3 Electrostatic Velocity Selection

Electrostatic velocity selection is achieved by exploiting the interaction of polar molecules with an applied inhomogeneous electric field. This interaction results in a shift in the internal energy states of the molecules according to the Stark effect, which perturbs the energy by $E_{\text{Stark}} = \vec{\mu} \cdot \vec{E}$ (where $\vec{\mu}$ is the molecule’s dipole moment and $\vec{E}$ is the applied external electric field).

A gas at a given temperature T exhibits a Maxwell-Boltzmann distribution of translational velocities. From the shape of this distribution, we can see that even at high temperatures, there is a non-zero probability of a molecule exhibiting a low velocity *i.e.* it is translationally “cold” (see Figure 2.3). Unlike other methods to produce cold molecules, described in Section 1, electrostatic velocity selection selects these naturally occurring “cold” molecules preferentially rather than directly cooling the molecules.

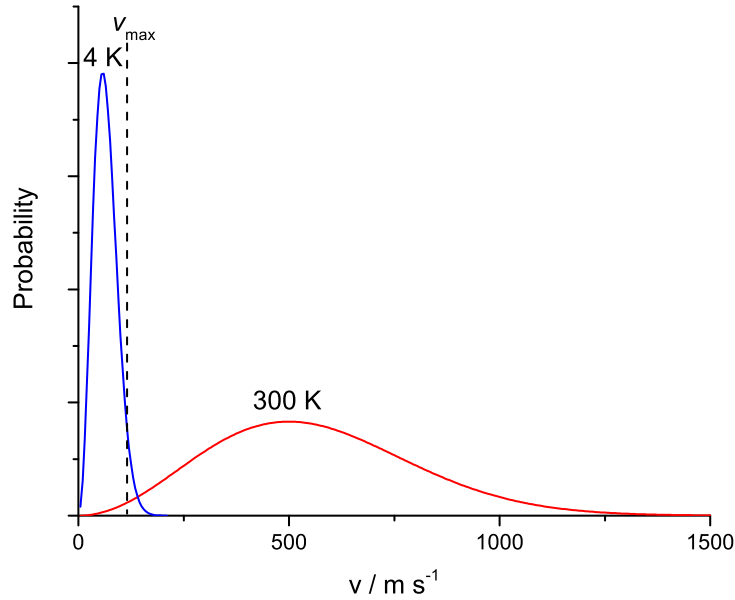


Figure 2.3: Maxwell-Boltzmann velocity distributions for ND_3 at 300 K and 4 K. It can be seen that there is a fraction of low-velocity molecules even at 300 K, and by pre-cooling the sample using the buffer gas cell the fraction of molecules below a threshold velocity $v_{\max}$ increases.

The velocity selecting guide consists of four stainless steel rods in a quadrupolar arrangement, spaced 1 mm apart from each other and measuring 2 mm in diameter. The applied electric field forms a potential energy well in the centre of the rods (see Figure 2.5 a)) for molecules in low-field seeking Stark states *i.e.* those states which increase in potential energy with an increase in applied field. This is due to the quadrupolar arrangement resulting in zero field in the centre and high fields on the

perimeter of the guide. Experimentally, voltages of ± 5 kV are applied to the guide, resulting in fields up to 100 kV cm^{-1} at the surface of the electrodes. The Oxford guide consists of straight sections and bent sections (where the guide makes a 90° turn); it is principally in the bent sections where the velocity selection happens. The curved guide distorts the trapping potential by rotating the field minima around the bend, giving a transverse component to the potential. Molecules which experience a centripetal force $F_C = mv^2/R$ (arising from their longitudinal velocity) that is less than the centripetal force due to the Stark effect (the force containing the molecules within the guide $F_{\text{Stark}} = \nabla W_{\text{Stark}}$ – approximately $= W_{\text{Stark}}/r$ (where R is the radius of curvature and r is the inner radius of the quadrupole) for a state exhibiting a linear Stark shift, will be guided around the bend. Only low field seeking states *i.e.* those states for which the potential energy increases with increased electric field can be guided around the bend. A plot showing the potential energy of low lying rotational states of ammonia against applied electric field is given in Figure 2.4. For high velocity molecules, which will experience a much higher centrifugal force, the trapping potential will not be great enough to contain them within the guide and hence they will be lost from the guide. This is shown graphically in Figures 2.5 and 2.6. Overall, we can combine the expressions above to give a formula for the maximum velocity v_{max} for a molecule in a given low-field state to be successfully guided around a bend:

$$v_{\text{max}} = \sqrt{\frac{W_{\text{Stark}} R}{mr}} \quad (2.2)$$

For the $|J, MK\rangle = |1, -1\rangle$ state of ND_3 ¹ (the lowest lying low field seeking rotational state), we find a maximum longitudinal velocity of 240 m s^{-1} for our experimental setup ($R = 100 \text{ mm}$, $r = 1.12 \text{ mm}$). To obtain a translationally colder

¹ J is the total rotational angular momentum, K is the projection of J on the molecular axis and M is the projection of J on the external electric field axis. The Stark shift is dependent on the product MK . For further information see Section 4.1 and Equation 4.11

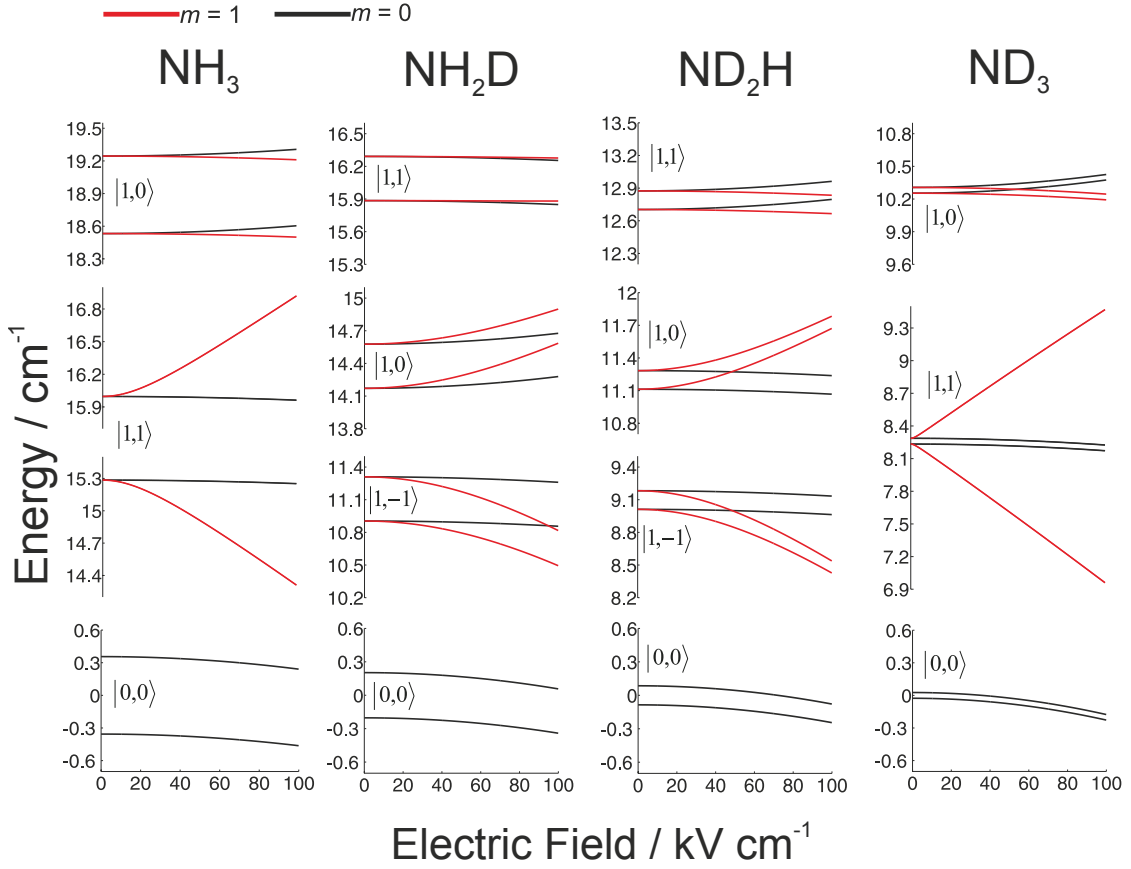


Figure 2.4: Plot showing the calculated rotational ($J = 0, 1$) energy levels of ND_3 , ND_2H , NH_2D and NH_3 with increasing external electric field magnitude. The zero point on the energy scale corresponds to the energy of the $|J, K\rangle = |0, 0\rangle$ state in the absence of inversion splitting or applied electric field.

beam, either the radius of curvature could be decreased or a lower guide voltage (hence lower W_{stark}) can be used. For example, using a guide voltage of ± 3 kV gives $v_{\text{max}} = 190 \text{ m s}^{-1}$ for ND_3 $|1, -1\rangle$. Principally, the translational temperature is determined by the buffer-gas cell temperature rather than the guide.

K. Twyman [128] carried out simulations to investigate the outcome of using a hexapole guide instead of a quadrupole guide. The trapping potential in a hexapole guide was found to be shallower and wider. This would have the advantage of a wider acceptance region into the guide, hence coupling the guide and buffer-gas cell would be technically simpler (a ± 5 kV hexapole guide using the same diameter rods has a region of approximate zero field ± 1 mm either side of the centre, whereas the

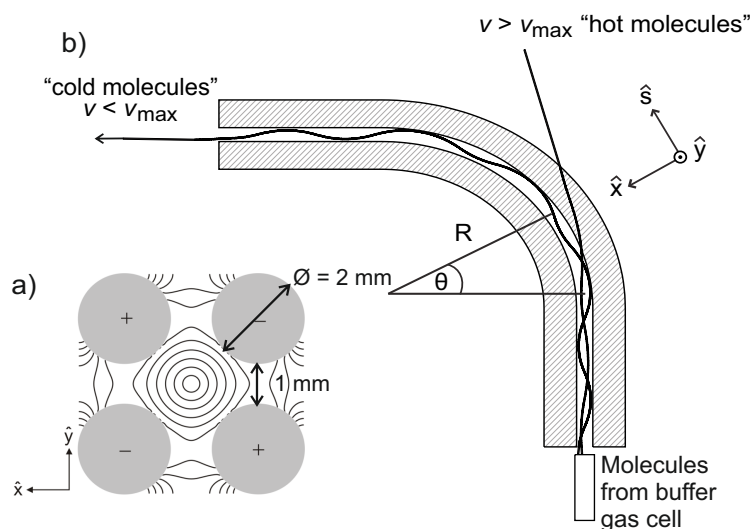


Figure 2.5: a) Electric field contours for a quadrupole guide operated at ± 5 kV. The inner contour line corresponds to 5 kV cm^{-1} and the outer to 90 kV cm^{-1} , with 15 kV cm^{-1} intervals. b) Schematic of electrostatic velocity selection. Only molecules in the low-velocity tail ($v < v_{\text{max}}$) of the distribution are guided around the bend. Adapted from [100].

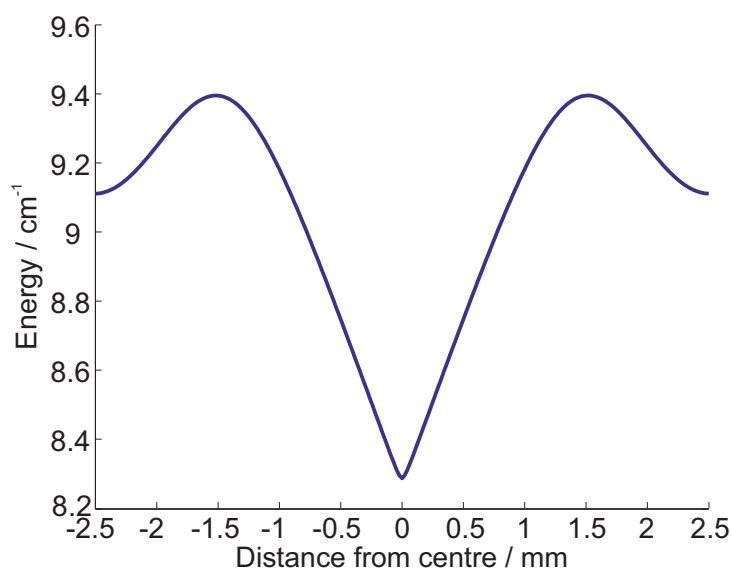


Figure 2.6: Trapping potential created by the quadrupole guide for the $|1, -1\rangle$ state of ND_3 arising from the Stark effect.

same region is less than ± 0.1 mm for the quadrupole (see Figure 2.6)). However the shallower trapping potential would result in greater losses from the guide and fewer molecules guided around the bends, hence a lower flux. Alternatively, higher voltages would have to be used. A full discussion of the merits of both quadrupole and hexapole guides can be found from p73 in [128].

The guide employed in the experiments described in this thesis is 2148 mm in length, consisting of three bends. The guide is made from hand polished stainless steel (316L grade) cylindrical rods 2 mm in diameter. The guide has several sections, due to the technical challenges of manufacturing and installing a single rod of such length. The overall length of the guide allows molecules to be transported from the buffer gas cell to a detection region which can be differentially pumped and isolated from the relatively high pressures of the buffer gas cell. Where two sections of guide are joined, the gap between adjacent sections is always less than 1 mm. Monte Carlo trajectory simulations run by K. Twyman [128] found negligible losses for a gap of < 1 mm, but losses are $> 50\%$ for a gap of 5 mm.

The guide is supported throughout by insulators made of Macor (a type of vacuum-compatible ceramic). A pin in the insulator contains a spring-loaded M1.6 screw which screws into a tapped hole on the outer face of the quadrupole, providing a retaining force preserving the quadrupolar geometry and preventing major distortions due to the natural curvature of the metal. A schematic of an assembled insulator is shown in Figure 2.7. The insulators are designed such that there is a long path length between rods to prevent surface flashovers between rods of opposite polarity, where electricity conducts across the face of the insulator causing a short circuit between adjacent rods. Frequent surface flashovers were found to be a problem with a previous quadrupole guide which utilised PEEK insulators to retain the structure [100].

The Macor insulators described above are regularly spaced at intervals of 16 cm

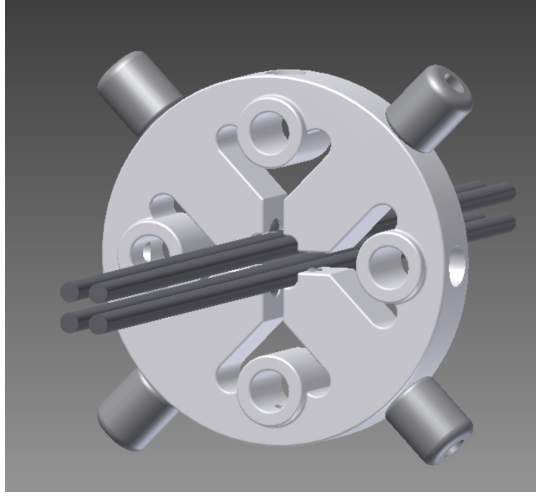


Figure 2.7: Schematic of an assembled Macor insulator with the guide passing through, showing the 4 pins, each containing a spring loaded M1.6 screw providing a retaining force on the guide rods.

along the straight sections of guide, and more regularly at the bends where the curvature of the guide means more support is required to retain the structure.

Due to the compact size of the ion trap [142] and the need for extra ports on the vacuum chamber to allow for additional feedthroughs and functionality, it is not possible to connect the ion trap to the rest of the experiment through the “standard” DN100CF flanges. Instead, a DN35CF flange and a reducer piece were used to connect the two chambers.

To feed the guide through the reducer piece, the spacing between insulators was increased from 16 cm to 22 cm in this section. The insulators themselves, without any pins, measure 35 mm in diameter, the same diameter as the vacuum chamber in this section, hence no insulators could be placed in this region. After installing this, pumping down and commencing the normal conditioning process (described below), the guide would frequently arc between rods at a potential difference of 9 kV (± 4.5 kV, or at an asymmetric $+/-$ voltage giving the same potential difference). This arcing caused surface damage to the rods, shown in Figure 2.8, from the high local temperatures in the arc, which further hindered the ability

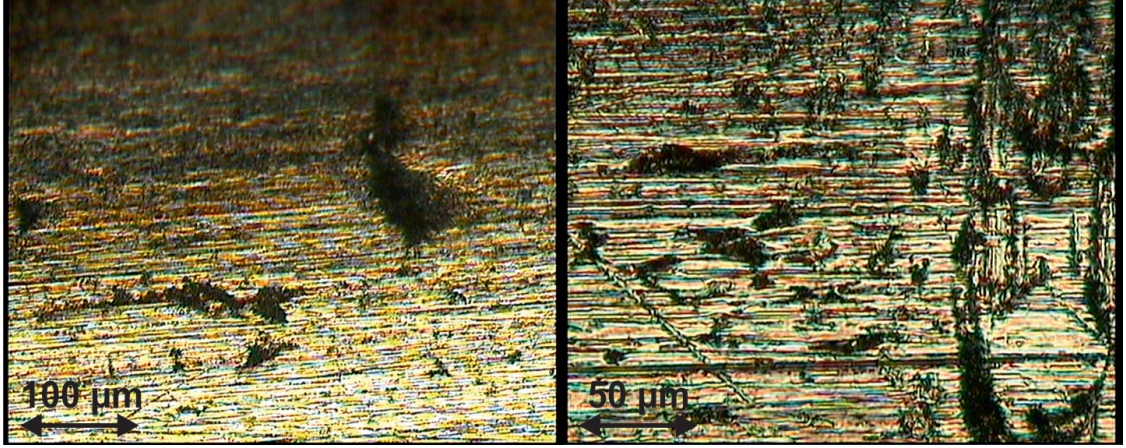


Figure 2.8: Microscope images showing surface damage caused to the guide rods due to an electrical breakdown (arc) at ± 4.5 kV.

of the guide to hold voltage.

A diagnostic experiment where the straight section of guide was removed and was conditioned in a vacuum chamber with viewports along the length of guide found the unsupported section curved inwards just below the breakdown voltage. The Coulombic force between the two oppositely charged rods was great enough to overcome the rigidity of the metal and hence reduce the distance between the rods. The voltage at which electrical breakdown will occur, V_B is given by Paschen's law [143]:

$$V_B = \frac{apd}{\ln(pd) + b} \quad (2.3)$$

where a and b are empirical parameters depending on the residual gas in the vacuum system, p is the background pressure in the system and d is the inter-electrode distance. The consequence of Paschen's Law is that the breakdown voltage depends on the product of pressure and distance between conductors pd . Hence, any decrease in d will lower the breakdown voltage.

In order to give the guide extra rigidity through this section, a smaller insulator has been designed and is used (shown in Figure 2.9). This insulator was also made



Figure 2.9: The new smaller Macor insulator designed for use in the $\varnothing = 35$ mm tube of the reducer piece. The left image shows a CAD drawing of the insulator and the right image is a photo of the insulator after installation.

from Macor due to its favourable properties (low thermal expansion, low outgassing, non-conductive, machinable). The new insulator took design elements from the previous insulators in order to ensure compatibility and ensure a quadrupolar structure for the electrodes. Rather than using a pin and screw design, in order to save space the “pin” was machined into the Macor such that there was a larger hole for the spring and screw to be inserted, then a ridge inside for the spring to press against and a smaller hole for the M1.6 screw to pass through to the rods.

2.4 High Voltage Conditioning

For the guide to support the high voltages required to perform the experiments without arcing or electrical breakdown, the guide rods must be conditioned. This process must be carried out before use after initial installation and when they have been exposed to the atmosphere. The rods were initially prepared by hand polishing with fine grades of sandpaper and then with 10 μm and 2 μm diamond paste to give a highly polished surface. Despite this, small protrusions and defects in the surface can limit the ability to sustain high voltages. The conditioning

process aims to reduce the severity of these defects such that it is more capable of holding a high voltage. An overview of the theories behind high voltage conditioning and its physical interpretation can be found in [144]. In the current apparatus, conditioning is achieved by applying static DC voltages to the guide under high vacuum conditions ($p < 10^{-7}$ mbar) and slowly increasing the voltage, usually in increments of ± 0.25 kV over a period of several hours until ± 6 kV has been reached. The current drawn from the power supplies is measured on digital multimeters during this process and the conditioning is stopped if a current of more than a few μA is drawn. A small current implies small breakdown events which help remove surface defects and further “polish” the electrodes, however high currents imply more significant breakdowns which could cause damage to the guide electrodes. If the guide fails to condition, the process can be repeated under a pressure of an inert gas such as He or Ar which increases the dielectric constant of the vacuum hence allowing for these “polishing” events to occur. Conditioning is carried out up to ± 6 kV, although the guide is operated with a maximum voltage of ± 5 kV, to ensure the guide will reliably hold voltage while performing experiments.

2.5 Buffer Gas Cell - Experimental Design

In the experimental setup, the buffer gas cell is mounted to the second stage of a low vibration He pulsed tube cryocooler (see Figure 2.10), and reaches an equilibrium temperature of 6 K. The buffer gas cell is made from oxygen-free copper and measures 40 mm x 40 mm x 20 mm. There are 3 ports - one for capillary filling of the buffer gas, one for the molecular gas and an exit aperture, coupled to the acceptance region of the electrostatic guide. Oxygen-free copper was used for the buffer gas cell due to both its high thermal conductivity and because defects in standard copper (which contains some oxygen) could result in temperature

gradients and non-equilibrium conditions in the cell.

The He gas line, from which He is introduced into the cell, is thermally connected to both stages of the cryocooler (the first stage reaches 32 K). The design of the gas line is such that it allows the He to thermalise to the cold environment before entering the buffer-gas cell (see Figure 2.10). The part of the He gas line within the cryocooler is made from copper due to its high thermal conductivity and is mounted to the cryocooler stages *via* a tightly fitting copper block. *Apiezon N* vacuum grease is used at the interface of the copper block and gas line to further enhance thermal conductivity. He gas enters the buffer gas cell through a 6.3 mm diameter aperture in the cell wall, behind a copper block ensuring thermal equilibrium between the cell and gas line. A 130 μm piece of In foil is placed over the copper block, further improving the thermal conductivity to the gas line and also sealing the entrance. Conversely, the molecular (ND_3) gas line needs to be isolated as much as possible from the cryogenic environment, to prevent molecular ices blocking the line before the gas enters the buffer gas cell. The interface between the molecular gas line and the buffer gas cell is provided by a copper ring around the inlet, covered with a sheet of Kapton (poly-oxydiphenylene-pyromellitimide) film which is at cryogenic temperature. The stainless steel gas line is mounted to a trigonal shaped copper plate, which is then mounted to the cryogenic copper ring via stainless steel pegs. In order to reduce thermal conductivity, there is a small glass ball held between the copper plate and a peg made of borosilicate (Pyrex) glass, which has a low thermal conductivity ($0.10 \text{ W m}^{-1} \text{ K}^{-1}$ @ 4 K [145]), and which along with the small surface area in contact between the warm side, glass ball and cold side, results in low thermal transfer. Despite attempts to thermally isolate the molecular gas line, the gas inside is prone to freezing due to the cold ambient environment. To counter this, two cartridge heaters are placed on the gas line in order to provide a controllable, warmer local environment for the gas prior to entering the buffer

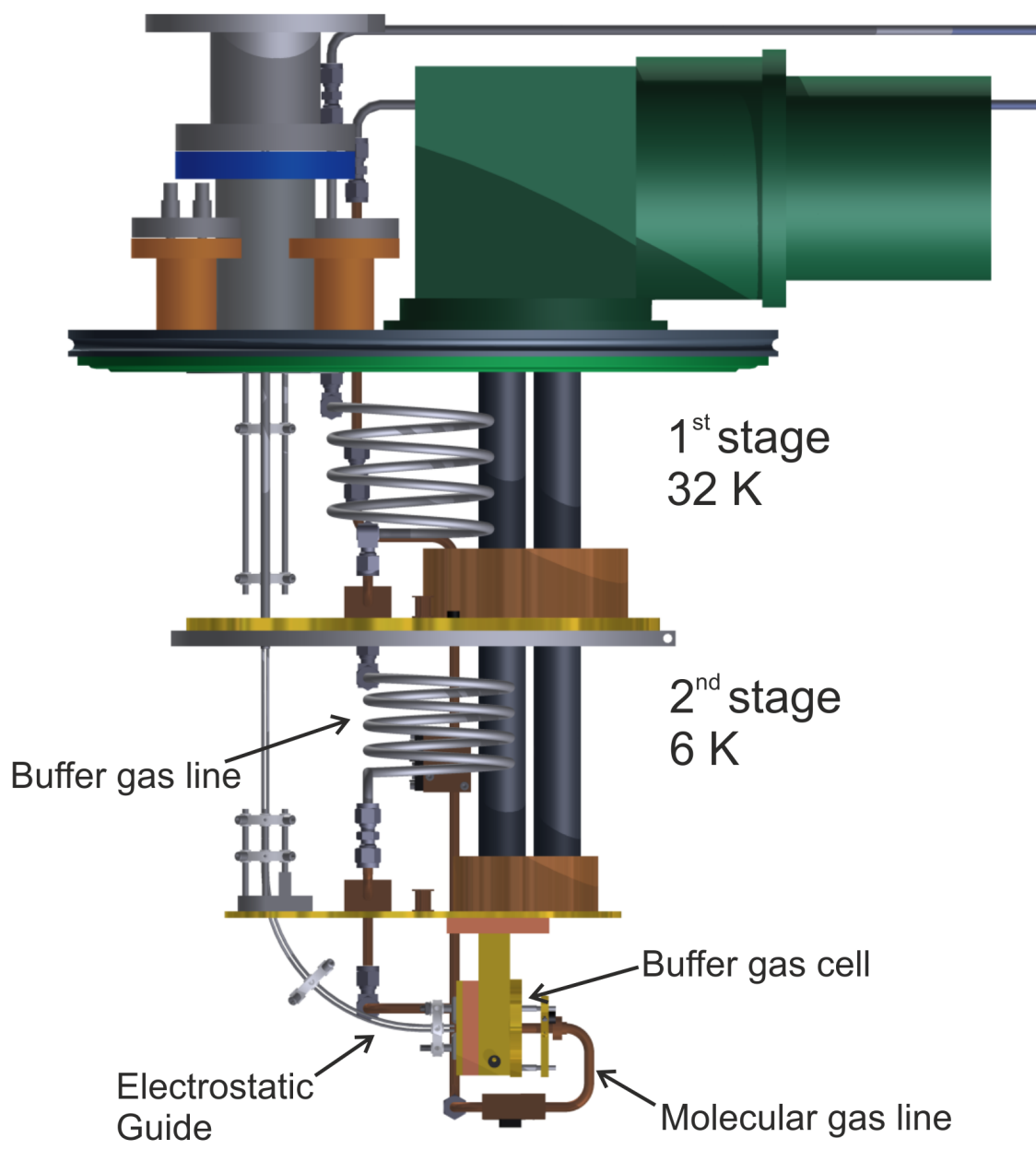


Figure 2.10: CAD drawing of the cryostat, showing the external He pump (top) and the two stages of the cryostat, the buffer-gas cell, gas lines and guide. Note the long path length of the buffer gas line to allow thermalisation with the cryogenic environment. Adapted from [128].

gas cell and prevent the formation of ices. The molecular gas line is also made of copper, so that the heaters are effective along the entire length of the line and temperature gradients are minimised, and the entire line is wrapped in Mylar film² to insulate it from the cryogenic environment.

The He flow is regulated by a thermo-mechanical leak valve, which can be either be controlled by hand or electrically by a resistive heater which causes a bolt connected to the sealing surface to contract. To allow for precise regulation of the He flow, the thermo-mechanical mode is used, in combination with an adjacent ceramic (Al_2O_3) diaphragm pressure gauge which measures the pressure in the gas line leading to the buffer-gas cell. The pressure readout is received by a LabVIEW computer program which uses a proportional-integral-derivative (PID) algorithm to adjust the current flow to the resistive heater in the leak valve, based on the pressure reading. The molecular gas flow is regulated by a commercial mass flow controller (Bronkhorst F-200CV-002-AAD-22-E) calibrated for ammonia, and is capable of delivering a flow of 0.1 to $5 \text{ cm}^3 \text{ min}^{-1}$, with an uncertainty of $\pm 1\%$. While this meter is calibrated for ammonia, it can be used with other gases. To obtain the flow rate when using other gases, a gas calibration factor, C can be calculated using the expression in Equation 2.4

$$C = \frac{C_{p,1}\rho_1}{C_{p,2}\rho_2} \quad (2.4)$$

where $C_{p,x}$ is the specific heat capacity at constant pressure of gas x and ρ_x is the density under standard conditions of gas x . For example, using the values of C_p and ρ for ND_3 and CH_3F ,³ $C = 0.906$ for CH_3F *i.e.* if a flow rate of $2 \text{ cm}^3 \text{ min}^{-1}$

²Mylar (biaxially-oriented polyethylene terephthalate) has a low thermal conductivity ($0.038 \text{ W m}^{-1} \text{ K}^{-1}$ @ 4 K). By contrast, copper has a thermal conductivity of $640 \text{ W m}^{-1} \text{ K}^{-1}$ @ 4 K

³ $C_{p,\text{ND}_3} = 2.192 \text{ J g}^{-1} \text{ K}^{-1}$, $\rho_{\text{ND}_3} = 0.769 \text{ g dm}^{-3}$, $C_{p,\text{CH}_3\text{F}} = 1.102 \text{ J g}^{-1} \text{ K}^{-1}$, $\rho_{\text{CH}_3\text{F}} = 1.534 \text{ g dm}^{-3}$ [21]

is measured while using CH_3F , the actual flow rate is $2 \times 0.906 = 1.812 \text{ cm}^3 \text{ min}^{-1}$.

2.5.1 Heat Shields

All matter, at temperatures $T > 0 \text{ K}$ emits (and absorbs) electromagnetic radiation. This process is the conversion of a particle's internal energy into electromagnetic radiation. It can be considered that this arises as a consequence of the Second Law of Thermodynamics, as the emission of such radiation results in a increase of the entropy of the universe. Such radiation is generally referred to as "blackbody radiation". While technically incorrect, as a blackbody is an idealised surface that absorbs all incident electromagnetic radiation, regardless of frequency or angle of incidence and emits a spectrum of radiation dependent upon its temperature, it is a good approximation for a wide variety of commonly encountered materials. Real materials can be characterised by their emissivity, ϵ , which is the fraction of radiation emitted compared to a true black body (a true black body has $\epsilon = 1$). The radiative flux from a surface is given by the Stefan-Boltzmann law (Equation 2.5). The power of the radiation emitted is obtained by multiplying the flux by the surface area.

$$j = \sigma \epsilon T^4 \quad (2.5)$$

where σ is the Stefan-Boltzmann constant. From this equation, we can see that the radiative flux is dependent strongly on temperature.

Given the size of the outer heat chamber containing the cryostat (600 mm high, 406 mm outer diameter, 403 mm inner diameter), the heat exchange due to blackbody radiation on the cryocooler from the chamber surface is 3.88 W. This heat load prevents the cryocooler from reaching 6 K and will only reach 17 K unless additional shielding is in place. To reach the lower temperature, two heat shields are employed. One is a smaller heat shield with encloses the buffer gas cell and the second stage

of the cryocooler, where it is critical to reach the lower temperatures. The other heat shield encompasses the entire cryocooler and fits inside the main chamber. The heat shields need to have a low surface emissivity, so that their own blackbody field does not distort the cold environment. Cu (1.2 mm thick) was chosen due to its low surface emissivity, however copper readily oxidises to CuO which has $\epsilon = 0.6$. To prevent oxidation, the copper heat shields were electroplated with a 0.25 μm layer of Au which is resistant to oxidation and has $\epsilon = 0.02$ [145]. Adding the larger heat shield reduces the heat load on the buffer-gas cell itself from 0.16 W to 1.85×10^{-5} W and with both heat shields the heat load on the buffer-gas cell from blackbody radiation becomes negligible.

For the guided molecules to exit the buffer gas cell into the guide and be transported to the detection region, collisions between background gas and the molecules in the guide need to occur with negligible frequency, as collisions will result in the molecules being lost from the guide. For this to be the case, the pressure needs to be 10^{-6} mbar or lower (low pressures also decrease the dielectric constant of the atmosphere and prevent arcing between the guide rods). Due to the continuous flow of He and molecular gasses into the buffer-gas cell, the environment inside the inner heat shield may no longer resemble high vacuum conditions. To increase the pumping efficiency in this region, the inner heat shield is coated with fine grains of activated charcoal. Charcoal (carbon) acts as an effective helium pump at low temperatures ($T < 10$ K) by absorbing helium into its porous structure. This He is released from the charcoal at higher temperatures ($T > 20$ K) allowing it to be pumped away by the turbomolecular pumps when the experiment is warming up. Activated charcoal has an effective “pumping speed” of $4.3 \text{ dm}^3 \text{ s}^{-1} \text{ cm}^{-2}$ at 4 K [146]. The inner surface area of the inner heat shield is approximately 1500 cm^2 , giving a pumping speed of $6500 \text{ dm}^3 \text{ s}^{-1}$, a value comparable to many turbomolecular pumps, hence allowing high vacuum conditions to be retained during operation.

2.6 Detection Methods and Characterisation

In order to characterise the molecular beam exiting the guide, a method of detection is required. The guide exit is in a vacuum chamber after three 90° bends in the quadrupole and after a final 69.3 cm straight section of guide. The detection chamber, located where the ion trap was eventually installed (see Figure 2.1), is differentially pumped, reaching a lower pressure of 10^{-8} mbar or lower, compared to the $10^{-6} - 10^{-7}$ mbar reached in the cryostat. When combined with the ion trap later, further differential pumping is implemented to reach the ultrahigh vacuum regime ($< 10^{-9}$ mbar).

Detection of the molecular beam is achieved through two different methods, mass spectrometry (using a compact quadrupole mass spectrometer (QMS)) and resonance-enhanced multi-photon ionisation (REMPI) spectroscopy. Mass spectrometry is easier to deploy, as it does not require the use of laser systems and is not sensitive to correctly tuning the wavelength of a laser; however it is not quantum-state or species selective (unless soft-ionisation techniques are used).

