



A New Instrument to Study Vibrationally Enhanced Chemistry on Metal Clusters in the Gas Phase

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I dedicate this thesis to Anna

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Error is ever the sequence of haste.

— Arthur Wellesley, First Duke of Wellington

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Abstract

Vibrational excitation of molecules prior to collision and subsequent reaction can change the outcome of the reaction by either enhancing or diminishing reaction rates or even changing product distributions. Studies of the effects of vibrational excitation on reactive outcomes have been limited to extremely simple gas phase systems or extended metal surfaces. The first part of this thesis details the design, development and construction of a new instrument to study the effects of vibrational excitation on the reactions of ionic metals species (single atoms or clusters) reacting with neutral species in the gas phase. Starting from a collision cell designed from a simple theoretical model of collisions, a tandem ToF mass spectrometer was designed from scratch to collide ionic metal species with single neutral gas molecules with controlled energies and good spatial focus prior to detection of the collision products. Laser ablation sources provide very poorly spatially and energetically resolved ion packets requiring extensive ion optics to control them. While the instrument development is still ongoing, due to difficulties associated with controlling ion kinetic energies and maintaining good transmission, an instrument capable of carrying out reactive collisions has been successfully developed.

The second part of the thesis presents infrared multi-photon dissociation spectroscopic studies of Ho^+ cations with CO_2 and OCS molecules. Both $\text{Ho}(\text{CO}_2)_n^+$ and $\text{Ho}[\text{O}(\text{CO}_2)_n]^+$ are obtained when Ho is ablated in the presence of CO_2 seeded into Ar . Spectra were recorded in two spectral ranges: $1650\text{--}1950\text{ cm}^{-1}$ and $2300\text{--}2450\text{ cm}^{-1}$ and assigned using predicted structures (generated from potential energy surface searches) using density functional theory (DFT). CO_2 binds in a molecular/end-on fashion to Ho^+ in $\text{Ho}(\text{CO}_2)_n^+$ complexes and showed little evidence of activation. $\text{Ho}[\text{O}(\text{CO}_2)_n]^+$ complexes in which $n \geq 3$, by contrast, show clear spectroscopic evidence of the formation of a carbonate radical anion moiety ($\{\text{CO}_3\}^{\delta-}$). The characteristic vibrational band of this structure red-shifts with increasing CO_2 coordination displaying clear evidence of charge transfer between ligands mediated by a metal centre. $\text{Ho}[(\text{OCS})_n]^+$, $\text{Ho}[\text{S}(\text{OCS})_n]^+$ and $\text{Ho}[\text{O}(\text{OCS})_n]^+$ complexes, are generated when Ho is ablated in the presence of OCS seeded into and He . Spectra of each molecule were recorded between $1200\text{--}2400\text{ cm}^{-1}$ and assigned based on DFT calculations. OCS was found to react with Ho^+ ions to form both $\text{HoO}^+ + \text{CS}$ and $\text{HoS}^+ + \text{CO}$ as well as bind in a molecular fashion analogous to CO_2 . Both HoO^+

and HoS^+ were observed to produce $\{\text{CO}_2\text{S}\}^{\delta-}$ and $\{\text{COS}_2\}^{\delta-}$ respectively that preferentially bound to the Ho^+ via sulphur atoms. The COS_2 C=O bond stretch is observed to red-shift with increasing complex size illustrating that additional OCS ligands donate electron density to stabilise the thiocarbonate in an identical fashion to the behaviour seen in $\text{Ho}[\text{O}(\text{CO}_2)_n]^+$ species.

List of Publications

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List of Abbreviations

CAD		Computer Aided Design
CCS		Collision Cross Section
		CMB Crossed Molecular Beam
COM		Centre Of Mass
DFG		Difference Frequency Generation
DFT		Density Functional Theory
IR		Infrared
IVR		Internal Vibrational Redistribution
MFP		Mean Free Path
MOSFET		Metal-Oxide-Semiconductor Field-Effect Transistor
OPO		Optical Parametric Oscillator
OPA		Optical Parametric Amplifier
PES		Potential Energy Surface
PEL		Potential Energy Landscape
RCS		Reactive Cross Section
reToF		Reflectron Time Of Flight
RF		Radio Frequency
SHG		Second Harmonic Generation
ToF		Time Of Flight
YAG		Yttrium Aluminium Garnet

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1 | Introduction

On a microscopic level, for a reaction to occur, the reactant species must collide, bringing them close enough in space to exchange atoms or electrons. However, mere collision is not sufficient; the colliding species must also have the correct orientation and ample energy to overcome any energy barrier to reaction. Consequently, in the majority of cases, colliding species simply scatter, exchanging translational or even internal energy, without reacting. Under specific conditions where both orientation and energy requirements are met, chemical bonds may be broken or formed, resulting in a reaction. It is precisely this latter scenario that captures the interest of chemists and forms the focus of this thesis. Specifically, this work details the design, development and construction of a novel instrument to investigate how the addition of energy in both vibrational and translational degrees of freedom influences the outcomes of reactive collisions between gas-phase transition metal ions/clusters and small, neutral gas molecules.

In addition to the developmental work associated with the new instrument, several infrared (IR) spectroscopic studies have been performed on cationic complexes formed when Holmium is ablated in the presence of CO₂ and OCS seeded into Ar/He. In order to carry out these spectroscopic experiments, multiple upgrades to the experimental apparatus were also carried out.

1.1 Motivation

1.1.1 Molecular Activation on Metals and Catalysis

Catalysts are materials that can increase the rate of a chemical reaction, without themselves being consumed. The addition of a catalyst to a reaction provides an alternative, lower energy, path through which the reactants can form the products, as illustrated by the red route in Figure 1.1. With fixed external conditions (e.g. temperature), the catalyst increases the rate of reaction, as a greater fraction of the reacting species will have the required energy to pass over the barrier upon collision which, for a fixed collision rate, will result in a higher number of "successful" reactive collisions. Catalysts may also change the

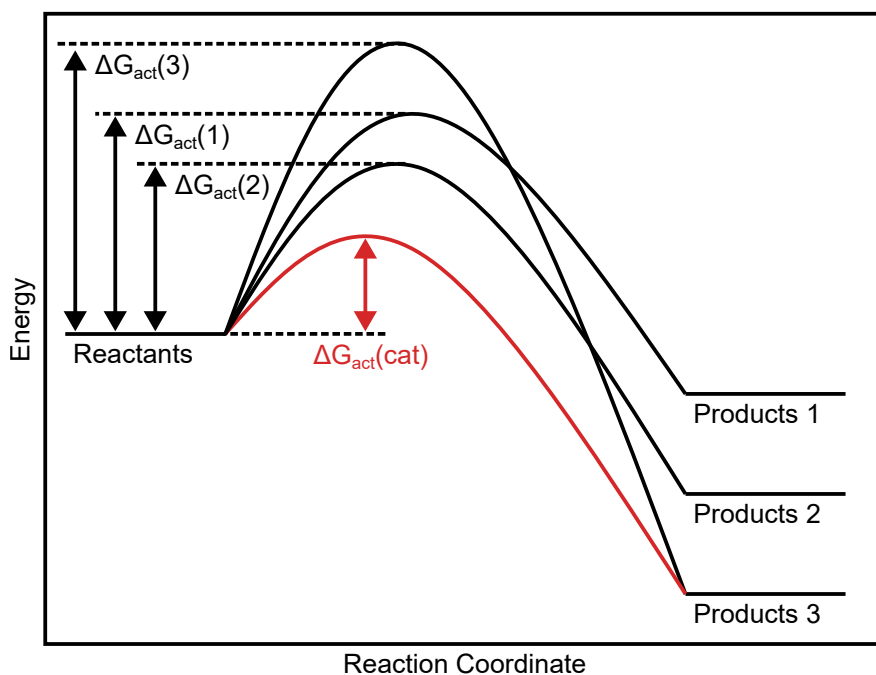


Figure 1.1: Cartoon potential energy surface showing a series of energy paths that a system of reactant molecules may take to generate a series of three different product molecules. The red path represents the path enabled through the addition of a catalyst.

product distribution within a given reaction. Within Figure 1.1, there are three possible outcomes from the reaction. Without the catalyst, product set 2 is kinetically favoured as it has the lowest barrier, however, upon addition of the catalyst, product set 3 is favoured as its barrier has been lowered below the other routes, meaning that a collision between the reactants is more likely to generate product set 3 than any other product set.

As a concept, catalysts were first described by Elizabeth Fulhame in 1794.^[1–3] Throughout the early 18th century, many different researchers (including Berzelius, Faraday, Davy and Döbereiner)^[4] began to report examples of catalysis. However, it was not until the 1880s that a systematic study of catalysis of reactions (by acids and bases) would be undertaken by Ostwald (earning him the Nobel Prize in 1907).^[5] Vladimir Ipatieff, termed the father of catalysis, then took the concepts of catalysis from the previous century and developed them into industrially relevant applications.^[6] Today, more than 80% of chemicals produced in the world rely upon catalysis, meaning that catalysts represent a 33.9 billion dollar industry.^[7, 8] Products from reactions involving catalysis touch almost every aspect of modern life from transport (e.g. catalytic converters within vehicle exhausts)^[9], to agrochemicals (e.g. NH_3 production)^[10], through to fine chemical production (e.g.

catalytic cracking)^[11].

The production of chemicals imparts a huge burden on the environment. Around 7% of global anthropogenic global greenhouse gas emissions result from the energy production required to support the industry.^[12] Catalysts offer a route by which these energy requirements may be reduced, both minimising costs and the environmental impact of modern industrial chemical manufacture. Hence, research into and improvement of catalysis is of key importance for the future.

Two categories of catalysts exist: homogeneous or heterogeneous. Heterogeneous catalysis occurs when the catalyst functions in a different phase than the reactants. Due to the phase difference between the (usually solid-state) catalyst and the gas/liquid phase reactants, catalysis occurs on the surface of the catalyst material itself (the gas/liquid-solid interface). Many industrially relevant catalysts are formed from transition metals and their oxides^[13] such as the Harber-Bosch process where an iron catalyst is used^[14] or in steam reformation where a nickel catalyst is used.^[15] The surface of catalysts is far from uniform and usually contains numerous defect sites (edges, grooves or protruding atoms) where catalytic activity occurs due to their instability.^[16] The majority of industrial catalysis are heterogeneous in nature due to their robustness and lower operational cost compared to homogeneous catalysts.

Despite its ubiquity, heterogeneous catalysis is (generally) much more poorly understood. This stems from the fact that looking at detailed chemistry on surfaces remains challenging, requiring highly specialised experiments under ultrahigh ($< 1 \times 10^{-8}$ mbar) vacuum conditions. Exacerbating this further, theoretical models of surfaces are still too computationally intensive or inaccurate to model surface chemistry at the level of detail needed to properly understand the underlying chemistry. Many of the inaccuracies associated with these models result from poor approximations of surface effects or ignoring them entirely. Gas-phase metal ions and clusters can provide tractable models for the defect/active sites on the catalytic materials without the disadvantages of surface experiments or additional complicating effects from surface perturbations.^[17–20]

Homogeneous catalysis occurs where the catalyst is in the same phase as the reactants and typically is carried out in the solution phase. Outside of biological catalysis (with

enzymes) and organocatalysis (catalysis with small organic molecules), the majority of heterogeneous catalysis involves (transition) metal ions/clusters.^[21] The study of these systems within the gas phase elucidates the structure and dynamics without complicating factors such as solvent molecules and counter-ions. Metal clusters and ions may be catalytic in their own right and can be dispersed within silica or zeolite materials to form novel single-site type catalysts.^[22–24]

Through an improved understanding of the gas-phase reactions of metal atoms and clusters, it is hoped that better and more effective catalysts can be developed, thus reducing energy consumption and producing useful chemicals in a faster and cleaner manner than previously possible. Part II of this thesis concerns the spectroscopic investigation of Ho^+ cations and their reactions with CO_2 and OCS in order to determine whether or not holmium can act as a catalyst.

1.1.2 Vibrations and Reactivity

Selective bond cleavage and formation could be considered as one of the "holy grails" of chemistry, as it would provide unprecedented control over building molecules. Currently, selective bond cleavage and formation is possible only in limited scenarios, and to understand reactivity, the concept of a potential energy surface (PES) must first be understood. Developed in 1913^[25], a PES is a $3N$ dimensional surface providing the complete description of the potential energy of a system of N atoms based on their positions. They have been extensively detailed previously.^[26, 27] Briefly, a sufficiently complex PES contains features that represent all key aspects of chemical reactions between the atoms within the system that they represent. Its minima indicate stable configurations of molecules and its local maxima (specifically saddle points) represent transition states. For a reaction to occur, the system of atoms must pass from one minimum to another via a transition state. As the transition states lie higher in energy relative to the minima, energy must be supplied to the reactant molecules and it is this energy that represents the energy barrier to the reaction.

With enough energy, the arrangement of atoms may pass from a minimum, over the transition state, to another minimum thus overcoming the energy barrier. Under ther-

mal conditions, the energy is statistically partitioned into a series of quantised modes: translational, rotational, vibrational and electronic. Energy associated with rotational, vibrational and electronic energy is considered to be internal to the molecule whereas translational energy is considered to be external to the molecule. The different forms of energy within the molecule are nonequivalent in the way that they couple to and aid the reactive species in passing over the transition state. For a collection of molecules under thermal conditions, the energy is distributed into all modes (dependent upon their quantised energy level separation) and any resulting reaction results from a combination of all of the forms of energy making their individual contributions hard to distinguish from one another.

If, in theory, a collision between two molecules with perfectly defined translational energy in defined quantum states can be modelled, then the effects of adding energy into the different modes can then be predicted. The addition of rotational energy and electronic excitation on the outcomes of reactivity falls outside the scope of this thesis so is not considered here.^[28–31] The earliest theoretical framework through which the difference between vibrational and translational energy can be understood was developed by Polanyi in the 1970s based on observations from a wealth of experimental and theoretical data.^[28] He predicted that the outcomes of reactions in which the transition state was early, central or late with respect to the reaction coordinate would differ in their response to the addition of translational or vibrational energy, based on how type of molecular motion coupled to the transition state. Figure 1.2 illustrates three possible reactions for the simple exchange of atom B, between atoms A and C as shown in Reaction 1:



in terms of bond distances (A–B and B–C). Figures 1.2 (a) and (c), illustrate the case in which the transition state is early, whereas Figures 1.2 (b) and (d) show the case in which the transition state is late.

Where the transition state is early, the translational energy vector couples much more effectively with the transition state as compared to the vibrational energy of AB, as the translational energy vector aligns with the motion needed to overcome the transition state.

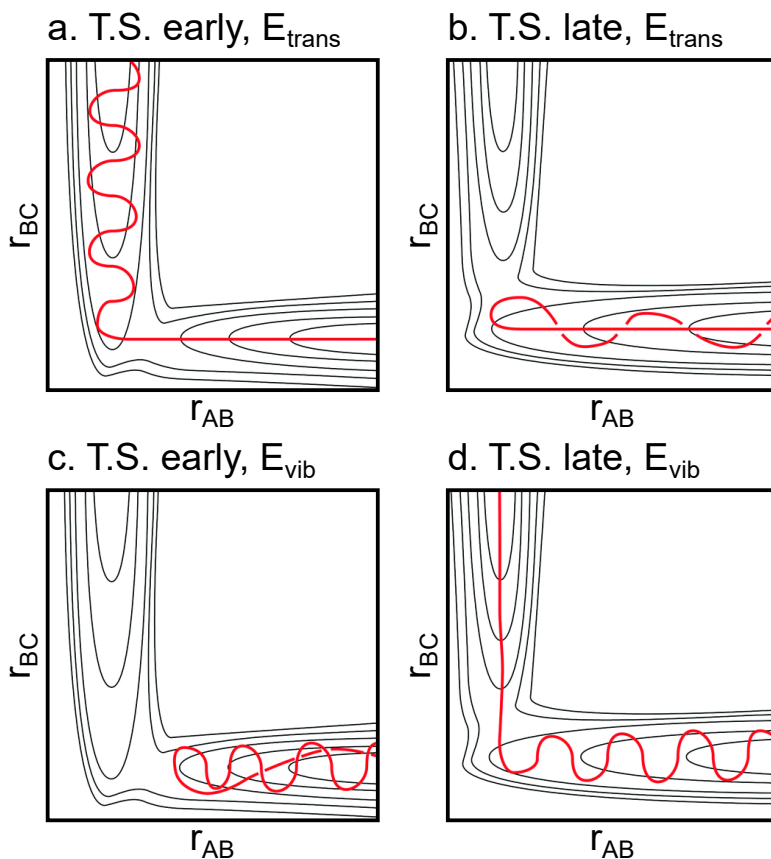


Figure 1.2: Schematic diagrams illustrating potential energy surfaces encountered as function of the bond lengths A–B and B–C within a triatomic system of three atoms: A, B and C. An energy maximum (transition state) is encountered within each of the subfigures, although its position is moved between a/c and b/d from "early" to "late". This nomenclature refers to where the transition state occurs relative to the bond length A–B - i.e. the transition state is considered to be early when the A–B distance is long and vice versa. (a) Illustrates the case where energy is placed into the translational motion of A relative to BC with an early transition state. (b) Illustrates the case where energy is placed into the translational motion of A relative to BC with a late transition state. (c) Illustrates the case where energy is placed into the vibrational motion of BC with an early transition state. (d) Illustrates the case where energy is placed into the vibrational motion of BC with a late transition state. This figure is adapted from the work of Beck and coworkers.^[32]

Once the exchange of B occurs, the translational energy is localised into the BC bond as the BC vibrational energy vector is in the same plane as the original translational vector. In the other extreme case, where the transition state is late, the vibrational energy within AB couples much more effectively with the transition state, as they overlap much better than the translational energy which is almost orthogonal to the transition state vector. Equally, the AB vibrational energy is deposited into translational energy of BC and A moving apart as these vectors are parallel. Although Polanyi's rules are a simplification of the markedly more complex reality, they do illustrate the fact that the type of energy added to systems can influence the outcome of a chemical reaction. Since the development of Polanyi's rules almost 50 years ago, a variety of improved models that can (at least) partially capture the behaviour in polyatomic systems have been developed.^[33–55] These are discussed in more detail later in this section.

While there has been a wealth of experimental evidence for vibrationally altered chemistry recorded within simple gas phase systems^[46, 56–74], the effects of adding vibrational energy to reactions involving metal species have been limited. Aside from a singular study from the Mackenzie group^[75], the majority of work carried out has focused on the dissociative adsorption of methane on metal surfaces.^[76–101] By way of example, CH₄ has been observed to adsorb to Ni(100) surfaces in a dissociative fashion although there is a significant barrier to dissociation. The effect of adding vibrational energy to the system (as opposed to translational energy) has been observed to be highly non-statistical. Exciting CH₄ to the first excited state of its symmetric stretching (a_1) mode ($v_1 = 1 \leftarrow v_1 = 0$) is an order of magnitude more effective at promoting CH₄ chemisorption to an Ni(100) surface than adding the equivalent amount of translational energy to the CH₄^[82], whereas exciting the asymmetric stretching (t_2) mode to its first excited state ($v_3 = 1 \leftarrow v_3 = 0$) was shown to be fractionally less effective than adding the equivalent amount of translational energy.^[88] Not only does adding vibrational energy, as opposed to translational energy, to the reactive species have an effect on the reactive outcomes, but the specific mode to which the vibrational energy is added may also have an effect. The Beck and Utz groups have carried out a wide range of similar studies on the behaviour of methane (and its deuterated analogues) on various metal surfaces including Pt(110/111/210/211/531) and Ni(100/110/111).^[76–78, 80–101] Both vibrational enhancements and suppression (relative to

translational energy) have been observed in all systems, but these vary dramatically with the metal type and specific surface structures. In addition to the mode selective effects observed, in experiments involving the deuterated analogues, vibrational energy placed into specific modes (e.g. C-H in CD₃H) were able to promote the selective breaking of bonds, illustrating the potential for selective bond breaking using vibrational energy.

The highly non-statistical nature of the behaviour observed readily evinces the use of dynamics to understand the behaviour. Before dynamical studies can be performed, accurate potential energy surfaces must be generated. This is an extremely challenging process, especially for larger systems with many degrees of freedom. Previously, these limited the studies of CH₄ dissociatively binding to metal surfaces to low dimensional PESs in which the CH₄ is modelled as a pseudo diatomic^[33, 34, 44, 49–55] or in reduced dimensionality.^[102] More recently, with advances in computational power and improved methodologies, full dimensional PESs have been developed.^[103] Developed by Guo and coworkers, the first 15-dimensional PES was defined using DFT for the CH₄ dissociating on Ni(100). They were then able to use this PES in a quasi-classical dynamics study that was able to capture the mode selective effects observed experimentally.^[35] More recently the Zhang and Guo groups have developed 15-dimensional PESs of CH₄ and on Ni(111) and Ni(100) surfaces using neural networks and have used them in quantum dynamical studies.^[36–41] The use of neural networks dramatically reduces the computational cost of developing highly dimensional PESs by predicting potential energy surfaces based on a model as opposed to having to calculate them directly.

The fact only three groups have developed PESs for these CH₄-metal surface systems and carried out dynamical studies on these systems highlights the difficulty associated with their generation, and as such, other work has been carried out simplifying the PESs. One such approach taken by Jackson and coworkers utilised the concept of the reaction path Hamiltonian (RPH) first postulated by Miller *et al.*^[104, 105]. The RPH simplifies the N -dimensional PES to a 1-dimensional reaction path leading from the reactants to the products (via a transition) state, massively reducing the number of data points required to define the surface to the point where full *ab initio* calculations could be used to determine points on the surface. Jackson’s (quantum) RPH method has since been

used to successfully describe the experimentally observed mode selective effects of CH_4 dissociation on both Ni and Pt.^[42, 43, 106–110] An even simpler model, the sudden vector projection model, was developed by Guo and coworkers as an extension of Polanyi’s rules for polyatomic molecules and has been applied successfully to rationalise experimentally observed behaviours.^[45]

Outside of the work with methane and surfaces, vibrational alterations to chemistry occurring with metals and small neutral molecules have been previously observed within the Mackenzie group. In these infrared photodissociation (IRPD) experiments, excitation of the asymmetric stretching (t_2) mode of methane prior to its interaction with Au^+ cations was seen to enhance the proportion of methane that dehydrogenated upon binding to the Au^+ cation.^[75] This work, coupled with the rich vibrationally enhanced chemistry seen on surfaces previously, inspired the development of a new instrument within the group to study the reactions of metal ions under single collision conditions with vibrational enhancements. The preliminary design, development and construction of this instrument forms the basis of this thesis. The difficulty of performing surface experiments cannot be understated, and the convoluted effects of the metal surfaces are still poorly understood despite very complex theoretical models. By performing similar experiments with gas-phase metal clusters or atoms instead of surfaces, the behaviours should be easier to model, as well as understand, while retaining a higher degree of control over the collisions themselves. Beyond this, the size-dependent properties of metal clusters (unlike bulk surfaces) could generate highly interesting chemistry and the new instrument enables the study of all of these.

1.2 Studying Gas-Phase Reactions of Metals

The past 60 years have seen a remarkable amount of work examining the reactions of single atoms and clustered transition metal and lanthanide ions in the gas phase with a huge variety of different molecules including CO_2 , N_2O and CH_4 .^[111–143] A variety of methods have been employed ranging from selected-ion-flow mass spectrometry, Fourier transform ion-cyclotron resonance and guided ion beam mass spectrometry. Often performed under multiple collision and thermalised conditions, these studies showcase the possible reactions

of gas-phase metal ions but often provide little insight into the non-statistical effects of energy placed into the reactions as already discussed in the previous section.

Ideally, investigations into the non-statistical effects of energy type on reactions would consist of performing collisions between reactant species with perfect energy resolution (i.e. in defined quantum states) being intersected followed by recording the spatial and temporal evolution of the scattered products. Such experiments would allow for a full understanding of the structural outcomes as well as the disposal of energy within the products. While experiments such as this do exist for simple systems such as NO/rare gas atoms collisions^[144–147], they are often restricted to specific and simple systems thus proscribing their use in the metal-gas reactions of interest in this thesis.

Supersonic molecular/ion beams make ideal tools for the study of reactions in the gas phase as they can form rotationally and (mostly) vibrationally cool beams in which the species within the beam are spatially isolated from one another.^[148] The isolation of the species within the beam prevents the exchange of energy with other species in the beam through collision, allowing for higher control over the internal energy of the reactants. Many advances within recent years have been made in controlling and selecting not only the translational energy but also the internal states of molecules and ions within molecular beams.^[149–152] According to Armentrout^[153], there are four possible collision experiment types that may be performed with ion beams:

1. Ion beam and gas experiments
2. Crossed ion/molecular beam experiments
3. Merged ion/molecular beam experiments
4. Guided ion beam and gas experiments

Ion beam-gas experiments represent the earliest and simplest of all of these experimental methods used to measure reaction cross-sections. Within an ion beam experiment, energy-selected and mass-selected ions are passed through a collision cell containing the reactant gas at low pressure (to prevent multiple collisions from occurring). If angular distribution measurements are desired, then the cell can be fitted with a wide exit aperture or a rotatable aperture. However, if only the identities of the products are of interest,

then they can simply be detected using mass spectrometry. While simple compared to the other techniques, these types of experiments have been widely employed with some success to measure both collision cross-sections as well as some reactive cross-sections and their dependence on translational energy.^[154–164] Despite their success, there are issues associated with their performance. Loss of signal at low ion energies is the most notable issue, although poor product collection efficiencies have also been identified.^[153] Signal loss at low collision energies can be partially mitigated in heavy ion/light neutral collisions due to more of momentum being excluded from the centre of mass collision frame.^[165]

Crossed molecular beam (CMB) methods involve the intersection of two molecular beams and the detection of scattered products. Initially developed by Taylor and Datz for metal atom reactions in the Oak Ridge National Labs^[166], early crossed molecular beam (CMB) experiments were constrained to alkali earth metals for a number of years due to limitations in detection technology.^[167] It was not until the 1960s that Lee and coworkers were able to develop a so-called "universal" CMB experiment which, coupled with the concurrent development of supersonic beam sources and the development time-of-flight (ToF) method of velocity analysis, allowed the CMB method to be applied to the study of the (translational) energy dependence of reactions over the past 60 years.^[168–179] While the crossed molecular beam methodology has been by far the most successful methodology for the examination of collision and reactive cross-sections, it suffers from the same issue as the collision cell methodology in that it struggles to obtain data on low-energy collisions without considerable loss of signal.^[153]

In an attempt to address the lack of experiments measuring the effects of low translational energies on reaction cross-sections, the merged ion beam technique was developed.^[180, 181] Merged ion beam techniques are able to achieve low collision energies (between 0.3–10 eV) within the lab frame with excellent energy resolution by propagating two different molecular beams along a common axis at fractionally different speeds. While they have been employed with some success in the study of ultra-cold reactions^[182–188], difficulties, such as low reactive yields and the enormous expense associated with running these experiments, have limited their use.^[189–191]

Guided ion beam experiments improve upon the two major weaknesses of ion beam-gas

experiments by both increasing the collection efficiency of the reaction products and maintaining ion signals at low ion energies through the use of radio-frequency (RF) ion guides to radially confine ions during the collision processes.^[192] Initially developed by Teloy and Gerlich in 1974^[193], the use of guided ion beams in measuring ion-neutral translational energy dependence was sparse^[194, 195] until Armentrout and coworkers developed a new guided ion beam mass spectrometer.^[196]

Whilst the preceding methods have seen some use in investigations of the reaction dynamics of metal containing systems^[197], this thesis focuses on reactions of transition metal ions with more complex neutral molecules which have seen little investigation with these methods. Armentrout and coworkers have used the guided ion beam methodology to carry out hundreds of investigations into the translational energy dependence of transition metal and lanthanide cations with many different gas phase neutral molecules.^[198–250] Armentrout and coworkers generate metal cations using a variety of different methods including electron impact, glow discharge, laser vaporization, microwave discharge or surface ionization to generate an ion beam which is then decelerated to a known kinetic energy before being passed into an octupole. The octupole ion guide then passes through a collision cell filled with the reaction gas of interest at a low enough pressure to achieve single ion-molecule collisions. The reaction products are detected using a quadrupole mass filter and dynode combination.^[251] With this apparatus, it is possible to measure the reaction cross-section for an ion-neutral collision over a range of user-defined energies. The apparatus is optimised for the transmission of ions rather than for mass (or energy) resolution, as without good transmission, reaction cross-sections are impossible to measure.^[251]

From the brief literature review presented within this section, it should be clear that although a variety of different experiments have been successfully performed to measure the effects of vibrational energy on the outcomes of reactions, these studies have been limited to very simple gas-phase systems or to the dissociative chemisorption reactions of methane taking place on transition-metal surfaces. Although the work of Beck, Utz, and their co-workers has demonstrated mode selective chemisorption of methane, these experiments have not been used to investigate other gas phase molecules or more complex surfaces. The theory underpinning these surface experiments has also remained extremely

difficult, limiting its use to only a select few groups specialising in wavepacket propagation techniques. Whilst Armentrout and coworkers have investigated a multitude of reactions of ionic metal clusters and complexes with neutral gas-phase molecules, these studies have remained limited to measuring only translational energy dependence.

An experiment that is able to measure both the translational and vibrational energy dependence of the reactions of ionic metal clusters and complexes with neutral gas-phase molecules would extend the work of Armentrout and coworkers with an additional degree of control, whilst expanding the possible range of reactions on which vibrationally enhanced or mode selective experiments could be performed compared to the surface experiments of Beck and Utz. Performing experiments on ionic clusters and complexes, as opposed to extended metal surfaces, would significantly reduce the complexity associated with theoretically modelling the effects of vibrational energy addition, whilst simultaneously allowing the size effects often seen within metal clusters to be investigated. Part I of this thesis concerns the development of a novel instrument capable of measuring both the translational and vibrational energy dependence of the reactions of ionic metal clusters and complexes with neutral gas-phase molecules under single collision conditions.