2.6.1 Mass Spectrometry

Mass spectrometric measurements were obtained on the guided molecular beam using a commercial quadrupole mass spectrometer (QMS) (also known as a residual gas analyzer (RGA)) mounted at the base of the detection chamber. The QMS has a yttria (Y_2O_3) coated iridium filament, which ejects high energy electrons ($E_K = 70$ eV) that collide with molecules in the detection chamber, ionising them. Electric fields in the QMS head guide these ions into a quadrupole mass filter and are then detected using a Channeltron detector. To shield the QMS from the high electric fields within the guide, which could impair its operation, a grounded “cup” was placed at the end of the guide with a Ni mesh (85% transmittance),

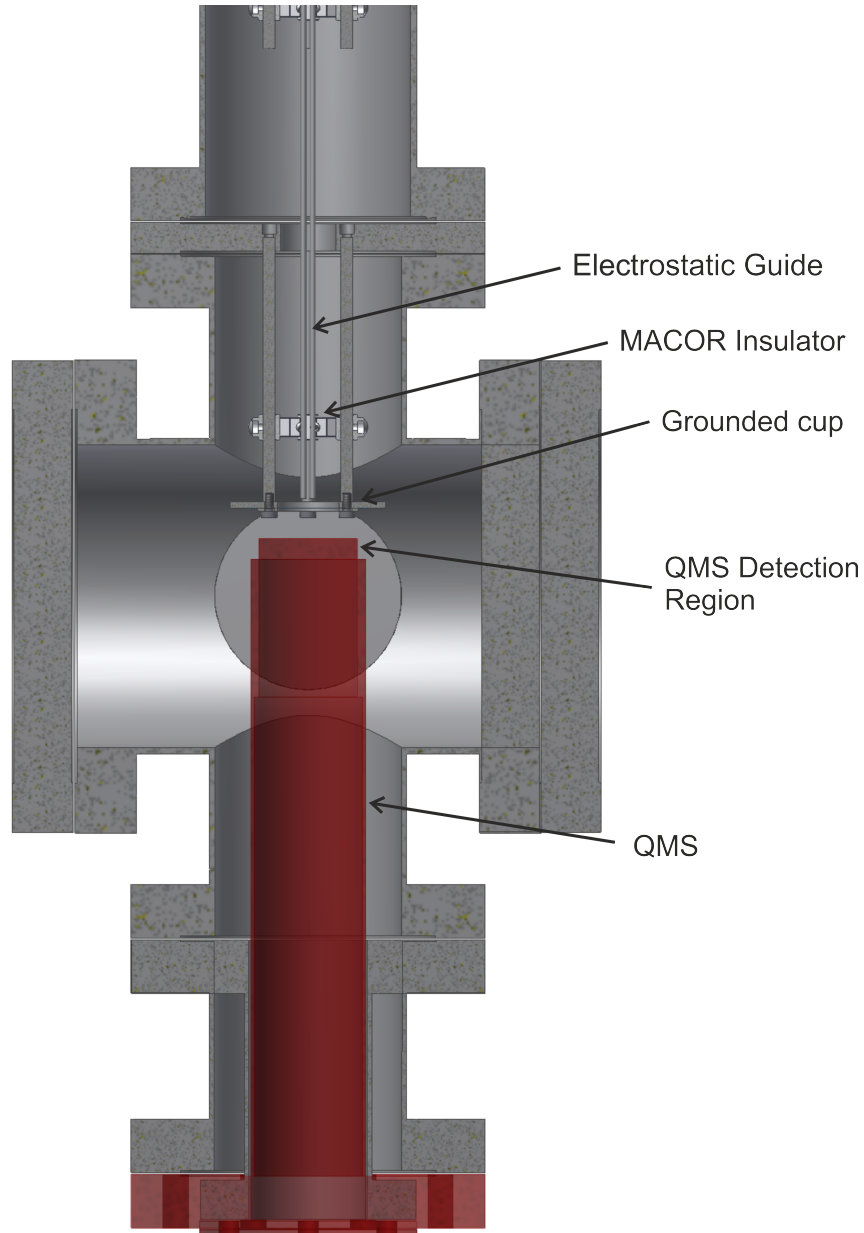
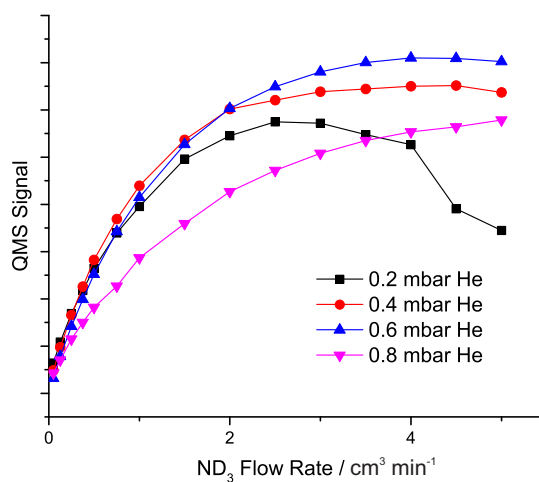


Figure 2.11: CAD drawing showing the end of the electrostatic guide and the QMS (red). A grounded cup with a high transmission mesh encloses the end of the guide to shield the QMS from protruding electric fields. The distance between the bottom face of the cup and the QMS is 6 mm (8 mm from the guide exit).

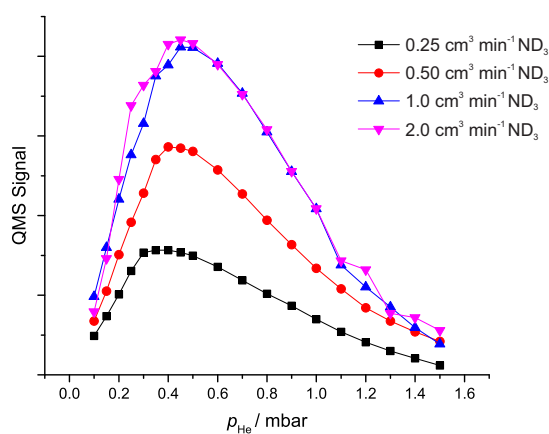
as shown in Figure 2.11.

The QMS was used to characterise and optimise the experimental parameters. This was done by guiding ND_3 , measuring the ion current at $m = 20$ u on the QMS while varying parameters such as the molecular gas flow, He buffer gas pressure and guide voltage, with results shown in Figure 2.12.

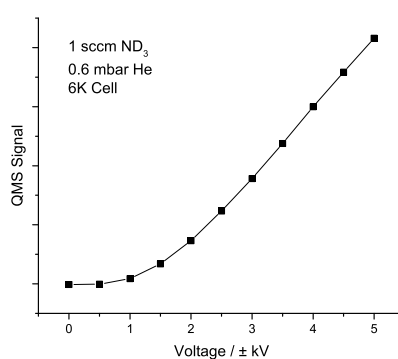
If the density of He in the buffer gas cell is too low, the molecular gas does not undergo sufficient collisions with the He to thermalise to the cryogenic temperature, hence the molecules exiting the cell are “hot”. Conversely, if the He density is too high, the flow of molecules from the aperture is hindered and the molecules exiting the cell can be velocity boosted as they enter a region of higher vacuum, leading to losses in the guide as a greater proportion will have $v > v_{\text{max}}$ at the bend in the guide. Similarly, if the molecular gas flow is too high, insufficient cooling will occur and if the flow rate is too low, the guided flux will be too low to detect. Therefore, an intermediate regime for both buffer gas and molecular gas flow is optimal. The optimal settings were found for ND₃ to be 0.6 mbar He and a flow rate of 1 cm³ min⁻¹ ND₃ at a guide voltage of ± 5 kV (see Figure 2.12). Full details of the characterisation can be found in [128].



(a)



(b)



(c)

Figure 2.12: Results from characterisation experiments showing QMS signal for mass 20 u against a) flow rate of ND₃, b) He pressure in the buffer gas cell, c) electrostatic guide voltage.

The QMS was also used to verify that the guided molecules were translationally

cold. By pulsing the guide, at 2.5 Hz, and measuring the arrival times of the molecules using the QMS, a velocity distribution for the guided molecular beam can be obtained. The cumulative QMS signal against time is recorded and is processed using a MATLAB program to give the velocity distribution, using a process described from p134 of [128]. A plot of the raw data and velocity distribution is shown in Figure 2.13. For a 6 K cell with He buffer gas, the modal velocity of ND₃ is found to be 70.3 m s⁻¹. If a 17 K buffer-gas cell is used, the modal velocity of ND₃ is found to be 70.1 m s⁻¹ with Ne buffer gas, and 112.4 m s⁻¹ with He. To give a comparable molecular velocity (and hence translational temperature) between the two buffer-gas cell temperatures, Ne buffer gas is generally used with a 17 K cell.

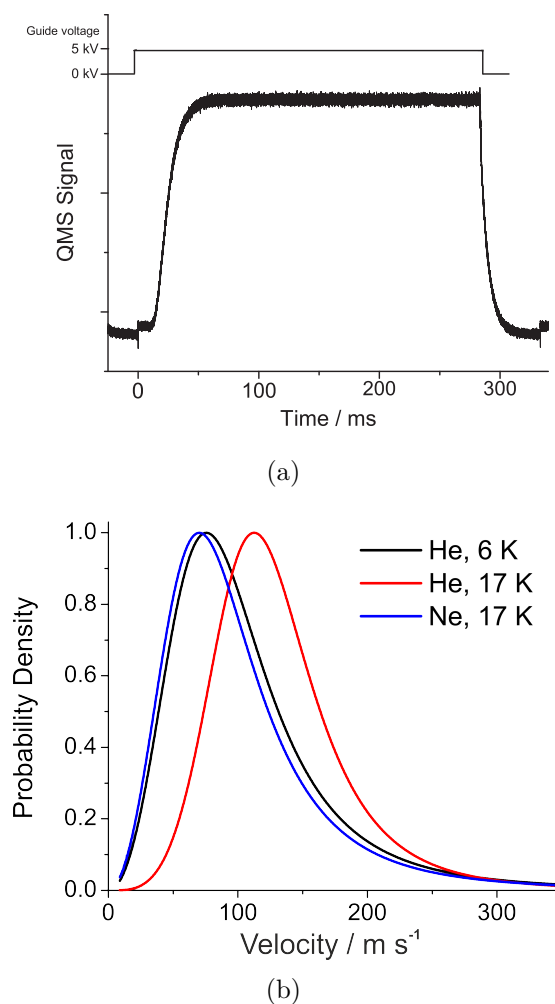


Figure 2.13: Results from pulsed guide measurements a) the raw data recorded by the oscilloscope over the duration of one pulse. b) the recorded velocity distribution of the guided molecular beam, for a variety of cell temperatures and buffer gases. Figure b) is adapted from [128].

An issue which needs to be considered with the QMS is that the high energy electron-impact ionisation technique it uses for detection can cause fragmentation. A model was developed to deconvolute the signals arising from the molecular and fragment ions, which is discussed in Chapter 3.

During the combination process with the ion trap, it was noted that the REMPI spectra being recorded at that point no longer indicated as low a rotational temperature. Analysis of the spectra indicated $T_{\text{rot}} \approx 100$ K. Upon inspection of the buffer gas cell, it was found the Kapton film wall surrounding the molecular inlet had

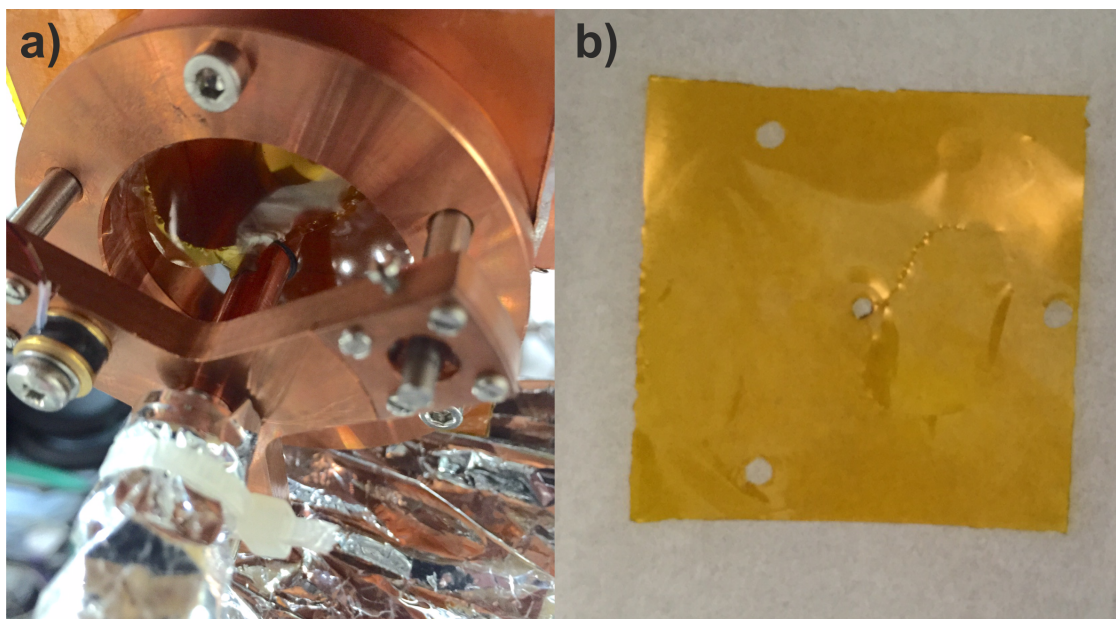


Figure 2.14: a) Photograph showing the buffer-gas cell after the rotationally hot beam had been detected, showing the damaged Kapton film *in situ*. b) Photograph showing the extent of damage to the Kapton film.

become damaged (see Figure 2.14), allowing the cryogenic He to leak out of the cell.

Once repaired, it was found the run time of the experiment was drastically reduced, from *ca.* 5 h to 30 min, before major instabilities in the gas flows presented. The rate of decay of ND₃ |1, 1⟩ peak at 63024.4 cm⁻¹ was measured over several hours (see Figure 2.15) to characterise the reduction in flux with time. An exponential of the form $y = Ae^{-t/\tau} + c$ can be fitted to the data to obtain the relative signal at a given time t .

2.6.2 Flux determination

To fully understand the properties of the quadrupole guide, the rate of transmittance of molecules or flux is determined to an order-of-magnitude precision. This is done using the QMS. ND₃ is cooled and guided and the ion current at $m = 20$ u is measured. ND₃ molecules which are transmitted through the guide but are subsequently fragmented in the ionisation region of the QMS, and therefore do

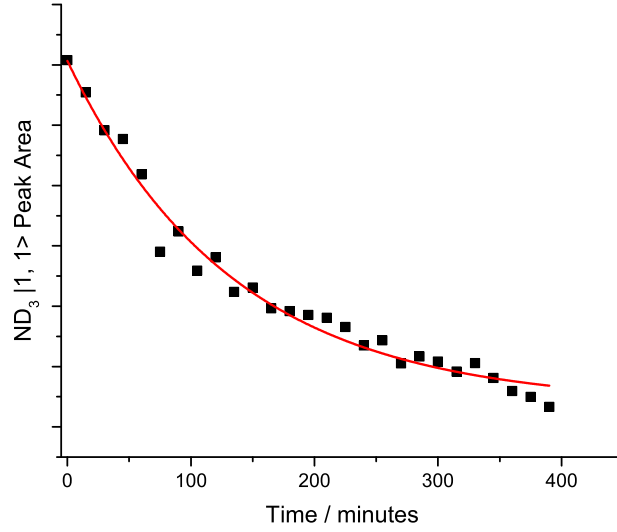


Figure 2.15: Figure showing the decay in the peak area of the ND₃ |1, 1> peak at 63024.4 cm⁻¹ with experiment run time.

not contribute to the ion signal at 20 u, are considered using the fragmentation model presented in Chapter 3.

To determine the flux, the apparatus was operated using the original optimal settings described above ($p_{\text{He}} = 0.6$ mbar, ND₃ flow rate of 1 cm³ min⁻¹ at a guide voltage of ± 5 kV). ND₃ was admitted to the chamber *via* the guide until a detectable rise in pressure was recorded, and the time taken for this was measured. The detection chamber pressure was measured using a Bayard-Alpert type hot cathode ionisation gauge (Leybold Ionivac ITR 90). The van der Waals' equation of state (Equation 2.6) is used to convert the pressure rise into the number density.

$$\left[p + a \left(\frac{n}{V} \right)^2 \right] \left(\frac{V}{n} - b \right) = RT \quad (2.6)$$

where a and b are the empirical non-ideality parameters, accounting for the deviation from ideal behaviour for each gas. For ND₃, these parameters are $a = 0.417$ Pa m⁶ mol⁻¹ and $b = 3.71 \times 10^{-5}$ m³ mol⁻¹ [147]. The quantity of

gas exiting the guide which reached the QMS was estimated by the solid angle subtended from the guide exit that intersects the QMS detector region. The QMS is mounted below the guide exit on an angled port, and the angle between the guide and QMS is 11.3° . Using the modal velocity as determined in Section 2.6.1 and the fragmentation ratio in the QMS detector as determined in Chapter 3, the flux can be determined. Furthermore, between the guide exit and the QMS is a grounded Ni mesh with a transmittance of 88%, which is accounted for. For ND_3 , the flux was determined to be $1.64(26) \times 10^{12} \text{ s}^{-1}$, which is comparable to the flux determined for the similar quadrupole guide experiment in the group of G. Rempe [148]. A conversion factor between the background-subtracted QMS ion current and molecular flux was also determined, allowing for the flux to be determined during experiments in the ion trap.

2.6.3 REMPI Spectroscopy

Complementary to the QMS measurements, resonance-enhanced multi-photon ionisation (REMPI) spectroscopy is used. REMPI is a species- and quantum-state selective technique, which was used to establish the rotational populations of the buffer-gas cooled and guided molecules.

To conduct REMPI spectroscopy on ND_3 , the molecular beam after the guide is intersected by a laser which excites the two-photon transition to form the intermediate Rydberg state and then a further photon forms the molecular ion. The frequency doubled output of a dye laser at $\sim 317 \text{ nm}$ (capable of an output power up to $\sim 8 \text{ mJ/pulse}$, frequency doubled using a $\beta\text{-Ba}(\text{BO}_2)_2$ (BBO) crystal, tuned to individual transitions) was used to perform the ionisation. The dye laser is pumped by a frequency doubled Nd:YAG laser at 532 nm with a 5 ns pulse length and a repetition rate of 10 Hz . For REMPI measurements of ND_3 , the laser is tuned to the $\tilde{B}(v'_2 = 5) \leftarrow \tilde{X}(v''_2 = 0)$ transition and the wavelength is

stepped, exciting different ground rotational states to the $\tilde{B}$ state as they come into resonance. A discussion of this choice of Rydberg state can be found in Section 4.2. A (2+1) REMPI scheme is used in these measurements. The notation ($m+n$) refers to the number of photons (m), required to excite the ground state molecule to the Rydberg state (in this case, the $\tilde{B}$ state) and then the number of photons (n) to ionise the Rydberg molecule. The majority of REMPI experiments are (2+1) or (3+1) schemes; the absorption cross sections become prohibitively small for $m > 3$ [149] and few molecules have sufficiently long-lived Rydberg states for multi-photon ionisation from the excited state.

Detection of these ions is achieved using a Wiley-McLaren type time of flight (TOF) tube [150] in combination with a microchannel plate (MCP) detector. The TOF tube has 3 plates - repeller, extractor and ground and is situated at the guide exit, as shown in Figure 2.16. The ions are formed between the repeller and extractor plates, which are held at potentials of 330 V and 217 V respectively, accelerating the ions through the grounded tube towards the MCP. A large negative potential is applied to the MCP surface (-1900 V). The MCP has a diameter of 25 mm and is made of a lead oxide glass producing a cascade of electrons when impacted by an ion; these electrons can be detected by an oscilloscope and an ion current recorded.

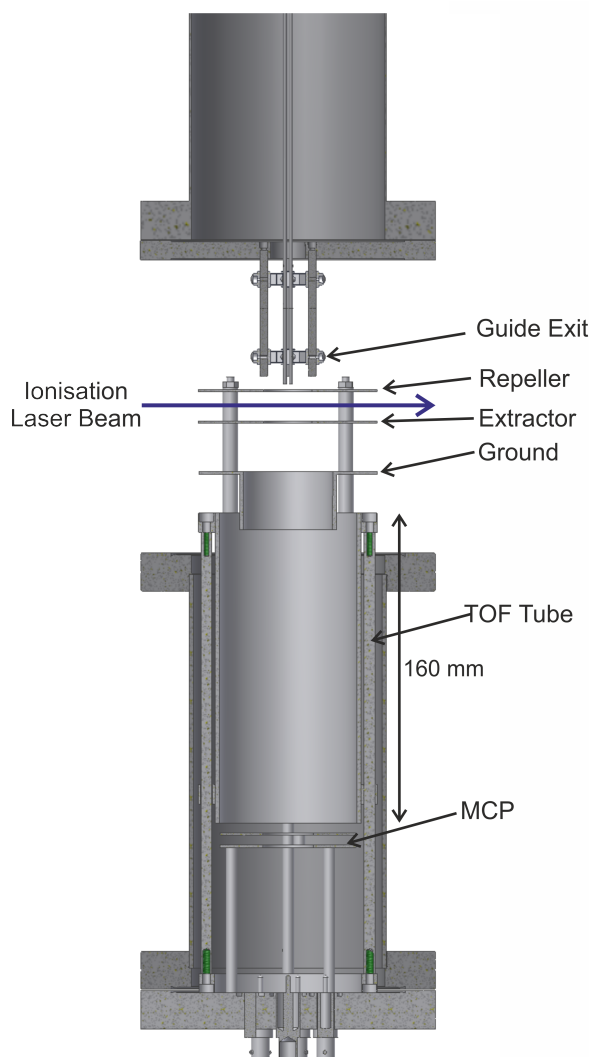


Figure 2.16: Schematic of the Wiley-McLaren type time of flight tube used to detect the ions formed by REMPI. The outer vacuum chamber enclosing the guide exit and TOF apparatus is omitted for clarity.

As REMPI is quantum state selective, it was used to determine the internal (rotational) state distribution of the guided ND_3 molecular beam. The REMPI spectra obtained, shown in Figure 2.17, were compared to simulations produced using PGOPHER [151] to assign the transitions, and the intensities of the experimental spectra can be fit to extract the relative populations of each rotational state. From this, the rotational temperature of the guided molecules can be obtained. The final rotational population of molecules at the end of the guide exhibits Boltzmann

statistics (with high field seeking states removed, as the electrostatic guide only guides low-field seeking Stark states), hence the rotational temperature can be ascertained using the Maxwell-Boltzmann function. Utilising Monte Carlo trajectory simulations (see [128] and Chapter 3), a “guidability factor” is calculated, which is a scaling factor which represents how the guide perturbs the initial population. Using the PGOPHER fit and this “guidability factor”, the rotational temperature is obtained. It was found that for a 6 K buffer gas cell with He buffer gas, $T_{\text{rot}} = 9$ K and for a 17 K buffer gas cell with Ne buffer gas, $T_{\text{rot}} = 15$ K. It is noted that due to the spin isomers of ND_3 (*ortho*- ND_3 and *para*- ND_3), and the lack of interconversion between them, it is technically incorrect to describe a sample of ND_3 with a single rotational temperature. However, under these conditions, the given T_{rot} is a fairly accurate measure of the rotational energy of the ND_3 sample. Fitting T_{rot} separately for *ortho* and *para* states showed little deviation from that obtained by fitting a single temperature [169]. Further details on the spin isomers in ammonia are given in Section 4.1.

Further details on subsequent REMPI experiments can be found in Chapter 4.

2.7 Ion Trap

The ion trap is a linear Paul ion trap, based on the initial ion trap first developed by Wolfgang Paul in the 1950s [152, 153]. The ion trap uses static direct current (DC) and radiofrequency (RF) voltages to confine cations spatially. The theory of ion trapping is described in detail in Chapter 5. This section is concerned with the experimental design of the ion trap itself and the combination with the buffer-gas cell and guide apparatus.

The ion trap used in this experiment, shown schematically in Figure 2.18 was initially designed and built by L. Pollum [142], who used the ion trap as a standalone

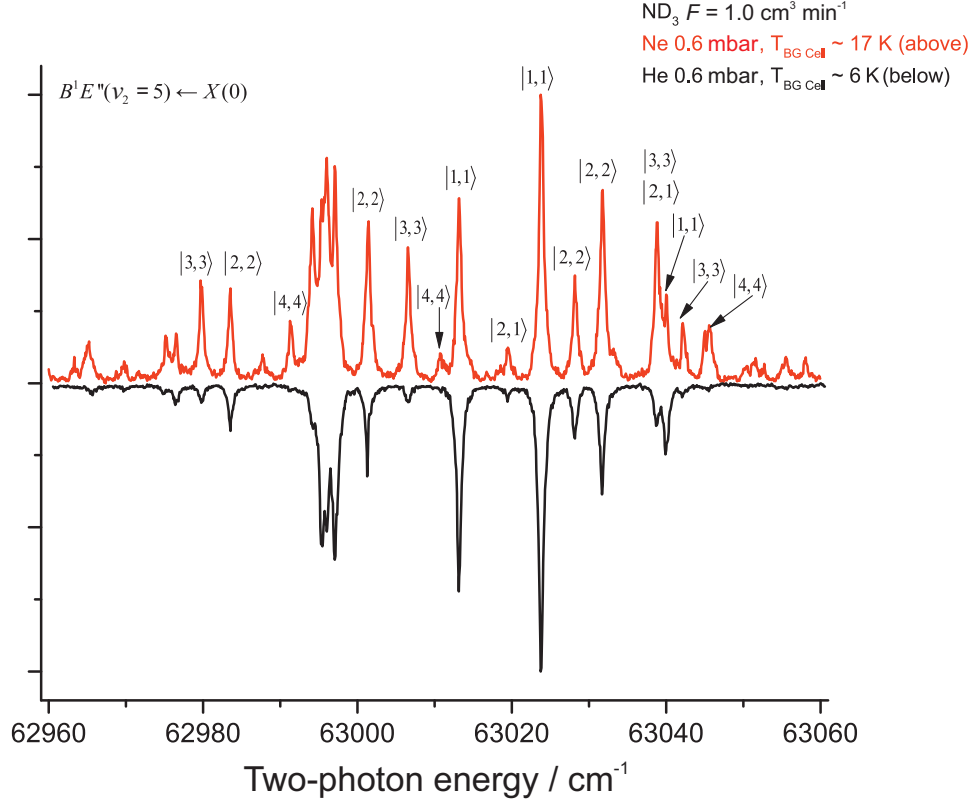


Figure 2.17: REMPI spectra of ND₃ taken with a buffer-gas cell temperature of 6 K (bottom) and 17 K (top), demonstrating the variability of rotational temperature with buffer-gas cell temperature. The buffer gas cell temperature can be altered by adding/removing the heat shields described in Section 2.5. Peaks are labelled as $|J, K\rangle$ Figure adapted from [128].

experiment [154]. However, the ion trap was built with the ultimate intention of combination with the quadrupole guide and several design features show this. During my project this apparatus was physically combined with the electrostatic guide and minor modifications to the design of L. Pollum were made to improve robustness and compatibility with the rest of the experiment.

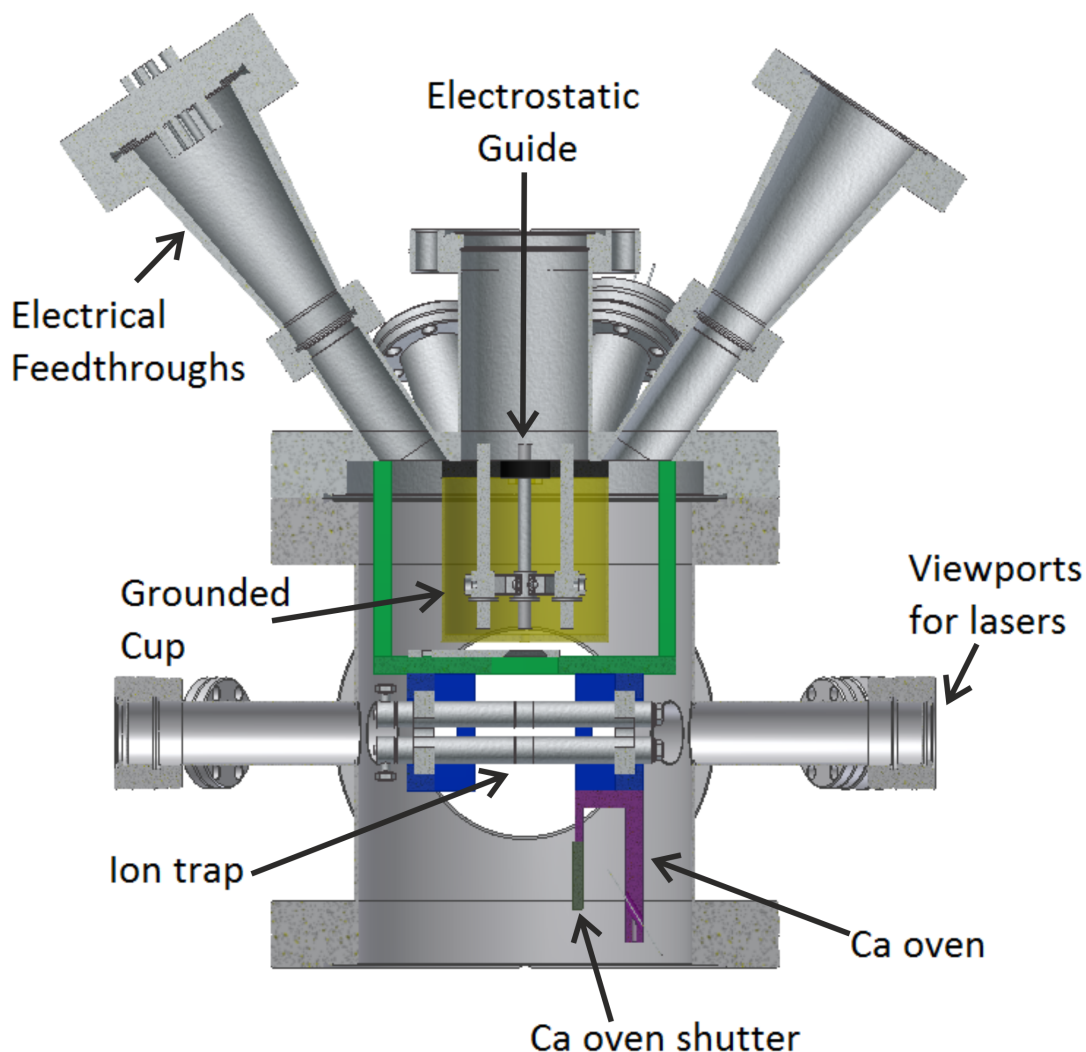


Figure 2.18: CAD drawing of the ion trap apparatus, showing the end of the guide, ion trap electrodes, Ca oven and vacuum chamber design.

The design of the ion trap must be such that it is compatible with the existing quadrupole guide apparatus, which places constraints on the orientation of the trap. Additionally, to perform cold chemistry experiments using the ion trap, ports for cooling lasers, high energy ionisation lasers, imaging of the trapped ions and for ejection of the ions (using the ion trap mass spectrometry approach developed in the group [154, 155]) are required. All of these ports need a direct line of sight to the ion trap. Additional functionality required on the trap chamber is a leak valve for directly introducing gases and an extra turbomolecular pump to maintain

ultrahigh vacuum conditions, as well as electrical feedthroughs for the ion trap and Ca oven. These ports do not require a direct line of sight to the trap. A base pressure of 5×10^{10} mbar is achievable in the trap chamber.

The ion trap electrodes are arranged in a quadrupolar arrangement, as shown in Figure 2.19, with each electrode having three disconnected segments, allowing for static DC voltages to be applied to the “endcaps” (outer electrodes) and RF to all electrodes. The electrodes themselves are made from stainless steel and are made by manufacturing the centre electrode with a small diameter thread which extends to the edge of the array, allowing electrical connections to the centre to be made. To form the entire array, a Macor insulator is placed over this thread and then the endcaps slide over this insulator. The endcaps do not touch the centre electrode and hence are disconnected electrically from it. The 4 individual electrode arrays are held together in a quadrupole arrangements by 2 PEEK brackets at either end of the trap.

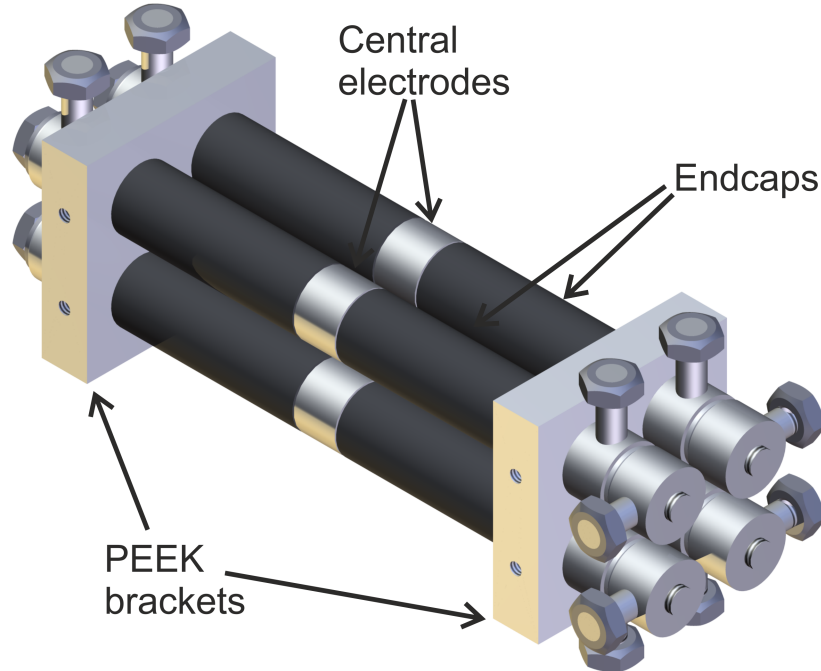


Figure 2.19: CAD drawing of the linear Paul ion trap used in this work. Dimensions are given in Table 5.1.

The ion, to which laser cooling is applied in our experiments, is singly charged

calcium, Ca^+ . To introduce Ca^+ into the trap, it must be produced *in situ* from Ca metal vapour. To do this, a resistively heated Ca oven is placed below the ion trap. A high resistance Ta wire is tightly wrapped around a threaded Macor insulator, which holds a Ta tube containing Ca powder. Ta was chosen due to its high resistivity ($1.24 \times 10^{-7} \Omega \text{ m}^{-1}$, by contrast this is ~ 10 x greater than Cu) and thermal conductance ($57 \text{ W m}^{-1} \text{ K}^{-1}$) [156], yet a low thermal expansion coefficient ($6.4 \times 10^{-6} \text{ K}^{-1}$) [157]. Passing a current on the order of 2 A through the Ta wire heats the oven sufficiently to produce a beam of Ca, which is skimmed by a $\varnothing = 1 \text{ mm}$ hole in a plate attached to the oven. This is to prevent deposition of Ca on the ion trap electrodes which may lead to patch potentials and distortion of the trapping fields. This plate can be adjusted by a linear actuator on the vacuum chamber to block the Ca beam entirely. The third harmonic of a pulsed nanosecond Nd:YAG laser (355 nm), or a tunable high power dye laser, can be introduced through two viewports 30° to the trap axis to ionise the Ca atoms to form Ca^+ in a non-resonant two-photon process.

A grounded mesh “cup” is used to shield the ion trap from the electric fields protruding from the guide. The cup encloses the final 45 mm of the guide and is made from solid stainless steel with a $\varnothing = 3 \text{ mm}$ hole in the base to allow the guided molecular beam to pass through. This hole is covered with a grounded mesh (Ni, 88% transmittance) to further prevent fringe fields. To vary the degree to which the molecular beam is skimmed (hence removing warmer divergent parts of the beam) and to vary the differential pumping, the cup can be replaced with another cup with a $\varnothing = 1 \text{ mm}$ hole and an “open cup”, in which the stainless steel body is open and is replaced with 3 thin poles to hold the mesh. Uses for these additional cups will be discussed later.

The electrical connections to the ion trap were improved in order to increase the robustness of the trap. Originally, the wire from the electrical feedthrough fed into

a hole on the edge of the trap assembly and looped around to form a “hook” to hold it in place. This configuration was subject to wires becoming dislodged and moving when the outer vacuum chambers were re-installed or from vibrations. To improve this, the wires were soldered on to the trap assembly and a sub-D connector (shown in Figure 2.20) was added between the vacuum feedthrough and trap, allowing the trap to be disconnected from the chamber for diagnostics and maintenance.

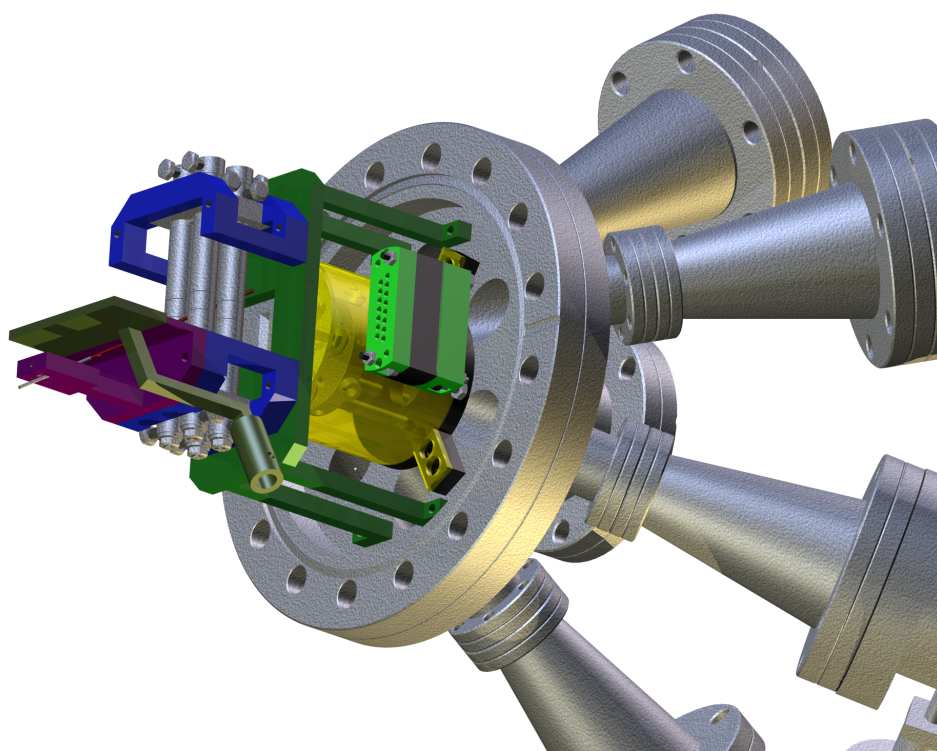


Figure 2.20: Oblique view of the ion trap assembly (excluding outer chamber) showing the sub-D connector, which makes the connection from the vacuum feedthrough to the ion trap and can easily be connection and disconnected. The wires are omitted for clarity.