1.3 Generating Metal Clusters in the Gas-Phase With Laser Ablation

According to an excellent review by Duncan and coworkers^[252], gas-phase metal clusters have been generated in a huge variety of different ways including: Knudsen ovens^[253–261], thermionic emission from heated metal salt cathodes^[262], decomposition of volatile organometallics^[252], discharge sputtering sources^[263–266], electrospray ionisation^[267–271] and laser vaporisation (ablation)^[272–278]. The work presented in this thesis relies exclusively on laser vaporisation to produce ions in the gas phase, so only this method of cluster generation is explored in detail here. For information on other cluster generation methodologies, readers are directed to a review by De Heer.^[279]

Developed independently by both Smalley and Bondybey in 1981^[272–278], the source uses ablation to generate a plasma from a metal surface prior to seeding the plasma into a rare

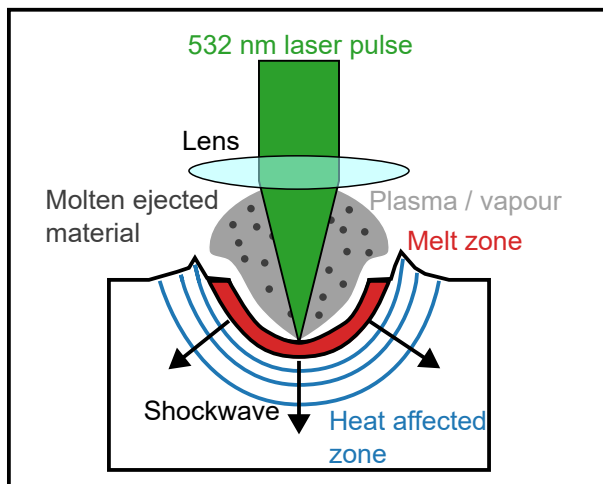


Figure 1.3: Ablation of a metal surface. The ablation laser causes local super-heating of the metal surface which, in turn, causes the ejection of plasma / vapour along with molten material. This Figure is adapted from the work of Van Der Heide and coworkers.^[284]

gas atom pulse that is supersonically expanded to generate a molecular beam.

1.3.1 Laser Vaporisation

Laser ablation is the process in which laser light, focused onto a small point of a (metal) surface, generates a plasma containing atoms, ions (even doubly charged ions^[280]) and electrons.^[252] While poorly understood, it is thought that laser light hitting the surface excites internal degrees of freedom (rotational, vibrational and electronic) within the surface structures of the material. This energy can remove electrons from atoms generating ions but, through various mechanisms, can also be transferred into kinetic energy of the atoms/ions causing them to eject from the surface and form a vapour and a plasma containing cations, neutral species and anions (and electrons). The plasma conditions can be tuned to favour the production of particular species.^[274–276, 281–283] The ablation process is illustrated in the cartoon in Figure 1.3.

A variety of different laser systems have been used for laser ablation including excimer lasers, Cu vapour lasers and various harmonics of Nd:YAG laser systems.^[252] The pulse energy is the most important parameter for the laser used, and it depends heavily upon the system selected. Transition metals typically require between 10-20 mJ for optimal ablation.^[285–287] Beyond the pulse energy, the pulse duration and wavelength as well as the focus of the laser beam have all been shown to influence the ablation dynamics.^[252, 288] The

focus of the beam onto a small point has been demonstrated to be of critical importance making the Gaussian beams (from Nd:YAG laser systems) preferable to rectangular beams from excimer laser systems.^[252] The experiments presented within this thesis all use the second harmonic of an Nd:YAG laser system (532 nm) focused to a point on the metal target. It is common to rotate the target being ablated to ensure the ablation occurs from "fresh" material.

Laser vaporisation, although something of a "black box" approach due to the generally poor understanding of ablation, does present significant advantages over the other methods of generating gas-phase metal atoms/clusters. Relative to the methods presented previously it uses very little sample within each laser shot and is applicable to a much wider range of systems. With a stable light source, laser ablation sources are considerably more stable when compared to many other sources.^[252]

1.3.2 Gas Pulse

Having produced the plasma via laser vaporisation, Smalley and Bondybey pulsed an inert gas through the plasma in such a manner that supersonic expansion occurred.^[272–278] Developed by Kantrowitz and Grey^[289], supersonic expansion involves expanding gas from a region of high pressure (P_1) to a region of low pressure (P_2) through an orifice in which the orifice diameter (Φ) is smaller than the mean free path of the gas (λ) or alternatively, the expansion must have a Knudsen number (K_n) defined as

$$K_n = \frac{\lambda}{\Phi}, \quad (1.1)$$

greater than one.

The pressure differential between the two regions draws the molecules, through the orifice, to the low pressure region. Due to the molecular mean free path being markedly shorter than the orifice diameter, molecules passing through the orifice (as well as in the region immediately after), they undergo many collisions with one another. Collisions between molecules that impart velocity along the same axis as the orifice are ultimately more successful in passing through aperture than those that do not.^[290] The net result of the

supersonic expansion is a molecular beam within which most, if not all, of the (random) translational, rotational and vibrational energy of the metal clusters generated in the plasma is converted into translational energy in the direction of the beam. If the neutral expansion gas is modelled as an ideal gas, the beam velocity can be calculated using:

$$u_{\max} = \left(\frac{2k_B T}{m} \frac{\gamma}{\gamma - 1} \right)^{\frac{1}{2}}, \quad \text{where } \gamma = \frac{C_p}{C_v}, \quad (1.2)$$

k_B is the Boltzmann constant, T is the temperature, m is the mass of the gas molecule, C_p is the specific heat capacity of the molecule at constant pressure, and C_v is the specific heat capacity of the molecule at constant volume.^[148, 291] The resulting supersonic expansion is illustrated in Figure 1.4 (a) along with shock-waves resulting from the the molecules passing through the sound barrier. These shock-waves, if allowed to continue unimpeded, will disturb the beam downstream of the zone of silence.^[292] To avoid this, the expansion is skimmed within the zone of silence to generate a molecular beam as shown in Figure 1.4 (b).

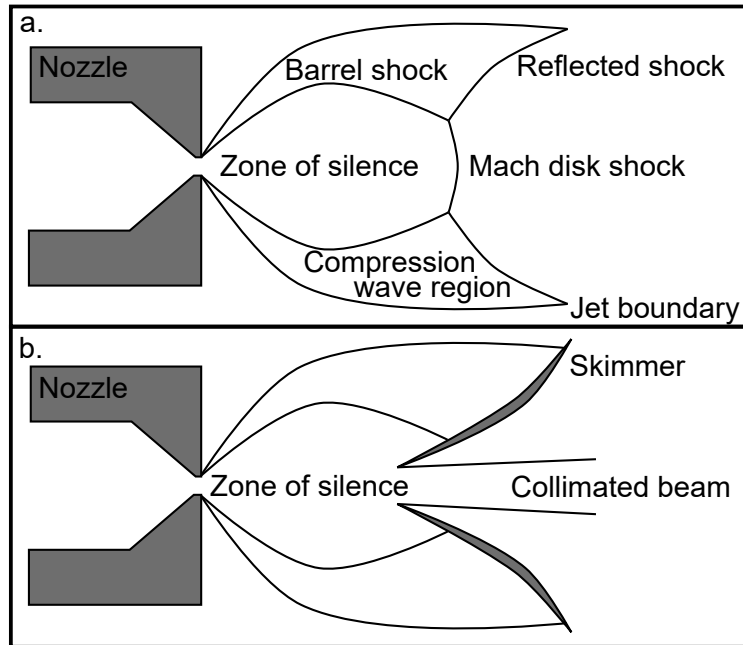


Figure 1.4: (a) Diagram of the supersonic expansion from a nozzle. The various shock waves associated with supersonic expansion are also illustrated. (b) The same supersonic expansion as illustrated in (a) with the addition of a skimmer within the zone of silence that generates a collimated molecular beam. These figures are adapted directly from Claire Vallance's reaction dynamics lecture notes.^[290]

Within the experiments presented in this thesis, metals are ablated into the supersonically expanding gases to generate the metal clusters or metal ligand complexes. Initial cluster formation occurs through three-body collisions shown in Figure 1.5 (a) rather than two-body collisions. Conservation of energy prevents the production of stable species in two-body collisions, meaning that three-body collisions, as opposed to two-body collisions, are the only route through which initial cluster formation can occur. Clusters may also cool through the loss of constituent atoms via evaporative cooling, shown in Figure 1.5 (b). Radiative cooling, shown in Figure 1.5 (d), is slow on the timescale of most experiments so contributes very little to cluster cooling and growth.

Collisional cooling, shown in Figure 1.5 (c), is a major route (during supersonic expansion) by which both translational and internal (rotational, vibrational or electronic) energy is removed from excited state species. Translational energy is transferred most efficiently, followed by rotational energy and then vibrational energy. Electronic quenching efficiency is heavily dependent upon the species and the excited states in question.^[293] While supersonic expansion is often able to produce rotationally and vibrationally cool species, there is often a non-equilibrium distribution of electronic states of metal species within molecular beams.^[294, 295] Collisions also allow for the generation of cations, neutrals and anions through the exchange of electrons.^[296, 297]

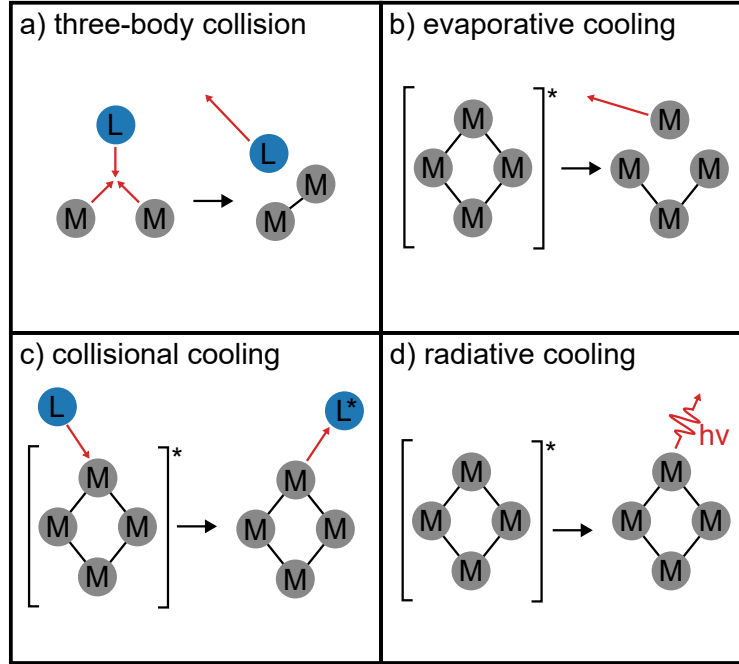


Figure 1.5: (a) Three-body collisions between two constituent cluster atoms and a gas molecule. The gas molecule removes the excess energy generated upon bond formation in the collision. (b) Evaporative cooling from an excited state metal cluster through loss of a constituent atom. (c) Collisional cooling of an excited state metal cluster through the transfer of energy to a neutral gas atom in a collision. (d) Radiative cooling from an excited state metal cluster through the emission of a photon.

1.3.3 Laser Vaporisation Source Designs

There are a multitude of different source designs within the community, with each design optimised to generate a certain type of species.^[252, 298–303] However, only the two source geometries used to generate the cationic metal species presented within this thesis are explored here. The two geometries used are each shown in Figure 1.6.

Figure 1.6 (a) shows the cutaway source design inspired by the work of Duncan and coworkers.^[252] The source geometry allows the ablation plume to be generated in the throat of the supersonic expansion, allowing the ablation to occur into an almost free jet expansion of the gas. It reduces the pressure of neutral gas that the ablation plume encounters, which avoids metal-metal condensation, favouring the production of single metal species and generating an extremely cold supersonic expansion which allows for tagging of metals with rare gas atoms.^[252]

The geometry shown in Figure 1.6 (b) is the channel source and represents a "standard" design. The supersonic expansion in the gas pulse is directed into a channel which fills with gas prior to ablation. As the gas pulse occurs into a channel rather than a vacuum, the gas does not undergo a supersonic expansion (at this point), allowing metal-metal condensation to occur along the length of the channel. Thermalisation of the gas and ablated material occurs with the block held at room temperature.

Figure 1.6 (c) illustrates the way in which the source block is mounted within the experiment. In both cases, the ablation laser is brought in via a small channel within the block to strike a metal disk target mounted to a rotating stage rotated by a Faulhauber 8016006SR-K2570 motor. The target assembly may be translated relative to the source block to allow ablation on tracks at different radii on the target (also driven by a Faulhauber 8016006SR-K2570 motor). The mounting plate is joined to three rods set into a flange. The source blocks are electrically isolated from other parts of the source and can be floated at a potential relative to the skimmer. This can aid in generating larger number densities of ions from the source.

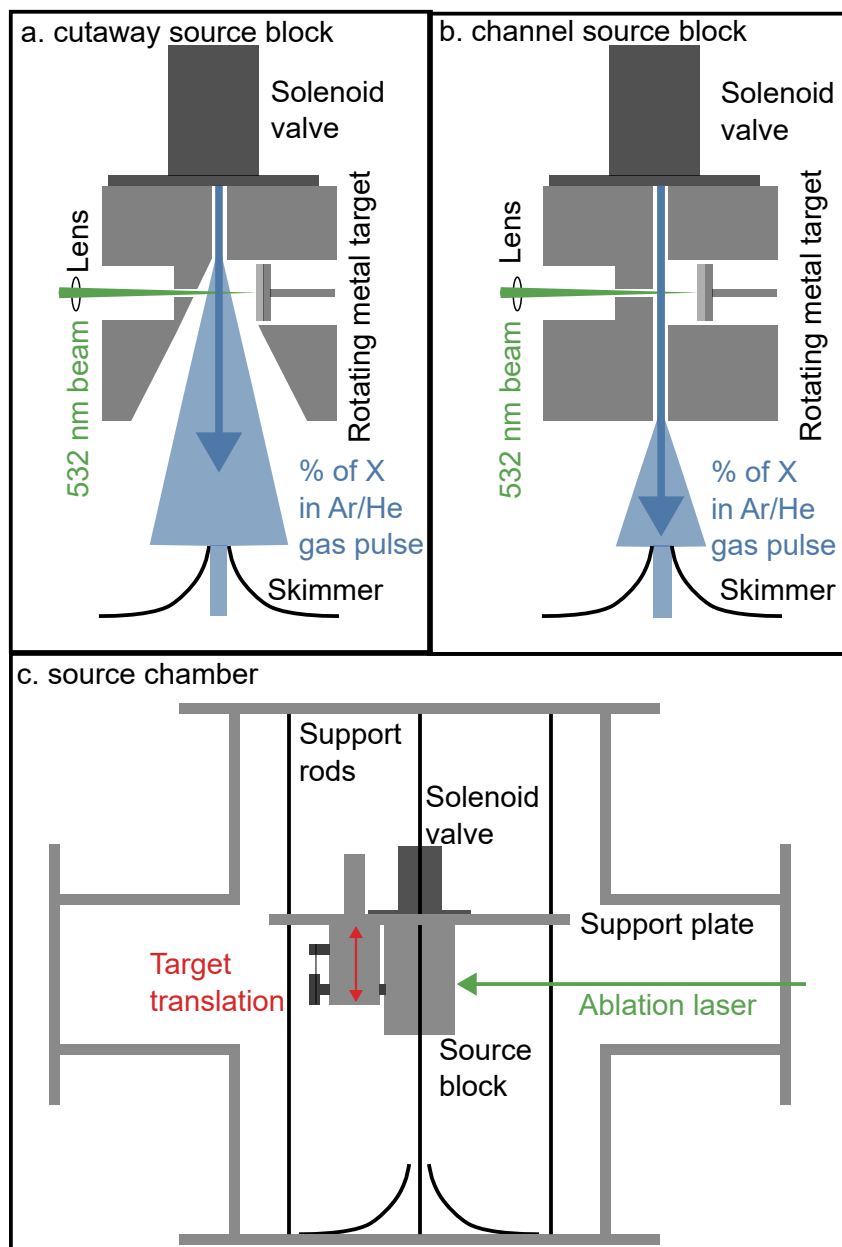


Figure 1.6: (a) A schematic diagram of the cutaway source block used to generate ions via laser ablation. (b) A schematic diagram of the channel source block used to generate ions via laser ablation. (c) A schematic diagram of how the source is mounted and arranged within the chamber.