2.8 Summary

To summarise, a novel apparatus combining buffer-gas cooling, electrostatic velocity selection and ion trapping for the investigation of cold ion-molecule chemical reactions has been constructed, developed and characterised. A variety of detection

methods (QMS, REMPI/Time-of-Flight and ion trap radial ejection) are implemented for detection of guided molecules and reaction products. The molecular beam flux has been optimised to give sufficient density to perform experiments and for reliable detection of molecules. Based on early usage of the apparatus, improvements have been made to enhance reliability and robustness and add additional functionality. This apparatus will now be employed in a range of experiments involving cold ions and molecules.

3

Using mass spectrometry to analyse the molecular beam

As the most abundant species in the universe, the chemistry of hydrogen atoms – and, by extension, hydrogen-containing molecules – is ubiquitous. The role of H-transfer in reaction mechanisms can be examined by exploiting the kinetic isotope effect; by monitoring the change in reaction rate with selective deuteration, one can elucidate the role played by the substituted hydrogen in the reaction process. H-transfer and H/D-exchange reactions play an important role in the chemistry of the interstellar medium (ISM). Approximately 30 deuterated molecular species have been identified in the ISM [158], with the prevalence of deuterated isotopologues significantly higher than that anticipated from the cosmic abundance of deuterium [159]. The density of ND₃ in selected regions of the ISM, for example, indicates a

deuterium enhancement (also termed fractionation) several orders of magnitude in excess of that predicted by the ISM D/H ratio of 1.5×10^{-5} [160, 161].

The mechanism for this enrichment is yet to be fully understood. It is postulated that ion-molecule reactions between HD and other mixed isotopic species with species such as H_3^+ , CH_3^+ and C_2H_2^+ are important mechanisms for deuterium enhancement, where H/D exchange is exothermic due to zero point energy considerations. As temperatures in the ISM are typically on the order of 10 - 20 K, the reverse (hydrogenation) reaction is suppressed – very little energy is available to surmount the reverse reaction barrier. The resulting deuterated ions, H_2D^+ , CH_2D^+ and C_2HD^+ , can undergo additional reactions, leading to deuterium fractionation in a diverse range of species [162].

To develop an understanding of deuterium fractionation, a method for the study of H/D exchange reactions at low temperatures in the laboratory is required. The experimental apparatus described in this thesis (see Chapter 2 and Figure 2.1) was designed with the intention of performing such reactions. In characterising and determining the properties of the cold molecular beam, ammonia is used because the buffer-gas cell and the guide have been characterised and optimised previously using ammonia, the results of which are shown in Section 2.6. Ammonia, and the deuterated isotopologues of ammonia, are fundamental small molecules in the chemistry of the interstellar medium [132, 163], giving a direct link to the motivation for studying these reactions and the types of reactions we wish to study.

For accurate reaction-rate measurements, the quantity (concentration) and characteristics of the molecular reactants needs to be known. While this can be determined fairly easily in the previous work with this apparatus using pure ND_3 or NH_3 gases, it is more challenging when considering the mixed ammonia isotopologues. Due to facile H/D exchange, it is not possible to obtain a pure sample of ND_2H and NH_2D ; instead, any gas mix containing these species will contain ND_3 , ND_2H ,

	ND ₃	ND ₂ H	NH ₂ D	NH ₃
<i>A</i>	-	7.445	9.678	-
<i>B</i>	5.143	5.344	6.411	9.444
<i>C</i>	3.120	3.753	4.696	6.196
μ_a	-	-	-0.185	-
μ_b	-	0.210	-	-
μ_c	1.497	1.470	1.465	1.497
$\tilde{\nu}_{\text{inv}}$	0.0680	0.1705	0.4060	0.7935
References	[100, 164]	[165, 166]	[165, 167]	[168]

Table 3.1: Rotational constants, dipole moments and inversion splittings for ND₃, ND₂H, NH₂D and NH₃. Dipole moments are given in Debye, all other quantities in cm⁻¹.

NH₂D and NH₃. As all of these species can be guided, the resulting molecular beam will contain all 4 species in differing concentrations depending on the initial concentration exiting the buffer-gas cell and the guiding efficiency.

A model for establishing the relative abundances of ND₃, ND₂H, NH₂D and NH₃ in the final molecular beam has been developed in this work, in order to ascertain the relative concentrations from the mass spectrometry signature of the beam, recorded using the QMS. As the four ammonia isotopologues have different rotational constants, dipole moments and – of particular importance – internal energy levels with widely differing Stark shifts (see Table 3.1 and Figure ??); for a full discussion of the molecular Stark shift see Section 4.5.1.), differing fractions of ND₃, ND₂H, NDH₂ and NH₃ reach the detection chamber. Thus the relative concentrations of each species in the resulting molecular beam does not match the initial distribution prior to electrostatic velocity selection.

Processes occurring in the QMS (such as ion fragmentation) are explicitly considered in the model and the electrostatic guiding process is modelled by Monte Carlo trajectory simulations. Considering both experimental findings and the Monte Carlo simulations together, the components of the final molecular beam are quantified. The total fraction of each species present and the relative populations of each rotational state are determined.

3.1 Trajectory Simulations

Monte Carlo trajectory simulations are performed to model the electrostatic guiding of the different buffer-gas cooled ammonia isotopologues. The trajectory simulation code, originally developed by M. Bell [100] and K. Twyman [128] and modified for this application by myself, is written in FORTRAN and an in-depth discussion of the mechanics of the program can be found in Chapter 2 of [128].

10^5 particles are initialised with a $T_{\text{trans,rot}} = 9$ K Boltzmann distribution, consistent with the energy distributions observed in previous measurements [169]. Further codes were developed by myself in order to create the effective potential experienced by the molecular in the guide, which is input into the FORTRAN program. To create the effective fields experienced by the molecules, the quadrupole velocity guide is modelled using SIMION 8.0 software with an applied voltage of $V_{\text{guide}} = \pm 5$ kV. Then, a MATLAB program solves the symmetric (ND_3 , NH_3), or asymmetric top (ND_2H , NH_2D) Hamiltonian for each isotopologue to calculate the Stark shifts at the voltage of interest. These Stark shifts are shown in Figure 2.4. A third program combines the output from the SIMION and MATLAB calculations, enabling the total effective field experienced by a molecule in a specific rotational state to be established. The simulations explicitly consider each rotational state of all of the ammonia isotopologues considered here (ND_3 , ND_2H , NH_2D and NH_3) up to $J = 5$. Previous characterisation of the buffer-gas cooled, guided beam of ND_3 by rotationally resolved REMPI spectroscopy found a negligible population in $J \geq 5$ under equivalent experimental conditions [169, 170].

As particles are propagated along the full length of the three-bend experimental guide, the guiding efficiency (or “guidability factor”) of a particular state is defined as the fraction of molecules in that state which reach the guide exit. Taking the guidability factor of each state and summing over all rotational states (weighted by

the initial Boltzmann population) gives a numerical handle on the overall relative guiding efficiency of each isotopologue, as provided in Table 3.2.

The decreasing guidability on increasing the H content of the isotopologue is principally a consequence of the lower population of the levels that are guided most strongly – for example, the energy gap from the ground state to the $J = 1$ levels increases as the rotational constant increases, hence the population of $J = 1$ decreases. There are also more subtle effects associated with the large inversion doubling in NH_3 , leading to a non-linear Stark effect at low fields, and the asymmetric top levels also have a non-linear Stark effect in the mixed isotopologues (see Figure 2.4), reducing the guidability.

	ND_3	ND_2H	NH_2D	NH_3
Guidability	0.4795	0.2714	0.1809	0.06823

Table 3.2: Overall relative guidability (normalised) of the deuterated isotopologues of ammonia under the experimental conditions described above.

3.2 Experimental

To produce a mixture of ammonia isotopologues, ND_3 and NH_3 are mixed in a sealed gas-mix bottle and left for 24 hours. Previous studies have reported that mixtures of ammonia equilibrate to yield a statistical distribution of the four isotopologues [171, 172, 173]. For a mixture with a 1:1 ratio of NH_3 and ND_3 , for example, a statistical distribution would result in relative concentrations of 1:3:3:1 for ND_3 : ND_2H : NH_2D : NH_3 . Experiments are conducted with pure ND_3 , pure NH_3 and three gas mixes containing different concentrations of ND_3 and NH_3 (termed Mixture A, Mixture B and Mixture C, corresponding to approximately 50:50, 75:25 and 25:75 mixtures of ND_3 and NH_3 , respectively)

Molecules exiting the guide are detected by the QMS located 25 mm from the guide exit, as described in Section 2.6.1. The QMS employs hot-cathode electron-

impact ionisation with an electron energy of 70 eV. As a result, fragmentation is a significant effect and must be accounted for when analysing the resulting ion signal. Subtraction of the QMS background signal is achieved by fitting a linear function to the background signal recorded before and after each experimental measurement with no voltage applied to the guide.

It is observed that at applied voltages above $V_{\text{guide}} = \pm 2$ kV, the QMS signal is linear with guide voltage (see Figure 3.1), confirming that the fragmentation branching ratios are due to processes in the QMS and not arising from the guiding process. Below $V_{\text{guide}} = \pm 2$ kV, a quadratic trend in signal is observed. The Stark effect for the ammonia isotopologues has a quadratic dependence on $|\mathbf{E}|$ at low electric field magnitude, becoming linear only at higher fields, and this quadratic behaviour is reflected in the transmission probability and hence the QMS signal.

The fragmentation patterns for pure ND_3 and pure NH_3 samples are shown in Figure [?] (a) and (b) for $m = 14 - 20$ u. Data for $m = 21$ u has also been recorded, however due to lack of signal (attributed to the low abundance of $^{15}\text{ND}_3$) the $m = 21$ u data was omitted from the modelling and analysis. As Figure 3.1 illustrates, single, double or triple fragmentation of the parent molecule occurs in the mass spectra (MS) of NH_3 and ND_3 , representing the loss of one, two or three D (H) atoms from an ND_3 (NH_3) parent molecule, respectively.

The ND_2H and NH_2D fragmentation probabilities are then estimated by taking a weighted average of the fragmentation patterns exhibited by ND_3 and NH_3 . For example, the relative magnitude of the signal at 18 u (representing the loss of one H atom from ND_2H), is estimated by taking the $\text{NH}_2:\text{NH}_3$ ratio from the single fragmentation of NH_3 and weighting it by $1/3$ to reflect the statistical probability that an H atom is lost from ND_2H compared to NH_3 . The signal at 17 u, representing the loss of one D atom, is established from the single fragmentation of ND_3 weighted by $2/3$. This process is continued down to 14 u, and is subsequently repeated for NH_2D .

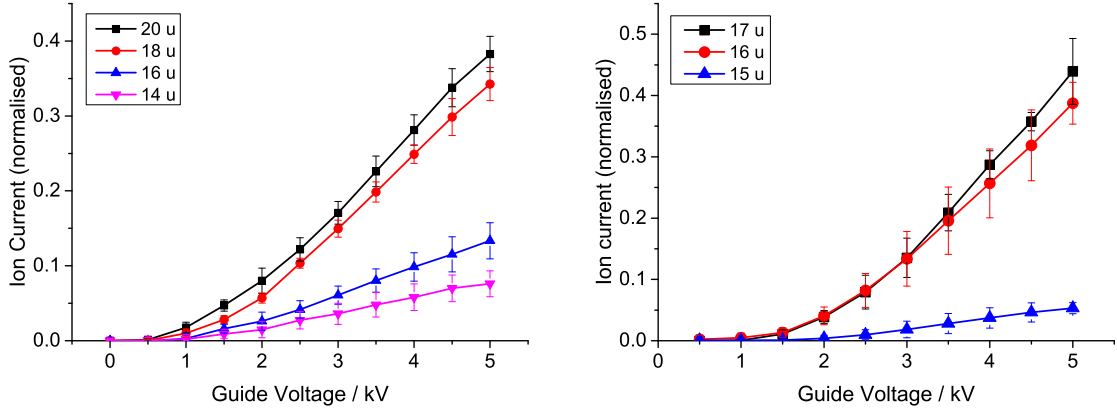


Figure 3.1: Relative ion currents recorded in the MS of ND_3 (left) and NH_3 (right) for $V_{\text{guide}} = 0 - 5$ kV. Masses giving a relative ion current of less than 0.05 at $V_{\text{guide}} = 5$ kV are not shown here for clarity. The full distribution is shown in Appendix A.2

For the loss of one H and one D from NH_2D , the estimated fragmentation is simply the average of the probabilities of losing two H atoms from NH_3 and two D atoms from ND_3 . Where there is more than one way of achieving a particular mass, such as loss of two H atoms or one D atom from NH_2D to yield a fragment of mass 16 u, contributions from all possible pathways are weighted appropriately and summed.

Taking the mass distribution observed for ND_3 and NH_3 with that predicted for ND_2H and NH_2D (outlined above), a 7×4 matrix (termed $\underline{\underline{A}}$ in the equations below) is formulated, indicating the relative contribution of each isotopologue to each mass peak. The two $\underline{\underline{A}}$ matrices, termed $\underline{\underline{A}}_{\text{guided}}$ and $\underline{\underline{A}}_{\text{non-guided}}$, refer to the two data sets recorded: the first from the buffer-gas cooled, velocity-selected, or “guided” samples; the second from the samples leaked directly into the detection chamber bypassing the guide (hence “non-guided”). The ND_3 and NH_3 columns in the $\underline{\underline{A}}$ matrices, defining the relative ion signals observed for each mass 20 – 14 u, are taken directly from the averaged QMS data. The mass distributions predicted for ND_2H and NH_2D can be seen in columns 2 and 3 (respectively) of the $\underline{\underline{A}}$ matrices (columns 1 and 4 depict the breakdown of ND_3 and NH_3 , respectively). Coefficients < 0.01 are denoted as 0 for clarity.

The $\underline{\underline{A}}$ matrices for the guided and non-guided (leak valve) data differ slightly (see

below). This is attributed to the different experimental conditions between the two measurements; the non-guided molecules are leaked directly into the detection chamber and hence exhibit a room temperature Maxwell-Boltzmann distribution of state populations, whereas the internally- and translationally-cooled guided molecules travel through the buffer gas cell and quadrupole guide, allowing time and more opportunity for H/D exchanges to occur.

$$\underline{\underline{A}}_{\text{guided}} = \begin{pmatrix} 0.38 & 0 & 0 & 0.02 \\ 0.04 & 0.40 & 0.01 & 0.01 \\ 0.34 & 0.14 & 0.43 & 0.02 \\ 0.02 & 0.25 & 0.28 & 0.46 \\ 0.14 & 0.10 & 0.16 & 0.41 \\ 0.01 & 0.05 & 0.06 & 0.06 \\ 0.07 & 0.06 & 0.04 & 0.03 \end{pmatrix}$$

$$\underline{\underline{A}}_{\text{non-guided}} = \begin{pmatrix} 0.43 & 0 & 0 & 0 \\ 0.02 & 0.44 & 0.04 & 0 \\ 0.34 & 0.12 & 0.47 & 0.04 \\ 0.01 & 0.24 & 0.26 & 0.50 \\ 0.18 & 0.10 & 0.14 & 0.40 \\ 0 & 0.08 & 0.08 & 0.03 \\ 0.02 & 0.02 & 0.01 & 0.03 \end{pmatrix}$$

As ND_3 is the only species with mass 20 u (ignoring minor H/D exchange from other isotopologues), the contribution of ND_3 fragments to the other mass peaks can be directly established from the ND_3 column in matrix $\underline{\underline{A}}$. However, it is not so straightforward to account for the contributions of the other three isotopologues within the various mixtures, as there are no other mass peaks attributable to only one parent molecule. To deconvolve the contributions of each isotopologue to each mass peak, a matrix equation $\underline{\underline{A}} \cdot \underline{x} = \underline{i}$ is solved for $\underline{x}$. Here $\underline{i}$ is a vector containing the background-subtracted ion currents for $m = 20 - 14$ u and $\underline{x} = [c_{\text{ND}_3}; c_{\text{ND}_2\text{H}}; c_{\text{NH}_2\text{D}}; c_{\text{NH}_3}]^T$, where c_x is the relative concentration of molecule X at the end of the guide, after accounting for fragmentation and exchange processes. A least squares fitting method is used to solve for $\underline{x}$. Fitting with and without

		Pure ND ₃	Pure NH ₃	Mix A	Mix B	Mix C
c_{ND_3}	guided	1	0	0.20	0.26	0.04
	non-guided*	1	0	0.19	0.28	0.04
	non-guided	1	0	0.08	0.15	0.01
$c_{\text{ND}_2\text{H}}$	guided	0	0	0.40	0.47	0.25
	non-guided*	0	0	0.40	0.47	0.24
	non-guided	0	0	0.38	0.44	0.13
$c_{\text{NH}_2\text{D}}$	guided	0	0	0.33	0.24	0.53
	non-guided*	0	0	0.35	0.22	0.53
	non-guided	0	0	0.40	0.31	0.44
c_{NH_3}	guided	0	1	0.07	0.04	0.18
	non-guided*	0	1	0.07	0.03	0.19
	non-guided	0	1	0.21	0.10	0.42

Table 3.3: Relative concentrations of ND₃, ND₂H, NH₂D and NH₃ in each gas mix, established from the guided and non-guided measurements. (*) indicates non-guided data multiplied by the appropriate guidability factors for comparison to the guided data.

the constraint of non-negative coefficients yields the same result. The relative concentrations of each isotopologue determined for the three buffer-gas cooled, guided gas mixtures are provided in Table 3.3.

As the efficiency of the guiding process varies for the different isotopologues (dependent on their Stark shifts, given in Figure 2.4), as indicated in Table 3.2, the post-guide relative concentrations will be different from those in the initial gas mix. To test both the validity of the fragmentation model described above and the accuracy of the Monte Carlo simulations, one can consider the non-guided leak valve data set recorded by the QMS. The concentrations of the isotopologues in each of the gas samples are established by leaking the gas directly into the detection chamber, and subsequently multiplied by the relevant guidability factor. This yields a prediction of the relative concentrations of the isotopologues in the guided sample, that can be directly compared to those obtained from the guided-beam analysis. These “corrected” leak valve concentrations are also presented in Table 3.3.

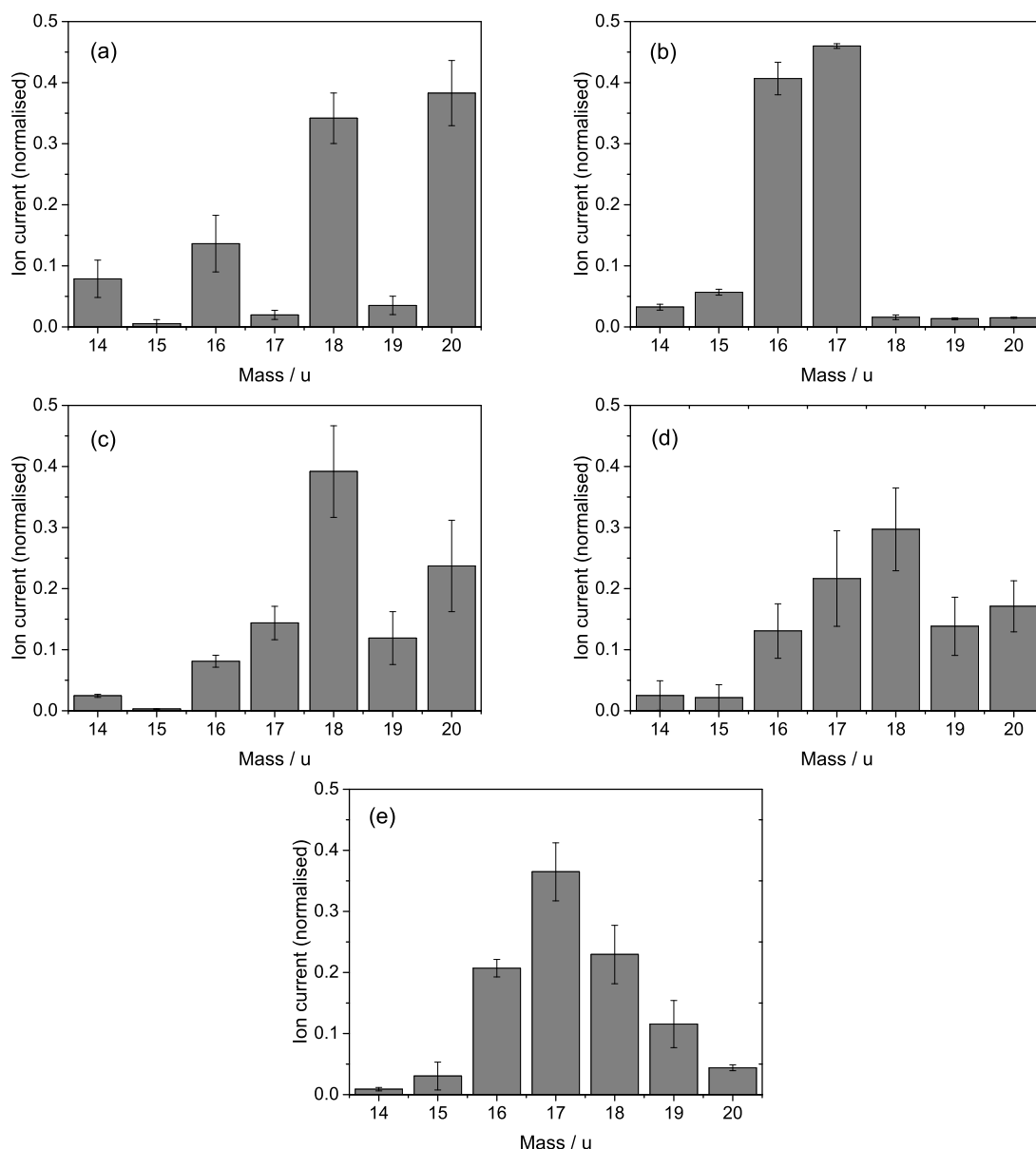


Figure 3.2: The QMS ion currents recorded for $m = 14 - 20$ u, from the five gas mixes examined in this work: (a) pure ND₃, (b) pure NH₃, (c) Mixture A, (d) Mixture B, and (e) Mixture C.

Quantitative agreement is demonstrated between the fractional abundances of the isotopologues in the buffer-gas cooled guided beam and those obtained from the room temperature data (modified using the guidability factors) in all three gas mixtures. In all instances the agreement is to within ± 0.02 . Given the not insignificant experimental uncertainty, with an upper error limit of ± 0.035 in the fractional

abundances, this agreement is excellent. As the various ammonia isotopologues are guided to differing degrees, mixtures that are richer in NH_3 will be guided less efficiently overall; the QMS ion signals recorded for NH_3 -rich mixtures will be smaller, with a reduced signal-to-noise ratio. This is seen experimentally, with the largest deviations between the two data sets occurring in Mixture C, which has the highest concentration of NH_3 . While the pure NH_3 sample has the lowest guiding efficiency of all, measurements on this sample do not suffer as significantly from poor signal-to-noise ratios as every molecule that makes it to the QMS is NH_3 .

Due to the cryogenic nature of the experiment, the buffer-gas cell is prone to “freezing over” during data collection, where molecular ice can temporarily hinder gas flow and block apertures – a phenomenon which was characterised in detail in [128] and Figure 2.15. The multiple repeats recorded for each gas sample serve to reduce the effect of any random errors introduced by changes in the buffer gas cell conditions, and the gas flow rates were closely monitored. Other potential sources of experimental error include contamination from adsorbates on the walls of the apparatus, regions of non-uniform electric fields in the guide due to material imperfections, and collisions or Majorana transitions causing loss of molecules from the guide. The high level of agreement demonstrated between the data sets indicates that the effect of these errors is likely to be minor.

The high level of agreement in the data sets imply little change in the relative abundances of the isotopologues as the gas mix is cooled, at least on the time scale that the gases reside in the buffer gas cell, *i.e.*, the isotopologue abundances of the source gas can be taken as equal to the abundances entering the guide.

The agreement confirms the validity of both the fragmentation modelling and the Monte Carlo trajectory simulations. Thus, the fraction of each isotopologue in a guided gas mixture can be determined, and when combined with absolute flux measurements, the density of each reactant species in the reaction region at the

end of the guide. The Monte Carlo simulations also output the rotational state population distributions for each species in the detection chamber. While we do not have sufficient molecular density of the mixed isotopologues to measure their rotational population distribution accurately, REMPI spectra recorded for ND₃ and NH₃ – from both pure samples and from the gas mixtures exhibit rotational populations in quantitative agreement with the Monte Carlo simulations [169] (see Section 2.6.3). The guidabilities for each rotational state are given in Appendix A.2.

3.3 Discussion and Conclusion

In this chapter, a model for determining the relative concentrations of ND₃, ND₂H, NH₂D and NH₃ from three different buffer-gas cooled mixtures of ammonia isotopologues transmitted through a quadrupole guide is demonstrated. The accuracy of Monte Carlo trajectory calculations in simulating the guiding process is confirmed through comparisons between guided and non-guided mass spectra of guided beams and room temperature samples admitted via a leak valve. With the ability to accurately determine the concentrations of each reactant species in ammonia mixtures – and, furthermore, to simulate the rotational population distributions – we can fully characterise the reactant molecules entering the ion trap *via* the guide.

Measuring the reaction rates for different gas mixtures, and hence the fractions of each isotopologue will facilitate the unscrambling of the reaction rates in future chemical reactions involving ammonia performed using this apparatus. With the ability to control and characterise the molecular reactants, one could probe the mechanism for deuterium fractionation in astrochemically important ion-molecule reactions. For example, the competition between H and D transfer could be examined, with the branching ratio between $\text{ND}_2\text{H} + \text{NH}_3^+ \rightarrow \text{ND}_2 + \text{NH}_4^+$ and

NDH + NH₃D⁺ products ascertained.

4

Using REMPI spectroscopy to probe the guided molecular beam

Resonance-enhanced multi-photon ionisation (REMPI) is a highly sensitive spectroscopic technique in which multi-photon transitions can be measured through the detection of molecular ions formed by ionisation of an intermediate excited electronic (Rydberg) state (see Figure 4.1). Molecules are excited from a specific rotational and vibrational state to an intermediate electronic state, which is then excited to the ionisation continuum. By scanning the ionisation laser in wavelength, different resonances can be found, hence building up a spectrum. A REMPI spectrum gives the initial quantum state distribution of the molecular sample.

With the ability to probe the internal state distribution, the rotational temperature of a molecular beam can be determined. As outlined in Chapter 1, part of the

rationale for the experiments described in this thesis is to investigate the effect of rotational temperature on reaction kinetics and dynamics. REMPI spectroscopy is used to verify that the guided molecular beam is rotationally cold, to determine the rotational state populations and to ascertain the degree of control over T_{rot} that is possible using this apparatus. Controlling the rotational temperature of reactants allows for finer control over the pathway reactants take on a reactive potential energy surface, compared to thermal ($T_{\text{rot}} \approx 298$ K) reactants. The emphasis of this chapter is that by using polarised laser light in conjunction with REMPI, the orientation of molecules in the molecular beam exiting the quadrupole guide, described in Section 2.3, can be probed. Molecular orientation is a factor which has been shown to affect the rate of some chemical processes [174, 175].

4.1 Rotational State Labels

The rotation of a symmetric top molecule, in the absence of additional angular momenta, can be described by the quantum numbers $|J, K, M\rangle$. Here, J is the total angular momentum quantum number of the molecule, K represents the projection of J on the primary molecular axis and M is the projection of J onto an external space-fixed axis, usually the axis of an applied field. In the case where additional angular momenta are present, an expanded basis set can be used, which is described in Section 4.5.2.

The rotational energy levels of a symmetric top molecule, in the absence of external fields and ignoring centrifugal distortion, are given by:

$$E_{\text{rot}} = BJ(J+1) \pm (A-C)K^2 \quad (4.1)$$

where the rotational constants are $A = \hbar/2I_a$, $B = \hbar/2I_b$ and $C = \hbar/2I_c$, and

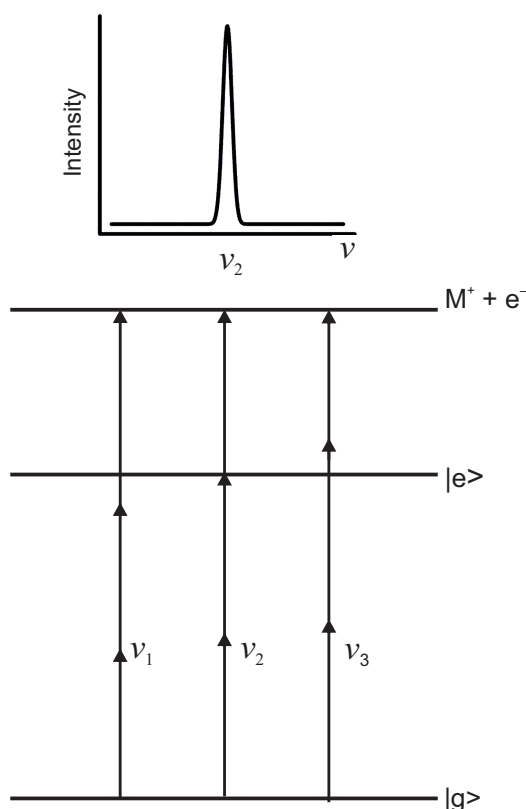


Figure 4.1: Schematic showing the principles of $(2 + 1)$ REMPI spectroscopy. A molecule is excited from the ground state $|g\rangle$ to an excited electronic state $|e\rangle$ by a number of photons and then to the ionisation continuum by further photon(s). Where the energy of the photon(s) (two in this instance) is resonant with the transition, as for ν_2 , an enhancement in the ionisation probability (resonance-enhancement) is observed and hence a greater signal is recorded.

$I_x = \sum_i m_i r_i^2$ is the moment of inertia around the a , b and c molecular axes. The positive combination applies for prolate symmetric tops (molecules where $I_a < I_b = I_c$) and the negative combination applies to oblate symmetric tops (molecules where $I_a = I_b < I_c$). ND_3 and NH_3 are oblate symmetric tops. NH_2D and ND_2H are asymmetric tops, where $I_a < I_b < I_c$. In the asymmetric top case, J is projected onto both the a and c axes leading to K no longer being a good quantum number. Instead, the projections are expressed independently as K_a and K_c . The pseudo-quantum number $\tau = K_a - K_c$ is often used to express the projection of J on to the molecular axes in the case of an asymmetric top. The energy levels of an asymmetric top have a more complex formulation than those of

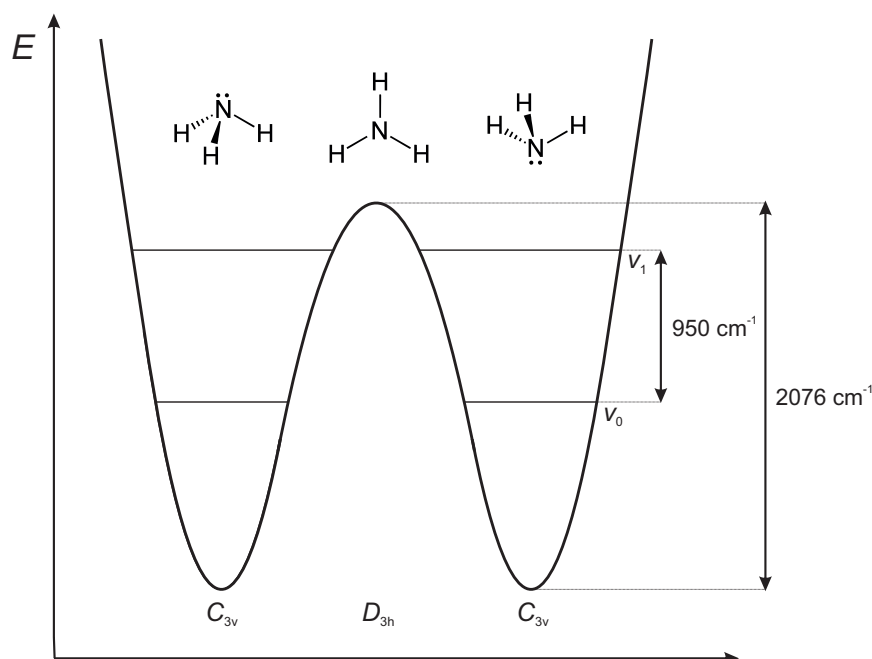


Figure 4.2: Double well potential arising from the inversion motion of the NH_3 molecule, with the vibrational energy level spacing ω_e and inversion barrier height shown. Values are from [178].

a symmetric top or linear molecule, the formulation of the asymmetric top energy levels can be found in references [176, 177].

ND_3 and NH_3 are pyramidal (C_{3v} symmetry) molecules in their electronic ground state. However, ND_3 and NH_3 can undergo inversion due to the N atom tunnelling through the plane of the H(D) atoms. This has the effect of inverting the ammonia molecule, *via* a planar (D_{3h} symmetry) intermediate. This inversion effect gives rise to a double-well potential, shown in Figure 4.2. In NH_3 , the barrier to inversion is 2076 cm^{-1} [178], compared to $k_B T \approx 210 \text{ cm}^{-1}$ at 300 K; hence inversion occurs due to tunnelling through the barrier rather than by thermal excitation. The rotational constants and inversion splittings for ND_3 , ND_2H , NDH_2 and NH_3 can be found in Table 3.1.

As a result of the tunnelling through the inversion barrier in ND_3 and NH_3 , the two inversion states (and hence the energy levels in each state) are not distinct,

instead the eigenstates are linear combinations of the two inversion states, *i.e.* $\psi = \frac{1}{\sqrt{2}} (\phi_1 \pm \phi_2)$. This gives symmetric (+) and antisymmetric (−) parity states. To include this effect, a parity quantum number $\epsilon = \pm 1$ is introduced, which expands the rotational (symmetric top) basis set from $|J, K, M\rangle$ to that given in Equation 4.2. The formulation of the inversion eigenstates and the basis set given assumes the Born-Oppenheimer approximation is valid *i.e.* the overall molecular wavefunction Ψ can be adiabatically separated into its components $\Psi = \psi_{\text{trans}}\psi_{\text{rot}}\psi_{\text{vib}}\psi_{\text{elec}}\psi_{\text{nuclear}}$. As the separation between internal states is greater than $k_{\text{B}}T$ at the temperatures in this work, the Born-Oppenheimer approximation is likely to be a valid assumption.

$$|JKM, \epsilon = \pm 1\rangle = \frac{1}{\sqrt{2}} (|JKM\rangle + \epsilon |J - K - M\rangle) \quad (4.2)$$

As mentioned in Section 2.6.3, NH_3 and ND_3 have *ortho* and *para* forms, arising from the nuclear spin of the H(D) atoms, which can be aligned parallel with each other (*ortho*) or aligned anti-parallel (*para*). In the absence of a catalyst (such as Ni metal), the two forms can not interconvert – interconversion is only possible by exchange of D atoms between ND_3 molecules. Due to the different alignment of the individual H(D) nuclear spin vectors in the *ortho* and *para* forms (see Figure 4.3, the total nuclear spin $\mathbf{I}_{\text{tot}}$ takes different values for the two forms (or spin isomers) - for *ortho*- NH_3 , $I_{\text{tot}} = 3/2$ and for *para*- NH_3 , $I_{\text{tot}} = 1/2$ (further coupling of the H(D) nuclear spin to the nuclear spin of N is possible).

In the case of NH_3 , the H nuclei are fermions ($I = 1/2$) hence the overall molecular wavefunction Ψ must change sign on interchange of identical nuclei (*i.e.* upon a C_3 rotation). As shown in Figure 4.4, ψ_{rot} has parity $(-1)^J$.

This parity of the rotational wavefunction results in “missing” rotational states for each spin isomer. ψ_{rot} couples to the nuclear spin component of the wavefunction, ψ_{nuc} , which is negative if the nuclei being interchanged have anti-parallel spins

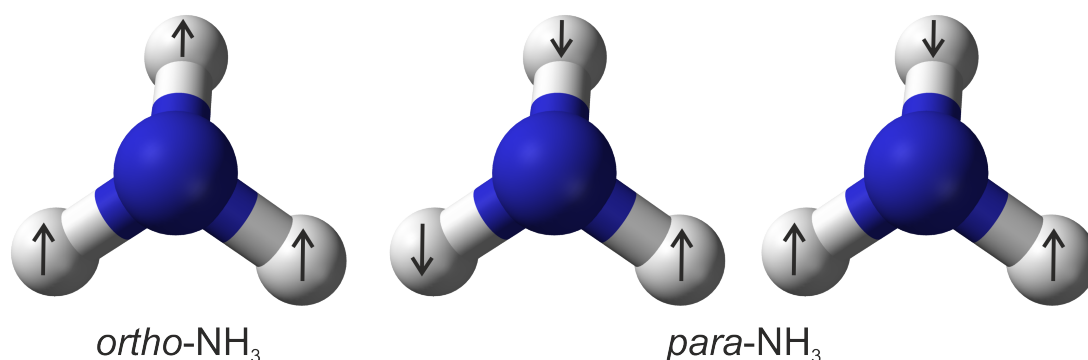


Figure 4.3: Molecular models of *ortho*- and *para*-NH₃, showing the H nuclear spins in both spin isomers. The N nuclear spin vector is not shown.

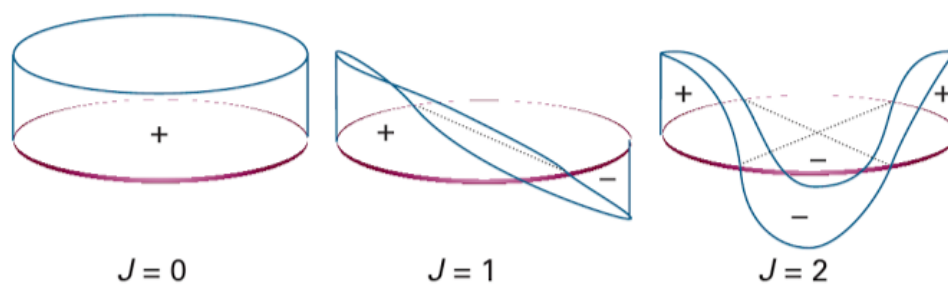


Figure 4.4: The symmetries of ψ_{rot} , for a 2D rotor, undergoing a rotation through 180° . It can be seen that the parity of ψ_{rot} is $(-1)^J$. Adapted from [21].

and positive if the spins are parallel. Hence, only even rotational (J) levels are present in the *para* form and odd levels in the *ortho* form. For ND₃, D is a boson ($I = 1$) and the condition for exchange of identical bosons is that Ψ must not change sign upon exchange, allowing for odd rotational levels in *para*-ND₃ and even levels in *ortho*-ND₃. As the lowest energy low-field seeking state is only present in *para*-ND₃, the ratio will be biased towards the *para* form by the guiding process, however as the guide transmits a range of rotational states, both *ortho* and *para*-ND₃ will be present in the guided sample, the *ortho:para* ratio depending on the buffer-gas cell temperature. As different rotational states are present in the two spin isomers of ND₃, *ortho* and *para*-ND₃ will thus thermalise separately to different equilibrium rotational state distributions. Nevertheless, excellent agreement between

the simulations (obtained assuming the same rotational temperature for both *ortho* and *para* components) and the experimental spectra indicates that the difference in rotational temperature between the *ortho* and *para* states is minimal under our conditions (see Section 2.6.3 and [169]).

4.2 Choice of intermediate Rydberg state

ND₃ and NH₃ have been extensively studied spectroscopically and many of the spectroscopic constants and Rydberg states are well characterised in the literature [179, 180, 181]. As noted previously, ND₃ and NH₃ have C_{3v} symmetry in the ground state. However, due to the rapid inversion motion in ND₃ and NH₃, it is often more appropriate to consider the average geometry of the two inversion states (see Figure 4.2), which has D_{3h} symmetry. In ammonia, the highest-occupied molecular orbital is the doubly occupied lone-pair ($3a_1$) orbital. Electronic excitation generally involves excitation of one of these electrons to a higher lying orbital ($n > 3$).

The first excited state of ammonia, the $\tilde{A}$ ($^1A_2''$) state has a very short natural lifetime ($\tau < 1$ ps) [182], which makes this state unsuitable for REMPI spectroscopy – as REMPI relies on the excited electronic state being long-lived enough for the molecule to absorb the necessary additional photon(s) for excitation to the ionisation continuum. In addition, the rovibronic levels of the $\tilde{A}$ state are substantially lifetime broadened.

Many REMPI studies on ammonia have utilised the $\tilde{C}'$ state [149]. However, the $\tilde{C}'$ state is ill-suited for obtaining populations from rotationally-resolved REMPI spectra as the predissociation rate of this state is somewhat dependent on the internal quantum state (rotational and vibrational) [183]. The lifetimes of $\tilde{C}'$ state levels decrease with increasing vibrational level in the excited state, and within each vibrational state the predissociation rate increases upon exciting to

higher rotational levels [179, 184, 185].

The singlet $\tilde{B} \left(^1E'' \right)$ state has a lifetime of 0.25 ns, independent of rotational state for vibrational levels $v' \leq 6$ [186]. The longer lifetime and lack of rotational state lifetime dependence makes this state ideal for extracting populations from rotationally-resolved REMPI studies. The $\tilde{B} \leftarrow \tilde{X}$ transition lies just below the $\tilde{C}'$ origin. Additionally, the $\tilde{B} (v' = 5) \leftarrow \tilde{X} (v'' = 0)$ transition lies near the peak output of the second harmonic of the dye laser in the configuration used for these experiments (given in Section 2.6.3)¹, and it is this transition that is used in all the REMPI studies presented here.

4.3 Alignment and Orientation

In spectroscopy and molecular dynamics, a distinction between *aligned* and *oriented* molecules is made. If we consider the angular momentum vectors $\mathbf{J}$ of an ensemble of molecules, in an oriented sample there would be a preferred direction of $\mathbf{J}$ in space. In an aligned sample, it can be distinguished if $\mathbf{J}$ is pointing either parallel or anti-parallel to a given reference but no distinction between parallel and anti-parallel can be made [174] (see Figure 4.5). Another way to consider this is that the distribution of the components of $\mathbf{J}$ on the reference axis, M_J , will be entirely positive (or negative) in an oriented sample, due to the fixed direction of $\mathbf{J}$ relative to the reference axis. In an aligned sample, M_J takes both positive and negative values, due to the alternation in the direction of $\mathbf{J}$ with respect to the reference axis. The resulting M_J distributions are shown in Figure 4.6.

In most spectroscopic experiments, there is a symmetry axis $\mathbf{Z}$, often based on laser polarisation, the lab-frame axis or the direction of a molecular beam. In our experiments, the linear polarisation of the ionisation laser defines the symmetry axis.

¹DCM laser dye is used in these experiments

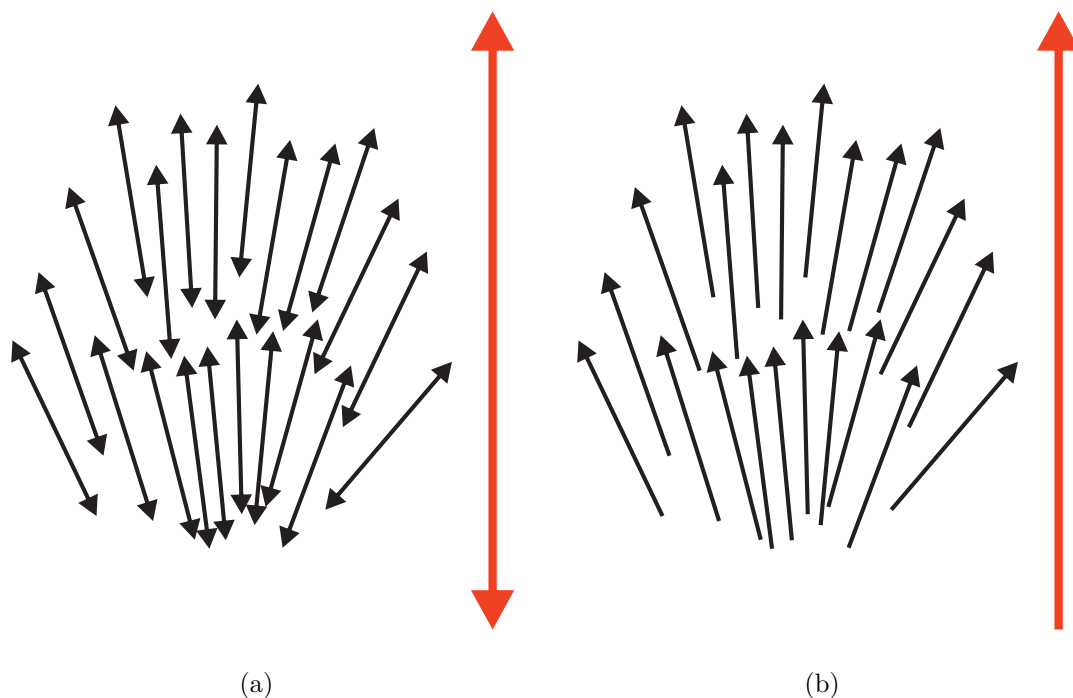


Figure 4.5: Schematic showing the potential direction of the angular momentum vectors $\mathbf{J}$ with a reference axis $\mathbf{Z}$ (shown in red) for an a) aligned sample and b) oriented sample.

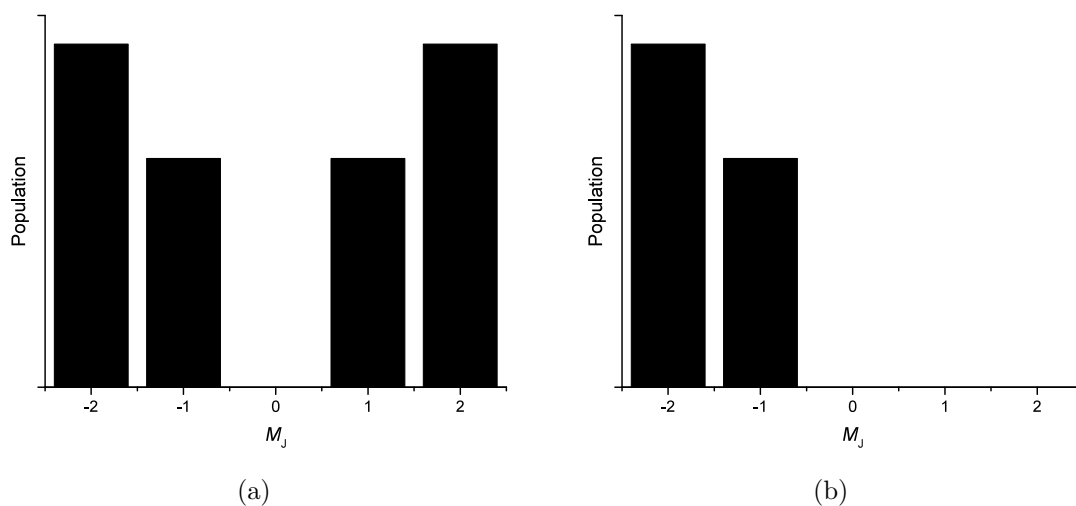


Figure 4.6: Resulting M_J distributions, arising from the projection of the molecular angular momentum vector $\mathbf{J}$ upon a symmetry axis $\mathbf{Z}$ for a) an aligned sample and b) an oriented sample.

It is also necessary to distinguish between molecular or bond axis orientation and alignment and angular momentum orientation and alignment, referring to the geometrical distribution of molecules around a given bond axis in space and the spatial distribution of the $\mathbf{J}$ vector, respectively. These two properties are not entirely decoupled, as a sample with angular momentum orientation will have a well-defined bond axis orientation [264]. The use of linearly-polarised laser light in the experiments described below allow us to probe the M -state distribution, which is related to the degree of angular momentum orientation.

4.4 Orientation effects

One aim of performing chemical reactions at cold temperatures is to gain a greater degree of control over the reactants. This includes controlling degrees of freedom which are generally lost at room temperature due to thermal averaging, such as the quantum state, collision energy and orientation of reactants. The orientation of reactants can affect the reaction rate constant, k , as the relative angle between reacting species can result in the reaction proceeding *via* a different pathway on the reactive potential energy surface. This can give more favourable (or unfavourable) conditions for the reaction [174] compared to where the orientation of the reactants is scrambled by thermal averaging. For example, it was observed in the group of J. Ye that by orienting the dipoles in a sample of KRb in an optical lattice trap, the rate of the $2\text{KRb} \rightarrow \text{K}_2 + \text{Rb}_2$ reaction could be suppressed [82]. This was achieved by tight confinement of the molecules such that only repulsive “side-by-side” collisions could occur, rather than attractive “head-to-tail” collisions. Y. Shagam *et al.* demonstrated that electric fields can be used to select a specific conformer of 3-aminophenol, and that a specific conformer of the molecule reacts more favourably with ultracold trapped Ca^+ ions [188]. External electric fields were shown to

increase the reactive cross-section in the ultracold $\text{Rb} + \text{ND}_3$ system (prepared by laser cooling and Stark deceleration, respectively) due to non-adiabatic transitions resulting from the competition between orientation of the molecules to the external field and the collision (dipole) axis [189]. The topic of controlling chemical reactivity *via* molecular orientation has been the subject of several reviews [174, 190, 191, 192]. Electric (magnetic) fields are commonly used to orient molecules that have a permanent electric dipole moment (magnetic moment). Orientation effects are molecule, and state dependent. The interaction energy between a permanent dipole, μ , and an external electric field, E , is (in scalar terms), $U_{\text{Stark}} = \mu E \langle \cos \theta \rangle$, where θ is the angle between the dipole and the field axis and $\langle \cos \theta \rangle = KM/J(J+1)$. The field required to orient a molecule, in a given $|J, K, M\rangle$ state, to an external field was reported in Reference [193] to be given by:

$$E_{JKM} = \frac{W_{\text{orient}}}{\mu} \frac{J(J+1)}{KM} \quad (4.3)$$

where W_{orient} is the minimum threshold energy required to rotate the molecule to be oriented with the field axis and depends upon the moment of inertia of a given molecule. For most small symmetric top molecules (such as ND_3) in low lying J states (typically $J < 7$), E_{JKM} is on the order of a few V cm^{-1} [194]. Hence the large-magnitude electric field present in the quadrupole guide in this experimental setup will orient all states in ammonia to the external field axis.

4.4.1 Oriented REMPI spectra

To probe orientation effects in molecules exiting the quadrupole guide, $(2+1)$ REMPI spectra of ND_3 and NH_3 are recorded using linearly-polarised laser light, aligned parallel (“vertical”) or perpendicular (“horizontal”) to the quadrupole axis. The detection region of the experimental setup to perform these REMPI experiments

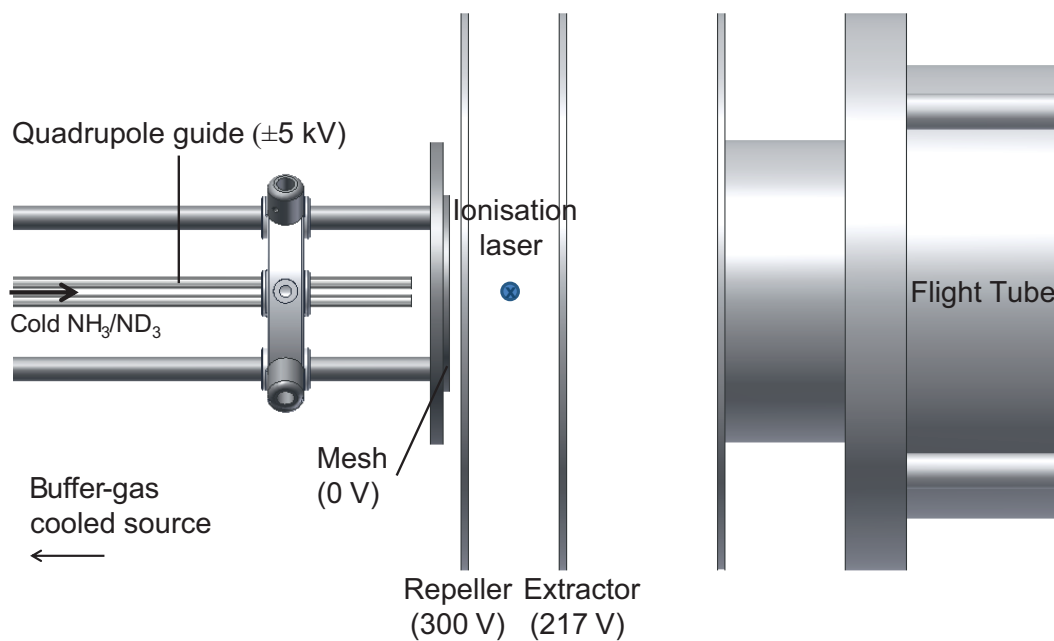


Figure 4.7: Schematic of the detection region in the experimental apparatus, located at the end of the quadrupole guide. Further details of this setup are given in Section 2.6.3.

is given in Figure 4.7, and a broader overview of the experimental apparatus can be found in Chapter 2. The polarisation of the laser light is controlled with a $\lambda/2$ plate and polarising beam splitter (PBS). A schematic of the beamline is shown in Figure 4.8.

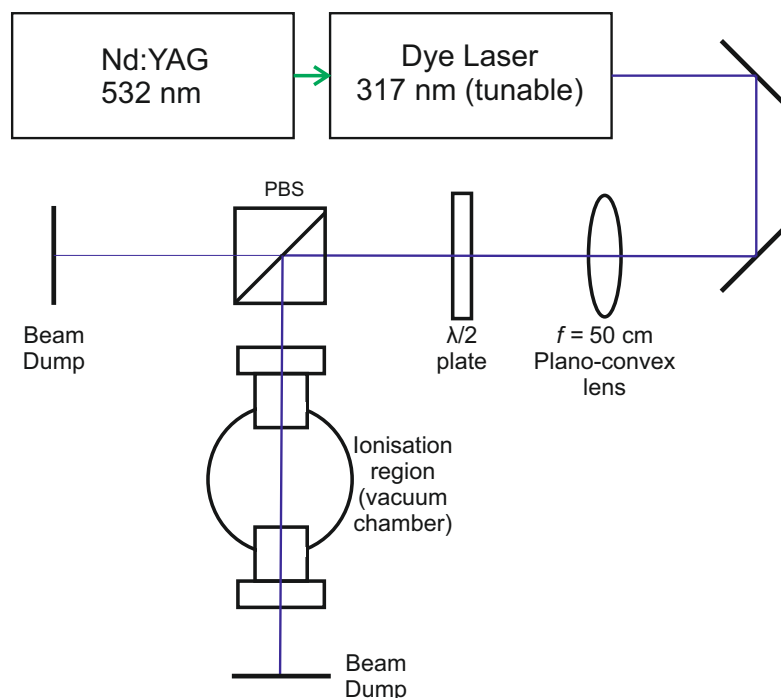


Figure 4.8: Schematic of the laser beamline used for performing the REMPI orientation experiments.

Use of linearly-polarised laser light allows different ΔM transitions to be probed independently, $\Delta M = \pm 2$ or 0 (horizontal) and $\Delta M = 0$ (vertical), allowing a picture of the M -state distribution at the point of ionisation to be constructed from the spectra.

4.4.2 Spectral analysis

The ND_3 and NH_3 REMPI spectra, shown in Figure 4.9 are analysed using the PGOPHER spectral fitting and simulation software package [151]. As the individual M -state populations needed to be explicitly considered in this case, a modification to the PGOPHER code was implemented by C. Western and is described in [257]. Due to the need to record repeat measurements to reduce uncertainties and to build up statistics, combined with the run-time limitations arising from the cryogenic

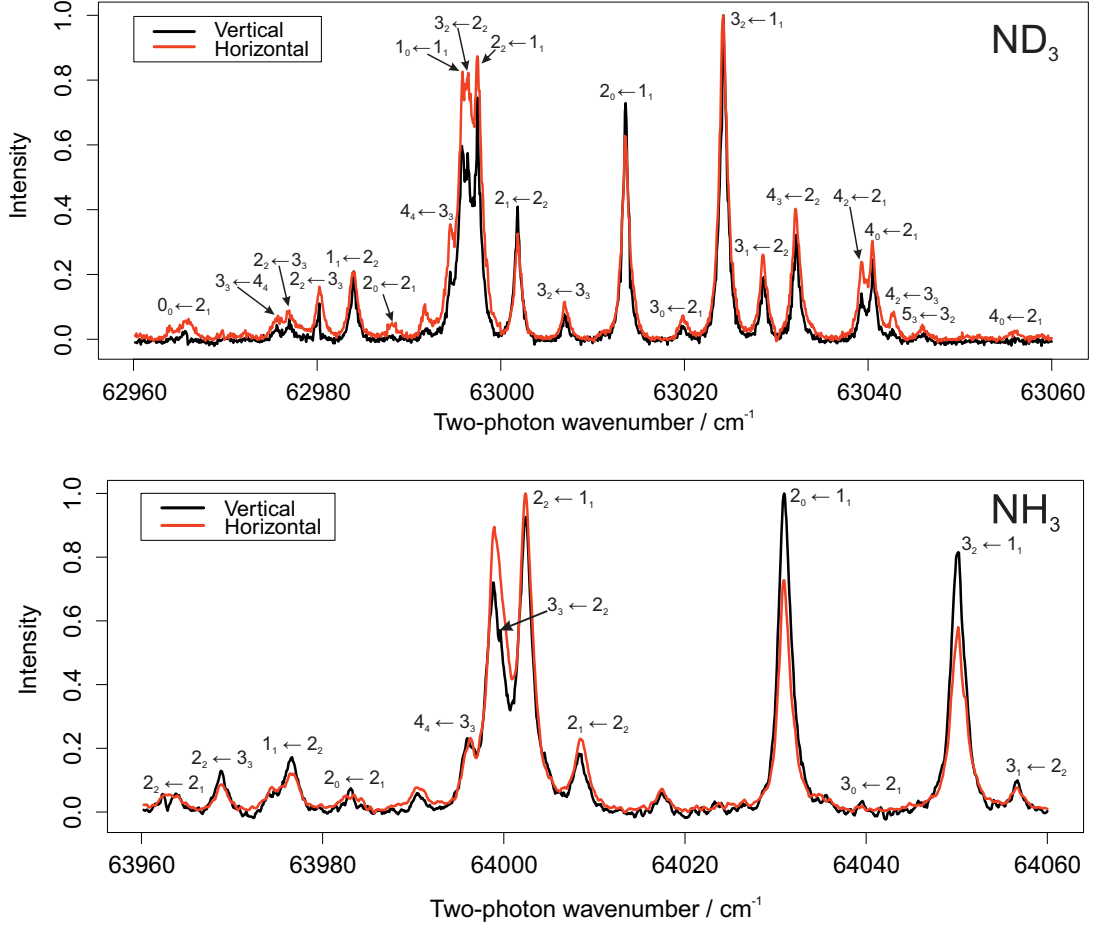


Figure 4.9: (2+1) REMPI spectra of ND₃ and NH₃, recorded on the $\tilde{B}(v=5) \leftarrow \tilde{X}(v=0)$ transition with horizontal and vertical linearly polarised laser light. $P_{\text{laser}} = 4.5$ mJ/pulse. The spectra were normalised by the overall integrated intensity of the entire spectral region.

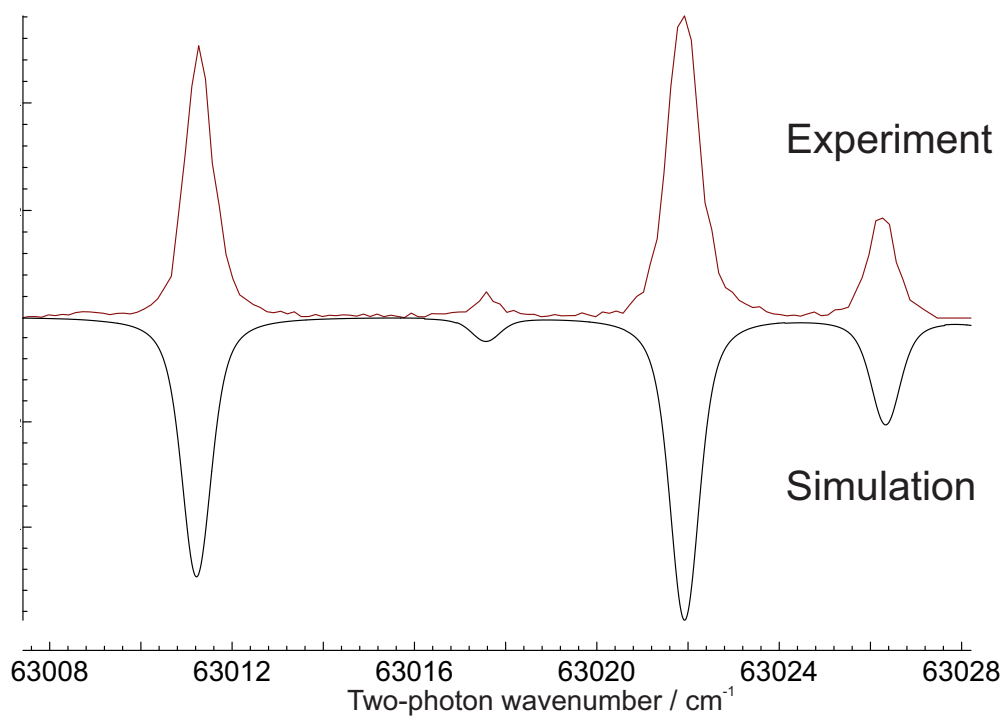
buffer-gas cell described in Figure 2.15, a small region of the spectrum is selected for more detailed analysis (63008 – 63028 cm⁻¹). This region exhibits a high signal-to-noise ratio, strong orientation effects, and includes peaks corresponding to isolated transitions (transitions with initial rotational state $J_K = 1_1$, 2_1 and 2_2). The analysis primarily focusses on ND₃, as it has a greater transmission efficiency through the quadrupole guide compared to NH₃, yielding spectra with an improved signal-to-noise ratio.

A contour fit is performed to the spectral region (63008 – 63028 cm⁻¹) with the populations of the rotational states floated. The rotational constants used in the fit

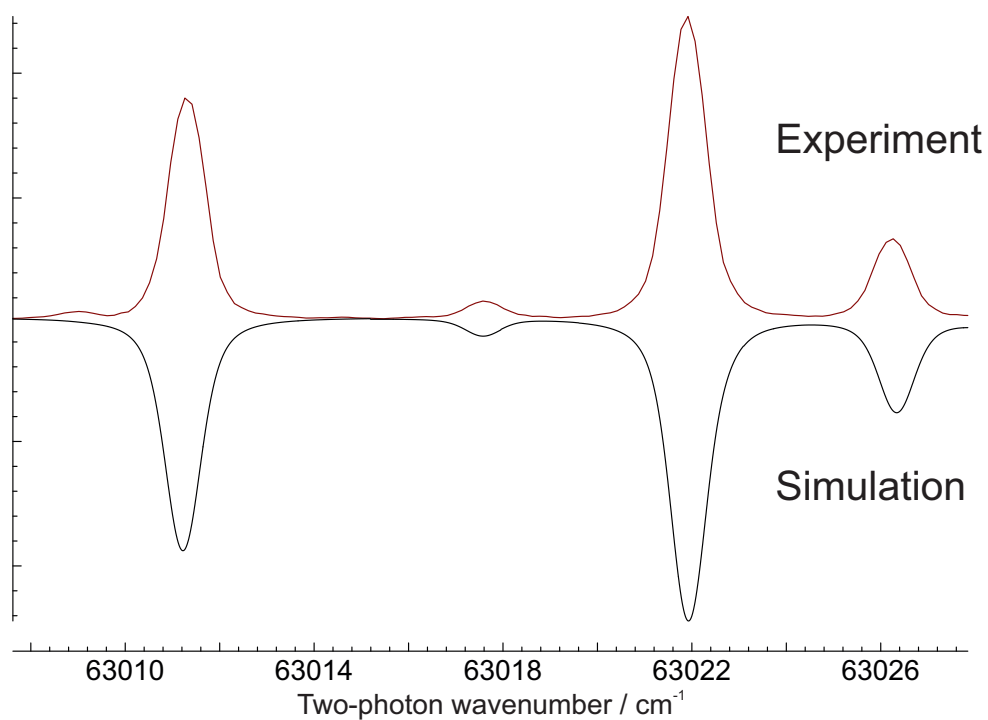
are given in Table 4.1. The fit is repeated for multiple cycles until the populations converge and the RMS error is minimised. The resulting experimental and simulated spectra are shown in Figure 4.10, and the rotational state populations obtained from the fit are provided in Table 4.2.

	$\tilde{X} (v = 0)$	$\tilde{B} (v = 5)$
B	5.1427599	4.4829
C	3.1141819	2.706138
$10^6 D_J$	197.8	196.7
$10^6 D_{JK}$	-349.0	-41.5453
$10^6 D_K$	200.1	789.0
$10^8 H_{JJJ}$	2.32	—
$10^8 H_{JJK}$	-6.60	—
$10^8 H_{JKK}$	7.20	—
$10^8 H_{KKK}$	0.00	—
ζ	—	0.8311
q_+	—	0.1589
q_-	—	0.1589
Band Origin	—	62992.58
References	[195]	[186, 196]

Table 4.1: Rotational constants for the $\tilde{X} (v = 0)$ and $\tilde{B} (v = 5)$ states of ND₃, as used in the PGOPHER simulations. All parameters have units of cm⁻¹, except for the Coriolis coupling constant, ζ , which is dimensionless.



(a)



(b)

Figure 4.10: Simulated and experimental (2+1) REMPI spectra of ND₃ in the region 63008 – 63028 cm⁻¹. Spectrum a) is recorded with vertically polarised laser light, and b) with horizontal polarisation.

$ J, K , MK\rangle$	Horizontal Norm. Population	Vertical Norm. Population	Statistical
$ 1, 1, 0\rangle$	0.3800(845)	0.3949(751)	0.3333
$ 1, 1, 1\rangle$	0.4006(1335)	0.4035(1369)	0.3333
$ 1, 1, -1\rangle$	0.2193(1509)	0.2016(1569)	0.3333
$ 2, 2, 2\rangle$	0.2244(365)	0.2562(830)	0.2000
$ 2, 2, 1\rangle$	0.1387(748)	0.1377(717)	0.2000
$ 2, 2, 0\rangle$	0.1730(777)	0.1803(810)	0.2000
$ 2, 2, -1\rangle$	0.2080(785)	0.1795(619)	0.2000
$ 2, 2, -2\rangle$	0.2560(342)	0.2462(525)	0.2000
$ 2, 1, 2\rangle$	0.2553(782)	0.2599(759)	0.2000
$ 2, 1, 1\rangle$	0.1318(1041)	0.1059(1012)	0.2000
$ 2, 1, 0\rangle$	0.1232(1134)	0.1129(1124)	0.2000
$ 2, 1, -1\rangle$	0.2072(823)	0.1823(319)	0.2000
$ 2, 1, -2\rangle$	0.2825(1061)	0.3390(1627)	0.2000

Table 4.2: Normalised (by the sum of populations in each J_K state) fitted populations, obtained from experimental spectra using PGOPHER. For comparison, the values for a statistical distribution across all M states is shown. The uncertainties (given in parentheses) are determined by varying the population of a given state until the integrated peak area of a peak corresponding to that state is 95% of the initial value.

The rotational state populations suggest significant, although not total, deorientation relative to the strong orientation of the molecules expected inside the quadrupole guide. This indicates that a small fraction of the molecules have retained their orientation to the external field axis (their M -state distribution). The observed deorientation is likely to arise from the molecules passing through a short region of near-zero field between the guide exit and the ionisation region, enabling the molecules to undergo M -state changing transitions. This low field region arises due to the presence of a grounded mesh after the guide exit, which results in fields in this region falling to values as low as 50 mV cm^{-1} . Calculated plots of the fields present in this region are given in Figures 4.15 and 4.19. Due to the weak M -state dependence of the REMPI transitions considered [197], the peak area is not very sensitive to the population of the initial state, hence the fits returned large margins of error. The margins of error give the possibility of a statistical distribution, although a consistent and reproducible residual orientation between

both sets of measurements (horizontal and vertical) is noted. To gain further insight into the orientation effects observed, the guide exit and time-of-flight tube are modelled using computer software, and the trajectories of ND₃ molecules through the apparatus to the point of ionisation are simulated.

4.5 Theory and Simulations

As noted above, the REMPI spectra recorded with polarised light showed significant, but not complete, depolarisation. However, total depolarisation (*i.e.* a statistical M -state distribution) is a possibility within the error bounds of the rotational population fits. To investigate if any orientation is retained as molecules pass through the different regions and electric field magnitudes in the apparatus, trajectory simulations of ND₃ molecules in the region of interest are conducted, tracking the quantum state of each molecule through the different regions of the apparatus until the point of ionisation.

4.5.1 The molecular Stark effect

The interaction of a molecule with a permanent dipole moment with an external electric field results in a perturbation of the energy levels of the molecule, as given by the Stark Hamiltonian operator (Equation 4.4).

$$H_{\text{Stark}} = \vec{\mu} \cdot \vec{E} \quad (4.4)$$

In general, $\vec{\mu}$ is defined along the molecular axis, whereas $\vec{E}$ is external to the molecule and is generally assumed to be aligned to the lab frame (z -) axis. This scalar product is often resolved as a product of irreducible first-rank spherical tensors T_q^1 which can be transformed between frames by a rotation operator. The electric

field vector can be written in terms of its components in the molecular frame [100]:

$$T_q^1(\vec{E}) = E D_{0q}^1(\Omega) \quad (4.5)$$

where $D_{0q}^1(\Omega)$ is the Wigner rotation (D -) matrix and $\Omega \in [\theta, \phi, \chi]$, the Euler angles, which define the orientation of the molecular frame with respect to the lab frame.

The dipole moment operator has the following components:

$$T_{\pm 1}^1(\vec{\mu}) = -\frac{1}{\sqrt{2}}(\hat{\mu}_x \pm i\hat{\mu}_y)T_0^1(\vec{\mu}) = \hat{\mu}_z \quad (4.6)$$

Thus, the Stark Hamiltonian can be expressed as [198]:

$$H_{\text{Stark}} = \sum_{q=-1}^1 (-1)^q T_q^1(\vec{\mu}) \cdot T_{-q}^1(\vec{E}) \quad (4.7)$$

Integrating over the Euler angles in the symmetric top basis set yields the individual H_{Stark} matrix elements in terms of the quantum numbers J , K and M .

$$\begin{aligned} \left\langle J'K'M' \left| \hat{H}_{\text{Stark}} \right| JKM \right\rangle = -E \sum_{q=-1}^1 (-1)^q T_q^1(\vec{\mu}) \times \\ \int \left\langle J'K'M' \left| \Omega \right\rangle D_{0-q}^1(\Omega) \langle \Omega | JKM \rangle d\Omega \end{aligned} \quad (4.8)$$

where X' represents the final value and X the initial value of the given quantum number. The Euler-angle representation of the symmetric top wavefunction and the Wigner rotation (D -) matrix are related by [198]:

$$\langle \Omega | JKM \rangle = \sqrt{\frac{2J+1}{8\pi^2}} D_{KM}^J(\Omega)^* \quad (4.9)$$

Combining Equations 4.8 and 4.9 gives the matrix elements of H_{Stark} in terms

of $3j$ symbols:

$$\begin{aligned} \left\langle J'K'M' \left| \hat{H}_{\text{Stark}} \right| JKM \right\rangle = -E \sum_{q=-1}^1 (-1)^{M-K'} T_q^1(\vec{\mu}) \times \\ \begin{pmatrix} J' & 1 & J \\ -M' & 0 & M \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ -K' & 0 & K \end{pmatrix} \quad (4.10) \end{aligned}$$

Due to the symmetry properties of the $3j$ symbols, the interaction between a molecule and an external electric field is invariant to rotation around the lab frame z -axis. Furthermore, the selection rules ($J' = J, J \pm 1$ and $K' = K, K \pm 1$) arising from the conservation of angular momentum result in H_{Stark} being tridiagonal in J and K . Due to the simplifications resulting from this, the first-order contribution to the Stark effect reduces to [199]:

$$W_{\text{Stark}}^{(1)} = \left\langle JKM \left| \hat{H}_{\text{Stark}} \right| JKM \right\rangle = -\frac{MK}{J(J+1)} \quad (4.11)$$

where $W_{\text{Stark}}^{(1)}$ is the energy shift of the rotational level due to the first-order Stark effect. If the density of rotational states is high, or the applied external electric field, E , is very large, adjacent energy levels can interact strongly and hence the first-order Stark effect does not fully describe the perturbation. In this case, the perturbed energy levels can be determined by diagonalising the Hamiltonian matrix in a given (symmetric- or asymmetric top) basis set.

$$\left\langle J'K'M \left| \hat{H}_{\text{rot}} \right| JKM \right\rangle = E_{\text{rot}}(J, K) \delta_{J',J} \delta_{K',K} + \left\langle J'K'M \left| \hat{H}_{\text{Stark}} \right| JKM \right\rangle \quad (4.12)$$

where $\delta_{x,y}$ is the Kronecker delta ($\delta_{x,y} = 1$ for $x = y$, otherwise 0). Diagonalisation of the resulting Stark matrix given by Equation 4.12 gives the Stark energy levels. A plot of the Stark energy levels for ND_3 and NH_3 is provided in Figure 4.11

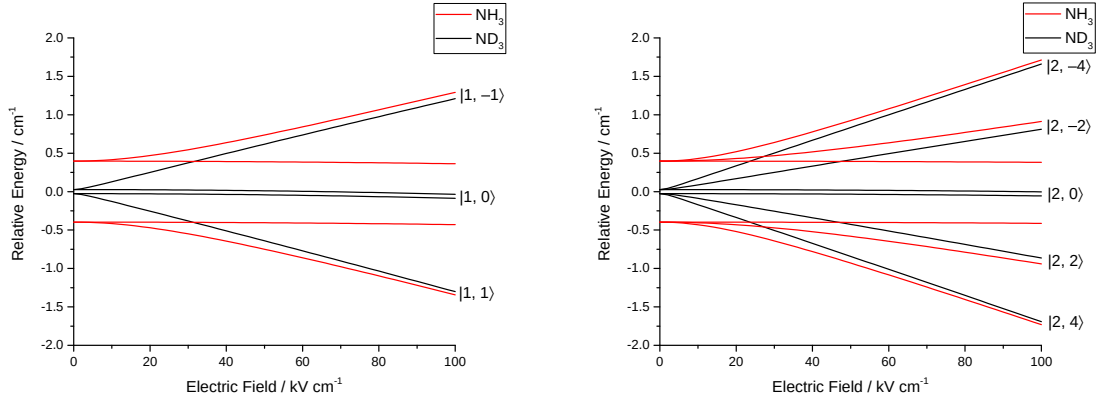


Figure 4.11: Relative Stark shifts for ND_3 (black) and NH_3 (red) ($J = 1, 2$), plotted against applied electric field. States are labelled $|J, MK\rangle$.