1.4 Molecular Collisions

For a reaction between two species to occur, the first thing that must occur is a collision. The mathematical descriptions of collisions between molecules are presented here.

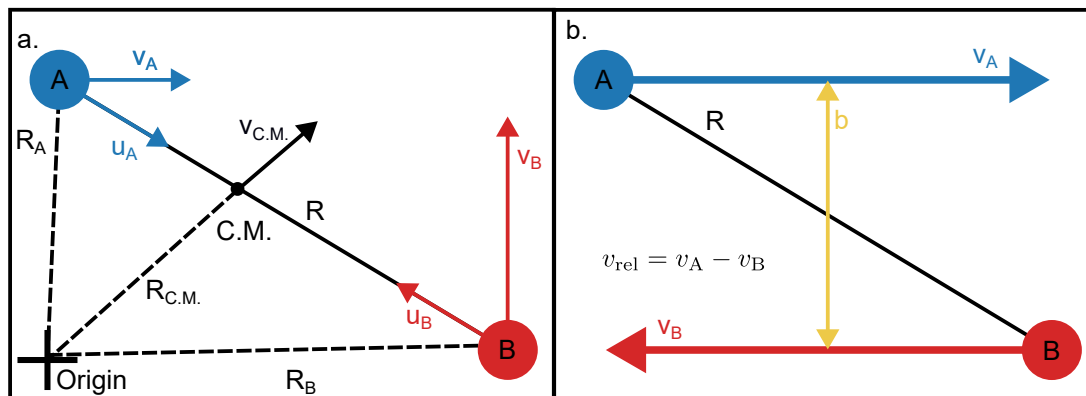


Figure 1.7: (a) Schematic diagram illustrating the motion of two particles A and B moving with velocities v_A and v_B respectively. The system can be described with respect to the lab frame of reference or the centre of mass (COM) frame of reference and both are illustrated. Within the centre of mass frame, the particles move relative to the centre of mass which also moves. Collisions are much easier to examine within the COM frame. (b) A schematic diagram of two particles moving relative to one another. The separation of the velocity vectors of each particle at this time is described by the impact parameter b (shown in yellow). These figures are adapted from "Molecular Reaction Dynamics" by Levine.^[304]

1.4.1 Motion in the Centre of Mass Frame

Given a single collision between two molecules, A and B, in order to describe the collision fully in 3D space with reference to an arbitrary origin, 2 sets of time dependant ($3N$) coordinates would be required (assuming no external force acts). To simplify this, the collisions can be considered with respect to the centre of mass (COM) frame as opposed to the laboratory frame.

Two molecules (A and B) are illustrated undergoing motion in Figure 1.7. As only their relative motion contributes to their collision dynamics, consideration of their motion is limited to the centre-of-mass (COM) frame rather than the laboratory frame (LF) which massively simplifies the number of vectors needing to be considered simultaneously.^[304] Within the COM frame, the particles are separated by a vector R and move with respect to one another with (relative) velocity v . The COM itself is also moving with a constant momentum.

1.4.2 Collision Probability

If molecule A is passed through a volume containing a high enough number density of molecule B, then they will collide (the "volumes" of two species A and B must overlap in space). The mean free path (MFP/ λ) represents the distance that molecule A, on average, will travel before it collides with B (for a given number density of B).^[305] It is related to the collision cross section (CCS/ σ) (a measure of collision probability) through the expression:

$$\lambda = \frac{1}{\sigma n_B}, \quad (1.3)$$

where n_B represents the number density of the species.^[305] Physically, the CCS represents an area that generates an extruded volume as A moves through the distribution of B. Any particles of B falling within this volume can be considered to collide with A. The CCS can essentially be thought of as a measure of the likelihood that two species will collide and it is typically used in place of the MFP as it is not dependant on the number densities of the molecules involved. The collision cross-section (σ) is related to the impact parameter shown in Figure 1.7 through the integral:

$$\sigma = \int_0^\infty 2\pi b db, \quad (1.4)$$

over the range of values of b that lead to a collision.^[304]

1.4.3 Reactive Collisions

Not all collisions that occur lead to a reaction - for every impact parameter, a proportion of the collisions that occur will not result in reaction. This is defined by a parameter known as the opacity function P . The differential reaction cross-section ($d\sigma_R$) is related to the opacity function (P) and the impact parameter b by:

$$d\sigma_R = 2\pi b P(b) db. \quad (1.5)$$

Integrating Equation 1.5 across all impact parameters yields the integrated reaction cross-section as shown in the expression:

$$\sigma_R = 2\pi \int_0^\infty bP(b)db. \quad (1.6)$$

The integrated reaction cross-section represents the probability that two species will collide and react. The reaction cross-section depends upon the collision energy, a relationship quantified by the excitation function, $\sigma_R(E_{\text{coll}})$.^[290] There are two broad categories of excitation function, corresponding to reactions without a barrier and reactions with an activation barrier respectively, and each are illustrated in Figure 1.8. For reactions without a barrier, even with very low collision energies, the reaction will occur due to attractive forces acting over large distances. The picture is different for reactions with barriers as only once the barrier to reaction is exceeded is a non-zero reaction cross-section encountered. The reaction cross-section increases up to a maximum where the relative approach velocities of the species allow the reaction barrier to be overcome and place the colliding species close enough together for the barrier to be overcome. In both cases, reactions cross sections decrease to the hard sphere limit at non-zero impact parameters at high collision energies due to the fact that their high relative velocities prevent the attractive forces between the reactants acting for long enough to pull them together.

1.4.4 Collision Energy

Within the COM frame, only the kinetic energy associated with the relative velocity of the species A and B is available in the collision. The rest of the energy is associated with the movement of the centre of mass, which must be conserved in the collision. The distribution of the energies is determined by the relationship:

$$E_{\text{tot}} = \frac{1}{2}Mv_{\text{COM}}^2 + \frac{1}{2}\mu v_{\text{rel}}^2 \quad (1.7)$$

where M represents the mass of the COM frame (defined as $m_A + m_B$), v_{COM} represents the velocity of the COM (defined by $(m_A v_A + m_B v_B)/M$), μ represents the reduced mass of the particles, $(m_A m_B)/(m_A + m_B)$, and v_{rel} represents the relative velocity of A and B,

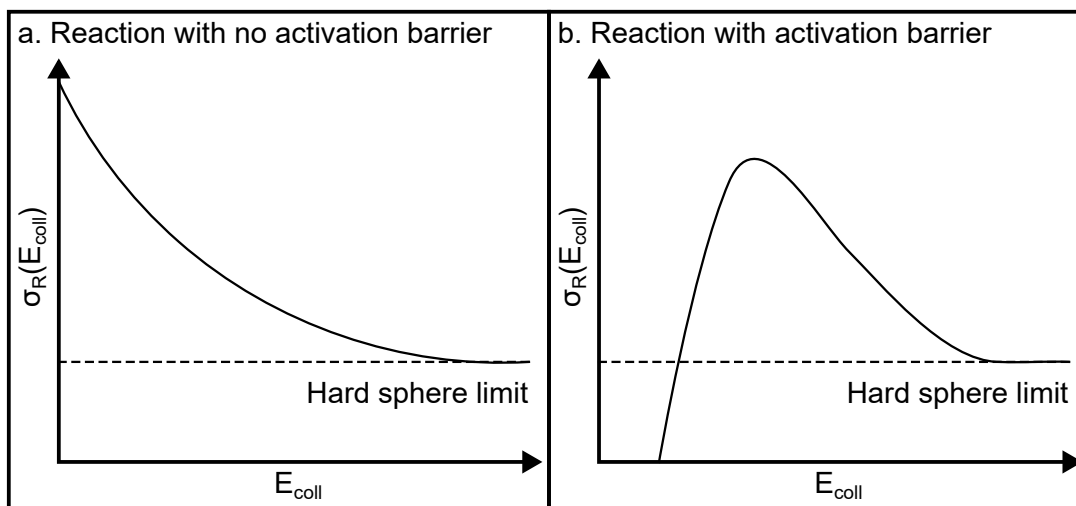


Figure 1.8: Examples of the two broad categories of excitation function as a function of the collision energy (E_{coll}) (a) Excitation function for reactions with no activation barrier. (b) Excitation function for reactions with an activation barrier. These Figures are adapted directly from Claire Vallance's reaction dynamics lecture notes.^[290]

which is determined by the difference in velocity vectors: $v_A - v_B$.^[290] Equation 1.7 shows that the lab-frame kinetic energy is partitioned into the relative motion of the particles (shown in red in Equation 1.7) and the motion of the centre of mass (shown in blue in Equation 1.7).

Previously, the vector $\mathbf{R}$ was defined - it describes the separation of the particles. As the particles come together, both the direction and magnitude of $\mathbf{R}$ change, meaning the kinetic energy associated with the relative motion of the two particles may also be split into two components: the energy associated with the change in distance between the particles and the energy associated with the change in direction (i.e. the energy associated with the orbital angular momentum) of the system.^[304] The energy associated with the orbital angular momentum cannot be used within the collision to overcome any energy barriers (this concept forms the basis of the centrifugal barrier), meaning that the total energy actually available within a collision is given by:

$$E_{\text{col}} = \frac{1}{2}\mu v_{\text{rel}}^2 - \frac{\dot{R}^2 b^2}{2r^2} \quad (1.8)$$

where μ is the reduced mass of the colliding particles A and B, v_{rel} is their relative velocity, $\dot{R}$ is the rate of change in the vector $\mathbf{R}$, b is the impact parameter and r separation of

the particles (magnitude). As the particles approach one another, an increasing amount of energy is transferred into the orbital angular momentum term, preventing a closer approach than the impact parameter (b).^[290]

1.5 Mass Spectrometry

The work presented within this thesis relies heavily upon mass spectrometry to separate ions of different mass-to-charge ratios for both detection and filtration purposes. Both the novel experiment presented in Chapters 2 through 4 as well as the spectroscopy experiment presented in Chapters 6 through 7 rely on ToF mass spectrometry for the detection of mass-resolved ions.

1.5.1 Time-of-Flight Mass Spectrometry

An ion of charge q moving through a potential difference of ΔV will acquire kinetic energy E_k defined by:

$$E_k = \Delta V q = \frac{1}{2}mv^2 \quad (1.9)$$

where m is the mass of the ion and v is the velocity after acceleration.^[306] If a series of ions with different masses start from the same point within the electric field, each ion will be imparted with identical kinetic energy. Based on the relationship shown in Equation 1.9, if the ions are then allowed to fly freely over an arbitrary distance D , ions of different masses will separate in time and space, allowing ion masses to be measured as a function of their time-of-flight (ToF). The principle of this is illustrated in Figure 1.9 (a). In reality, it is impossible to impart ions within a packet with identical kinetic energies and have them start from the same single point, as ion packets always have a spatial distribution which means ions are imparted with energy distributions, complicating matters.

In 1955, Wiley and McLaren developed a system of three electrodes (repeller, extractor and ground), allowing for ion acceleration in two stages which, through careful control of the ratios of potential applied to the electrodes, uses the kinetic energy distribution imparted to the ions to spatially focus them at position D downstream of the electrode system.^[307] The system of plates is illustrated in Figures 1.15 a and b. The total kinetic

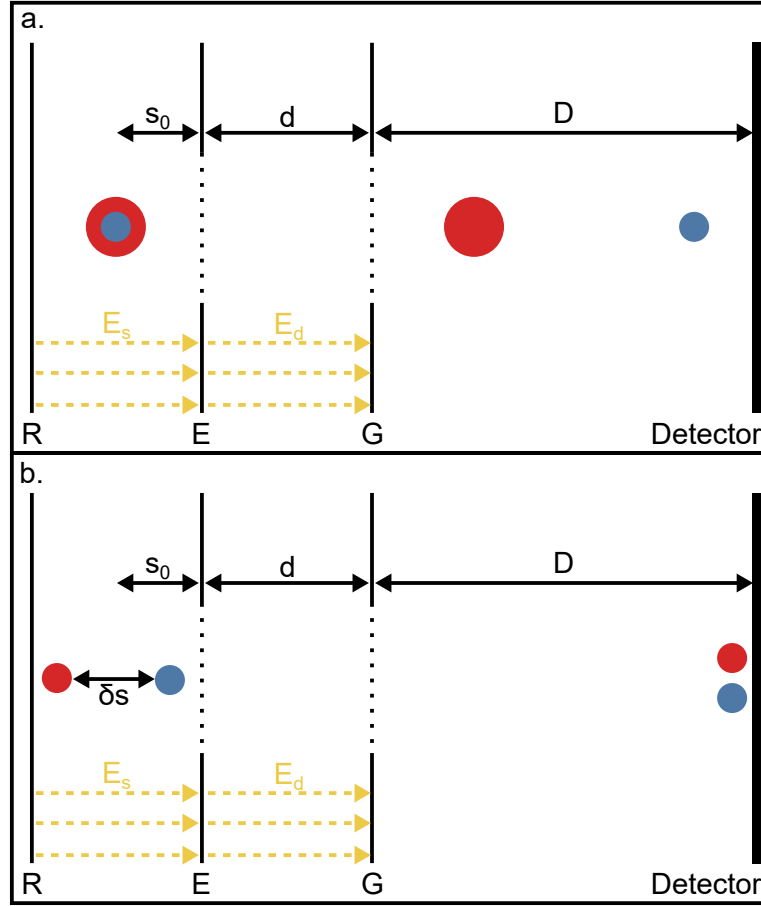


Figure 1.9: Both sub-figures illustrate Wiley-McLaren lenses used to accelerate ions for ToF mass spectrometry. The lens consists of three electrodes: the repeller (R), the extractor (E) and the ground electrode (G). The electric field in yellow (E_s and E_d) are generated by pulsing potentials onto R and E. Ions are detected at the end of the flight tube. (a) The red and blue circles indicate ions of different masses separating in time-of-flight. (b) Illustrates ions of identical mass but different starting positions within the electrodes arriving at the detector at the same time due to the spatial focusing achieved by Wiley-McLaren lenses.

energy (U) of the ion starting distance s from the extractor electrode in Figures 1.9 (a)/(b), imparted by the Wiley-McLaren lens is given by the relationship:

$$U_{\text{total}} = U_0 + qsE_s + qdE_d \quad (1.10)$$

where U_0 is the ion's initial kinetic energy, q is the charge on the ion, s_0 is the distance of the ion from the extractor plate (see Figure 1.10 (b)), E_s is the electric field within the repeller and extractor region, d is the extractor ground plate separation and E_d is the electric field generated between the extractor and ground plates. The total time-of-flight

(ToF) of the same ion under the same conditions is given by the sum:

$$t_{\text{total}} = t_s + t_d + t_D = \frac{(2m)^{\frac{1}{2}}}{E_s q} \left((U_0 + E_s q s)^{\frac{1}{2}} - U_0^{\frac{1}{2}} \right) + \frac{(2m)^{\frac{1}{2}}}{E_d q} \left(U_{\text{total}}^{\frac{1}{2}} - (U_0 + E_s q s)^{\frac{1}{2}} \right) + (2m)^{\frac{1}{2}} \frac{D}{2U_{\text{total}}^{\frac{1}{2}}} \quad (1.11)$$

where m is the mass of the ion, D is the free flight distance, and all other parameters were defined previously.