4.5.2 Hyperfine effects

In a system with additional angular momenta (arising from nuclear or electron spin), the basis set needs to be expanded beyond J , K and M . The coupling of angular momenta results in $\mathbf{J}$ no longer being well defined; instead, $\mathbf{J}$ couples to $\mathbf{I}$ (and/or $\mathbf{S}$) which precesses around the total angular momentum $\mathbf{F}$. The projection of $\mathbf{F}$ onto the molecular axis gives rise to K and the projection of $\mathbf{F}$ onto the external field axes gives the projection M_F . The coupling and precession of angular momenta in a system with nuclear spin are shown in Figure 4.12. Time-dependent hyperfine depolarisation effects have been previously observed in several small molecules, including HD [200], D_2 [201] and HCl [202].

Hyperfine effects need to be considered for ammonia due to the quadrupolar nuclei present. ^{14}N , the predominant isotope of N, has $I = 1$. D is also a quadrupolar nucleus with $I = 1$. Ammonia is a closed shell molecule, hence $S = 0$. The matrix elements of H_{Stark} are thus:

$$\left\langle J'K'I'_{\text{tot}}F'M'_F \left| \hat{H}_{\text{Stark}} \right| JK I_{\text{tot}} F M_F \right\rangle \quad (4.13)$$

where I_{tot} is the magnitude of the total nuclear spin vector, formed by the Clebsch-

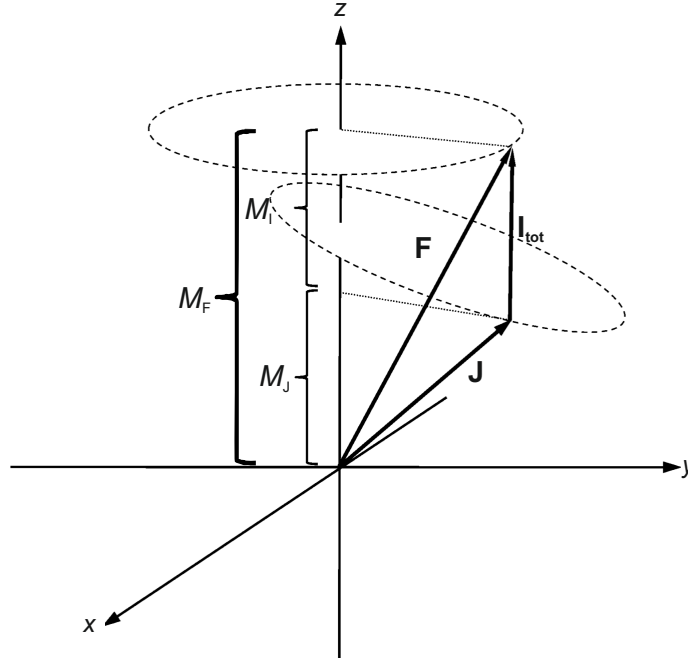


Figure 4.12: Precession of angular momenta in a system with rotational ($\mathbf{J}$) and nuclear spin ($\mathbf{I}$) angular momenta. $\mathbf{J}$ couples to $\mathbf{I}_{\text{tot}}$ to give the total angular momentum, $\mathbf{F}$ with projection M_F onto the external axis.

Gordan series of the individual nuclear spin vectors $\mathbf{I}$. Diagonalisation of the matrix described in Equation 4.13 yields the full energy level structure, accounting for hyperfine effects.

As J is no longer a well-defined quantum number in the presence of nuclear spin, this can cause states to become “scrambled” when labelled using the typical rotational state labels (J, K) . The effect of the hyperfine interaction gives off-diagonal matrix elements in the Hamiltonian which mixes states with $J \pm 1$. The hyperfine interaction shifts the rotational energy levels by [168]:

$$E_{\text{hyp}} = \frac{\chi \left[\frac{3K^2}{J(J+1)} - 1 \right]}{2I(2I-1)(2J-1)(2J+3)} \left(\frac{3}{4}C(C+1) - I(I+1)J(J+1) \right) \quad (4.14)$$

where $C = F(F+1) - I(I+1) - J(J+1)$. Effective mixing of levels occurs when the energy shift due to the quadrupole interaction is comparable to the rotational

energy level spacing. As can be seen in Equation 4.14, the energy shift depends on the quadrupole coupling constants, χ , of the nuclei with $I > \frac{1}{2}$ (see Table 4.3).

Isotope	I	χ / kHz	Reference
^{14}N	1	4090	[203]
^{15}N	$\frac{1}{2}$	-	
H	$\frac{1}{2}$	-	[204]
D	1	-0.096 (χ_z) 0.159 (χ_{x-y})	

Table 4.3: Nuclear quadrupole coupling constants for the isotopes present in the ammonias used in these experiments. The subscripts refer to the components of χ along the stated axes.

The rotational energy level spacing is on the order of 8 cm^{-1} (240 GHz) in ND_3 and 15 cm^{-1} (450 GHz) in NH_3 . As such, any mixing of rotational energy levels due to the hyperfine interaction is negligible and, in practice, the basis set in Equation 4.12 can be used to calculate a REMPI spectrum. However, the presence of the hyperfine interaction provides additional angular momentum in the molecule, which can result in orientation effects at low applied electric field, as well as population transfer due to mixing of M_J sublevels near energy level crossings. For this reason, hyperfine effects are included in the trajectory simulations described in this chapter. These effects are discussed further in Section 4.5.4.

4.5.3 Modelling the electric fields

The electric fields present in the experimental apparatus are modelled using SIMION 8.0 software, as shown in Figure 4.13. The experimental apparatus, including the guide exit and the entire time-of-flight tube, is drawn using CAD software. Voltages are applied to the various elements in SIMION, which uses a high resolution grid over the dimensions of the system and solves the Laplace equation, $\nabla^2\phi = 0$, on the grid, hence modelling the electric fields.

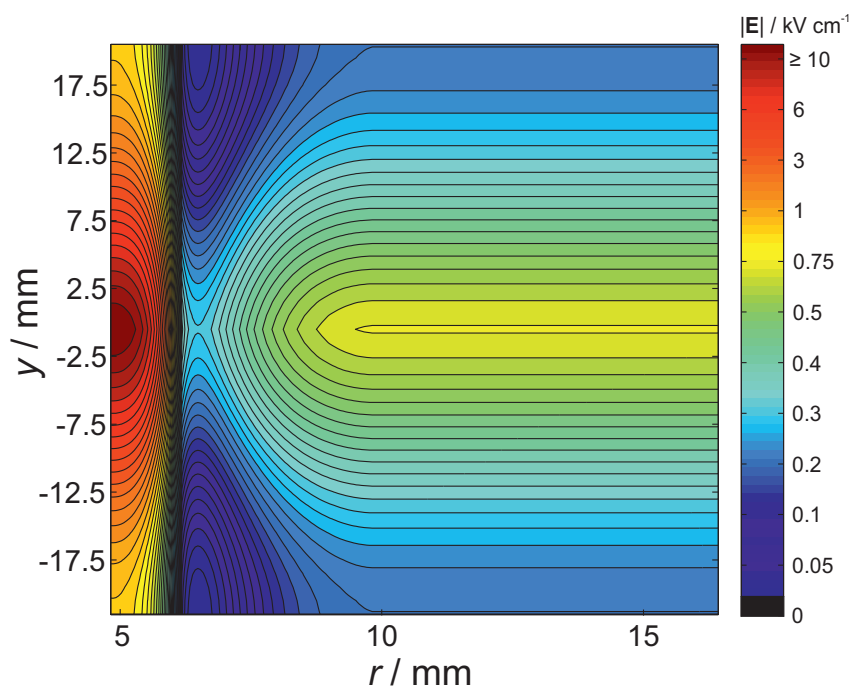


Figure 4.13: Electric fields present in the time-of-flight (TOF) tube, modelled using SIMION 8.0 software.

The electric fields are modelled in 3 parts (potential arrays), one for the quadrupole guide, one for the time of flight tube and one for the grounded mesh. The mesh is a Ni wire mesh with square pores and is modelled according to the dimensions obtained from microscopy on a piece of the mesh from the same batch (46 wires cm^{-1} , wire width = $12.7 \mu\text{m}$, pore area = 0.042 mm^2 , 88% transmittance). Using an accurate mesh rather than an idealised (100% transmittance) grounded mesh in the simulations yields accurate modelling the electric fields in this region, accounting for any effects due to micro-focussing and fringe fields.

The fields are input into a MATLAB program, adapted from [205], which propagates ND_3 molecules in a pre-defined quantum state and set velocity. The program tracks the time-evolution of the quantum state of the molecules throughout the experimental setup by solving the time-dependent Schrödinger equation (Equation 4.15) with the Stark Hamiltonian given in Equation 4.7. Hyperfine and inversion

doubling effects are explicitly included, using the hyperfine parameters of van Veldhoven *et al.* [206]. This enables the shifts due to hyperfine effects in the presence of an external applied electric field to be calculated using a tensor coupling scheme [206, 207].

$$i\hbar \frac{\partial}{\partial t} \psi(t) = \hat{H} \psi(t) \quad (4.15)$$

As the fields in the experimental apparatus are inhomogeneous, as shown in Figure 4.13, solving the time-dependent Schrödinger equation in a rotating field basis with a fixed lab-frame coordinate system is time consuming and computationally inefficient [208]. To improve the efficiency of the calculations, the coordinate system is rotated so that the z -axis is aligned with the local field direction at time t . This approach assumes that population changes are only due to the magnitude of the field, not the direction (*i.e.* molecules follow the field direction adiabatically). As the field rotates at a rate which is slow relative to the rotational frequency of the molecules, this assumption is valid in this case. The instantaneous Hamiltonian is then $\hat{H}' = E_{\text{rot}} + \hat{H}_{\text{Stark}}(\epsilon(t))$ (*cf.* Equation 4.12 in the non-rotated coordinate system), where $\epsilon(t)$ is the local electric field magnitude at time t . This is achieved by rotating the original Hamiltonian $\hat{H}$ through an angle β about the y -axis, such that $\hat{D} \hat{H} \hat{D}^{-1} = \hat{H}'$ and $\hat{D}$ is the rotation operator $\hat{D} = e^{-i\hat{N}_y \beta / \hbar}$ and the operator $\hat{N}_y$ is defined as [205]:

$$\left\langle F, M_F \pm 1 \left| \hat{N}_y \right| F, M_F \right\rangle = \mp \frac{i\hbar}{2} \sum_F [(F \mp M_F)(F \pm M_F + 1)]^{1/2} \quad (4.16)$$

By applying $\hat{D}$ to both sides of Equation 4.15 and using the fact that $\hat{D}$ commutes with $\hat{N}_y$, Wall *et al.* showed that the time-dependent Hamiltonian operator can be expressed as [208]:

$$\left(\hat{H} + \omega(t)\hat{N}_y\right) |\alpha'\rangle = i\hbar \frac{d|\alpha'\rangle}{dt} \quad (4.17)$$

where $|\alpha'\rangle$ is the eigenvector of the molecular state in the rotated frame and $\omega(t) = d\beta/dt$. For small values of t , ω is approximately constant and hence the time-dependent wavefunction is:

$$\psi(t) = \psi(0) e^{i(\hat{H}' + \omega\hat{N}_y)t/\hbar} \quad (4.18)$$

By calculating the wavefunction at small timesteps δt between 0 and t using

$$\psi(t' + \delta t) = \psi(t') e^{i(\hat{H}' + \omega(t')\hat{N}_y)\delta t/\hbar} \quad (4.19)$$

where t' is a value between 0 and t , the wavefunction can be calculated. The time propagation is performed by multiplying the matrices of the time evolution operator (Equation 4.19) with the wavefunction vector.

In the simulation, voltages are applied to all electrodes constantly to match experimental conditions. The z -axis is defined based on the local electric field direction (the “local field frame”). The orientation of the molecules in the lab frame can be recovered using the orientation probability functions introduced by Choi and Bernstein [209]. Applying a rotation transforms the original frame (x , y , z) to a new frame (x' , y' , z'), with a common origin. Upon a rotation, the eigenstate $|J, M\rangle$ of the total angular momentum operator $\mathbf{J}^2$ is transformed into a linear combination of M -states [198]. The probability of $\mathbf{J}$ having a projection M' onto the new z' axis (corresponding to the lab frame z -axis) for a given $|J, K, M\rangle$

state is given by the following function [210]:

$$P_{JKM}(\cos \theta) = \frac{2J+1}{2} (-1)^{M-K} \sum_{n=0}^{2J} (2n+1) \times \\ \left(\begin{matrix} J & J & n \\ K & -K & 0 \end{matrix} \right) \left(\begin{matrix} J & J & n \\ M & -M & 0 \end{matrix} \right) \times \mathcal{P}_n(\cos \theta) \quad (4.20)$$

where $\mathcal{P}_n$ is the n^{th} order Legendre polynomial and the preceding elements are $3j$ symbols (angular momenta coupling factors). This orientation is noted as the “fixed field frame.”

The code for these simulations can be found in Appendix B.1.

4.5.4 Simulation results

Using the MATLAB program described above, 10^5 ND_3 molecules in the quantum states $J_K = 1_1$, 2_1 and 2_2 with a Maxwell-Boltzmann distribution of velocities with modal velocity 70.29 m s^{-1} (corresponding to the modal velocity as determined in Section 2.6.1) are “generated” at the quadrupole exit and propagated through the modelled electric fields. The time evolution of the Stark Hamiltonian is tracked at each timestep (20 ns) and hence the M -state distribution with time is determined. The results of these simulations are shown in Figure 4.14.

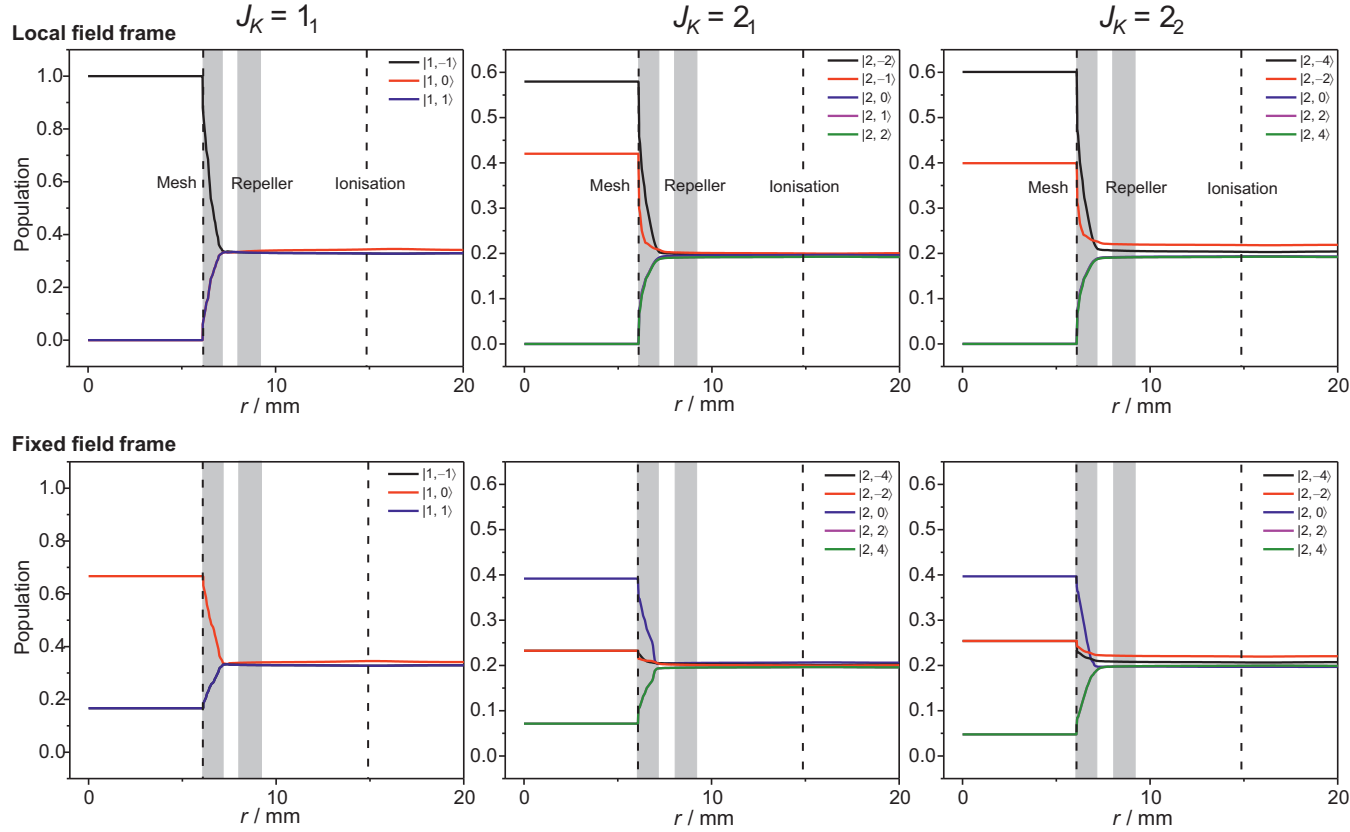


Figure 4.14: The M -state distribution of 10^5 ND_3 molecules propagated through the guide and time-of-flight tube, as established from trajectory simulations. The guide exit is at 0 mm, the grounded mesh is at 6.05 mm, the repeller plate at 8.00 mm and the point of ionisation is at 14.85 mm. States are labelled $|J, MK\rangle$. The top row shows the distribution with M defined along the local field z -axis and the bottom row shows the distribution with M defined along the laboratory frame z -axis.

For the rotational states considered in Figure 4.14, qualitative agreement is obtained with the M -state distributions obtained from fits to the experimental spectra (Table 4.2). While the majority of the molecules become deoriented and are no longer oriented to the external electric field axis at the point of ionisation, there is some residual retention of orientation. Hence, the M -state distribution is close to, but not exactly, what would be expected from a statistical distribution.

The loss of orientation in the regions of near-zero field is due to diabatic transitions, which arise when the molecules can no longer track the rotation of the quantisation axis, which occurs in the case of rapidly switching fields, or in regions of very low (or zero) field. Thus, deorientation occurs in the region of low-field near the grounded mesh. In this region, due to the low fields present (as low as $\lesssim 50 \text{ mV cm}^{-1}$, see Figure 4.15), the rotational angular momentum $\mathbf{J}$ couples to the nuclear spin $\mathbf{I}$ in preference to the external field. Coupling between $\mathbf{J}$ and $\mathbf{I}$ in the low-field region removes any spatial preference for the molecules, as $\mathbf{J}$ is not coupled to an external field axis, effectively scrambling the orientation of the dipoles and hence the molecules. In terms of the molecular eigenstates, the hyperfine interaction induces transitions between states of differing M_K but with an identical M_F quantum number. It is proposed that the minimal orientation observed at the point of ionisation occurs due to some of the molecules orienting to the ionisation region (acceleration) field direction after losing their orientation in the low-field region near the mesh. For example, it is noted that the acceleration field induces a slight enhancement in the population of the $|J, MK\rangle = |1, 0\rangle$ state, which is consistent with the experimental REMPI spectra where a slightly enhanced population in this state is observed.

For the $J_K = 1_1$ and 2_1 states, it is observed in the simulation that the population reaches an entirely statistical distribution at $r = 7.15 \text{ mm}$ (In the case of $J_K = 1_1$, some minor orientation is observed after the repeller plate.) The $J_K = 2_2$ state does show some residual orientation throughout, which we suggest arises from fringe

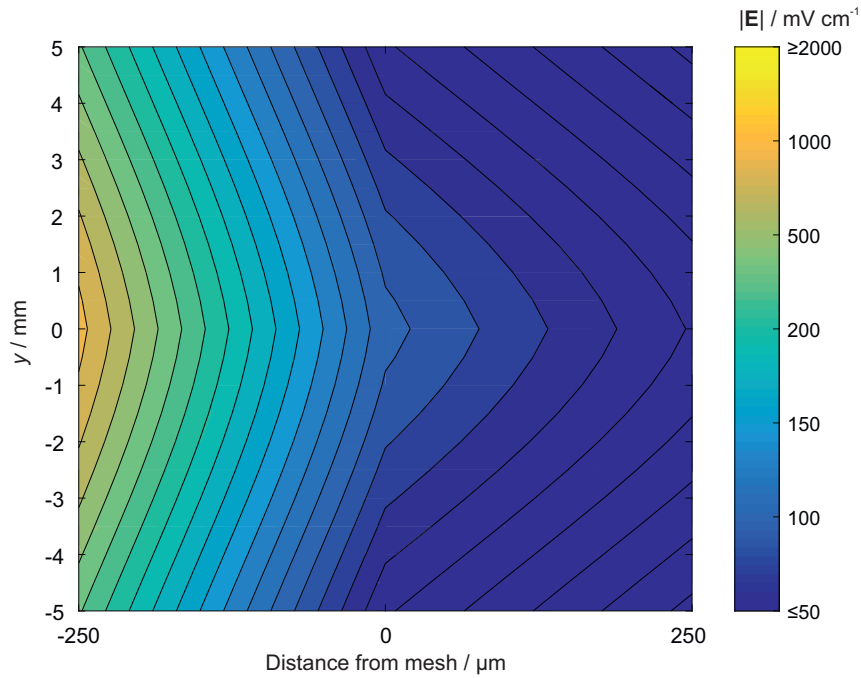


Figure 4.15: 2D slice illustrating the near-zero electric fields in the proximity of the grounded mesh. The y -axis scale is directly comparable to Figure 4.13.

field that penetrate through the pores in the mesh. Electric fields bounded by a mesh penetrate through the mesh to an extent equal to the width of the pore [211, 212], in this case $205\ \mu\text{m}$. While the magnitude of this fringe field is small and hence the majority of molecules do not orient to the axis of this weak field, its presence allows some polarisation to be maintained. As residual orientation is observed in the $J_K = 2_2$ state but not in the 1_1 or 2_1 states, additional effects besides the fringe fields (which is common to all states) must feature in preserving orientation in the 2_2 state. The Stark shifts for a given electric field (provided in Figure 4.11), are greater for the $J_K = 2_2$ state compared to the $J_K = 1_1$ or 2_1 states. Hence the MK -sublevels in the 2_2 states are further from degeneracy, even at low field, reducing the likelihood of diabatic transitions between sublevels, which will transfer population to other MK states.

It is noted that the transfer of population from the guided low-field seeking state to the other MK states of the same J_K occurs at the same rate. In the $J_K = 1_1$ state

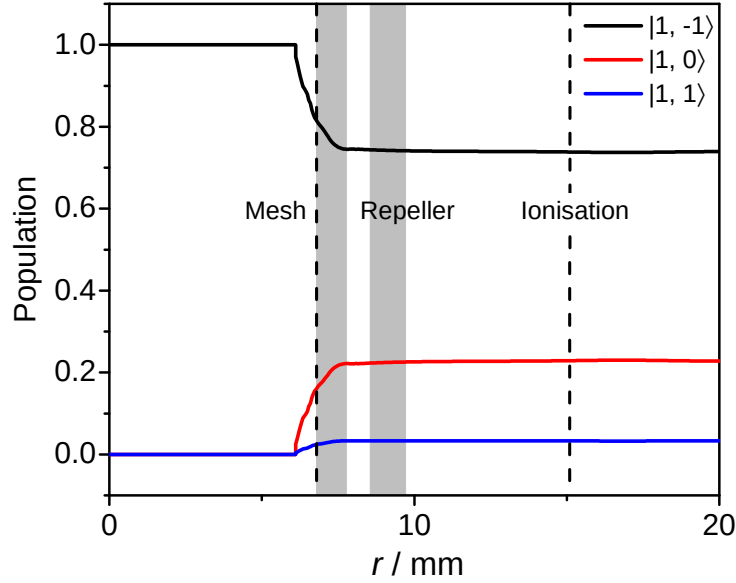


Figure 4.16: State-tracking trajectory simulation of 10^5 ND_3 molecules in the $J_K = 1_1$ state and local field frame, propagated through the guide and time-of-flight tube. The parameters for the simulations presented in Figure 4.14 are used, except $\tilde{\nu}_{\text{inv}} = 0.792 \text{ cm}^{-1}$, corresponding to the inversion splitting in NH_3 .

of ND_3 , it may be expected that due to the inversion splitting resulting in non-degeneracy of states even at zero field, population would preferentially transfer to the $|J, MK\rangle = |1, 0\rangle$ state instead of the $|1, 1\rangle$ state. If the larger inversion splitting for NH_3 , 0.792 cm^{-1} [168], is employed in the simulation rather than the inversion splitting for ND_3 , 0.053 cm^{-1} [168], this behaviour is observed (see Figure 4.16). Thus, the increased degree of deorientation observed in ND_3 is due to the magnitude of the inversion splitting in addition to the applied electric field magnitudes.

If a higher magnitude electric field is present throughout the experiment (*i.e.* in the absence of the grounded mesh), simulations indicate that the molecules will stay oriented to the external electric field axis, hence preserving the M -state distribution and giving some control over the orientation of molecules after the guide exit. A biased mesh would provide a small external field to retain orientation and eliminate any regions of zero- (or near-zero) field. This is investigated in Section 4.5.5.

Deorientation of the molecules can occur by other mechanisms than just *via* the hyperfine interaction. Collisional depolarisation, where collisions between molecules and other species (other molecules or background gases) result in either adiabatic M -state changing (but J preserving) transitions (sometimes termed *elastic depolarisation*) or inelastic rotational-state (J) changing collisions. Both of these phenomena alter the prior M -state distribution of the molecules affected and hence degrade the degree of orientation exhibited by the sample. Both the elastic and inelastic depolarisation processes have been studied in depth and models for their kinetics have been developed [265]. The rate of these processes is highly dependent on collision rate (and hence number density) [266]. The number density at the guide exit will depend strongly upon the buffer-gas cell conditions and experimental run time (see Figure 2.15); this factor is somewhat mitigated by only scanning a short region of the spectrum and averaging over multiple runs. Hence, any collisional depolarisation effects are likely to give a constant background rate of deorientation, and any modification of the electric fields in the experimental setup will affect the rate of hyperfine depolarisation.

4.5.5 Retaining orientation with a bias potential

Previous work on the orientation of molecules in electric fields, using hexapole guides, found that an external field magnitude as low as 3 V cm^{-1} was sufficient to retain orientation to the external field axis [193].

In the SIMION model of the experimental setup described in Section 4.5.3, the mesh after the guide exit is designated as an electrode, to which a potential can be applied. In the simulations described above, the potential applied to the mesh is 0 V, in accordance with the experimental conditions. To determine what field magnitude across the width of the mesh would be necessary to retain orientation, the potential is varied and the simulation run for $J = 1$. As shown in Figure

4.17, fields on the order of a few V cm^{-1} retain the majority of the population in the initial (guided) quantum states and fields greater than 6 V cm^{-1} entirely retain the initial state distribution.

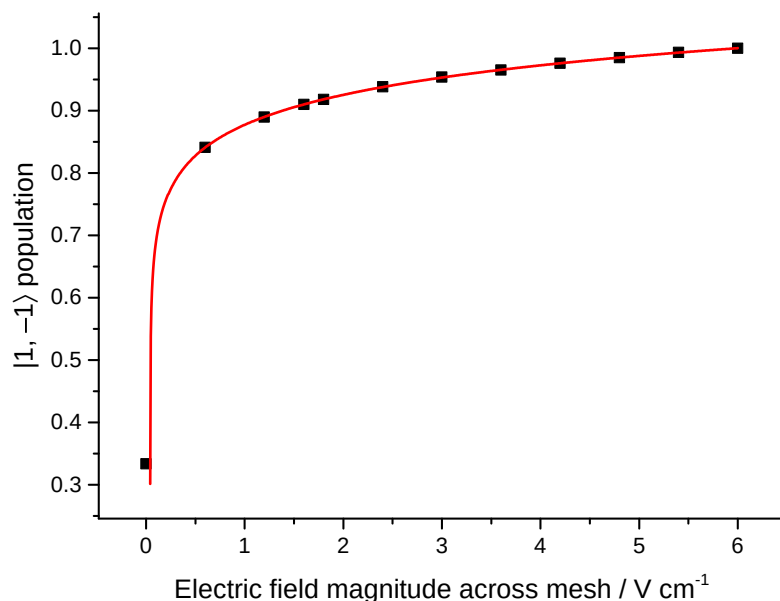


Figure 4.17: Population at the point of ionisation of the $|J, MK\rangle = |1, -1\rangle$ state of ND_3 , when a bias field is applied to the previously grounded mesh.

The results above show concordance with previous experimental studies investigating retention of orientation in low-magnitude electric fields. No such studies have been conducted on ND_3 , with the majority of literature studies focussing on the methyl halides, in particular CH_3I . CH_3I exhibits some similar physical properties to ND_3 – both are symmetric tops of C_{3v} symmetry and have a comparable permanent dipole moment (1.5 D [164] and 1.6 D [213], respectively), hence qualitative comparisons can be made regarding the behaviour of ND_3 . Harland *et al.* found that the orientation of a beam of CH_3I was entirely retained (within their error limit) with a bias field magnitude of $3 - 4 \text{ V cm}^{-1}$ [193]. The simulations presented in this work predict 95% – 97% retention of orientation in ND_3 over this range of bias fields. Brookes, Jones and Smith reported that complete orientation is retained at fields

greater than 10 V cm^{-1} [194], whereas a field of 6 V cm^{-1} is sufficient to retain orientation in this work, as determined from the simulations. The discrepancy is likely because the previous experimental study by Brookes *et al.* considered a mixture of CH_3I , CHCl_3 , CF_3I and *t*-BuI [$(\text{CH}_3)_3\text{CI}$], a series of molecules with different dipole moments and moments of inertia, properties which will affect the field required to orient the molecules (see Equation 4.3).

Our experiments and simulations show that some degree of orientation is retained even in the absence of an applied bias field *i.e.* with the mesh grounded. This is concordant with the work of Gandhi and Bernstein, and Kaesdorf, who reported observing significant orientational effects in CH_3I with fields as low as 0.3 V cm^{-1} [214, 215], a field magnitude below that required to fully orient a symmetric top molecule. According to Figure 4.17, the simulations indicate that 80% of ND_3 molecules will retain full orientation to the field at an external field magnitude of 0.3 V cm^{-1} , which corresponds to the signal recovery seen in the experiments described in [214, 215]. Orientation and focussing of asymmetric top molecules [216], including small organic molecules such as formaldehyde and acetic acid, has been observed using field magnitudes comparable to those to orient symmetric tops [217], suggesting that small bias fields could be used to align ND_2H and NH_2D in future experiments, in addition to ND_3 and NH_3 .

Where bias fields of sufficient magnitude to retain a large degree of orientation are applied, the simulations indicate oscillations in the state distribution around the point of the mesh. This is shown from $r = 3.75 \text{ mm}$ in Figure 4.18, and is attributed to the micro-focussing effect of fine meshes [218] and subsequent defocussing in the acceleration region, and the interference between the residual quadrupole guide fields, the bias field and the time-of-flight acceleration field. A plot of the electric fields present in the experiment with and without the bias field applied is shown in Figure 4.19.

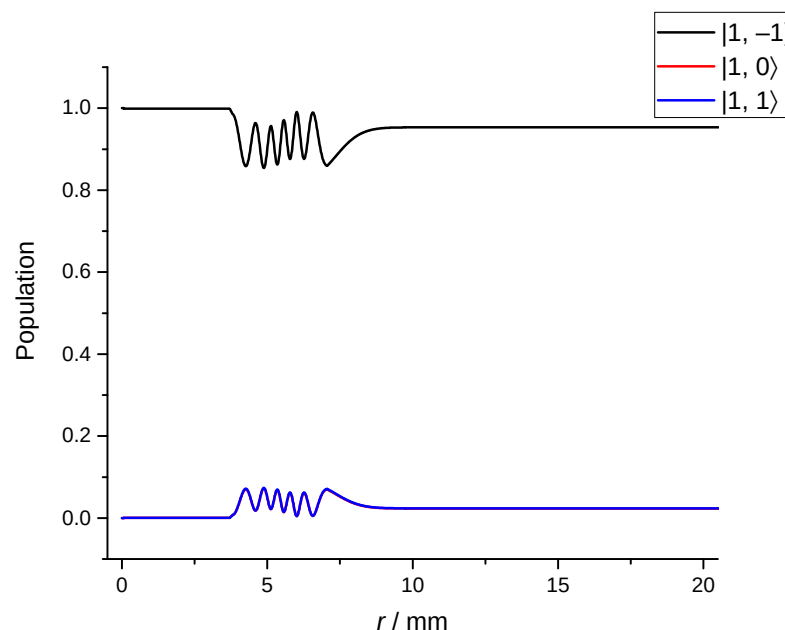


Figure 4.18: Simulated ND_3 quantum state distribution throughout the experimental apparatus with a bias field of 3 V cm^{-1} applied across the mesh. The oscillations observed are attributed to the micro-focussing effects of the mesh.

Practically, in the combined setup with the ion trap (see Figure 2.1), the ability to retain orientation of molecules through the use of a bias potential applied to the mesh is limited. Applying the necessary DC voltage to the mesh to generate the bias field could easily be achieved by implementing a vacuum feedthrough to connect the mesh to an external low-voltage power supply (to provide a 3 V cm^{-1} field across the mesh pores, a voltage of 17 V would need to be applied to the mesh). However, the method of operation of the linear Paul ion trap utilises (comparatively weak, compared to the guide) radiofrequency and static DC trapping fields. A full discussion of the theory of ion trapping is presented in Chapter 5. These fields will require shielding from the fields emanating from the guide to avoid interference with the trapping potential. Hence, the use of a biased mesh may be impractical in this experimental setup as the bias field will extend into the ion trap chamber and potentially interfere with the trapping fields, resulting in an unstable trap. Further simulations, explicitly including the trapping fields, are

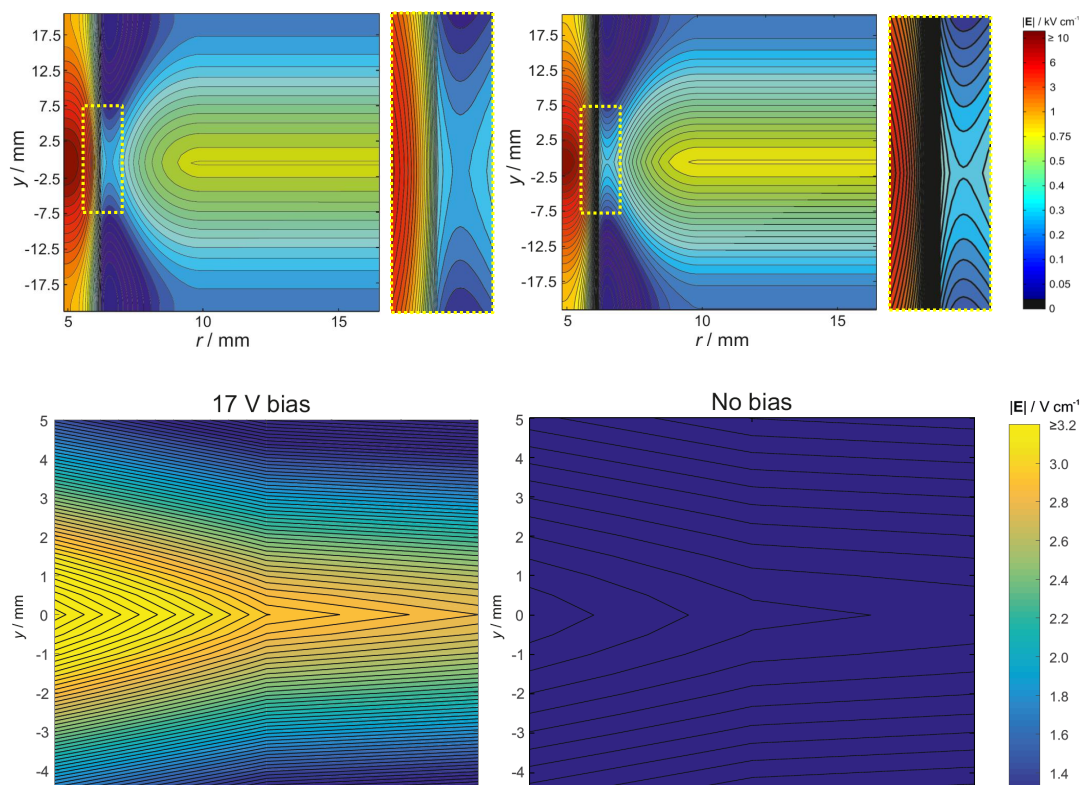


Figure 4.19: Simulated electric fields present in the time-of-flight (TOF) tube. The plots on the left show the fields with a 17 V bias applied (corresponding to a field of 3 V cm^{-1} across the mesh) and the plots on the right with no bias. The top row shows the fields up to the point of ionisation. The bottom row is zoomed in on the region $\pm 250 \mu\text{m}$ either side of the mesh.

required to investigate the feasibility of such an approach.

The loss of orientation to the external (quadrupole) electric field for molecules exiting the guide is time-dependent (and hence, distance dependent). An alternative approach to retaining (partial) orientation is to place the grounded mesh closer to the ion trap such that the M -state distribution is somewhat retained when the guided molecules reach the trapped ions in the trap centre. The simulations (see Figure 4.14) show near-complete loss of orientation within $\sim 1.5 \text{ mm}$ of the unbiased mesh. The trap centre lies 9.4 mm from the top face of the ion trap, and practically the grounded mesh could not be placed exactly at the top face due to the need of a vacuum gap for insulation, and due to penetration of fringe fields. Hence, the shortest possible distance between the mesh and trap centre is

~ 10 mm. At this distance minimal orientation is retained, suggesting this is not a feasible approach in the current experimental apparatus.

A potential alternative geometry for the use of a bias field applied across the mesh in conjunction with an ion trap would be to inject the guided molecules into the trap horizontally, rather than from above as in this experimental setup. This approach has been demonstrated in other experimental setups, including the previous Oxford electrostatic guide and ion trap experiment [131, 219, 220]. However, due to the radius of the electrodes, there will still be considerable distance between the mesh and the trap centre. Using the fact that some (but not total) orientation is retained at longer distances, the fraction of which will be greater with a bias field applied as the molecules no longer pass through zero field, a potential experiment could run with the bias on and subsequently off, and then the effect of orientation effects on an ion-molecule reaction could be deduced by comparison.

A further potential method to retain (partial) orientation throughout the low-field region is to reduce the width of the mesh. The current mesh is effectively 1.1 mm thick, consisting of a Ni wire mesh of thickness 100 μm affixed to a stainless steel disc of thickness 1 mm. By reducing the thickness of the mesh, the molecules experience a shorter low-field region. Trajectory simulations on the $J = 1$ state, using the parameters given in Section 4.5 but replacing the mesh holder with a “non-electrode” in the SIMION model of the experimental apparatus showed the degree of deorientation significantly reduced and a retention of orientation of $\sim 70\%$. The results are given in Figure 4.20. Experimentally, this setup could be realised by replacing the stainless steel holder disc with a disc made of a vacuum-compatible insulating material such as PEEK or MACOR.

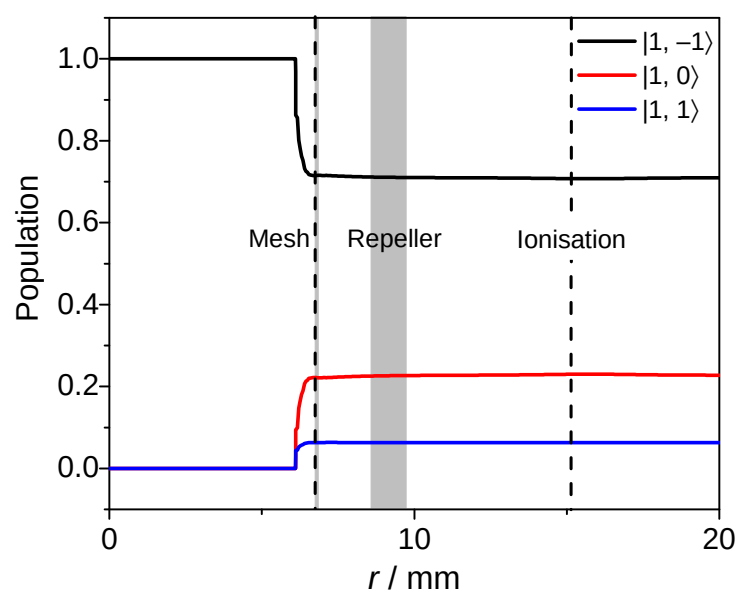


Figure 4.20: Trajectory simulation, in the local field frame, for $J_K = 1_1$. The parameters are the same as for the simulation shown in Figure 4.14, except that the mesh has been reduced in thickness to 100 μm .

4.6 Summary

In this chapter, previous work on the use of REMPI spectroscopy to characterise and investigate the molecular beam [128] has been expanded and an investigation into the orientation of ND_3 molecules exiting the guide has been conducted.

It was ascertained, by recording REMPI spectra with polarised laser light, that near-statistical redistribution of the projection onto the external field axis (M -state) takes place, due to the presence of a grounded mesh after the guide exit. By simulating the spectra and fitting the populations of each rotational state, it was deduced that a small fraction of molecules retain orientation to the external field (z) axis. State-tracking trajectory simulations were carried out and confirmed this result, and the effect of applying a bias field across the mesh pores or reducing the size of the mesh was investigated theoretically. This information would allow for further controlled reactions to be performed in the future, using cold oriented reactants.

The study of such reactions can be used to identify different orientation-dependent channels on the potential energy surface of reactions. Where reactions proceed along a different channel, this can lead to different products and/or branching ratios of products, hence being able to select a reactive channel will allow for a high degree of control over chemical reactions.

5

Investigating cold-ion molecule reactions using ion trapping

In this chapter, the theory of ion trapping is outlined, including laser cooling and sympathetic cooling of ionic species. A method for operating the ion trap is described, and a cold ion-molecule reaction between Xe^+ ions and ND_3 molecules is observed, in a cold trapped Ca^+ crystal. Observation of this reaction sets the groundwork for, and represents a fundamental step towards our aim of experimentally testing post-Langevin capture theories, as applied to ion-molecule reactions.

5.1 Chemical Reactions in ion traps

The ability to localise and accumulate ionic reactants at (ultra)cold temperatures make ion traps attractive for investigating the cold chemistry of ionic species. To date, a limited range of chemical reactions have been studied in ion traps, often between a laser-cooled ion and a small molecular reactant. Examples of such reactions include hydrogen extraction reactions, such as $\text{Mg}^+ + \text{H}_2 \rightarrow \text{MgH}^+ + \text{H}$ (and the corresponding deuteron transfer reaction, which showed a preference for forming MgD^+ over MgH^+) [221]. The analogous reaction $\text{Be}^+ + \text{H}_2 \rightarrow \text{BeH}^+ + \text{H}$ has also been observed [222]. Transfer of larger atoms or groups, such as halogens in the $\text{Ca}^+ + \text{CH}_3\text{F}$ reaction and hydroxyl groups in the $\text{Ca}^+ + \text{H}_2\text{O}$ (D_2O) reactions have been investigated previously using the trap described in this work [142, 154]. The oxidation of Ca^+ and Ba^+ with O_2 to give trapped CaO^+ and BaO^+ ions, respectively, has been reported [223, 224]. Chemical reactions involving sympathetically cooled ions (see Section 5.4.1 for details on sympathetic cooling) have been conducted, broadening the scope of the chemistry that can be studied beyond the direct reactions of laser-cooled ions. Examples of these reactions include the charge exchange process $\text{OCS}^+ + \text{ND}_3 \rightarrow \text{OCS} + \text{ND}_3^+$ (with Ca^+ as the laser-cooled ion) [29] and the proton transfer process $\text{H}_3\text{O}^+ + \text{NH}_3 \rightarrow \text{H}_2\text{O} + \text{NH}_4^+$ (with Mg^+ as the laser-cooled ion) [225]. Multi-step chemical reactions involving sympathetically cooled Ar^+ (with laser-cooled Be^+) have been utilised to form trapped ions of astrochemical interest, such as H_3^+ , D_3^+ and N_2H^+ [226].

To study reactions under cold conditions, both the ionic and the neutral reactant need to be translationally (and internally) cold. In a bid to study ion-molecule reactions under cold conditions, ion traps have been combined with a range of cold molecular sources. Examples of cold ion-molecule reactions studied using a cold molecule source (electrostatic velocity selection) combined with an ion trap included the $\text{Ca}^+ + \text{CH}_3\text{F}$, $\text{Ca}^+ + \text{CH}_3\text{Cl}$ and $\text{OCS}^+ + \text{ND}_3$ reactions [131, 227, 228]. In

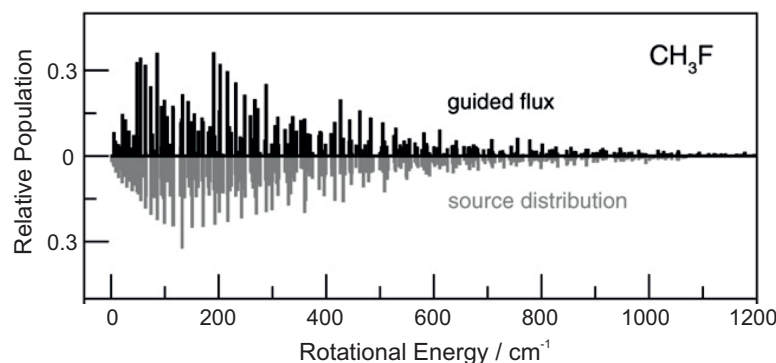


Figure 5.1: Figure showing the rotational state distribution in CH_3F from a room temperature source (lower) and after passing through an electrostatic velocity selector (upper). Figure reproduced from [229] with permission of The Royal Society of Chemistry.

contrast to the apparatus described in this work, the electrostatic velocity selector (quadrupole guide) used previously to study the $\text{Ca}^+ + \text{CH}_3\text{F}$ reaction was not combined with a buffer-gas cell; it used a room-temperature source for the guided flux of neutrals [227]. The quadrupole guide, while selective for translationally cold molecules, has little or no influence on the internal temperature of the molecules. Hence the CH_3F molecules had an approximately room-temperature Boltzmann distribution of internal states. It is noted, due to the low-field seeking state selectivity of the velocity selector (see Section 2.3), there is some minor rotational state selectivity, as shown in Figure 5.1.

Other cold molecule sources have been combined with ion traps, including a Stark decelerator [30]. In this case, the decelerated molecules are highly quantum-state selected, with almost all of the population in the $|J, MK\rangle = |1, -1\rangle$ rotational state. Stark deceleration also allows for variation in the translational energy of the molecules, and thus the collision energy of the reaction. The high quantum-state purity can be advantageous for investigating single reaction channels, however the lack of variability in internal temperature with such a source does not allow for the effect of rotational temperature on reaction rates to be measured. The combined buffer-gas cell, electrostatic guide and ion trap setup will allow internally

cold molecules to be introduced to the trap chamber (and hence react with laser- or sympathetically-cooled ions in the trap), with a rotational state distribution that can be varied between $T_{\text{rot}} = 9 - 20$ K, as detailed in Section 2.6.3. This controllable variation of rotational temperature – at a fixed translational energy – will allow the effect of internal temperature on reaction rates to be investigated, enabling us to ascertain the rotational state dependence of terms in post-Langevin capture theory, as outlined in Section 1.2.

5.2 Theory of ion trapping

Paul ion traps use a combination of static and time-variant electric fields, which interact with the electrical charge of the ions. These fields create an effective potential minimum which “trap” the ions in a localised region of space. Electric fields must obey the Laplace equation $\nabla^2\phi = 0$, which when written in 3 dimensions using Cartesian coordinates, is expressed as:

$$\frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2} + \frac{\partial^2\phi}{\partial z^2} = 0 \quad (5.1)$$

For a field to obey the Laplace equation, a potential minimum can not exist in all 3 dimensions at any given time; minima can only be achieved in 2 dimensions. This reflects the fact that a true minimum (or maximum) can not be achieved in all dimensions in free space, as this would be forbidden by Gauss’ Law, which states that the divergence of an electric field *in vacuo* is zero. It is from this fact that Earnshaw’s theorem is derived, which states that static fields can not contain charged particles in stationary equilibrium *via* the electrostatic interaction [152, 230].

Due to these constraints, ion trapping is achieved using a saddle point in the potential arising from the interactions of the ions with time-varying electric fields. In such a system, a potential maxima in one dimension prevents displacement

in that direction. The maximum is rapidly switched between orthogonal axes, on a shorter timescale than the displacement of the ions, effectively providing a potential well in two orthogonal dimensions. Static fields are used to provide confinement in the third dimension.

One design of ion trap that utilises these concepts is the linear Paul trap, which uses static DC voltages in combination with time-varying radio-frequency (RF) potentials. This design, which is used in this experimental apparatus, is discussed in the next section. Another design, the Penning trap, combines static electric and magnetic fields and has found extensive use in the fundamental physics community.

5.2.1 The Linear Paul Trap

The linear Paul trap (LPT) was developed in the 1950s by Wolfgang Paul [153], a development for which he shared the 1989 Nobel Prize in Physics [15]. The LPT has a quadrupolar design consisting of 4 electrodes, each of which is split into 3 segments.

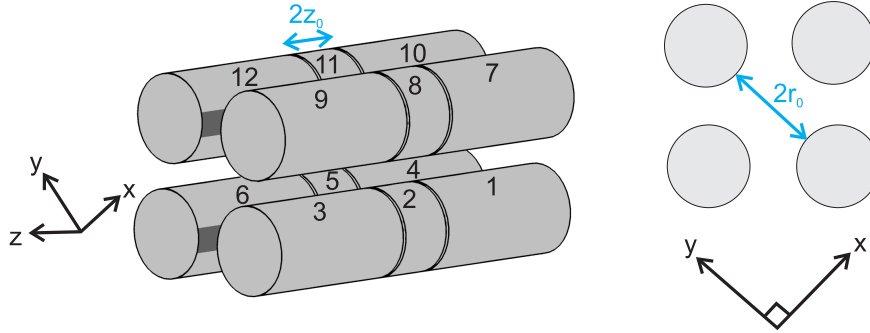


Figure 5.2: Schematic of a typical linear Paul trap, showing the 4 electrodes, each split into 3 segments. Static and RF voltages can be applied independently to each segment. The dimensions of the trap (r_0 and z_0) used in these experiments are given in Table 5.1. Figure adapted from [231].

Each segment is distinct and separated from the other segments by an insulator. Trapping is achieved in the x and y dimensions by applying time-dependent RF potentials to the centre electrodes $V_{\text{RF}} = \pm V_{\text{RF},0} \cos(\Omega_{\text{RF}} t)$, where V_{RF} is the effective

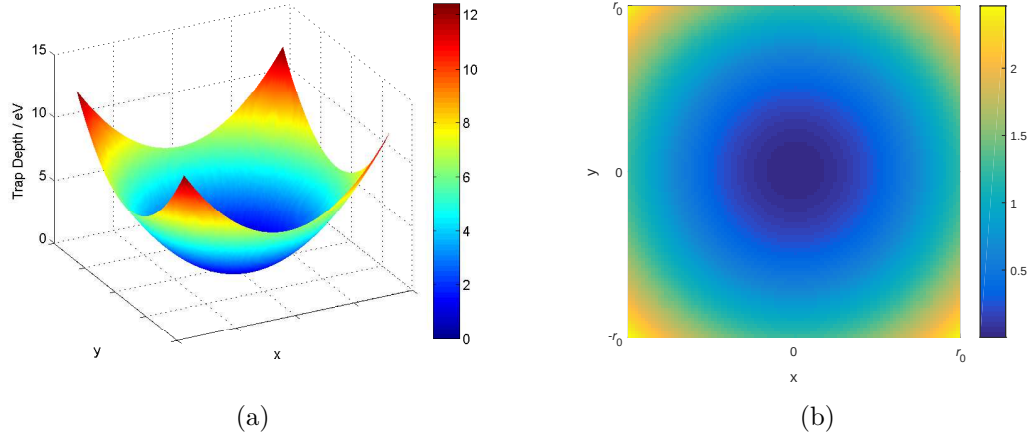


Figure 5.3: Figures showing the calculated pseudo-potential for the linear Paul trap used in these experiments. Figure a) shows the 3D potential and b) shows a slice through the x, y plane. The values represent the trap depth above the potential minimum, in units of eV.

RF potential, $V_{\text{RF},0}$ is the applied RF voltage and Ω_{RF} is the angular frequency of the RF waveform. Across the diagonal the RF potential is equal in magnitude and opposite in polarity, creating a saddle point which oscillates between the two dimensions once every RF period. If the RF frequency is large compared to the translational motion of the ions, this creates a time-averaged pseudo-potential with a minimum at the trap centre (see Figure 5.3). To confine the ions in the direction of the trap (z -) axis, a DC potential, U_{end} , is applied to the outer 8 electrodes (the “end-caps”). In such a quadrupolar trap, the idealised case would give harmonic trapping potentials which can be treated mathematically using the Mathieu equations (see Equations 5.3 to 5.5). Practically, a hyperbolic electrode geometry would be necessary to generate a truly harmonic trapping potential, although the potentials are typically near-harmonic in the trap centre [232].

5.2.2 Micromotion of trapped ions

The equations of motion for a charged particle in an oscillating one-dimensional trapping field can be reduced to a set of decoupled (Mathieu) differential equations.

The stability of an ion trajectory in such a field is dependent on two parameters (the Mathieu a and q parameters) and not on the initial state of the ion.

The total electric potential can be expressed as $\phi = \phi_{\text{RF}} + \phi_{\text{end}}$, where ϕ_{RF} and ϕ_{end} are the electric potentials arising from the RF fields and endcap voltages, respectively. The Newtonian equation of motion for an ion in the potential ϕ is:

$$\begin{aligned} F &= ma \\ &= -QE \\ &= -Q\nabla\phi \end{aligned} \tag{5.2}$$

where Q and m are the charge and mass of the ion, respectively and a is the acceleration of the ion. In this work, only singly charged ions are trapped, such that $Q = e$. Differentiating the above with respect to the x , y and z axes gives the following differential equations:

$$\frac{d^2x}{dt^2} + \left(\frac{QV_{\text{RF}}}{mr_0^2} \cos(\Omega_{\text{RF}}t) - \frac{\kappa QU_{\text{end}}}{mz_0^2} \right) x = 0 \tag{5.3}$$

$$\frac{d^2y}{dt^2} + \left(-\frac{QV_{\text{RF}}}{mr_0^2} \cos(\Omega_{\text{RF}}t) - \frac{\kappa QU_{\text{end}}}{mz_0^2} \right) y = 0 \tag{5.4}$$

$$\frac{d^2z}{dt^2} + \left(\frac{2\kappa QU_{\text{end}}}{mz_0^2} \right) z = 0 \tag{5.5}$$

where $2r_0$ is the surface separation between diagonal electrodes, $2z_0$ is the separation between adjacent endcaps, and κ is a trap geometry constant. These equations are all of the Mathieu type, the generalised form of which is:

$$\frac{d^2u}{d\tau^2} + (a - 2q \cos 2\tau) u = 0 \tag{5.6}$$

where a and q are referred to as the Mathieu a and q parameters, respectively. As described in Section 5.2.3, these parameters are key to determining the stability

of an ion in the trap. Equations 5.3 to 5.5 are expressed as the general form of the Mathieu equation (Equation 5.6) using the substitutions:

$$a_x = a_y = -\frac{4\kappa QU_{\text{end}}}{m\Omega_{\text{RF}}^2 z_0^2}; \quad a_z = -2a_x \quad (5.7)$$

$$q_x = -q_y = 2\frac{QV_{\text{RF}}}{m\Omega_{\text{RF}}^2 r_0^2}; \quad q_z = 0 \quad (5.8)$$

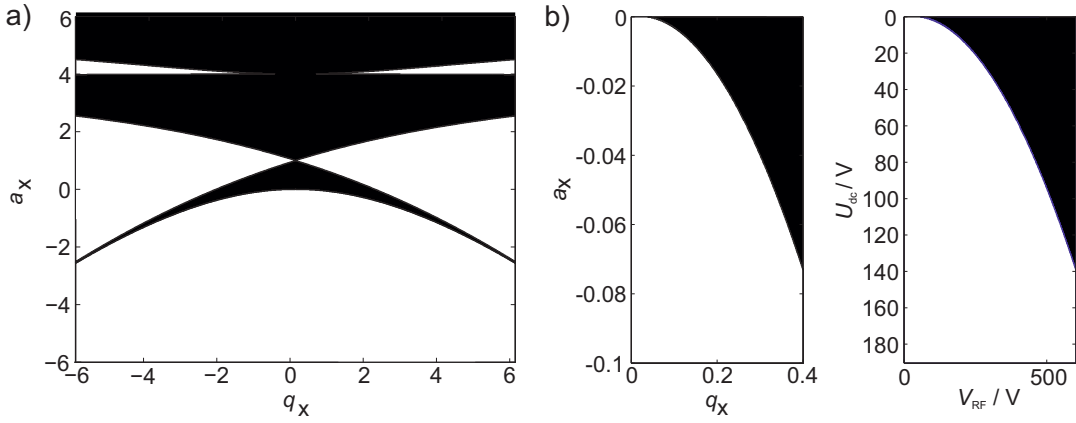
$$\tau = \frac{\Omega_{\text{RF}} t}{2} \quad (5.9)$$

The motion of an ion in these fields can be separated into two components – a low frequency motion along the trap axis, termed the secular motion, resulting from the thermal kinetic energy of the ions, and a higher frequency off-axis motion arising due to the oscillating RF fields, termed the micromotion. If the trap is unstable, the amplitude of the micromotion increases exponentially with time until the ions leave the trap.

5.2.3 Trap stability

Equations 5.6 to 5.9 can be used to determine whether an ion trajectory is stable for a given set of conditions *i.e.* if the ion will remain trapped. Trapping occurs when a trajectory satisfies the Mathieu equation (Equation 5.6), which is dependent on the parameters a and q . A “Stability Diagram” can be plotted, in terms of a and q , showing the regions for which trapping will be stable. Although the stability diagram (Figure 5.4) suggests a wide range of stable ion trajectories, experimental limitations result in only a small region of the diagram being accessible. This is due to limits on the potentials V_{RF} and U_{end} that can be practically applied, giving upper limits on the Mathieu parameters of $a_x \approx 0.063$ and $q_x \approx 0.4$. Typical trap parameters used in these experiments are given in Table 5.1.

Trap Parameter	Symbol	Value
RF frequency	Ω_{RF}	$2\pi \cdot 3.8727 \text{ MHz}$
RF amplitude	$V_{\text{RF},0}$	100-150 V
Endcap potential	U_{end}	1-4 V
Endcap electrode separation	$2z_0$	5.5 mm
Diagonal electrode separation	$2r_0$	7 mm
Geometric factor	κ	0.244
Electrode radius	R	4 mm

Table 5.1: Typical trapping parameters used in the experiments described in this thesis**Figure 5.4:** Stability diagram (calculated) for the ion trap used in this work with a cosine trapping field of $\Omega_{\text{RF}} = 2\pi \times 3.8727 \text{ MHz}$. Figure (a) shows the full range of stable trajectories and (b) the experimentally accessible region. The dark shaded regions represent stable trajectories.

5.3 Laser Cooling

Laser cooling is a well established technique for reducing the kinetic energy of an atom or ion *via* the Doppler effect, selectively enhancing photon absorption when a photon and the species of interest are travelling in anti-parallel directions. The theory of laser cooling was outlined in 1975 by Wineland and Dehmelt, and Hänsch and Schawlow [1, 2], and was first demonstrated experimentally for ions with Mg^+ and Ba^+ ions [233, 234]. A brief introduction to laser cooling is given in Chapter 1.

When an ion absorbs a photon, this process transfers momentum $p = \hbar k$, where $k = 2\pi/\lambda$, is the wavenumber of the photon. If the photon and ion are travelling in anti-parallel directions, the momentum transfer occurs in the opposite direction to the direction of travel of the ion. Over many cycles of absorption and re-emission, the kinetic energy of the ion is reduced. The photon emission from the ion is isotropic, resulting in a random recoil force on the ion which over many cycles reduces the velocity of the ion. The theoretical limit of laser cooling is the Doppler temperature, T_D , which is given by Equation 5.10 for low laser intensities (below the saturation limit):

$$T_D = \frac{\hbar\Gamma}{2k_B} \quad (5.10)$$

where Γ is the natural lifetime of the cooling transition. In this case temperature is defined as the average kinetic (translational) energy of the ions divided by the Boltzmann constant *i.e.* $T = \langle E_K \rangle / k_B$. To ensure that absorption only occurs when the photon and ion are travelling anti-parallel to each other, the laser is slightly detuned to a lower frequency from the atomic (cooling) transition. Typically, this detuning is ~ 45 fm. As the ion approaches the photon, the Doppler effect results in the apparent frequency of the photon being shifted towards the resonant frequency of the cooling transition. In the other case, if the motion of the ion and photon are parallel, the Doppler shift will result in the apparent frequency being further away from resonance, hence reducing the likelihood of absorption.

The principal cooling transition in Ca^+ (the laser-cooled ion used in these experiments) is the dipole allowed $4s\ ^2S_{1/2} \rightarrow 4p\ ^2P_{1/2}$ transition at 397 nm. Ions in the $^2P_{1/2}$ state can decay radiatively to the $^2S_{1/2}$ ground state, or to the metastable $3d\ ^2D_{3/2}$ state, with a branching ratio of approximately 12:1 [235]. As the $^2D_{3/2}$ state is long lived and the transition from this state to the ground state is formally forbidden, a “re-pump” laser at 866 nm is used to transfer the population in the

$3d\ ^2D_{3/2}$ state into the $4p\ ^2P_{1/2}$ state, and hence back into the cooling cycle. A schematic illustrating the relevant energy levels and transitions in Ca^+ is provided in Figure 5.5. From Equation 5.10, the minimum temperature obtainable for Ca^+ using this cooling scheme is ~ 0.5 mK. Additional techniques, such as Raman transitions between hyperfine states, have been developed to cool ions below T_D , into the μK and nK regime [236]. Experimental parameters mean that under normal operating conditions, the translational secular (ignoring micromotion) temperature of the ions is typically greater than T_D .

For cooling > 25 ions, generally the cooling lasers need only to be applied along the trap axis, as the ions form a semi-crystalline state (Coulomb crystal) and the translational motion of the individual ions are coupled *via* the Coulombic interaction (See Section 5.4 for further information). In small crystals or when cooling “strings” of ions, off-axis “radial” cooling is necessary to maintain an adequate secular temperature [142]. Radial cooling provides laser cooling in the (x, y) directions, in addition to the main cooling lasers along the trap (z -) axis.

Ca has 6 naturally occurring stable isotopes¹ (natural abundances in parentheses): ^{40}Ca (96.94%), ^{42}Ca (0.65%), ^{43}Ca (0.14%), ^{44}Ca (2.09%), ^{46}Ca (0.004%) and ^{48}Ca (0.19%) [238]. Isotope shifts in the energy level structure of the Ca^+ ion are on the order of several GHz and are outside the linewidth of the laser system, hence it is only possible to address one isotope at any given time. In this work we exclusively use the most abundant isotope, ^{40}Ca . Any other Ca isotopes present will not undergo laser cooling.

¹It is noted that ^{48}Ca is technically unstable with a half life of 4.3×10^{19} years, undergoing β decay to ^{48}Ti [237]. For practical purposes it can be considered stable.

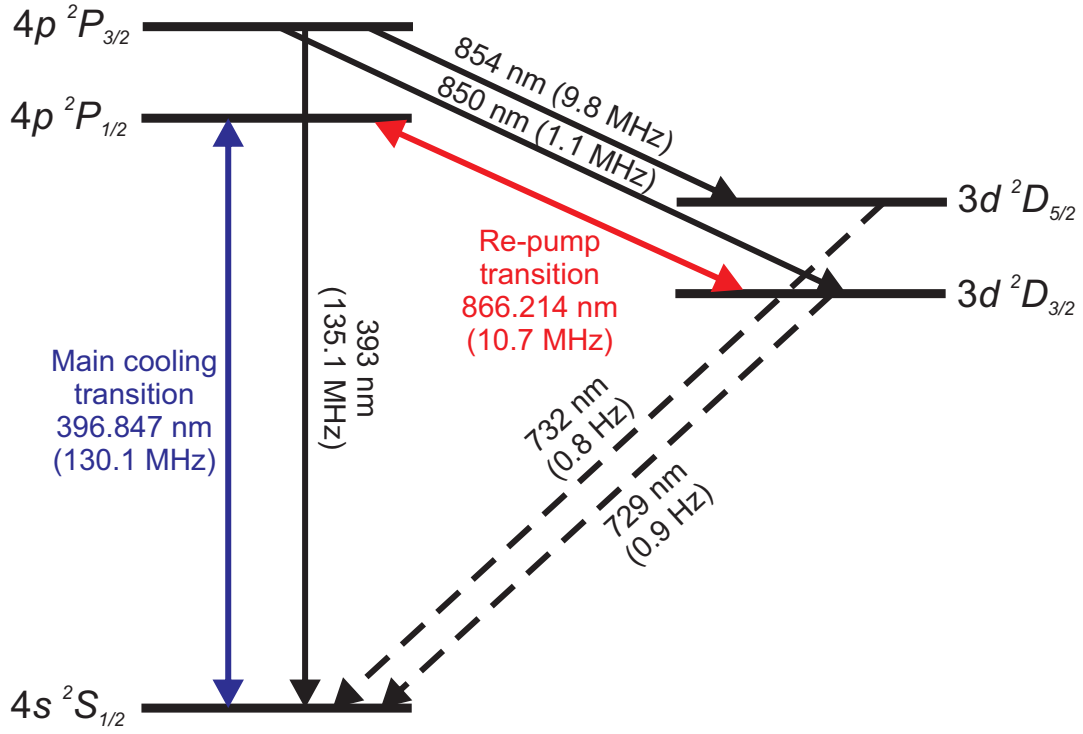


Figure 5.5: Energy level diagram for $^{40}\text{Ca}^+$ with the cooling and re-pump transitions used in these experiments shown. Other main transitions are given. The values in parentheses are the natural linewidths of the transitions [29].

5.4 Coulomb Crystals

The structure and morphology of an ensemble of ions in a trap, with identical mass and charge, is governed by the kinetic energy (or temperature) of the ions, the degree of electrostatic repulsion between the ions, and the trapping fields described in Section 5.2. At high temperatures, a given ion will have sufficient kinetic energy to overcome the potential minimum arising from the Coulombic repulsion with nearby ions and hence can move freely, as in the gas phase. At lower temperatures, a given ion will become increasingly localised in this potential minimum. At a critical temperature, the system will undergo a phase transition to a 3D lattice structure, known as a Coulomb crystal. Such a crystal is shown in Figure 5.6.

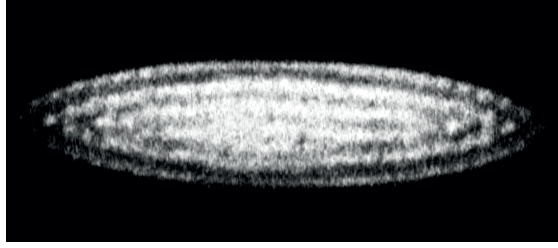


Figure 5.6: An experimental Ca^+ Coulomb crystal image, recorded with $V_{\text{RF}} = 255$ V and $U_{\text{end}} = 1.8$ V.

It is noted, that although the term “crystal” is used, a Coulomb crystal physically is reminiscent of a gas phase plasma and has no translational symmetry as conventional ionic crystals do². Ion spacings in a Coulomb crystal (for the trapping parameters in Table 5.1) are in the range $10 - 20 \mu\text{m}$ [100], approximately four orders of magnitude greater than in a typical solid-phase crystal such as NaCl [240]. Furthermore, in contrast to typical solid phase crystals, ions can diffuse throughout Coulomb crystals – images recorded of Coulomb crystals (such as Figure 5.6) represent the average positions of the ions.

The ratio between the kinetic energy of the ions and the Coulombic potential energy is given by the plasma coupling parameter, Γ , defined as:

$$\Gamma = \frac{E_{\text{P}}}{E_{\text{K}}} = \frac{Q^2}{4\pi\epsilon_0 a_{\text{WS}} k_{\text{B}} T} \quad (5.11)$$

Here, Q is the ionic charge and a_{WS} is the Wigner-Seitz ionic radius (which can be considered as a measure of the average inter-particle spacing), defined as $\frac{4}{3}\pi a_{\text{WS}}^3 = n_0^{-1}$, where n_0 is the ion (or number) density at $T = 0$ K. Γ is an indicator of the thermodynamic state of the ion plasma. For $\Gamma \gtrsim 2$, the ion positions are spatially correlated over short ranges and the ions are in a liquid-like state [241]; for $\Gamma \lesssim 2$ the system behaves as a gas. At values of $\Gamma \gtrsim 150$, crystallisation occurs [242, 243, 244]. Ion densities in a LPT are limited to $\sim 10^8 \text{ cm}^{-3}$ by the Coulombic repulsion. Using

²a body-centered cubic (bcc) structure has been observed in the core of very large Coulomb crystals [239].

Equation 5.11, this gives an ion temperature of ~ 100 mK for Ca^+ ions under our experimental conditions, ignoring any micromotion effects.

5.4.1 Sympathetic Cooling

Ionic species which are not directly addressed by laser cooling can be cooled by laser-cooled ions in a process known as “sympathetic cooling”. In sympathetic cooling, the laser-cooled ions (Ca^+ in this work) act as a heat sink, dissipating kinetic energy from the co-trapped non-laser-cooled ions. The “hot” ions interact with the laser-cooled ions *via* elastic collisions, resulting in a net momentum transfer to the cold Ca^+ ions. As Ca^+ ions are being continuously re-cooled (*via* the cooling cycle described in Section 5.3), the net result of this process is that the non-laser-cooled ions are also cooled. Sympathetic cooling is a versatile technique to produce multi-component crystals, without the need for extensive laser systems to address transitions in different ions or to incorporate ions that can not easily be laser cooled *e.g.* molecular ions.

Only ions that are being directly laser-cooled, and hence fluorescing, can be imaged using the CCD camera. Any other ions incorporated into the crystal are referred to as “dark ions” (see Figures 5.7 and 5.11). Any dark ions with a mass-to-charge (m/z) ratio less than that of the laser-cooled ion will reside in the centre of the crystal and form a dark core in the camera image. If m/z is greater than that of the laser-cooled ion, the ion will form a shell around the outer of the fluorescing Ca^+ core, which has the effect of “compressing” the fluorescent ion pattern. While these dark ions can not be imaged directly, the presence and identity of these ions can often be inferred from the resulting crystal morphology. Simulated Coulomb crystals, generated by molecular dynamics simulations, can be fitted to the experimental images to estimate the density of dark ions [245]. This requires knowledge of the identity of the dark ions, and becomes difficult for crystals with three or more

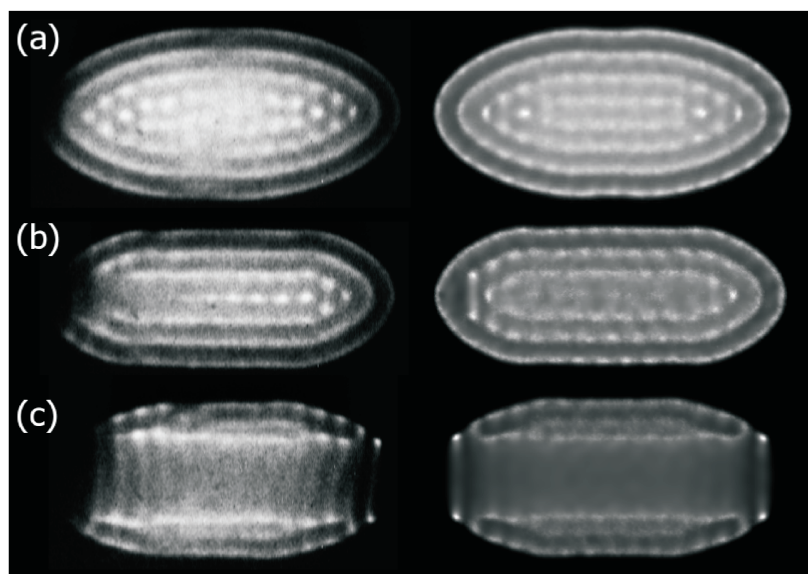


Figure 5.7: Experimental images (left) and simulated images (right) of Coulomb crystals containing a) Ca^+ only, b) Ca^+ and sympathetically cooled OCS^+ . c) Ca^+ , OCS^+ and ND_3^+ . Note that ions of a heavier mass than Ca^+ (40 u) form an outer shell and compress the Ca^+ core, whereas lighter ions form a dark core close to the trap axis. Figure reproduced from [29].

components, necessitating the need for more quantitative detection methods as described in Section 5.5. In some cases, where the reaction products and pathways are well characterised and ion densities are known, faster approximate methods such as aspect-ratio analysis can be used.