While the total ToF of an ion includes the time it takes for the ion to exit the Wiley-McLaren electrodes, the ToF of the ions within the Wiley-McLaren electrodes is generally very short relative to the free flight region, allowing the total ToF to be approximated to simply the free flight region ToF:

$$t_{\text{total}} \approx t_D = (2m)^{\frac{1}{2}} \frac{D}{2(U_0 + q s E_s + q d E_d)^{\frac{1}{2}}}. \quad [306] \quad (1.12)$$

Assuming that the initial kinetic energy of the ions (U_0) is negligible, the dependence of the ToF on the mass and charge can then be simplified by placing everything else within the constant α , yielding the linear relationship:

$$t_{\text{total}} \approx \alpha \left(\frac{m}{q} \right)^{\frac{1}{2}}. \quad (1.13)$$

The time it takes the ions to accelerate out of the Wiley-McLaren electrodes, whilst small, is non-zero. In addition to this, the electronics used to record mass spectra are imperfect, and there is a slight delay in the ion hitting the detector and a signal being registered. These small additional time components can be accounted for with a constant β yielding the final relation:

$$t_{\text{total}} \approx \alpha \left(\frac{m}{q} \right)^{\frac{1}{2}} + \beta \quad (1.14)$$

The α and β are easily determined through the assignment of known peaks within a ToF spectrum to their masses. The relationship in Equation 1.14 demonstrates that mass

separation using the Wiley-McLaren electrodes is possible.

The ion illustrated in red in Figure 1.9 (b) starts further back from the extractor electrodes as compared to the ion shown in blue. Despite the red ion's increased kinetic energy relative to the blue ion, it has further to travel. Thus, at some distance away from the Wiley-McLaren electrode, the red ion will catch up with the blue ion and overtake it. The position of this point at distance D downstream of the Wiley-McLaren lens, calculated based on the derivative of ToF with respect to the distance s being set to zero^[307],

$$D = 2s_0k_0^{\frac{3}{2}} \left(1 - \frac{1}{k_0 + k_0^{\frac{1}{2}}s_0} \frac{d}{s_0} \right), \quad \text{where} \quad k_0 = \frac{(s_0E_s + dE_d)}{s_0E_s}, \quad (1.15)$$

and s_0 is the distance halfway between the ions. If the detector is placed at a distance D from the lens, then ions with the same mass will arrive at detector D at the same time, despite being imparted with different kinetic energies and travelling different distances.^[307] The result of this is improved resolution compared to what was previously achievable. Equation 1.15 clearly shows that the "focal" distance D can be tuned through alteration of the lens geometry (d or s_0) and the ratio of the electric fields (E_s and E_d). With a fixed electrode geometry and fixed detector position, ions can be spatially focused onto the detector through tuning of the electric field ratio (E_s/E_d), i.e. tuning the applied potentials to the repeller and extractor electrodes.

1.6 Vibration of Molecules

The work presented within this thesis relies on vibrational excitation as both a structural probe and a means by which quantised energy can be added to molecules in a non-statistical manner. The theory that underpins molecular vibrations and how molecules absorb IR light is presented within this section.

1.6.1 Harmonic oscillator model

1.6.1.1 Classical harmonic oscillator model

Diatomic molecules (e.g. CO) may be modelled as harmonic oscillators and thus obey Hooke's law,

$$\vec{F} = -k_F \vec{x}, \quad (1.16)$$

where k_F is the force constant of the oscillator and $\vec{x}$ is the displacement vector from equilibrium.^[308] Simply put, this means that as the atoms within the diatomic species move apart, they experience a restoring force proportional to their displacement from equilibrium. The potential energy of this system is given by:

$$V(x) = \frac{1}{2} k_F x^2. \quad (1.17)$$

Based on Newton's second law, Equation 1.16 can then be written as,

$$\mu \frac{d^2 x}{dt^2} = -k_F x, \quad (1.18)$$

where μ is the reduced mass of the system and $-k_F$ and x represent the force constant and displacement respectively.^[305] One possible solution of the differential equation presented in Equation 1.18 is:

$$x(t) = A \cos \left(\sqrt{\frac{k_F}{\mu}} t + \phi \right) \quad (1.19)$$

where A represents the oscillation amplitude, and ϕ represents the phase shift of the oscillation.^[308] The relationship in Equation 1.19 shows that stronger bonds (higher force constants) have high oscillation frequencies, but species with a higher reduced mass will have lower oscillation frequencies.

1.6.1.2 Quantum harmonic oscillator model

This classical model may then be extended to the quantum regime (known as the quantum harmonic oscillator) by writing a Hamiltonian based on a nuclear wavefunction (describing

the coordinates of the nuclei):

$$\left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + \frac{1}{2} k_F(x)^2 \right] \psi_{\text{nuc}} = E \psi_{\text{nuc}} \quad (1.20)$$

where x is the displacement from equilibrium bond geometry, ψ_{nuc} is the nuclear wavefunction and E is the energy of the system.^[27] Determined through perturbation theory, the eigenvalues (G_v) from this Hamiltonian take give the quantised vibrational energy levels that take the form (in units of wavenumber):

$$\tilde{G}_v = \left(v + \frac{1}{2} \right) \omega_e \quad (v = 0, 1, 2, 3 \dots) \quad \text{where} \quad \omega_e = \frac{1}{2\pi\tilde{c}} \sqrt{\frac{k}{\mu}}, \quad (1.21)$$

where v is the vibrational quantum number, and ω_e (also shown in Equation 1.21) is the vibrational constant.^[309] The vibrational constant is dependent upon the reduced mass (μ) and bond strength (k) in the same way as the classical system. $\tilde{c}$ is the speed of light in cm s^{-1} .^[309] The major difference between the classical and quantum systems is that the energy levels within the quantum system are quantised into vibrational energy levels shown in Figure 1.10. Molecules may be excited between these vibrational levels through the absorption of (IR) photons resonant with the energy difference between the levels. The difference between two adjacent energy levels (v and v') and the energy of an absorbed photon is then given by:

$$E = \omega_e h \tilde{c}.^{[309]} \quad (1.22)$$

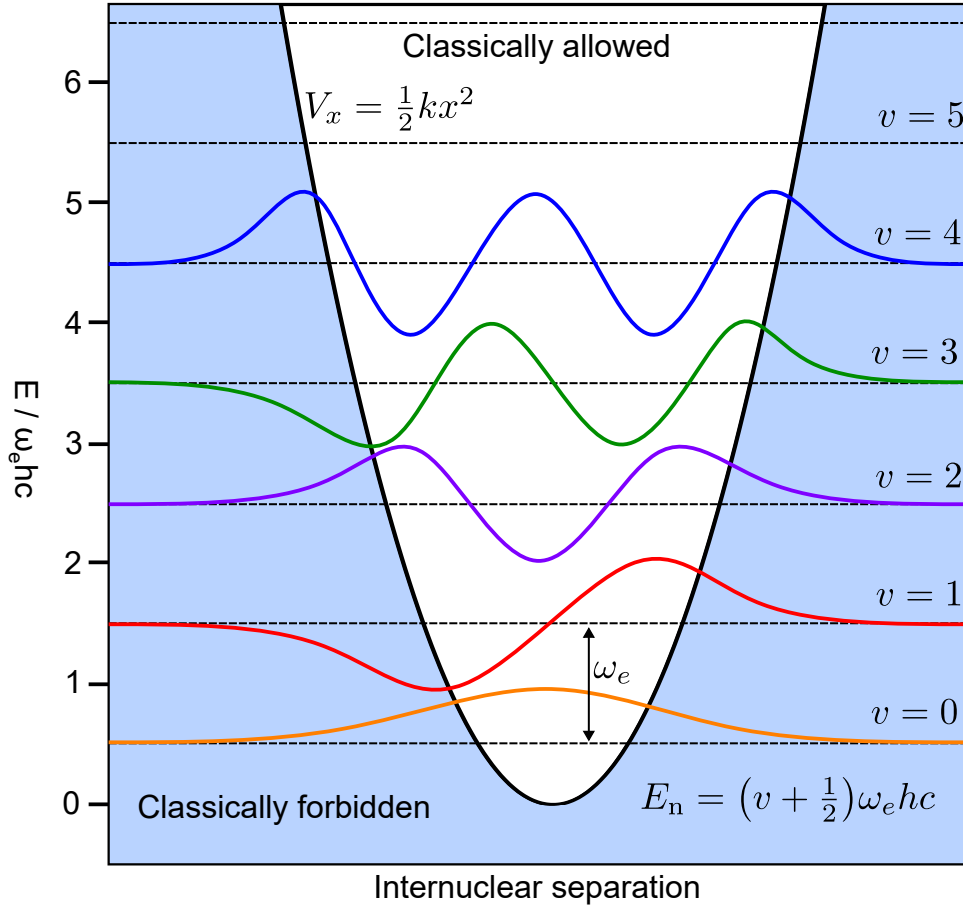


Figure 1.10: The simple harmonic oscillator potential energy well for a diatomic molecule. the first five wavefunctions of each state are illustrated at each vibrational energy level.

The wavefunctions $\psi_n(x)$ are eigenfunctions of Equation 1.20 that correspond to these energies and take the form of a Gaussian function multiplied by a Hermite polynomial ($H_n(\beta x)$):

$$\psi_n(x) = N_n \exp\left(\frac{-\beta^2 x^2}{2}\right) H_n(\beta x), \quad \text{where } \beta = \sqrt{\frac{m\omega}{\hbar}}. \quad (1.23)$$

N_n is the normalisation constant, m is the mass of the species and ω is the angular frequency.^[310] Hermite polynomials of degree n in x take the generic form:

$$H_n(x) = (-1)^n \exp(x^2) \frac{d^n}{dx^n} (\exp(-x^2)). \quad [311] \quad (1.24)$$

1.6.1.3 Selection Rules

Transitions between vibrational states within the quantum harmonic oscillator model are constrained by the selection rules derived in the following. For a vibrational transition to be allowed and observed (with high intensity), a change in the molecule's dipole moment must occur during the vibrational transition.^[310] The transition dipole moment ($R_{vv'}$) for a vibrational ($v - v'$) transition is determined by the transition dipole moment operator ($\hat{\mu}$) acting on the vibrational ground-state wavefunction (ψ_v) and the excited state wavefunction ($\psi_{v'}$):

$$R_{vv'} = \int_{-\infty}^{\infty} \psi_{v'} \hat{\mu} \psi_v dq, \quad \text{where} \quad \hat{\mu} = \sum_i -q_i r_i. \quad (1.25)$$

The transition dipole moment operator ($\hat{\mu}$) may also be written as a Taylor expansion in terms of scaled vibrational coordinates (q).^[312] The Taylor expansion, truncated at the second-order, is:

$$\hat{\mu} = \hat{\mu}_{q=0} + q \left(\frac{d\hat{\mu}}{dq} \right)_{q=0} + \frac{1}{2} q^2 \left(\frac{d^2\hat{\mu}}{dq^2} \right)_{q=0}. \quad [312] \quad (1.26)$$

The first term has no dependence upon q , hence is non-zero only where $v = v'$ (at which point there is implicitly no vibrational transition), meaning it is not important in terms of the selection rules.^[310] The second term has a dependence upon q , so the term has a contribution to the selection rules. The transition dipole moment (see Equation 1.25) can be written with only the first-order component contribution to the Taylor expansion as:

$$R_{vv'} = \int_{-\infty}^{\infty} \psi_{v'}^* \left[q \left(\frac{d\hat{\mu}}{dq} \right)_{q=0} \right] \psi_v dq = \left(\frac{d\hat{\mu}}{dq} \right)_{q=0} \int_{-\infty}^{\infty} \psi_{v'}^* q \psi_v dq. \quad [312] \quad (1.27)$$

Both factors (indicated in red and blue) must be non-zero in order for the entire term to be non-zero (and hence to obtain a non-zero transition dipole moment).

For the red factor in Equation 1.27 to be non-zero, the dipole of the molecule must change during the vibrational transition.^[310] This is termed the gross vibrational selection rule. To understand the blue term's contribution to the selection rules, consideration of ladder operators is required.^[310] The eigenfunction of state v is mapped onto the the eigenfunction

of state $v + 1$ ($\psi_v \Rightarrow \psi_{v+1}$) by the ladder operator:

$$\hat{Q}^+ = \sqrt{\frac{1}{2}} \left(q - \frac{d}{dq} \right) \quad (1.28)$$

and equivalently the eigenfunction of state v is mapped onto the onto the eigenfunction of state $v - 1$ ($\psi_v \Rightarrow \psi_{v-1}$) by the ladder operator:

$$\hat{Q} = \sqrt{\frac{1}{2}} \left(q + \frac{d}{dq} \right).^{[312]} \quad (1.29)$$

The ladder operators ($\hat{Q}^+$ and $\hat{Q}$) are related to the vibrational normal coordinate by:

$$\hat{Q}^+ + \hat{Q} = \sqrt{2}q, \quad (1.30)$$

which allows the blue term in Equation 1.27 to be rewritten in terms of the ladder operators as follows:

$$\frac{1}{\sqrt{2}} \int_{-\infty}^{\infty} \psi_{v'}^* (\hat{Q}^+ + \hat{Q}) \psi_v dq \neq 0.^{[312]} \quad (1.31)$$

The only case where the above expression is non-zero, and hence the blue factor of Equation 1.27 is non-zero, is in cases where $v' = v + 1$ or $v' = v - 1$.^[312] This yields the selection rule for a diatomic harmonic oscillator system that $\Delta v = \pm 1$.

1.6.2 Anharmonicity

Molecules are not harmonic oscillators. If their constituent atoms are separated infinitely, the bond between them will simply break. They will not feel an ever-increasing restoring force driving them back to their equilibrium bond length as defined by the harmonic oscillator potential. The potential energy well of a bond is better represented by a Morse potential:

$$V(R) = D_e \left(1 - \exp \left\{ \left(-\beta(R - R_e) \right) \right\} \right)^2, \quad (1.32)$$

where D_e is the well depth, β is a constant representing the width of the well, and R_e is the equilibrium bond length. The Morse potential and its parameters are illustrated in Figure 1.11.

The energy levels within a quantum-mechanical Morse potential (determined using the same methods as illustrated for the Harmonic oscillator approximation in Section 1.6.1) are shown in:

$$\tilde{G}_v = \left(v + \frac{1}{2}\right)\omega_e - \left(v + \frac{1}{2}\right)^2 \omega_e x_e, \quad \text{where} \quad x_e = \frac{\omega_e}{4D_e}. \quad (1.33)$$

Here, v is the vibrational quantum number, ω_e is the vibrational frequency seen previously (see Equation 1.21) and D_e is the well depth. x_e is often referred to as the anharmonicity constant. Equation 1.33 is made up of a harmonic and anharmonic term each highlighted in red and blue respectively. The anharmonic term varies with the square of the vibrational quantum number, causing the vibrational bands to coalesce in energy at high vibrational quantum numbers.

The anharmonicity leads to a relaxation of the selection rules established for the harmonic oscillator such that $v = \pm 1$ ($\pm 2, 3$ more weakly).

1.6.3 Polyatomic molecules

Additional complexity is encountered in the vibrational spectra of polyatomic molecules, which are the focus of the work presented in this thesis. When considering polyatomic molecules, it is useful to consider the concept of normal modes. Normal modes result from all parts of the system moving sinusoidally with an identical frequency as well as a fixed phase relationship. Also referred to as vibrational degrees of freedom, linear molecules have $3N - 5$ normal modes, whereas non-linear molecules have $3N - 6$ normal modes. The centre of mass of a molecule does not change during the vibrational motion associated with a normal mode.