5.5 Detection methods

To determine the identity of co-trapped sympathetically cooled (“dark”) ions and, in the case where a reaction has taken place in an ion trap, the identity and density of product ions, various detection methods have been developed for use in ion traps.

5.5.1 Photon counting

A method for detecting the number of laser-cooled ions non-destructively is photon counting, where the number of photons at a given wavelength emitted by an ion is counted over a period of time, usually using a PMT. As the number of ions is proportional to the emission rate, the number of fluorescing ions can be inferred from the photon count. This method has been employed in cases where a laser-cooled ion is a reactant [221] or a product [224] of a chemical reaction. However, this method can not detect or provide any information on dark ions. Additionally, a high degree of wavelength and power stabilisation of the cooling lasers is required to get reliable photon counts, which can be technically challenging to achieve.

5.5.2 Radial motion crystal excitation

Another non-destructive technique for crystal analysis is radial motion crystal excitation. As shown in Equations 5.3 to 5.5, the equations of motion for an ion in the trap depends on its mass. To excite the radial motion of the crystal, an additional oscillating excitation voltage V_{ex} is applied to the trap electrodes (or an electrode in close proximity to the trap). The frequency of V_{ex} is scanned and is correlated with the fluorescence intensity from the laser-cooled ions in the trap. A change in the fluorescence intensity occurs when the motion of the laser-cooled ions is excited, as the extra momentum changes the potential for absorbing (and re-emitting) a photon. When the motion of a sympathetically cooled “dark” ion is excited, the fluorescence intensity is also perturbed, due to the Coulombic interactions between sympathetically-cooled and laser-cooled ions in the trap.

This technique was pioneered by Baba and Waki, who used it to identify molecular ions in large ion clouds, and successfully detected NH_4^+ , H_3O^+ , C_2H_5^+ , COH^+ , and N_2H^+ ions [225, 246]. However, the technique is fairly insensitive to mass

and not suitable for detecting *e.g.* isotopically substituted products, where a resolution of < 1 u is required.

5.5.3 Axial motion crystal excitation

Similar to radial motion crystal excitation, axial motion crystal excitation uses an applied potential to excite the motion of the crystal (from which, the mass of components can be determined), except that the motion excited is along the trap axis in this instance. A pair of ions in a linear Paul trap, with masses m_1 and m_2 , has two modes of motion (v_+ and v_-):

$$v_{\pm}^2 = v_1^2 \left[(1 + \mu) \pm \sqrt{1 - \mu + \mu^2} \right] \quad (5.12)$$

where v_1 is the oscillation frequency in the trap of an ion with mass m_1 and $\mu = m_1/m_2$.

The excitation frequency V_{ex} is applied to two diagonal endcaps and the oscillation of the ion pair is observed using the CCD camera. From the oscillation of the ions, v_1 can be determined, and provided the mass of the laser-cooled ion is known, the mass of the sympathetically cooled ion can be determined [247]. This method has been used to analyse the charge exchange reaction between two calcium isotopes in an ion trap ($^{40}\text{Ca}^+ + ^{44}\text{Ca} \rightleftharpoons ^{40}\text{Ca} + ^{44}\text{Ca}^+$) [248]. However, as this technique can only be employed on a pair of ions, rather than crystals containing hundreds of ions, a considerable number of repeat measurements and averaging is required to build up sufficient statistics to extract chemical reaction rate constants. The resolution of the imaging system does limit the mass resolution, although mass resolution < 1 u has been reported using a standard CCD camera [247].

5.5.4 Mass-dependent ion ejection

In contrast to the previous methods, mass-dependent ion ejection is a destructive method, hence after detection the ions no longer remain in the trap and the crystal can not be re-formed. Mass dependent ion ejection utilises the different stabilities of trapped ions with different m/z ratios (see Equations 5.6 to 5.9). Ions with a larger m/z ratio require a larger Mathieu q parameter for stable trapping. As q is proportional to V_{RF} , and hence by reducing V_{RF} , ions with a higher mass-to-charge ratio can be ejected from the trap preferentially. In most setups where this method is employed, the ejected ions are detected by a Channeltron detector [249] with an extraction plate held at a large negative voltage (-1 kV) to attract the ions, which are ejected radially, towards the detector. By scanning V_{RF} and recording the ion counts, a mass spectrum can be built up. The acquisition time usually takes several seconds, as ramping down V_{RF} too fast can cause trap instabilities. Additionally, detection efficiencies of only $\sim 20\%$ have been reported for singly charged ions, when experimental mass spectra have been compared to those predicted from molecular dynamics simulations [250].

5.5.5 Time-of-flight (trap ejection) mass spectrometry

Time-of-flight (TOF) mass spectrometry is a destructive method, and is based on the Wiley-McLaren mass spectrometer [150], the principles of which are introduced in Sections 2.6.3 and 4.4. Schemes for TOF mass spectrometry have been developed for both axial and radial ejection of ions, although generally axial ejection is preferred due to the smaller spread of the crystal in this dimension, which minimises losses from ions being ejected into the chamber walls.

TOF mass spectrometry is used in the Stark decelerator ion trap experiment in our group. This method works by turning off the trapping voltages and applying

ejection voltages to each opposing set of trap electrodes (on the Stark decelerator ion trap, 217 V and 97 V, respectively), transforming them into repeller and extractor electrodes. The static electric field created by these electrodes has the effect of ejecting the ions out of the trap and into a time-of-flight tube, where they are detected by MCPs, held at -1900 V. From the flight time, the mass-to-charge ratio of the ions that formed the crystal can be determined. Ion trap mass spectrometry was first realised in our lab using a digital (square-wave) ion trap [142, 251]. In a digital ion trap, “square” RF pulses rather than sinusoidal waveforms provide the trapping potential. Due to the sharp rise- and fall time of the digital waveforms, the ejection voltages can be applied easily with minimal interference from the periodic trapping potential.

In a sinusoidal ion trap, with RF trapping potentials of the form $V_{\text{RF}} = \pm V_{\text{RF},0} \cos(\Omega_{\text{RF}} t)$, turning off the RF trapping fields on a short timescale can result in ringing of the form $V_{\text{RF},0} e^{-kt} \sin(t)$ (where k is a constant with a value ~ 1 MHz [142]), due to interference arising from the residual capacitance of the electrodes. The presence of this ringing can result in non-uniform extraction fields and deflection of ions away from the time-of-flight apparatus. This is overcome by actively damping the RF amplitude $V_{\text{RF},0}$ before applying the extraction voltages [154], hence reducing the degree of ringing present in the extraction pulses to a negligible level. The waveforms currently applied in our experiments are given in Figure 5.8. Simulations confirm that the detection efficiency is excellent ($\sim 100\%$) for all ionic species of interest and for crystals containing up to several hundred ions [154, 252].

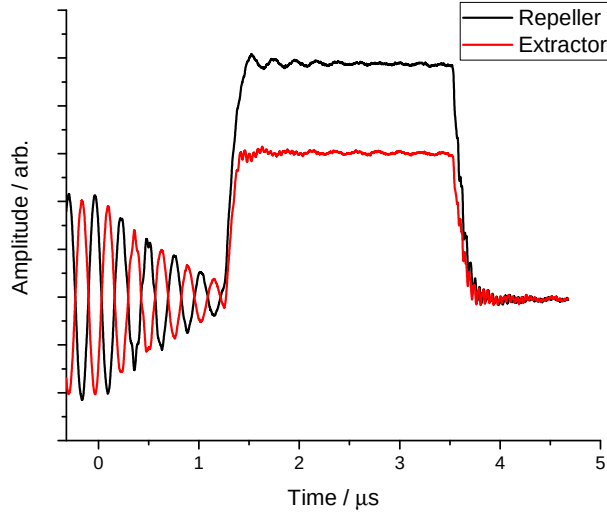


Figure 5.8: Plot of the waveforms applied to the trap during ejection, showing the normal trapping fields (before 0 μs), damping of the RF fields (0 – 1.27 μs) and application of the ejection voltages (1.27 – 3.5 μs).

5.6 Experimental procedure

5.6.1 Laser System

As outlined in Section 5.3, the main cooling transition in Ca^+ is the $4s\ ^2S_{1/2} \rightarrow 4p\ ^2P_{1/2}$ transition at 397 nm. To avoid a build-up of population in the metastable $3d\ ^2D_{3/2}$ “dark” (non-fluorescing) state, a “re-pump” laser at 866 nm is used to return population from this state to the cooling cycle. To generate the 397 nm and 866 nm laser light, two continuous-wave diode lasers are used. To maintain wavelength stability and obtain a well-defined detuning from the resonance point, the diode lasers are temperature stabilised and the current to the laser diode is controlled by a LabVIEW-based proportional, integral, differential (PID) controller (described in reference [231]) in conjunction with a wavelength meter. The software reads the wavelength from the wavelength meter and then adjusts the current setting on the laser diode. This system regulates the wavelength of the laser radiation to ± 1 fm for the 397 nm diode and ± 10 fm for the 866 nm diode.

The laser radiation is fibre coupled from a central laser table to the two ion trap experiments in our lab – the experiment described in this thesis and the Stark decelerator/ion trap experiment. A series of $\lambda/2$ plates and polarising beam splitters on the central laser table allow the laser power going to each experiment to be adjusted. A schematic of the diode laser system is given in Figure 5.9. Fibre coupling not only eliminates the need for separate lasers on each experiment, but also serves to improve the final laser beam profile due to the Gaussian acceptance profile of the optical fibres. The 397 nm and 866 nm laser beams are combined (such that they are colinear) using dichroic mirrors; a series of adjustable mirrors allow the laser beams to be aligned through the ion trap, as shown in Figure 5.9b). A mild focus lens is used prior to the viewport in the ion trap vacuum chamber to give sufficient intensity at the trap centre, but retain a wide beam profile such that the entire Coulomb crystal is illuminated.

An optional “retro-reflection” mirror can be introduced into the beamline. This reflects the laser radiation exiting the trap chamber back into the trap, such that the reflected beam is colinear with the exiting beam. Without the retro-reflected beam, Coulomb crystals show an asymmetry due to the uneven radiation pressure exerted on the ions in the crystal by the laser beam. The retro-reflected beam equalises the radiation pressure on the crystal and recovers the symmetry of the crystal.

5.6.2 Ca source

The Ca^+ source, outlined in Section 2.7 and reference [142], involves a resistively-heated oven and a high power Nd:YAG-pumped dye laser for ionisation. To trap Ca^+ ions, Ca^+ is formed *in situ* from Ca metal. The oven consists of a small Ta tube, which is packed with Ca powder. A current is applied to a high resistance wire wrapped around the tube, which acts as a heating element. This results in sublimation of Ca. The Ca sprays out of the oven, which is aligned with the

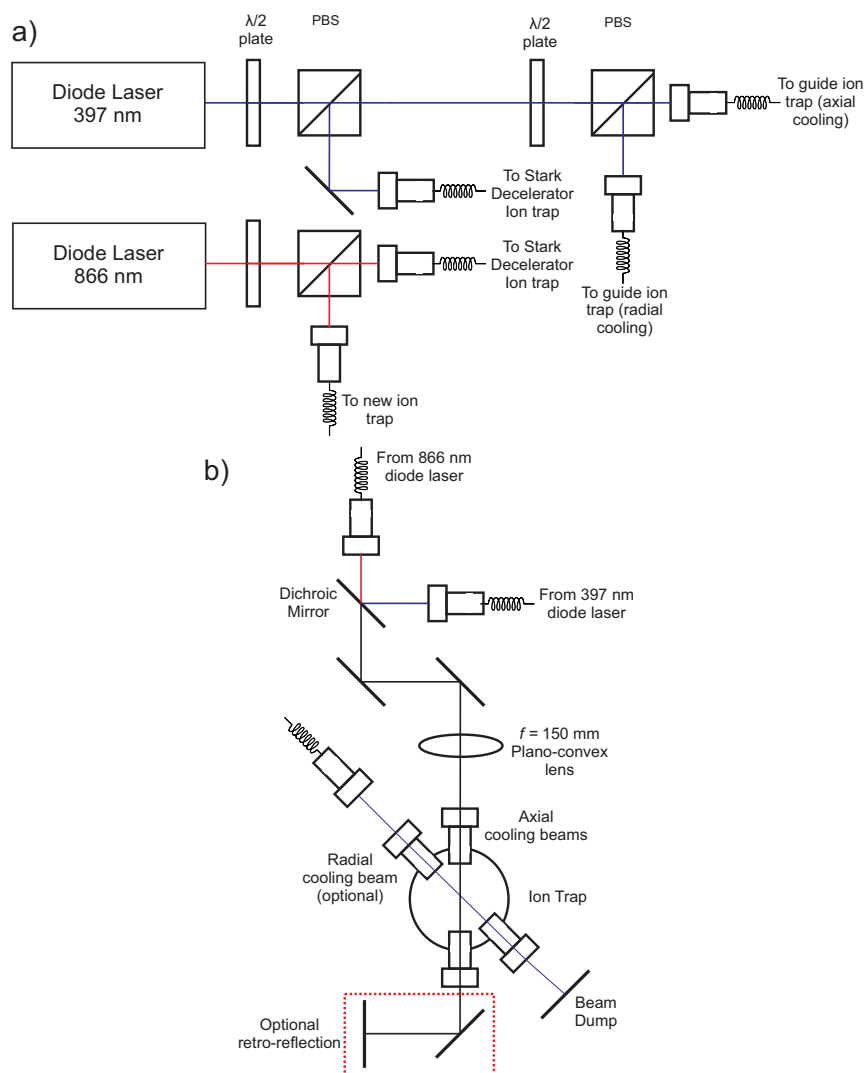


Figure 5.9: Schematic of the diode laser system, used to laser-cool trapped Ca^+ ions. Figure a) shows the setup on the central optical table, distributing the laser radiation to both ion trap experiments. Figure b) shows the setup at the new ion trap experiment.

trap centre. At this point the Ca beam is intersected by the dye laser (typically operated at $\lambda = 325$ nm and $P = 5.5$ mJ/pulse) which non-resonantly ionises the Ca in a two-photon process. Other groups have employed (2+1) REMPI on Ca, allowing the formation of Ca^+ without the need for high-powered pulsed lasers [253], however as suitable high-powered lasers were already present in the group, this methodology was not chosen. Due to their electronic charge, the Ca^+ ions will be affected by the trapping fields and will also interact with the cooling lasers, resulting in cold, localised Ca^+ crystals.

5.6.3 Imaging Trapped Ions

To detect the fluorescence from the laser-cooled Ca^+ ions, an electron-multiplying charged couple device (CCD) camera (Andor Luca DL-658M-TIL) is used. Alternatively, or in addition to the camera, a photomultiplier tube (PMT) can be used (Hamamatsu H10721P-110). The PMT is useful in detecting weak signals and is less dependent on the focal plane of the imaging setup, which is advantageous when initially searching for ion fluorescence before the setup is optimised.

The ions are imaged through a $\varnothing = 25$ mm quartz window using a $10\times$ microscope objective lens. The camera and PMT are mounted to a x, y, z -translation stage to manipulate the position and optimise the focus on the ions. To reduce the effect of background scatter and stray light, light passes through a 397 nm notch filter before it reaches the camera or PMT. A thin glass beamsplitter in the optical setup divides the light between the camera and PMT in a 24:1 ratio. The camera has been calibrated previously using a graticule; each camera pixel corresponds to an area $0.77 \times 0.77 \text{ }\mu\text{m}^2$ [142].

To assist in finding the location of trapped ions when using the trap for the first time, a retractable optical fibre on a x, y, z -translation stage has been added to the trap design. The fibre is ~ 2 mm long and $125 \text{ }\mu\text{m}$ in diameter, and the fibre material fluoresces when it is overlapped with the 397 nm laser beam. Using the translation stage, the fibre can be placed in the trap centre and when illuminated by the cooling lasers, it can be imaged using the camera. This gives the approximate focal plane and position of the trap centre and reduces the parameter space which needs to be explored with the camera or PMT to find ion fluorescence in the trap when setting up for the first time. When initially searching for ions, a lower endcap and RF voltage is used (typically $V_{\text{RF}} = 150 \text{ V}$, $U_{\text{end}} = 1 \text{ V}$) to create a wider trap, increasing the probability that the cooling lasers will overlap with the ions. However, such settings result in a shallow trap and hence the lifetime of trapped ions is short.

After aligning the camera to the trap centre, as determined by the fibre tip, and loading cold Ca^+ ions into the trap, it is possible that no ion fluorescence is initially observed. This is typically a result of the location of the effective trap centre not being at the physical centre of the trap. This can arise due to stray or asymmetric electric fields as a result of *e.g.* deposition of Ca powder or pump oils on the trap, manufacturing defects, or damage to the trap electrodes. To correct for this, small static DC offsets can be applied to individual electrodes to move the effective trap centre to the point at which the trap is being imaged. Once fluorescence is observed, the camera (or PMT) position, laser alignment and laser frequency are optimised to maximise signal.

5.7 Experimental crystals

Due to ongoing technical challenges in observing crystals in the ion trap combined with the buffer-gas cell and guide apparatus, some preliminary measurements, described in the following subsections, were made using the Stark decelerator ion trap. This ion trap has the same physical dimensions and trapping parameters (see Table 5.1), hence results from the two traps should be comparable. A schematic of the Stark decelerator ion trap experiment is given in Figure 1.7.

5.7.1 Bicomponent $\text{Ca}^+ - \text{Xe}^+$ crystals

To demonstrate the principle of sympathetic cooling and to show that a non-laser-cooled ion can be co-trapped with a Ca^+ Coulomb crystal, bicomponent Ca^+/Xe^+ crystals are loaded into the trap. To form these crystals, a Ca^+ crystal is loaded according to the experimental procedure outlined in Section 5.6. A partial pressure of approximately 1×10^{-9} mbar of Xe gas is leaked into the chamber through a precision leak valve and is ionised using a $(2 + 1)$ REMPI process *via* the $5p^56p^2P_{3/2}$

intermediate electronic state [254], using a frequency-doubled Nd:YAG-pumped dye laser at 40075 cm^{-1} with a power of $800\text{ }\mu\text{J/pulse}$. The laser is admitted to the chamber for up to 10 s to allow for the formation of a sufficient density of Xe^+ ions whilst minimising the probability of ionising contaminants.

The Xe^+ ions formed in the trap chamber interact with the laser-cooled Ca^+ ions, which cool the Xe^+ ions into the crystal by the process of sympathetic cooling. Due to the greater mass-to-charge ratio of Xe^+ compared to Ca^+ , Xe^+ does not interact with the trapping fields as strongly as Ca^+ and forms a shell around the outside of the Ca^+ core of the crystal, which compresses the core (see Figure 5.10). During the addition of Xe^+ ions, the crystal temperature increases due to the sympathetic cooling process – heat transfer takes place between the hot Xe^+ ions and cold Ca^+ ions, followed by re-cooling of Ca^+ . The camera images of the Coulomb crystals before, during and after loading are shown in Figure 5.11. Molecular dynamics simulations show that due to the weak interaction of Xe^+ with the trapping fields, the Xe^+ ions exist in a semi-liquid state, rather than a crystalline state.

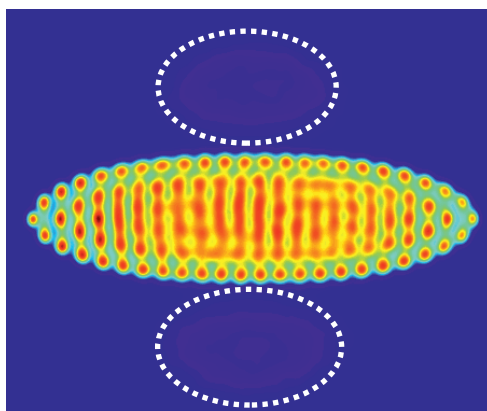


Figure 5.10: False colour image of a Ca^+ and Xe^+ bicomponent Coulomb crystal, as determined by molecular dynamics simulations conducted by B. Heazlewood. The white dotted circles give the region where the Xe^+ ions reside in the crystal.

To analyse the components of the crystals and to verify that the “dark ions” are Xe^+ , the trap-ejection mass spectrometry method is used, as described in Section 5.5.5

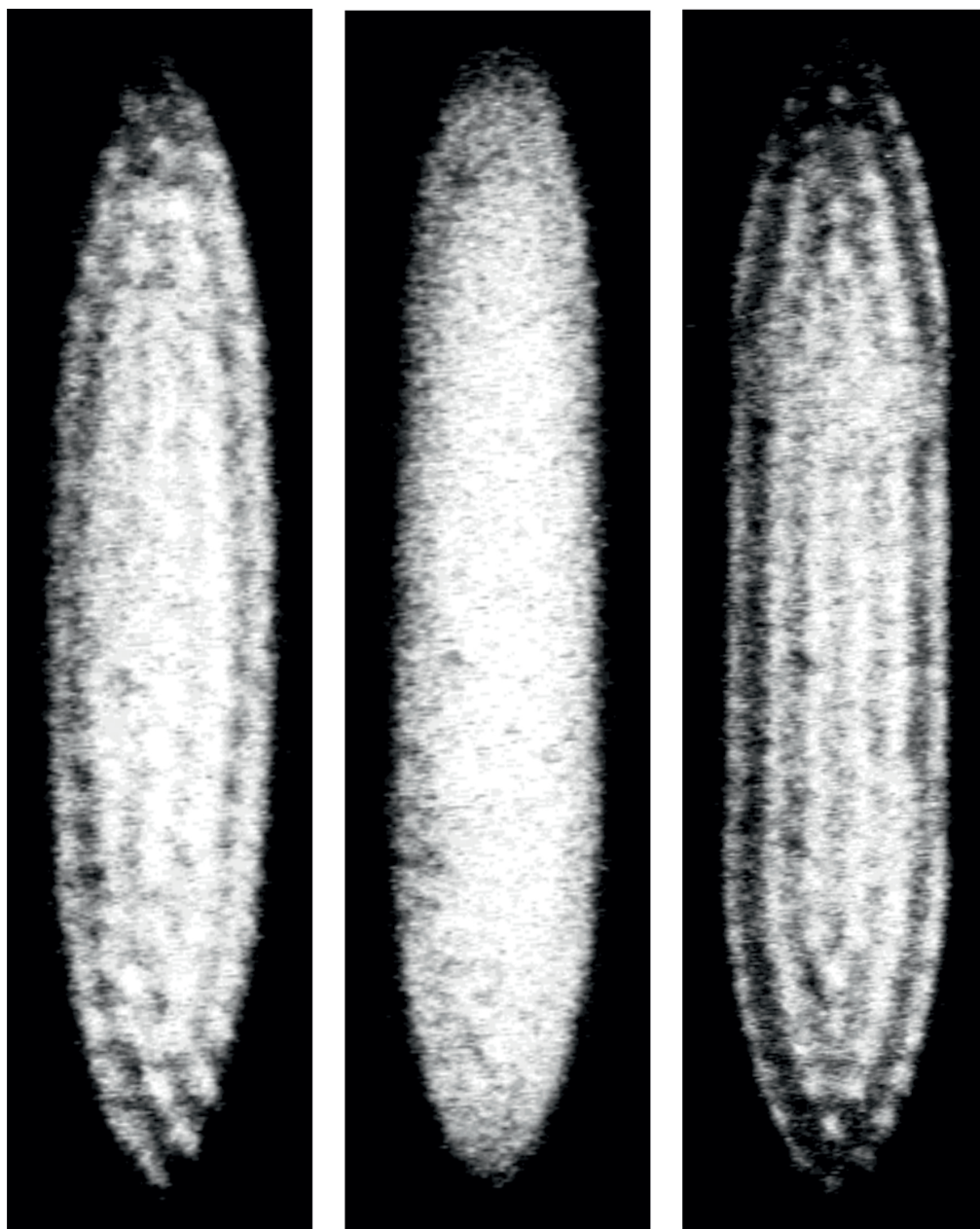


Figure 5.11: Experimental Coulomb crystal images of (left) Ca^+ only, (middle) immediately after ionisation of Xe, (right) a bi-component Ca^+ and Xe^+ crystal. Note that the Xe^+ ions are non-fluorescent, however their presence results in a compression of the fluorescing Ca^+ ions within the crystal.

and reference [154]. The resultant time-of-flight trace recorded following ejection of a bicomponent Ca^+ and Xe^+ crystal is given in Figure 5.12.

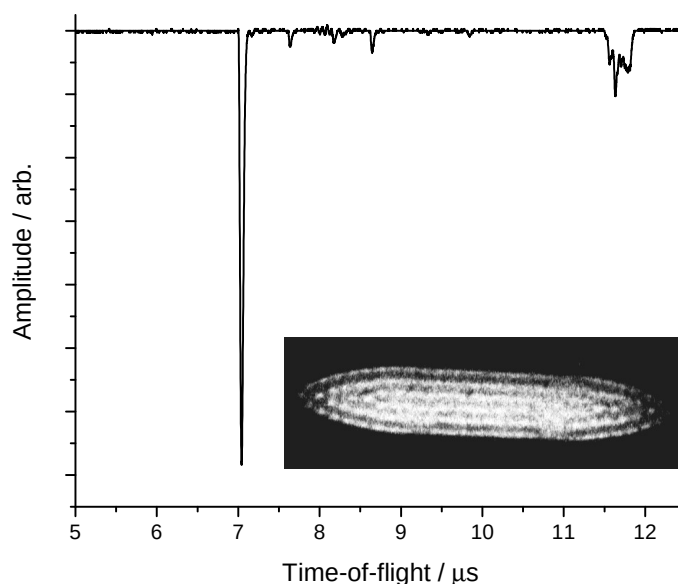


Figure 5.12: Time-of-flight trace obtained for the inset Ca^+/Xe^+ bicomponent crystal. The signal from Ca^+ is at 7 μs and from Xe^+ at 11.5–11.9 μs . Several Xe^+ peaks are seen due to the multiple stable isotopes of Xe. Other minor peaks are attributed to contaminants in the vacuum chamber.

5.7.2 The $\text{Xe}^+ + \text{ND}_3$ reaction

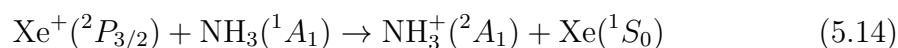
Following on from loading bicomponent Ca^+ and Xe^+ crystals in the ion trap, as described in Section 5.7.1, a neutral polar molecule (ND_3) was admitted to the trap chamber which would undergo a charge exchange process with the sympathetically-cooled Xe^+ in the following reaction:



5.7.2.1 Dynamics of the Xe^+ + ammonia reaction

The $\text{Xe}^+ + \text{ND}_3$ reaction is ideally suited for fulfilling our aim to test post-Langevin capture theories experimentally, as set out in Chapter 1. Theoretical work by D. Clary has been conducted, using rotationally-adiabatic capture theory, on an analogous reaction between neutral ammonia molecules and an atomic ion (the $\text{N}^+ + \text{NH}_3$ reaction) [31]. Hence, direct comparisons between theory and experiment (accounting for the mass differences between the reactants in the theoretical work and the experimental study) can be made.

Additionally, the reaction between NH_3 and Xe^+ has been investigated theoretically by Lavander and Chiu [259]. Thermochemical calculations show a single exothermic reactive channel, given in Equation 5.14, corresponding to a charge transfer process with $\Delta H = -2.1$ eV. All other channels were found to be endothermic ($\Delta H \geq 1.0$ eV). The energetics will be marginally different for ND_3 due to zero-point energy effects.



Scattering studies, also performed by Lavander and Chiu [259], suggest that Equation 5.14 proceeds *via* complex formation as a result of ion-molecule capture. Hence, the post-Langevin capture theories introduced in Section 1.2 should describe the reaction to a high degree of accuracy. L. Harper [30], calculated the temperature dependence of the rate constant for NH_3 in the $|J, MK\rangle = |1, -1\rangle$ rotational state (the rotational state selected by the Stark decelerator), using statistically-adiabatic capture theory [258]. The results of these calculations is shown in Figure 5.13.

Whilst little experimental data for this reaction is available at low temperatures, studies have been conducted at room temperature (300 K) using selected-ion flow tubes [262, 263] and ion-cyclotron resonance [260, 261]. These studies have

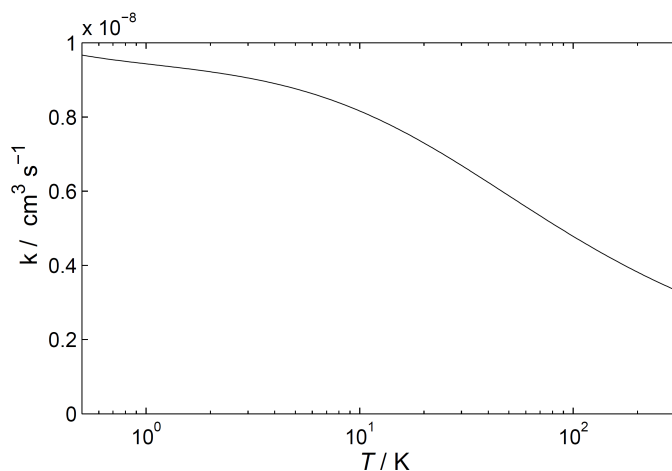


Figure 5.13: Calculated rate constant for the $\text{Xe}^+ + \text{NH}_3$ reaction, calculated using statistically-adiabatic capture theory. Adapted from [30].

yielded rate constants in the range $6.0 - 8.3 \times 10^{10} \text{ cm}^3 \text{ s}^{-1}$. These experimental rates constants are several times larger than that predicted by the work shown in Figure 5.13. This is not unexpected, given that the population of molecules in the $|J, MK\rangle = |1, -1\rangle$ rotational state at 300 K is much smaller, with a large proportion in higher rotational states. Molecules with greater rotational angular momentum possess a lower “effective” dipole moment, which in turn lowers the ion-molecule interaction potential and hence lowers the rate constant. The ability to collect data at low temperatures for such processes will allow for valid comparisons between theory and experiment to be made.

5.7.2.2 Experimental procedure

To introduce ND_3 into the trap chamber, the Stark decelerator is operated in “guiding mode”, where static high voltages are applied to the decelerator rather than switching voltages, resulting in the decelerator operating as an electrostatic guide. As Xe^+ has a greater mass-to-charge ratio, and ND_3^+ has a smaller mass-to-charge ratio, compared to Ca^+ , these ions sit outside and inside the Ca^+ core, respectively. Hence, the progress of the reaction can be tracked from the camera image by the

formation of a dark core and a reduction in compression on the sides of the imaged crystal. The experimental images from this reaction are given in Figure 5.14. The final crystal was analysed, as before, using trap-ejection mass spectrometry and was found to contain Ca^+ , ND_3^+ ions, as well as unreacted Xe^+ ions. The presence of ND_3^+ ions indicate a reaction has taken place. Due to the gas handling process, H/D exchange takes place giving a mixture of isotopologues in the crystal, hence four mass peaks are seen for ammonia, corresponding to ND_3^+ , ND_2H^+ , NH_2D^+ and NH_3^+ . The time-of-flight trace is given in Figure 5.15.

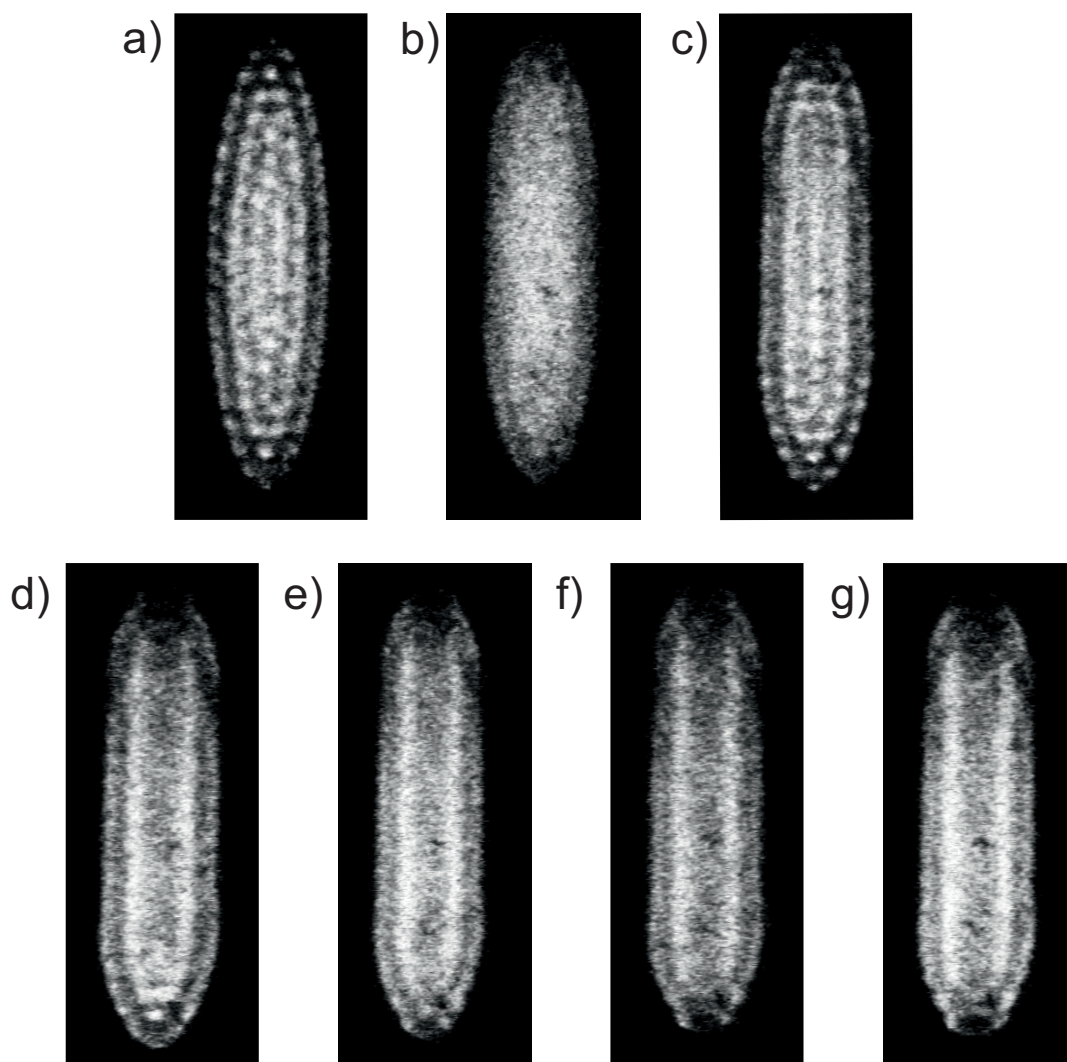


Figure 5.14: Series of experimental images showing the $\text{Xe}^+ + \text{ND}_3$ reaction, sympathetically cooled in a Ca^+ Coulomb crystal. a) Shows the Ca^+ Coulomb crystal. b) During the process of loading Xe^+ (details in Section 5.7.1). c) Ca^+ and Xe^+ bicomponent crystal. d, e, f, g) 1, 2, 4, 5 min, respectively, after introducing ND_3 into the trap chamber.

To extract a rate constant from the experimental images in Figure 5.14, molecular dynamics simulations of the crystals could be conducted, and the simulations compared to the experimental images. This method would be valid in this case, due to the large mass-to-charge difference between ND_3^+ and Xe^+ , and hence the two ions are spatially separated in the crystals. Such method would prove more difficult if both reactant and product ions were lighter, or heavier, than the laser-cooled

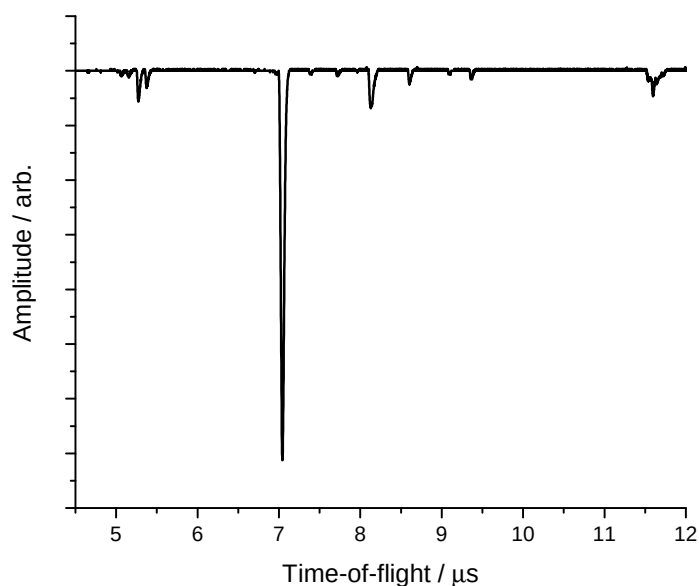


Figure 5.15: Time-of-flight trace resulting from the ejection of the crystal shown in Figure 5.14g). The signal arising from ammonia ions is at $\sim 5.3 \mu\text{s}$, Ca^+ is at $7 \mu\text{s}$ and Xe^+ at $11.5\text{--}11.9 \mu\text{s}$. Other minor peaks are attributed to contaminants in the vacuum chamber.

ion. From the simulations, a number density of each ion can be extracted and by analysing images taken at different times, the rate of change of a given ion can be determined. Core volume analysis, where the aspect ratio of the dark core is measured to give an approximate volume of the core, could be used to estimate the number of ammonia ions at a given time. Such an approach requires well defined initial densities and would need to be used in tandem with molecular dynamics simulations in order to calibrate the core volumes. More information on core volume analysis can be found in reference [30].

It is noted that, from the mass spectrum given in Figure 5.15, other ions are present in the crystal besides ammonia, Ca^+ and Xe^+ . These ions are likely to result from fragments of vacuum pump oil which dissociate and ionise (and hence are trapped) when the high-powered Ca ionisation and Xe REMPI lasers are admitted to the chamber. Such ions distort the morphology of the crystal and give the

impression of a higher density of reactant ions (as the contaminant ions have a greater mass-to-charge ratio than Ca^+ , but are typically below that of Xe^+). To reduce the density of such contaminant ions in the future, the vacuum chamber will be baked for a longer period of time to help remove contaminants adsorbed onto the chamber walls. Additional measures such as cryogenic foreline traps could be implemented if the presence of such ions persists, in order to reduce diffusion of pump oils into the chamber from the vacuum pumps.

In order to extract a pure rate constant for the charge exchange process between Xe^+ (or Ca^+) and ND_3 and rule out the possibility of any background reactions occurring between Xe^+ and contaminants in the vacuum chamber, a Ca^+ and Xe^+ Coulomb crystal can be loaded and monitored over a long timescale (~ 60 min) and changes in its morphology noted – this will give a rate of any background reactions. This rate can then be subtracted from the reaction rate observed with ND_3 , disentangling the effect of any side reactions that may occur in the trap chamber.

5.8 Summary

In this chapter, the theory of ion trapping, with a focus on the linear Paul trap, has been introduced. Experimentally, the ion trap apparatus introduced in Section 2.7 has been fully combined with the buffer-gas cell and electrostatic guide experiment. The theory underpinning, and the experimental realisation of, laser-cooling was described, with a focus on the Ca^+ ion used in these experiments. As a result of ongoing technical issues, Coulomb crystals were not observed yet in the combined experimental apparatus.

Utilising the Stark decelerator ion trap, which has the same geometry and technical design as the ion trap on the quadrupole guide apparatus, Coulomb crystals were observed. Both monocomponent Ca^+ and bicomponent Ca^+ and Xe^+ Coulomb

crystals were obtained, and a charge exchange reaction between Xe^+ and ND_3 was carried out in a Coulomb crystal. As this is one of the target reactions for the new setup, and this reaction is ideally suited for our aim of experimentally verifying post-Langevin theory, it provided valuable insights for future work on both experimental setups. Work to refine this process and extract chemical parameters such as rate constants from the $\text{Xe}^+ + \text{ND}_3$ reaction is ongoing. Further investigation on the buffer-gas cell and quadrupole guide ion trap is being conducted by L. Petralia, to resolve the remaining technical issues and observe crystals. Preliminary diagnostics show promising results and the observation of the first cold Coulomb crystals in this trap is imminent. Once resolved, the guide can be used as a cold molecule source to achieve the aim set out at the start of this project, the observation of translationally and internally cold ion-molecule chemical reactions.

6

Conclusion

In this thesis, a novel apparatus combining buffer-gas cooling, electrostatic velocity selection and a linear Paul ion trap has been characterised and developed. Various elements of the experimental apparatus, initially designed and constructed by K. Twyman (buffer-gas cell and quadrupole guide) [128] and L. Pollum (ion trap) [142], were further developed and improved in this work. Characterisation experiments were conducted to ascertain the optimal parameters for the buffer-gas cell and to achieve thermalisation of the molecular gas whilst maintaining a reasonable run time before molecular ices impeded operation. This will enable us to achieve a sufficient density of cold molecules to study cold ion-molecule reactions.

Experiments using a quadrupole mass spectrometer to detect and analyse the guided molecular beam were carried out to determine the identity and relative flux of various ammonia isotopologues. Using mass spectrometry and a model developed

to account for the typical fragmentation pattern of isotopically-pure samples of ND_3 and NH_3 , the initial relative concentrations of each isotopologue in a variety of ND_3/NH_3 gas mixtures was calculated. Such a technique is necessary as it is not possible to isolate pure samples of ND_2H and NH_2D : these species only exist in mixtures which also contain ND_3 and NH_3 . This model will allow for real-time detection of the output of the guide (and hence, the concentrations of reactants) when studying cold ion-molecule reactions involving ammonia isotopologues. The ability to detect the relative concentrations of individual ammonia isotopologues exiting the guide sets the foundation for studying deuterium fractionation reactions under cold conditions. Such reactions are believed to occur in the interstellar medium [160], however the mechanisms of such processes remain relatively uninvestigated due to the difficulties associated with forming internally cold neutral molecules at temperatures comparable to the interstellar medium in the laboratory. The apparatus described in this thesis, along with the preparatory characterisation work, will allow such investigations to be undertaken in the future.

Using REMPI spectroscopy with linearly-polarised laser light, the orientation of ND_3 molecules as they pass through the guide and into the detection region was investigated. Spectra recorded with the laser polarisation axis parallel to the electric fields (or “vertical”) and with the laser polarisation axis perpendicular to the field (or “horizontal”) showed a significant, reproducible difference in peak intensity for several transitions, arising from non-statistical M -state distributions. To further investigate the orientation of ND_3 molecules in the region after the guide, state-tracking trajectory simulations, in which ND_3 molecules were propagated through the detection setup, were conducted. These simulations confirmed a small, but non-negligible anisotropy in the M -state distribution at the point of ionisation. It was determined that, in the current configuration, the majority of orientation to the local field was lost a short distance after the molecules passed through a

grounded mesh, installed to shield the ion trap from the large-magnitude electric fields present in the guide. Hence, the degree of orientation retained by the point at which the ion trap is installed is too small to allow for the possibility of investigating the effects of orientation in ion-molecule reactions. Schemes for increasing the retention of orientation, such as through the addition of bias fields or modifying components of the experiment, were investigated theoretically. As detailed in Chapter 4, the addition of a small bias field (on the order of 3 V cm^{-1}) – or reducing the thickness of the grounded mesh by replacing the stainless steel mesh holder with an insulating material – would result in $>70\%$ of ND_3 molecules retaining their orientation to the local field at the point of detection. Implementing either of these minor modifications to the experimental set-up would allow for the influence of an additional degree of freedom, the orientation of the neutral reactant, to be investigated in ion-molecule reactions.

The proposed combination of the cold molecule source (buffer-gas cell and electrostatic quadrupole guide) with a linear Paul ion trap has been completed. Multiple modifications were made to the initial designs for the apparatus, for a number of reasons. A portion of the vacuum chamber was modified from a cylindrical shape to a conical shape (to aid differential pumping and impede gas flow into the ion trap chamber), and a grounded “open” cup was installed at the end of the guide (to improve the pumping efficiency before the ion trap and prevent rethermalisation of cold molecules by background gas collisions). Extra pumps were installed to improve differential pumping and maintain the low pressures required for stable ion trapping. The guide electrodes were marginally shortened and a new insulator designed, to achieve a good connection between the guide and ion trap and prevent stray fields from affecting the trap. An optical fibre was also installed to approximate the focal (imaging) plane in the ion trap.

While Ca^+ ion signal has been detected in the ion trap of the combined apparatus,

ion fluorescence has not been observed (yet). To continue investigations, the Stark decelerator ion trap was used, which has the same trap parameters. This allowed for progress to be made in our investigation of cold ion-molecule chemistry while the final technical issues were resolved with the ion trap, and data was collected on a proof-of-principle reaction. Using the Stark decelerator ion trap, bicomponent Coulomb crystals with laser-cooled Ca^+ and sympathetically cooled Xe^+ were trapped. ND_3 was guided into the chamber and the $\text{Xe}^+ + \text{ND}_3$ charge exchange reaction was observed within a Ca^+ Coulomb crystal. The reaction progress was monitored over time by the change in structure of the Ca^+ Coulomb crystal, with all ions ejected into a time-of-flight tube for mass sensitive detection at a given point in the reaction process. Hence, the identity of the ions and the relative abundance of each ion in the crystal could be determined. Such cold ion-molecule reactions, with ammonia as the neutral reactant and an atomic ion, are of particular interest as theoretical work considering the behaviour of a similar reaction (the $\text{N}^+ + \text{NH}_3$ reaction) using post-Langevin capture theory (rotationally-adiabatic capture theory) has been conducted [31]. Investigating similar ion-molecule reactions will allow for direct comparisons between theory and experiment to be made.

This thesis documents the significant progress made towards the observation of cold ion-molecule reactions at a variety of low internal temperatures in the laboratory. Ongoing work is being carried out by L. Petralia to resolve the final technical issues with the ion trap. Once Ca^+ fluorescence is observed and the resultant Coulomb crystals are optimised, the initial aim is to study the $\text{Ca}^+ + \text{CH}_3\text{F} \rightarrow \text{CaF}^+ + \text{CH}_3$ reaction. This reaction was previously studied by S. Willitsch *et al.* [131] using a translationally cold but rotationally hot source. The availability of existing data for comparison, and the relative simplicity of the reaction (as one of the reactants is the laser-cooled ion), make this an ideal candidate for testing the new combined apparatus and observing the effects of rotational temperature on reaction dynamics.

Due to the broad applicability of electrostatic velocity selection and sympathetic ion cooling, this setup can be utilised to probe a wide range of ion-molecule reactions involving small polar neutral molecules, and has the potential to significantly broaden the scope of cold chemistry that can be studied in the laboratory.

In particular, the apparatus has ideal characteristics for the study of deuterium fractionation, a process which is of significant astrochemical significance [160, 161]. Ion-molecule reactions with a protonated and deuterated product channel such as $\text{NH}_3^+ + \text{ND}_2\text{H} \rightarrow \text{NH}_4^+ (\text{NH}_3^+\text{D}) + \text{ND}_2 (\text{NDH})$ can be studied and analysed to determine if there is a preference for the deuterated or protonated product over the other. Due to the ability with this apparatus to vary the rotational temperature, which is not possible with other cold molecule sources such as Stark deceleration, the branching ratio at a variety of T_{rot} in the range 9 – 20 K can be determined. Experimental data recorded using this apparatus can be compared with outcomes predicted by post-Langevin theories, such as those proposed by Clary [28]. This will serve as an experimental verification of such theories – decades after the theories were first developed.



Using mass spectrometry to analyse the molecular beam – Further Data

A.1 Full fragmentation patterns in the QMS for ND₃ and NH₃

The full fragmentation pattern, recorded using the QMS at the end of the quadrupole guide, for ND₃ and NH₃ are shown below in Figure A.1. Masses $m = 14 - 20$ u are shown. Data for $m = 21$ u has been recorded, however due to lack of signal (attributed to the low abundance of ¹⁵ND₃) this data was omitted. The fragmentation pattern showing the most abundant masses only is shown in Figure 3.1.

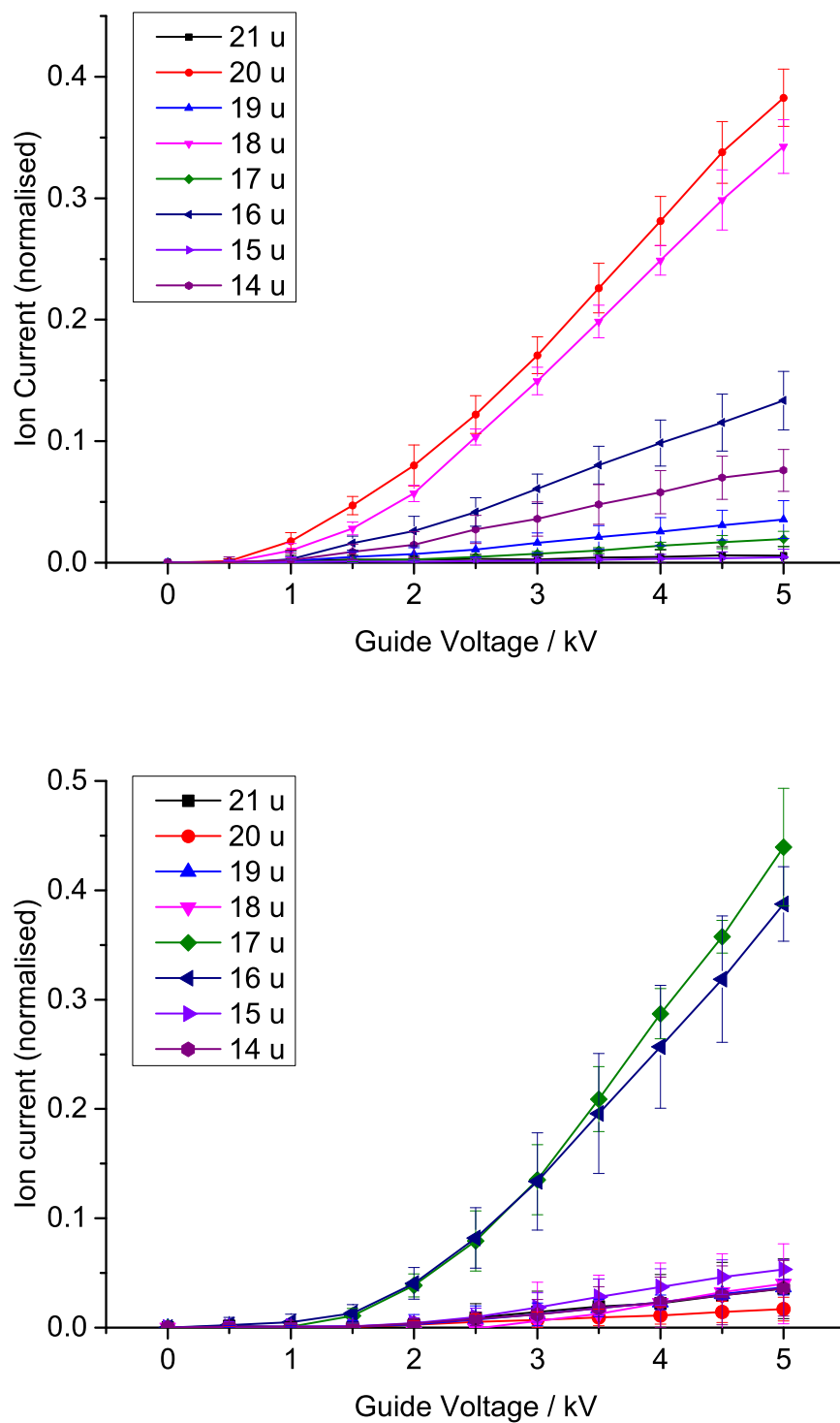


Figure A.1: Relative ion currents recorded in the MS of ND₃ (top) and NH₃ (bottom) for $V_{\text{guide}} = 0 - 5$ kV.

A.2 Guiding efficiency of each rotational state

As outlined in Chapter 3, the fraction of molecules transmitted through the guide, as established from Monte Carlo trajectory simulations, gives an overall “guidability factor” that is dependent on the guiding efficiency and thermal population of a given state.

Table A.1: The transmission efficiency (frac. trans.) and relative rotational population (rel. rot. pop.) at the guide exit for each $|J, K, M\rangle$ rotational state of ND₃ and NH₃, up to $J = 5$. The relative rotational population is the transmission weighted by a 9 K Boltzmann distribution for each state. Only low-field seeking states are included in the table.

				ND ₃		NH ₃	
J	K	M	MK	Frac. trans.	Rel. rot. pop.	Frac. trans.	Rel. rot. pop.
1	1	1	1	0.354	0.040	0.349	7.53E-03
2	1	1	1	0.194	1.56E-04	0.119	2.99E-07
2	1	2	2	0.292	1.00E-03	0.265	6.65E-07
2	2	1	2	0.295	1.02E-03	0.399	1.04E-05
2	2	2	4	0.407	1.40E-03	0.268	6.97E-06
3	1	1	1	0.104	5.15E-08	0.250	7.88E-13
3	1	2	2	0.192	9.49E-08	0.116	3.67E-13
3	1	3	3	0.250	1.24E-07	0.0295	9.29E-14
3	2	1	2	0.191	4.04E-07	0.117	3.83E-12
3	2	2	4	0.300	6.35E-07	0.300	9.78E-12
3	2	3	6	0.361	7.63E-07	0.364	1.19E-11
3	3	1	3	0.249	5.94E-06	0.249	4.00E-10
3	3	2	6	0.359	8.56E-06	0.359	5.76E-10
3	3	3	9	0.423	1.01E-05	0.422	6.76E-10
4	1	1	1	0.055	1.43E-12	0.0554	2.36E-21

Continues on next page...

J	K	M	MK	ND ₃		NH ₃	
				Frac. trans.	Rel. rot. pop.	Frac. trans.	Rel. rot. pop.
4	1	2	2	0.120	3.11E-12	0.0624	2.66E-21
4	1	3	3	0.172	4.44E-12	0.174	7.43E-21
4	1	4	4	0.172	4.44E-12	0.150	6.39E-21
4	2	1	2	0.121	1.34E-11	0.121	5.35E-20
4	2	2	4	0.221	2.44E-11	0.217	9.56E-20
4	2	3	6	0.284	3.13E-11	0.284	1.25E-19
4	2	4	8	0.327	3.61E-11	0.310	1.37E-19
4	3	1	3	0.174	2.16E-10	0.174	3.77E-18
4	3	2	6	0.280	3.48E-10	0.280	6.07E-18
4	3	3	9	0.347	4.32E-10	0.347	7.54E-18
4	3	4	12	0.390	4.86E-10	0.383	8.32E-18
4	4	1	4	0.216	7.97E-09	0.216	1.09E-15
4	4	2	8	0.330	1.22E-08	0.330	1.67E-15
4	4	3	12	0.389	1.44E-08	0.389	1.97E-15
4	4	4	16	0.434	1.60E-08	0.431	2.18E-15
5	1	1	1	0.077	3.79E-17	0.0773	5.71E-31
5	1	2	2	0.160	7.85E-17	0.160	1.18E-30
5	1	3	3	0.219	1.07E-16	0.234	1.73E-30
5	1	4	4	0.263	1.29E-16	-	-
5	1	5	5	0.300	1.47E-16	-	-
5	2	1	2	0.166	1.66E-16	0.166	1.07E-29
5	2	2	4	0.275	2.74E-16	0.139	8.97E-30
5	2	3	6	0.340	3.39E-16	0.158	1.02E-29
5	2	4	8	0.385	3.83E-16	0.222	1.43E-29
5	2	5	10	0.417	4.16E-16	0.268	1.73E-29

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ND ₃				NH ₃			
<i>J</i>	<i>K</i>	<i>M</i>	<i>MK</i>	Frac. trans.	Rel. rot. pop.	Frac. trans.	Rel. rot. pop.
5	3	1	3	0.121	6.65E-16	0.121	3.82E-28
5	3	2	6	0.220	1.22E-15	0.220	6.98E-28
5	3	3	9	0.281	1.55E-15	0.247	7.83E-28
5	3	4	12	0.330	1.82E-15	0.309	9.81E-28
5	3	5	15	0.366	2.02E-15	0.352	1.11E-27
5	4	1	4	0.158	2.58E-14	0.158	1.17E-25
5	4	2	8	0.263	4.31E-14	0.263	1.94E-25
5	4	3	12	0.330	5.42E-14	0.307	2.27E-25
5	4	4	16	0.373	6.11E-14	0.364	2.69E-25
5	4	5	20	0.407	6.67E-14	0.400	2.96E-25
5	5	1	5	0.190	2.43E-12	0.190	1.55E-22
5	5	2	10	0.298	3.82E-12	0.269	2.20E-22
5	5	3	15	0.364	4.66E-12	0.363	2.97E-22
5	5	4	20	0.405	5.19E-12	0.402	3.29E-22
5	5	5	25	0.439	5.63E-12	0.439	3.60E-22

Table A.2: The transmission efficiency (frac. trans.) and the relative rotational population (rel. rot. pop.) at the guide exit for each $|J, \tau, M\rangle$ rotational state of ND₂H and NH₂D, up to $J = 5$. The relative rotational population is the transmission weighted by a 9 K Boltzmann distribution for each state. Only low-field seeking states are included in the table. τ is equal to $K_a - K_c$.

ND ₂ H			NH ₂ D			
<i>J</i>	τ	<i>M</i>	Frac. trans.	Rel. rot. pop.	Frac. trans.	Rel. rot. pop.
1	1	1	0.288	0.025	0.215	0.0142
2	-1	1	0.235	0.00184	0.167	0.000575
2	-1	2	0.387	0.00297	0.362	0.00125

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ND ₂ H					NH ₂ D	
J	τ	M	Frac. trans	Rel. rot. pop.	Frac. trans.	Rel. rot. pop.
2	1	1	9.99E-03	1.59E-05	-	-
2	1	2	0.0499	7.78E-05	3.28E-03	1.39E-06
2	2	1	0.00339	4.83E-06	0.0198	7.37E-06
2	2	2	4.40E-04	6.27E-07	0.106	3.95E-05
3	-2	1	0.238	5.33E-05	0.207	8.9E-06
3	-2	2	0.359	8.02E-05	0.348	1.5E-05
3	-2	3	0.423	9.46E-05	0.417	1.79E-05
3	0	1	9.40E-03	2.96E-07	5.07E-03	1.68E-08
3	0	2	0.0604	1.9E-06	1.63E-03	5.41E-09
3	0	3	0.142	4.36E-06	0.068	2.26E-07
3	1	1	2.40E-04	5.15E-09	-	-
3	2	1	1.63E-03	6.08E-09	-	-
3	2	2	3.93E-03	1.43E-08	-	-
3	2	3	9.07E-03	3.3E-08	-	-
3	3	1	1.47E-03	5.35E-09	8.41E-03	1.36E-09
3	3	2	3.60E-03	1.28E-08	3.45E-03	5.57E-10
3	3	3	8.24E-03	2.93E-08	0.045	7.2E-09
4	-1	1	0.019	3.28E-09	6.91E-03	4.08E-11
4	-1	2	0.102	1.84E-08	0.040	2.38E-10
4	-1	3	0.206	3.62E-08	0.102	5.99E-10
4	-1	4	0.291	5.11E-08	0.174	1.02E-09
4	-3	1	0.217	4.65E-07	0.140	1.85E-08
4	-3	2	0.329	7.2E-07	0.327	4.33E-08
4	-3	3	0.391	8.37E-07	0.391	5.17E-08
4	-3	4	0.433	9.28E-07	0.432	5.72E-08

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ND ₂ H					NH ₂ D	
J	τ	M	Frac. trans	Rel. rot. pop.	Frac. trans.	Rel. rot. pop.
4	1	1	7.50E-04	1.28E-11	3.30E-04	8.56E-14
4	1	2	3.48E-03	5.93E-11	1.00E-04	2.59E-14
4	1	3	0.0102	1.74E-10	-	-
4	1	4	0.0226	3.84E-10	-	-
4	2	1	3.80E-04	5.71E-12	1.87E-03	4.15E-13
4	2	2	1.00E-04	1.47E-12	0.0106	2.35E-12
4	2	3	-	-	0.0294	6.52E-12
4	2	4	-	-	0.0550	1.22E-11
4	4	1	0.185	1.27E-09	0.170	1.74E-11
4	4	2	0.300	2.06E-09	0.296	3.04E-11
4	4	3	0.365	2.51E-09	0.364	3.74E-11
4	4	4	0.410	2.81E-09	0.408	4.19E-11
5	-2	1	0.040	1.23E-11	0.0128	3.02E-14
5	-2	2	0.178	5.49E-11	0.0169	3.97E-14
5	-2	3	0.279	8.58E-11	0.161	3.79E-13
5	-2	4	0.341	1.05E-10	0.245	5.76E-13
5	-2	5	0.385	1.18E-10	0.310	1.36E-12
5	-4	1	5.90E-04	6.01E-13	3.45E-03	1.46E-14
5	-4	2	1.00E-03	1.02E-12	0.0169	7.13E-14
5	-4	3	1.63E-03	1.66E-12	0.0434	1.83E-13
5	-4	4	-	-	0.0768	3.24E-13
5	-4	5	0.441	4.5E-10	0.441	8.46E-11
5	-5	1	6.60E-04	6.89E-13	-	-
5	-5	2	9.50E-04	9.92E-13	-	-
5	-5	3	1.75E-03	1.84E-12	-	-

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			ND ₂ H		NH ₂ D	
J	τ	M	Frac. trans	Rel. rot. pop.	Frac. trans.	Rel. rot. pop.
5	0	1	8.50E-04	1.81E-14	5.30E-04	3.82E-17
5	0	2	5.92E-03	1.26E-13	1.93E-03	1.39E-16
5	0	3	0.0193	4.1E-13	-	-
5	0	4	0.0408	8.7E-13	0.0104	7.49E-16
5	0	5	0.0691	1.47E-12	-	-
5	1	1	4.00E-05	5.22E-16	-	-
5	3	1	0.160	1.19E-12	0.130	2.64E-15
5	3	2	0.275	2.05E-12	0.263	5.37E-15
5	3	3	0.341	2.54E-12	0.337	6.88E-15
5	3	4	0.386	2.87E-12	0.386	7.87E-15
5	3	5	0.420	3.13E-12	0.419	1.6E-14
5	4	1	1.70E-04	2.06E-16	-	-
5	4	2	5.40E-04	6.53E-16	-	-
5	4	3	1.28E-03	1.55E-15	-	-
5	4	4	2.41E-03	2.92E-15	-	-
5	4	5	4.53E-03	5.48E-15	-	-
5	5	1	2.20E-04	2.55E-16	1.63E-03	1.94E-18
5	5	2	2.90E-04	3.36E-16	9.06E-03	1.08E-17
5	5	3	3.80E-04	4.4E-16	0.0242	2.89E-17
5	5	4	6.40E-04	7.41E-16	0.0567	6.75E-17
5	5	5	9.20E-04	1.07E-15	0.0708	1.57E-16

B

MATLAB code for the state-tracking trajectory simulation

B.1 Trajectory Simulation Code

The following code was employed in the state-tracking trajectory simulations of ND₃ throughout the detection region as described in Chapter 4. In the simulations presented in this work, the code is run on a Windows 7-based desktop PC running MATLAB R2013a. The code employs the *EField* class developed by C. Rennick [255] to import SIMION potential arrays into the MATLAB workspace as matrices. Functions *mFmat* and *mFed* provide the energy level structure of ND₃, including hyperfine sublevels. These arrays were calculated by van Veldhoven *et. al.* [206].

```
function ND3depolarise(tau)
```

```

% Read in SIMION fields

ef1 = EField.EField3D ('Quad x direction high res', [5000 -5000 -5000 5000 217],
, 1, [-67 -17 -17]*1e-3)

ef2 = EField.EField2D ('REMPI plates (5gu-mm)', [217 300 0 -1900], 1)
ef_mesh = EField.EField2D ('Mesh', [217 217 217 217 0], 0.0013)

ef = EField.EFieldCombined ({ef1 ef_mesh ef2 });

xlin = linspace(0, 1000, 5*500);
xlin = xlin';
grad = ef.gradient([ zeros(size(xlin)), zeros(size(xlin)), xlin]);

figure(1);
plot (xlin, grad(:,1));
figure(2);
quiver3(ones(size(xlin)), 0*ones(size(xlin)), xlin, ...
grad(:,1), grad(:,2), grad(:,3))
grad_norm = sqrt(sum(grad(:,1).^2,2));
depolarise(tau, sqrt(sum(grad(:,1).^2,2)))

end

function [s, logt] = depolarise(tau, E)

```

```

n = []; m = [];
ef = E(:);

for mF = -4:1:4
    % Generate Hamiltonian matrix
    P1 = mFmat(mF);
    maxP1 = max(P1);
    ct = maxP1(1);
    L = (-1 + sqrt(1+8*ct))/2;
    a = 1:L.^2;
    a = reshape(a,L,L);
    H = zeros (L);
    H(triu(a) ~= 0) = P1(:,2);
    Htemp = (H + transpose(H)) - (diag(diag(H)));
    if mF == -4
        H0 = Htemp;
    else
        L0 = length(H0);
        H0 = [H0 zeros(L0, L); zeros(L, L0) Htemp];
    end

P1 = mFed(mF);
maxP1 = max(P1);
ct = maxP1(1);
L = (-1 + sqrt(1+8*ct))/2;
a = 1:L*L;
a = reshape(a,L,L);

```

```

He = zeros(L);
He(triu(a) ~= 0) = P1(:,2);
Hed = He + He' -diag(diag(He));

Hstemp = Hed - Htemp;
if mF == -4
    Hs = Hstemp;
else
    L0 = length (Hs);
    Hs = [Hs zeros(L0, L); zeros(L, L0) Hstemp];
end

% Quantum number labelling
n1 = zeros(L);
n1(triu(a) ~= 0) = P1(:,4);
n2 = diag(n1)';
m1 = ones(1, length(n2)).*mF;
n = [n n2];
m = [m m1];
end

% Initial state

Hstark = H0 + Hs.*ef(1);
[wf, e] = eig(Hstark);
e = diag(e);
[foo, ii] = sort(e);

```

```

wf = wf(:,ii);
iw = 2; % Chosen energy level of ND3
c = wf(:,iw);

% Spatial wavefunctions
th = linspace(-pi/2,pi/2,1000);
cth = cos(th);
sth = sin(th);
P = [];

for ni = unique(n);
    pp = legendre(ni, cth, 'norm');
    mi = abs(m(ni == n));
    pp = pp(mi+1, :)';
    P = [P, pp];
end

[m, ii] = sort(m); % Tidy up matrix
n = n(ii);
P = P(:,ii);

% Evolution of rotational/hyperfine state
nt = length(ef);
logt = linspace(-12, -2, nt);
t = exp(log(10)*logt);
ef; beta = getfield (t, E, tau);

% Plot output

```



```

s = zeros(nt, 1);
figure(3)
p1 = plot(logt, s, 'b-');
hold on;
p2 = plot(logt, beta(1:end)./max(beta(1:end)), 'r--')
xlabel ('log_{10} t');
ylabel ('Population')
hold off;
drawnow

figure(4)
plot(logt,s,'b-')
xlabel ('log_{10} t');
ylabel ('Population');

figure(5)
plot(logt, 1-(beta(1:end)),'r--')
xlabel ('log_{10} t');
ylabel ('Population')

% Time stepping
Ny = angmom(n, m);
wfo = wf;
pp = zeros(length(nt), length(n));

for it = 1:nt-1
    b = beta(it+1);

```

```

    dt = t(it+1) - t(it);
    db = (b - beta(it))./dt;
    U = expm (-1i*dt*((H0 + ef(it).*Hs) + db*Ny));
    c = U*c;
    Pt = transpose(wf)*c;
    Pt = conj(Pt).*Pt;
    pp(it, :) = Pt;
    s(it) = 0;
    for x = 1:144;
        s(it) = s(it) + Pt(x);
    end
    wf; e = eig(H);
    e = diag(e);
    over = abs(wfo'*wf);
    [foo, ii] = max(over, [], 2);
    wf = wf(:,ii);
    % e = e(ii);
    wfo = wf;
    plotwf(P, b, th, cth, sth, c);
    set(p1, 'Xdata', logt(1:it), 'Ydata', s(1:it));
end

plotwf(P, beta(end), th, cth, sth, c);

end

%-----

```

```
function Ny = angmom (n,m)
```

```
% Matrix formulation of the J_y angular momentum operator
```

```
n = repmat (n, length(n), 1);
```

```
m = repmat (m, length(m), 1);
```

```
Ny = zeros (length(n),length(n));
```

```
ii = m'-1 == m;
```

```
n' == n;
```

```
Ny(ii) = -0.5*1i*sqrt((n(ii)-m(ii)).*(n(ii)+m(ii)+1));
```

```
ii = m'+1 == m;
```

```
n' == n;
```

```
Ny(ii) = 0.5*1i*sqrt((n(ii)+m(ii)).*(n(ii)-m(ii)+1));
```

```
end
```

```
%-----
```

```
function [ef, beta] = getfield (t, E, tau)
```

```
% Calculate electric field magnitude and angle from the lab frame z-axis
```

```
for i = 1:length(t)
```

```
    Ez(i) = E(1)*exp(-t(i)/tau(1));
```

```
    Ex(i) = E(2)*(1-exp(-t(i)/tau(2)));
```

```
    ef(i) = norm([Ex(i) Ez(i)]);
```

```
    beta(i) = atan(Ex(i)/Ez(i));
```

```
end
```

```
end
```

```
%-----
```

```
function plotwf (P, beta, th, cth, sth, c)
```

```
% Plots wavefunction in the xz plane
```

```
a = P*c;
```

```
a = abs(a).^2;
```

```
z = a.*cth';
```

```
x = a.*sth';
```

```
area = polyarea(z, x);
```

```
a = 0.5*a./sqrt(area);
```

```
R = [cos(beta) -sin(beta); sin(beta) cos(beta)];
```

```
r = R*[z'; x'];
```

```
z = r(1,:);
```

```
x = r(2,:);
```

```
end
```

B.2 Computation of Wigner-3j symbols

The following MATLAB code was employed to compute the Wigner 3j symbols in Equation 4.20, which provides the rotation operation between the local field frame and fixed field frame.

```
function wigner = Wigner3j( j123, m123 )

    % Compute the Wigner 3j symbol using the Racah formula.
    %
    % W = Wigner3j( J123, M123 )
    %
    % J123 = [J1, J2, J3], with the condition:
    %      |Ji - Jj| <= Jk <= (Ji + Jj)    (i,j,k are permutations of 1,2,3)
    % M123 = [M1, M2, M3], with the conditions:
    %      |Mi| <= Ji    (i = 1,2,3)
    %      M1 + M2 + M3 = 0
    % All Ji and Mi have to be half integers (correspondingly).
    %
    % Reference:
    % Wigner 3j-Symbol entry of Eric Weinstein's Mathworld:
    % http://mathworld.wolfram.com/Wigner3j-Symbol.html

    j1 = j123(1); j2 = j123(2); j3 = j123(3);
    m1 = m123(1); m2 = m123(2); m3 = m123(3);

    if ( j3 > (j1 + j2) ) || ( j3 < abs(j1 - j2) )
        wigner = 0;
    return
```

```

end

% Simple common case
if ~any( m123 ) && rem( sum( j123 ), 2 )
% m1 = m2 = m3 = 0 & j1 + j2 + j3 is odd
    wigner = 0;
    return
end

% Calculation
t1 = j2 - m1 - j3;
t2 = j1 + m2 - j3;
t3 = j1 + j2 - j3;
t4 = j1 - m1;
t5 = j2 + m2;

tmin = max( 0, max( t1, t2 ) );
tmax = min( t3, min( t4, t5 ) );

t = tmin : tmax;

wigner = sum( (-1).^t .* exp( -ones(1,6) * ....
gammaln( [t; t-t1; t-t2; t3-t; t4-t; t5-t] +1 ) + ...
    gammaln( [j1+j2+j3+1, j1+j2-j3, j1-j2+j3, ...
-j1+j2+j3, j1+m1, j1-m1, j2+m2, j2-m2, j3+m3, j3-m3] +1 ) ...
    * [-1; ones(9,1)] * 0.5 ) ) * (-1)^( j1-j2-m3 );
end

%-----

```


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