1.6.3.1 Selection rules

As previously stated in Section 1.6.1.3 and shown in Equation 1.25, in order for a vibrational transition to occur, the transition dipole moment must be non-zero. In a polyatomic molecule the transition dipole can change in any (or a combination) of the three different axes: x , y and z . Thus for a transition to occur, at least one of following Equations must

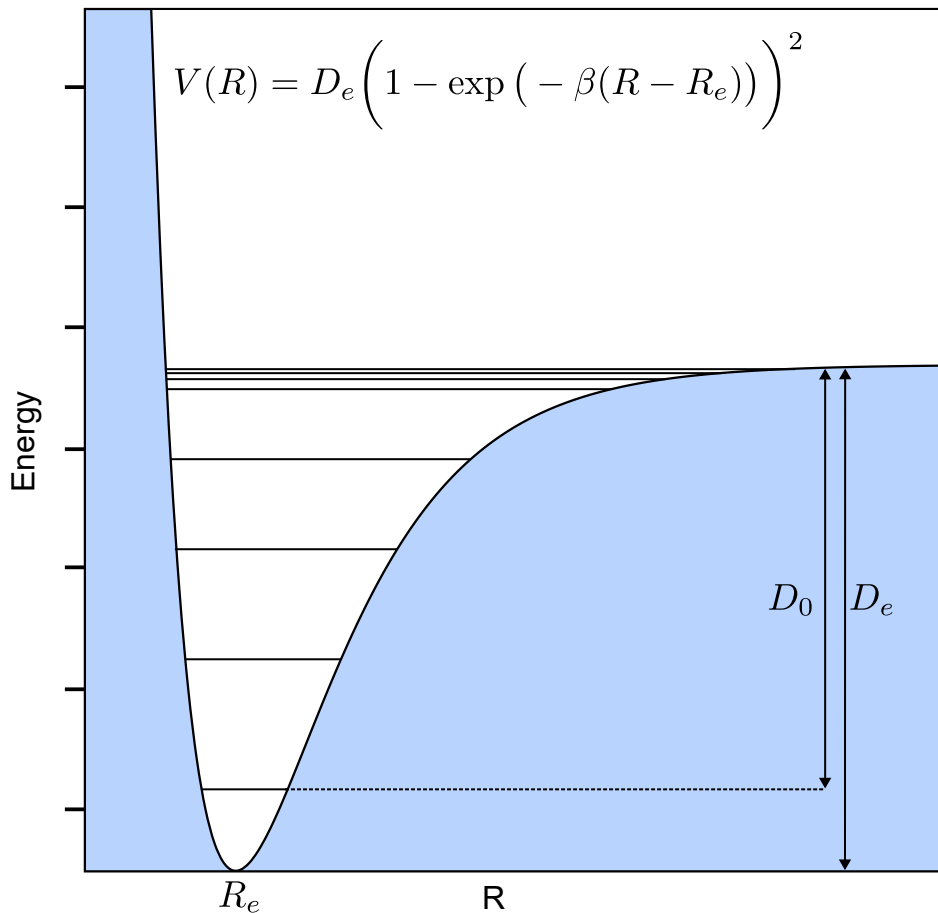


Figure 1.11: A Morse potential energy well. The potential is defined in Equation 1.32 and the energy levels are defined in Equation 1.33.

hold true:

$$R_{vv'(x)} = \int_{-\infty}^{\infty} \psi_{v'} \hat{\mu}_x \psi_v dx \neq 0, \quad (1.34)$$

$$R_{vv'(y)} = \int_{-\infty}^{\infty} \psi_{v'} \hat{\mu}_y \psi_v dy \neq 0, \quad (1.35)$$

$$R_{vv'(z)} = \int_{-\infty}^{\infty} \psi_{v'} \hat{\mu}_z \psi_v dz \neq 0. \quad [312] \quad (1.36)$$

The values of the transition dipole moments can be determined through the application of symmetry. While the details are not included here for brevity, provided the symmetry of the transition dipole moments in one axis transforms as the totally symmetric irreducible representation of the molecules point group, then the transition is allowed. The symmetry

of the transition dipole moment (μ_{xyz}) in one axis is defined by:

$$\mu_{xyz} = \Gamma_{v'} \otimes \Gamma_{\hat{\mu}_{xyz}} \otimes \Gamma_v, \quad (1.37)$$

where $\Gamma_{v'}$ is the symmetry of the vibrationally excited state wavefunction ($\psi_{v'}$), $\Gamma_{\hat{\mu}_{xyz}}$ is the symmetry of the transition dipole moment operator and Γ_v is the symmetry of the vibrational ground-state wavefunction (ψ_v).^[312] The first vibrationally excited state wavefunction ($\psi_{v'=1}$) always transforms as the same symmetry associated with the normal mode.^[305]

1.7 Infrared Spectroscopy

1.7.1 Absorbance Infrared Spectroscopy

Most infrared spectroscopy is carried out through the measurement of the transmission of IR light through a sample by recording the intensity of light before (I_0) and after (I) passing through the sample. The two intensities are related to one another via the Beer-Lambert law:

$$I = I_0 \exp\{(-\varepsilon CL)\} \quad (1.38)$$

where ε is the molar extinction coefficient (usually measured in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$), C is the concentration in (usually measured in mol dm^3) and L is the path length (usually measured in cm^{-1}).^[313] This form of measurement requires a volume density of 10^{10} molecules cm^{-3} of the species of interest to generate a measurable decrease in the intensity of the light.^[314, 315] Performing these experiments in multi-pass cells (which increase the effective path length through the sample) reduces the volume density requirement down to 10^8 molecules cm^{-3} .^[316] Typically, only volume densities of 10^7 molecules cm^{-3} are possible with ion beams (due to the effects of space-charge repulsion) meaning that alternative methods to record the infrared spectrum are required.^[316]

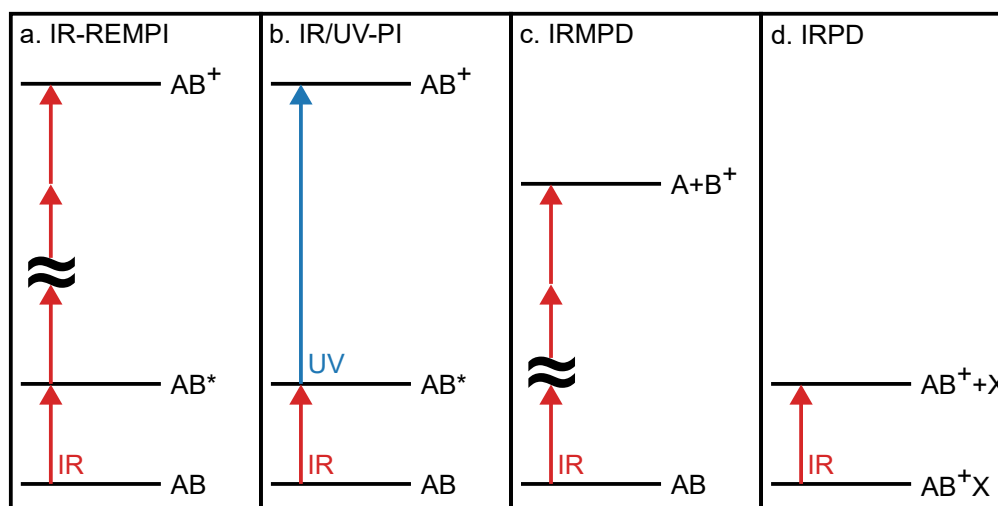


Figure 1.12: (a) Infrared resonantly enhanced multi-photon ionisation. (b) Two colour IR-UV photoionisation. (c) Infrared multiple photon dissociation. (d) Infrared photodissociation. This Figure is adapted from the thesis of Ethan Cunningham.

1.7.2 Infrared Action Spectroscopy

Action spectroscopy is a form of spectroscopy performed by measuring an outcome of the absorption of light rather than the absorption itself e.g. photodissociation.^[317] Action spectra are frequently recorded through photodissociation of the species of interest by detecting the resulting fragments using mass spectrometry. Action spectroscopy using mass spectrometry overcomes the volume density requirements of conventional spectroscopy by harnessing the sensitivity of mass spectrometry / ion detection for spectroscopy. In addition to the lower volume density requirements, action spectroscopy allows for the simultaneous measurement of multiple species within the molecular beam or (if additional beam modulations are carried out) measurements of single species may also be performed.

Infrared action spectroscopy can be classified into four distinct groups: infrared resonantly enhanced multi-photon ionisation (IR-REMPI)^[318], two colour IR-UV photoionisation (IR/UV-PI)^[319], infrared multiple photodissociation (IR-MPD)^[320] and infrared photodissociation.^[321] Each technique is illustrated schematically in Figure 1.12.

IR-REMPI relies on the sequential absorption of a series of IR photons, via virtual states, to remove an electron from the species of interest.^[318] IR/UV-PI works via the absorption of a single photon to an excited state prior to the absorption of a UV photon that ionises the species.^[319] Neither photon on their own would photo-ionise the species. The species of

interest examined by these methods are typically neutral, as photoionization of a cation requires very powerful lasers. Ionisation results in the generation of a charged species which can then be steered using ion optics before being measured via mass spectrometry. Neither method is explored in great detail here as they fall outside the scope of this thesis, which focuses on cationic systems.

Charged clusters are typically examined using IRMPD or IRPD.^[321] IRMPD relies upon the absorption of multiple photons to excite an ionic species over a dissociation threshold, causing the parent ion to fragment.^[320] The IR spectrum can then be recorded by measuring the intensity of the parent or daughter ions as a function of wavelength.

The process by which IRMPD occurs in small isolated molecules is illustrated schematically in Figure 1.13.^[322-324] Initially, IR photons can be sequentially absorbed, as the anharmonicity of the vibrational modes is accounted for by the line-width of the laser system and rovibrational states (stage (a) in Figure 1.13). The anharmonic bottleneck is reached when the laser can no longer excite the system further due to no resonant absorption being available to the excited state species. However, as the internal energy of the molecule increases, the vibrational density of states, ρ_i , increases according to the relationship:

$$\rho_i \approx E_i^N, \quad (1.39)$$

where N is the number of vibrational number of vibrational degrees of freedom.^[325] Eventually, the density of states within the molecule becomes so high that it is able to transition into the "quasi-continuum" region, in which the energy in the mode being pumped redistributes into other vibrational modes due to anharmonic coupling - a process called internal vibrational redistribution.^[326] The de-excitation of the pumped mode allows it to absorb additional photons which eventually push the molecule over the dissociation threshold. The short vibrational lifetimes within the quasi-continuum region often lead to some broadening in spectral peaks recorded in this manner.

The clusters and complexes investigated within this thesis differ due to the much higher density of states often present in these systems. The higher density of states permits fast deactivation of the $v = 1$ state through IVR (on a ps timescale) which allows absorption of additional IR photons of the same energy.^[321] Absorption of photons followed by deac-

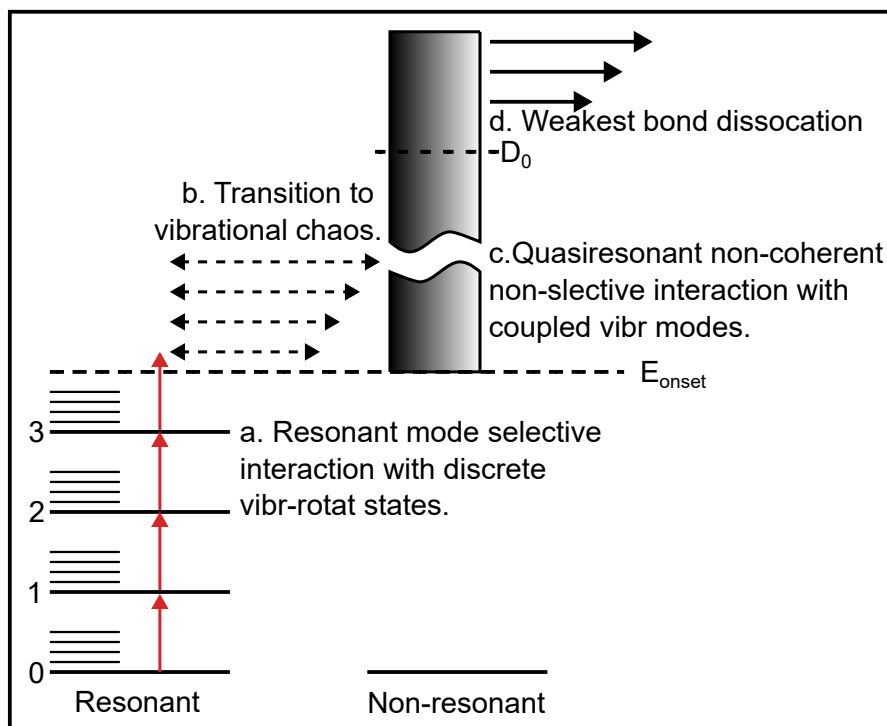


Figure 1.13: The process by which infrared multiple photon dissociation occurs through internal vibrational redistribution (IVR) for small isolated molecules. Figure adapted from previous work of Letokhov.^[322]

tivation through IVR can continue until the bond dissociation threshold is passed and the complex can dissociate. As such, the IRMPD spectroscopy performed on the complexes and clusters within this experiment can be much higher resolution than that of the small molecules presented in Figure 1.13.

IRPD relies upon the parent ion complex being extremely weakly bound, so that absorption of only a single IR photon can induce dissociation.^[321] As such, IRPD is limited to complexes with either a large number of ligands in a secondary/ tertiary solvation shell or inert messenger tagging. Inert messenger tagging involves attaching an inert gas atom/molecule such as He or Ar to the complex of interest.^[327] The inert tag binds to the complex relatively weakly, facilitating IRPD via its loss upon single IR photon absorption. The binding should also be weak enough that the structure is unperturbed. However, this is not always the case so binding motifs with inert tags should always be checked by simulation of the species of interest both with and without the inert messenger tag.^[321]

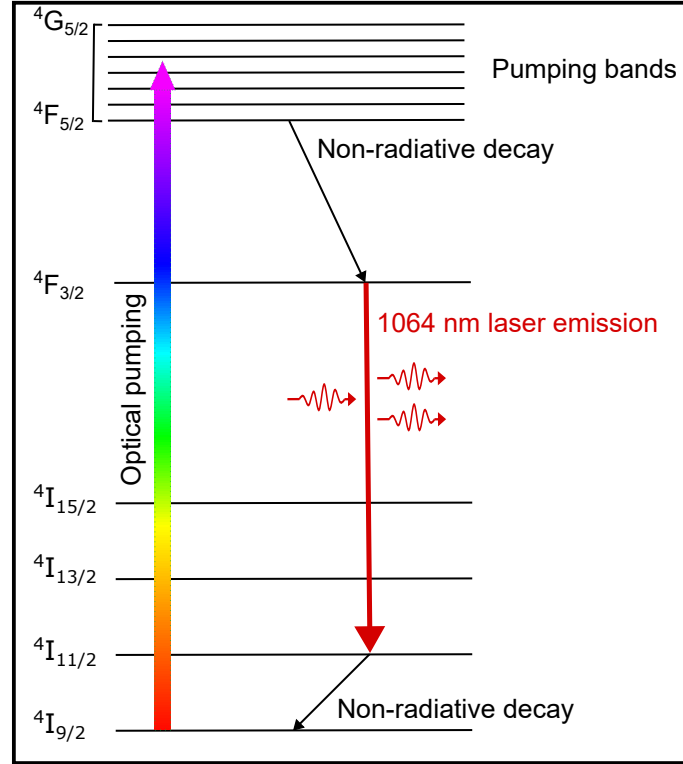


Figure 1.14: Schematic diagram showing four-level lasing within an Nd^{3+} ion in an Nd:YAG laser crystal. Lasing occurs between the $^4\text{F}_{3/2}$ and $^4\text{I}_{11/2}$ levels.

1.8 Lasers

1.8.1 Nd:YAG Lasers

Demonstrated in 1964^[328], neodymium-doped yttrium aluminium garnet (Nd:YAG) lasers have found a wide variety of applications within the medical, military and research sectors.^[329–331] They are four-level solid-state lasers relying on the excited states of the Nd^{3+} ions doped into YAG crystals to generate 1064 nm radiation. Within the context of the work presented in this thesis they are used to generate gas-phase metal ions via laser ablation (see Section 1.3) and to pump a commercial OPO/OPA system (LaserVision) to generate tuneable IR light detailed in the next section (Section 1.8.2).

1.8.2 Generating Different IR Frequencies: Non-Linear Optics

The infrared radiation used within the work presented in this thesis is generated from the output of a commercial OPO/OPA system (LaserVision), which is pumped by the 1064 nm

output of Nd:YAG laser system (Continuum Powerlite II). The commercial OPO/OPA system uses a combination of both optical parametric oscillation and amplification in non-linear optical crystals to generate wavelengths between 600-4000 cm^{-1} .^[332, 333] The mathematical theory underpinning optical parametric oscillation and amplification is presented briefly in this section.

Radiation passing through atoms within a crystalline lattice that do not absorb the photons will induce oscillations in the valence electrons that cumulatively generate a moving dipole within the crystal.^[334] This moving dipole may be modelled as a time-dependent polarisation density.^[334] The polarisation density does not respond in a linear fashion to the incident radiation, and it can be expressed as the Taylor expansion of incident electric fields ($E(t)$) and n^{th} order electric susceptibility ($X^{(n)}$) of the crystal in:

$$\vec{P}(t) = \epsilon_0 \left(\chi^1 \vec{E}(t) + \chi^2 \vec{E}^2(t) + \chi^3 \vec{E}^3(t) + \dots \right), \quad (1.40)$$

where ϵ_0 is the vacuum permittivity.^[335] The generated polarisation density itself generates an electric field, and the relationship between each is shown in:

$$\nabla^2 \vec{E} - \frac{n^2}{c^2} \frac{\partial^2}{\partial t^2} \vec{E} = \frac{1}{\epsilon_0 c^2} \frac{\partial^2}{\partial t^2} \vec{P} \quad (1.41)$$

where $\vec{E}$ is the electric field, n is the order of the field, c is the speed of light, t is the time, ϵ_0 is the vacuum permittivity and $\vec{P}$ is the polarisation density.^[336] The second-order differential relationship indicates that only accelerating polarisation density generates an electric field, hence only the X^2 term is of consequence in the Taylor expansion in Equation 1.40, allowing the relationship to be approximated to:

$$\vec{P}(t) = X^2 \vec{E}^3(t). \quad (1.42)$$

Taking the Fourier transform of Equation 1.42 yields a series of Taylor coefficients dependent upon frequency $X^n(\omega)$. The polarisation coefficient X^2 for anisotropic media is a third-order tensor that operates on three frequencies (ω) that are related by Equation

1.43:

$$\omega_P = \omega_{S(1)} + \omega_{I(2)} \quad (1.43)$$

based on the conservation of energy. ω_3 is the pump electromagnetic radiation that drives the generation of the polarisation density in the first place and the two other frequencies are formed from the non-linear polarisation wave resulting from ω_3 . The larger of the two is known as the signal, and the smaller is known as the idler. Based on this, the time-dependent electric field generated from the accelerating component of the polarisation wave can be written as shown in:

$$\vec{E}(t) = \vec{E}_1 e^{-i\omega_1 t} + \vec{E}_2 e^{-i\omega_2 t} + \vec{E}_1^* e^{-i\omega_1 t} + \vec{E}_2^* e^{-i\omega_2 t}. \quad [337] \quad (1.44)$$

Substituting Equation 1.44 into Equation 1.42 yields:

$$\begin{aligned} \vec{P}^{(2)}(t) = & \epsilon_0 X^{(2)} \left(\vec{E}_1^2 e^{-i2\omega_1 t} + \vec{E}_2^2 e^{-i2\omega_2 t} + 2\vec{E}_1 \vec{E}_2 e^{-i(\omega_1 + \omega_2)t} + 2\vec{E}_1 \vec{E}_2^* e^{-i(\omega_1 - \omega_2)t} + c.c. \right) \\ & + 2\epsilon_0 X^{(2)} \left(\vec{E}_2 \vec{E}_1^* + \vec{E}_2^* \vec{E}_1 \right). \quad [337] \end{aligned} \quad (1.45)$$

Four key processes can be picked out from Equation 1.45: second harmonic generation (2ω , shown in red), sum frequency generation ($\omega_1 + \omega_2$, blue), difference frequency generation ($\omega_1 - \omega_2$, shown in yellow) and optical rectification (terms with no frequency components, shown in green).^[334] Only the first three processes are used within the OPO/OPA system.

1.8.2.1 Phase Matching

Whilst it appears as if all three wavelength-dependant processes happen simultaneously (first three terms in Equation 1.45), they cannot because an additional condition, phase matching, must be met. Under normal experimental conditions, it is possible to phase match for a single process in a single crystal, and it allows for field contributions for a given process at different locations within the crystal to coherently add up at the exit face of the crystal. Conservation of energy and momentum both apply to the production

of the signal and idler beams from the pump beam. This concept is illustrated with wave vectors ($\vec{k}$) in the relationship:

$$\vec{k}_P = \vec{k}_S + \vec{k}_I + \Delta\vec{k} \quad (1.46)$$

where $\vec{k}_{P/S/I}$ is the wavevector of the pump/signal/idler radiation and $\Delta\vec{k}$ is the phase mismatch.^[338, 339] In any case where $\Delta\vec{k} \neq 0$, the waves generated from each non-linear optical process will destructively interfere and cancel out (to any experimentally meaningful degree) as the dispersion relationship ($\omega = \Omega(\mathbf{k})$) is not satisfied, meaning that when phase matching is satisfied, Equation 1.46 can be rewritten as:

$$\vec{k}_P = \vec{k}_S + \vec{k}_I. \quad [339] \quad (1.47)$$

Typically, optical birefringent materials are used to cancel the phase mismatch, however, other methods are often employed simultaneously (e.g. critical phase matching, co-linear phase matching etc).^[338, 340–342]

Uniaxially birefringent materials have two refractive indexes resulting from the differences in polarisation relative to the optical axis of the material. Electromagnetic radiation with polarisation perpendicular to the optic axis is governed by a fixed refractive index n_{ordinary} which is dependant only on wavelength, whereas electromagnetic radiation with polarisation parallel to the optic axis is governed by a different refractive index: $n_{\text{extraordinary}}$.^[343] $n_{\text{extraordinary}}$ is dependent on both the wavelength and the angle of the crystal relative to the electromagnetic radiation.^[343] There are two types of phase matching within non-linear and birefringent crystals shown below.

- Type I Phase Matching: Signal and idler have the same polarisation with respect to the optical axis. These can be referred to in terms of the beam polarisation of the pump, signal and idler in terms of their behaviour in the crystal (i.e. ooe/eoo).^[344]
- Type II Phase Matching: Signal and idler have different polarisation with respect to the optical axis (i.e. oeo/eoe).^[344]

The OPO and OPA stages in the system used within the experiments presented with this

thesis both use type II oeo phase matching.

1.8.2.2 Tuning in OPO OPA systems

The tuning in the OPO/OPA system is carried out using sum frequency generation and difference frequency generation in the OPO and OPA regions respectively. In both systems, optically non-linear and birefringent crystals are used. While the crystals in the OPO are phase matched for sum frequency generation, and the crystals in the OPA are phase matched for difference frequency generation, both use optically non-linear and birefringent crystals, which allow different frequencies to be generated by rotating the crystals relative to the beam. This stems from the conservation of momentum relation outlined in Equation 1.47 previously.^[339] The normal of a wave vector is related to the refractive index of a medium (n), its frequency (ω), and speed of light c by:

$$||\vec{k}|| = \frac{n(\omega)\omega}{c} \quad (1.48)$$

where n is the refractive index of the material, ω is the frequency of the light and c is the speed of light.^[345] This allows the phase matching condition (Equation 1.47) to be rewritten as:

$$n_P\omega_P = n_S\omega_S + n_I\omega_I \quad (1.49)$$

The crystals within the OPO/OPA are all type II phase-matched, meaning the pump and idler are polarised relative to the crystal, such that they are normal waves. This means that their refractive indexes (n_P/n_I) do not depend on the angle of the crystal. The signal beam, however, is polarised relative to the crystal such that it is an extraordinary wave, and its refractive index (n_S) does depend upon the angle of the crystal, meaning that Equation 1.49 can be rewritten from the type II phase-matched crystals in the OPO/OPA:

$$n_P\omega_P = n_S(\omega_S, \theta)\omega_S + n_I\omega_I. \quad (1.50)$$

Equation 1.50 illustrates that by rotation of the crystals within the system both the frequency of the signal and idler can be tuned simultaneously, allowing for the generation of tuneable radiation from a single pump beam.

1.9 Computational Methods

1.9.1 Density Functional Theory

The ground-state structure of molecules may be determined by finding solutions to the time-independent Schrödinger equation shown below:

$$\hat{H}\psi_0(r_n, R_m) = E_0\psi_0(r_n, R_m) \quad (1.51)$$

where $\hat{H}$ is the Hamiltonian operator, ψ_0 is the ground-state wavefunction of the molecule and E_0 is the ground-state energy. The wavefunction is written in terms of a radial (R_m) and angular (r_n) component. In cases where there are more than one interacting body, analytical solutions to the Schrödinger equation are not possible, and numerical approximations must be used.

Out of the many different approximations that can be made, density functional theory (DFT) represents one of the most dominant due to ease and (relatively) low computational cost compared to other methods.^[27] It is used extensively within Chapters 6 and 7 to generate low-lying isomers on the potential energy landscape which are then used to generate predicted infrared spectra to aid in structural assignment. Beyond predicted infrared spectra generation, the structures from DFT can also be used to estimate charge distributions within the structures which is also used within the final chapters of this thesis to help rationalise observed trends.

1.9.1.1 Theoretical Basis

Postulated in 1964, the Hohenberg-Kohn existence theorem demonstrates that the ground-state electron density of a system defines a unique external potential, which itself determines a unique Hamiltonian, and thus a wavefunction.^[346] The Hamiltonian and wavefunction allow, in theory, the energy of the system to be determined; however, for many body systems, analytical solutions are not possible.

The breakthrough for DFT came in 1965 when Kohn and Sham proposed that the energy of an interacting system of electrons with density ρ could be determined by calculating

the energy of a system of non-interacting electrons with density ρ and adding a small correction for their interaction energy.^[347] The Hamiltonian for a system of non-interacting electrons can be expressed as a sum of one-electron operators and has eigenfunctions that are Slater determinants of individual one-electron eigenfunctions. Using both the Hohenberg-Kohn existence theorem and the Kohn-Sham model, the energy of the system E can be expressed in terms of a sum of energies, each dependent upon the electron density ($\rho(\mathbf{r})$):

$$E[\rho(\mathbf{r})] = T_{\text{ni}}[\rho(\mathbf{r})] + V_{\text{ne}}[\rho(\mathbf{r})] + V_{\text{ee}}[\rho(\mathbf{r})] + \Delta T[\rho(\mathbf{r})] + \Delta V_{\text{ee}}[\rho(\mathbf{r})] \quad (1.52)$$

where, T_{ni} represents the kinetic energy of the non-interacting electrons, V_{ne} represents the energy of the electron nucleus attraction, V_{ee} represents the classical electron repulsion, ΔT represents the classical correction to the kinetic energy and ΔV_{ee} represents all of the non-classical corrections to the electron-electron repulsion energy.^[27] Equation 1.52 can then be rewritten in terms of an orbital expression of the electron density:

$$\begin{aligned} E[\rho(\mathbf{r})] = & \sum_i^N \left(\langle \chi_i | -\frac{1}{2} \nabla_i^2 | \chi_i \rangle - \langle \chi_i | \sum_k^{\text{nuclei}} \frac{Z_k}{|\mathbf{r}_i - \mathbf{r}'|} | \chi_i \rangle \right) \\ & + \sum_i^N \langle \chi_i | \frac{1}{2} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}_i - \mathbf{r}'|} | \chi_i \rangle + E_{xc}[\rho(\mathbf{r})] \end{aligned} \quad (1.53)$$

where the electron density is related to the single electron Kohn-Sham orbitals, χ_i , by:

$$\rho = \sum_{i=1}^N \langle \chi_i | \chi_i \rangle. \quad (1.54)$$

The classical and quantum corrections to the non-interacting energy (ΔT and ΔV_{ee}) are combined into a single term (E_{xc}) which is known as the exchange-correlation functional.

The methods used to generate the energy for the system of non-interacting electrons are identical in both Hartree-Fock theory and DFT methodologies. The two methods differ only in the way that they calculate the exchange-correlation component of the energy. Copious numbers of different functionals are available for use, each having been developed to agree with the experiment or higher levels of theory. There are three broad categories of

functionals which can be considered in terms of a Jacob's ladder shown in Figure 1.15.^[348] Their relative position on the ladder gives an indication of their accuracy.

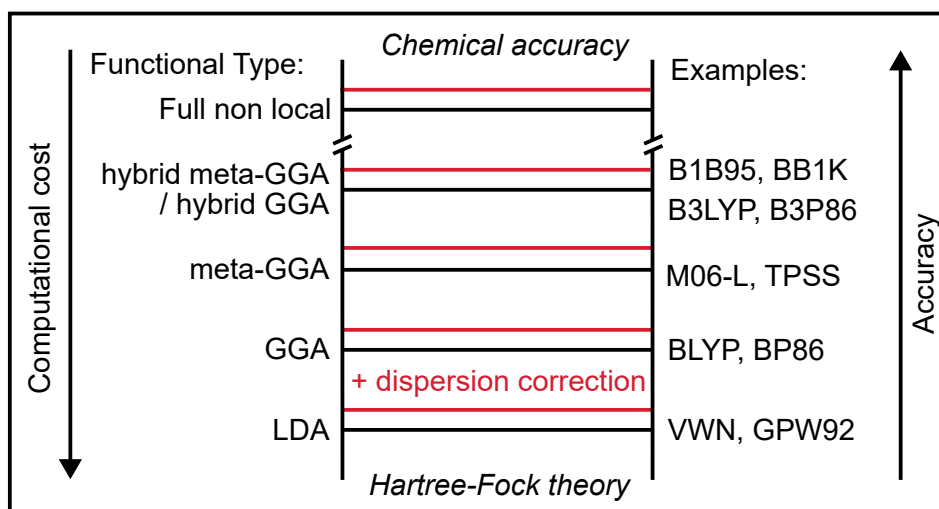


Figure 1.15: The Jacobs ladder illustration of the different types of DFT functionals including local density approximation (LDA), generalised gradient approximation (GGA), meta-GGA approximation and hybrid methods (hybrid GGA or hybrid meta-GGA). The red lines on the ladder indicate the improvement over each method including dispersion correction terms add to the functional's performance. Examples of each type of functional are also shown.^[348–358] This Figure is adapted from the work of Perdew and coworkers.^[348]

Representing the earliest and simplest method, the local density approximation (LDA) assumes that the local electron density behaves as a uniform electron gas.^[359, 360] LDA methods tend to underestimate exchange and overestimate correlation energies. The generalised gradient approximation methods do not assume a uniform electron gas and account for both local and longer-range gradients in electron density. The specific methodologies used within GGA methods differ greatly between individual functionals, and their details are well beyond the scope of this thesis.^[359, 361] Meta-GGA functionals advance the original GGA method through the addition of second-order differentials and orbital angular momentum.^[359] As they rely on the second-order differentials of electron density in space, they are considerably more expensive than regular GGA methods.^[360] The final functional type is the hybrid method, which calculates a portion of the exchange energy using Hartree-Fock theory with the rest contributed through GGA or meta-GGA methods.^[360] The correlation term is made of purely GGA or meta-GGA energy.^[360]

The single electron orbitals are calculated using a self-consistent-field (SCF) method which

works by selecting an initial set of guess orbitals and solving the Kohn-Sham expression. The newly generated orbitals from the solutions to the Kohn-Sham expression can be then fed back into a new Kohn-Sham expression. This process is repeated until the differences between the original and newly generated orbitals are minimised in energy (within a user-defined threshold).

Kohn-Sham orbitals, χ_i , are generated from a linear combination of basis functions, ϕ_α :

$$\chi_i = \sum_{\alpha}^{M_{\text{basis}}} c_{\alpha i} \phi_{\alpha} \quad (1.55)$$

where $c_{\alpha i}$ represents the coefficients of each basis function (i.e. how much it contributes to the Kohn-Sham orbital).^[27] Basis functions are obtained from basis sets which are a set of atom-centred mathematical functions (usually Gaussian) used to represent atomic orbitals. A wide variety of basis sets have been developed. These often differ based on the number of functions they use to represent the orbitals. Other modifications to orbital diffuseness and polarisation can be included to provide a more accurate description of the electron density.^[362] These are often highly system specific. Generally, using basis sets with a greater number of functions will yield a more accurate answer at the expense of increased computational cost. In some cases, where the core electrons are not involved in chemical bonding, they can be approximated with an effective core potential (ECP) rather than being modelled explicitly.

1.9.1.2 Searching the DFT defined Potential Energy Surfaces

While DFT offers a means by which the stationary points on a PES of a molecule may be efficiently calculated, it does not offer a method by which the PES can be searched. Within this thesis, two key structural motifs on the PES are of interest: minima and transition states, both shown in Figure 1.16. Starting from an initial structure, the structure can be optimised to either the minimum (or other features) using one of three methods:

- Steepest descent method
- Conjugate gradient method
- Newton-Raphson method

From Figure 1.16 the PES at a non-minimum/maximum point will have a non-zero gradient associated with the energy in terms of atomic displacements. Directed by a line search, the calculation of the energy gradient with respect to atomic displacement followed by a step (change in geometry) in the negative gradient direction will lead towards the minimum and is the principle of the steepest gradient decent method. In theory, if enough steps are taken, the minimum energy geometry will always be reached. However, this method suffers from slow convergence and large step sizes, rendering optimisation inefficient in some cases.^[360] The conjugate gradient method addresses some of the issues with the steepest descent method by allowing the previous search step direction to influence the new step taken in a variety of different ways.^[360] The Newton-Raphson method differs from the other methodologies in that it relies on a Taylor expansion of the PES and thus uses the second derivative, rather than only the first derivative. The second-order Taylor expansion can be unitarily transformed into a coordinate system in which the Hessian matrix is diagonalised. Using this, the most efficient step towards the minimum can be achieved. Most modern computational codes rely upon Newton-Raphson methods as they offer considerably faster optimisation compared to the other methods (despite their increased cost from the transformation and calculation of the Hessian matrix).

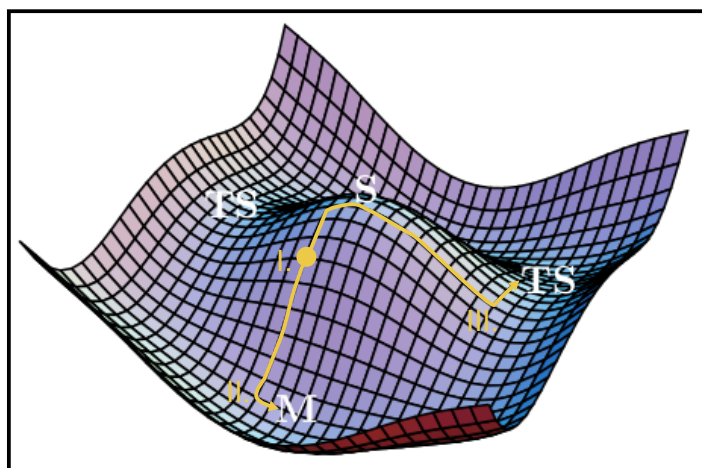


Figure 1.16: An example PES adapted from Wales^[363] with a random starting geometry (I), a possible route taken to optimise a minimum structure (II) and a possible route taken to optimise a transition state geometry (III).

PES searches presented within this thesis were all carried out using the Gaussian16 suite of software.^[364] While the Gaussian16 software is capable of optimising structures at the DFT level of theory, it cannot search the PES itself as it simply takes input structures

and optimises them. PESs are extremely complex and contain potentially huge numbers of minima and maxima. As a result, a large number of different starting geometries must be fed into Gaussian for minimisation to ensure that the PES is sampled effectively (i.e. minima from a large proportion of the PES are found). While these could be generated manually, randomly generated structures generated using the Kick³ algorithm^[365, 366] developed by Addicoat and co-workers have increased the rate at which large potential energy landscapes can be sampled. All of the computationally generated structures presented within Chapters 6 and 7 were initially generated using the Kick³ algorithm before being minimised in Gaussian16.

1.9.2 Predicting IR Spectra

The interpretation of experimentally generated IR spectra is aided by a comparison of computationally generated IR spectra from the energetically low-lying isomers found within the potential energy landscape search in the previous section. Theoretical spectra are calculated both in terms of the expected vibrational frequency and the intensity of the transition and Gaussian16 is able to calculate both.^[364] This section expands on how it is able to do both of these things.

1.9.2.1 Predicting Vibrational Frequencies

Within the harmonic approximation, any stationary point on the potential energy surface may have its potential energy written as a Taylor expansion with respect to Cartesian coordinates truncated at the second-order:

$$V(\mathbf{x}) = V(\mathbf{x}_0) + \left(\frac{dV}{d\mathbf{x}} \right)_{\mathbf{x}_0} (\mathbf{X} - \mathbf{X}_0) + \frac{1}{2} \left(\frac{d^2V}{d\mathbf{x}^2} \right)_{\mathbf{x}_0} (\mathbf{X} - \mathbf{X}_0)^2 \quad (1.56)$$

where $V(\mathbf{x}_0)$ is the starting energy, $\mathbf{X}$ is the vector of atomic coordinates, $\mathbf{X}_0$ is the equilibrium structure. Implicitly, at a stationary point the first order differential is equal to zero ($dV/d\mathbf{X} = 0$).^[360] This coupled with the fact that the exact potential energy is unimportant, allows Equation 1.56 to be simplified to:

$$V(\mathbf{x}) = \frac{1}{2} \Delta \mathbf{x}^t \mathbf{F} \Delta \mathbf{x} \quad (1.57)$$

where $\Delta \mathbf{x} = \mathbf{X} - \mathbf{X}_0$ and $\mathbf{F}$ represents the Hessian matrix ($3N \times 3N$ matrix of second derivatives).

Thus, the vibrational Schrödinger equation for the system of N atoms can then be written as:

$$\left[-\sum_i^{3N} \frac{1}{2m_i} \frac{\partial^2}{\partial x_i^2} + \frac{1}{2} \Delta \mathbf{x}^t \mathbf{F} \Delta \mathbf{x} \right] \psi_{\text{nuc}} = E \psi_{\text{nuc}}.^{[360]} \quad (1.58)$$

The Cartesian coordinate system is poorly suited for vibrational frequency calculations and it is convenient to transform the system into mass-weighted spatial coordinates and passed through a unitary transformation ($\mathbf{U}$) to yield:

$$\left[-\sum_i^{3N} \frac{\partial^2}{\partial y_i^2} + \frac{1}{2} \mathbf{y}^t (\mathbf{F} \mathbf{G}) \mathbf{y} \right] \Psi = E \Psi, \quad (1.59)$$

$$\left[-\sum_i^{3N} \frac{\partial^2}{\partial \mathbf{q}_i^2} + \frac{1}{2} \mathbf{q}^t (\mathbf{U} (\mathbf{F} \mathbf{G}) \mathbf{U}^t) \mathbf{q} \right] \Psi = E \Psi, \quad (1.60)$$

in which $y_i = \sqrt{m_i} \Delta x_i$, $\mathbf{q} = \mathbf{U} \mathbf{y}$, and $\mathbf{G}$ is a $3N \times 3N$ matrix containing the inverse square root of the atomic mass of the atom at that index ($1/\sqrt{M_a}$).^[360] Transformation into the vibrational normal coordinate system then allows $3N$ dimensional Schrödinger equation to be rewritten as a sum of $3N$ one dimensional Schrödinger equations:

$$-\sum_i^{3N} \left[\frac{\partial^2}{\partial \mathbf{q}_i^2} + \frac{1}{2} \epsilon_i \mathbf{q}_i^2 \right] \Psi = E \Psi, \quad (1.61)$$

each with an eigenvector ($\mathbf{q}_i$) and an eigenvalue (ϵ_i).^[360] Due to the numerical methods used in the minimisation, the structure is seldom in a perfect stationary point; rather, it is very close to one. The result of this is that within the $\mathbf{F} \mathbf{G}$ matrix there are translational and rotational components which need to be removed. These are commonly removed through projection into a translating and rotating frame.^[364] The vibrational frequency is related to the eigenvalue ϵ_i in Equation 1.61 through the relationship:

$$v_i = \frac{1}{2\pi} \sqrt{\epsilon_i}.^{[360]} \quad (1.62)$$

Calculating anharmonic frequencies is considerably more difficult and involves the addi-

tion of higher-order differential terms in the Taylor expansion. Anharmonic frequencies are typically calculated in one of two ways: either with second-order perturbation theory or vibrational mean-field theory.^[367–370] These are not discussed here as they are not used in the work presented in this thesis.

1.9.2.2 Predicting Vibrational Intensities

The prediction of IR intensities requires knowledge of how the electronic dipole changes with respect to the motion along a normal mode ($\mu = (\mu_x, \mu_y, \mu_z)$) - i.e. the derivative of μ with respect to the nuclear displacements.^[371] The electronic dipole can be split into two contributions:

$$\mu = \mu_n + \mu_e, \quad (1.63)$$

where μ_n is the nuclear contribution and μ_e is the electronic contribution.^[371]

The nuclear contribution to the electronic dipole is simply the sum of the Cartesian coordinates (R_K) of the nucleus K multiplied by its charge (Z_K):

$$\mu_n = \sum_K Z_K R_K \quad (1.64)$$

The derivative of the nuclear contribution of the electronic dipole moment can be obtained in an analogous way to that in which the Hessian matrix for energy can be generated: through the solution of coupled perturbed self-consistent field equations which are well beyond the scope of this thesis.^[371]

The electronic contribution to the electronic dipole (μ_e) is related to both the one-particle density matrix ($D_{\kappa\lambda}$) and the dipole moment integrals in the atomic orbital basis ($\mu_{\kappa\lambda}$) by:

$$\mu_e = \sum_{\kappa\lambda} D_{\kappa\lambda} \mu_{\kappa\lambda} \quad (1.65)$$

The derivative electronic contribution to the electronic dipole with respect to the normal mode motion is much more complex and requires derivatives of both the perturbed density and dipole integrals, again, well beyond the scope of this thesis.^[371]

The IR transition dipole moment can be calculated through the dot product dipole mo-

ment gradient and Cartesian normal modes. IR intensity for each normal mode can then be calculated from this by taking the square or the normal of the corresponding IR transition dipole moment before converting them into the output units of km mol^{-1} .

1.9.3 Hirshfeld charge distributions

Much of the interpretation of the behaviour observed in the final two chapters of this thesis is rationalised based on the charge distributions within the species of interest. These charge distributions are determined from the structures (and orbitals) generated from the minimisation process within the Gaussian16 software suite. A variety of different methods to analyse populations exists in order to understand charge distributions within structures. Examples of these include: Mulliken, CHelp/CHelpG and Hirshfeld charges (among many others).^[372–374] According to many previous studies, Hirshfeld population analysis performs much better when compared to other methods and as such should be preferred; hence, the work presented within the thesis uses Hirshfeld charge analysis to calculate localised charges within complexes.^[375–378]

Calculation of Hirshfeld charge requires density matrices for both the molecule and isolated atoms. The charge on an atom (q_A) is related to isolated ground-state density ($\rho(\mathbf{r})$) and the molecular density ($\rho(\mathbf{r})$) by:

$$q_A = Z_A - \int d\mathbf{r} \frac{\rho_A^0(\mathbf{r})}{\sum_B \rho_B^0(\mathbf{r})} \rho(\mathbf{r}) \quad (1.66)$$

where Z_A is the nuclear charge on A and B represents the other atoms in the molecule.^[374]

1.10 Thesis Overview

This chapter has provided a brief overview of the key background science associated with this thesis, including heterogeneous catalysis, vibrationally enhanced and mode-selective chemistry in the gas phase, and spectroscopic theory. The thesis is split into two conceptually different parts. Part I concerns the design, development and construction of the new instrument to study vibrational altered chemistry in single collisions between ionic metal species and neutral molecules in the gas phase. Part II concerns spectroscopic studies

using an infrared photodissociation experiment in addition to experimental modifications made through the course of the work presented in this thesis.

The new experiment to study vibrationally altered chemistry is presented in Part I. Based on theoretical modelling presented in Chapter 2, the collision cell forms the basis of the newly developed experiment. Based around the collision cell, Chapter 3 then introduces the rest of the experiment designed around a laser ablation source and the collision cell and its characterisation alongside the many iterations the experiment went through as part of its development. It should be noted that the experiment remains under active development at this time due to multiple factors discussed in Chapters 2 through 4. As such, there are currently no results, beyond the development data and preliminary characterisation data presented within this thesis. Chapter 4 summarises the work completed as part of this project as well as outlining the future work required.

Part II begins with Chapter 5 which details the numerous upgrades made to the infrared photodissociation experiment. Chapters 6 and 7 present (infrared) spectroscopic studies of $\text{Ho}[\text{O}_x(\text{CO}_2)_y]^+$ and $\text{Ho}[\text{O}_x\text{S}_y(\text{OCS})_z]^+$ ion molecule complexes. Finally, the conclusions and future directions are presented in Chapter 8. Due to the nature of experimental development, vast amounts of characterisation, computer aided design (CAD) data and other information are left out main body of the thesis; thus, an appendix containing much of this information is attached to the thesis.

Part I: Development of a New Instrument to Study Vibrational Enhancement in Gas-Phase Metal Ion Reactions

2 | Collision cell

In order to measure the effect of vibrational energy on reactions between ionic metal species and neutral molecules in the gas phase, we require single collisions at known and controllable collision energy. While there are many possible ways of achieving this, discussed in Section 1.2, the simplest method of passing the ion beam through a collision cell filled with a gas at low pressure was selected to make the initial experimental design as simple and easy to as possible. Should the collision cell method used here be found inadequate, then a more complex method, such as using a an octupole ion-guide, could be introduced to the experiment.

Previous experiments^[379, 380] using collision cells consist of a cylinder with apertures at either end to allow ions to pass through and allow neutral gas to leak out in order to maintain constant pressure. The design of the collision cell used in this experiment is much the same. However, the collision cell also needs to maintain a constant (measurable) pressure within the cell whilst gas leaks out of apertures. Thus appropriate gas leak valves and pressure gauges must be selected for use with the cell. To ensure optimal design of the dimensions of the collision cell and that appropriate leak valves and pressure gauges were selected, collisions within the cell were modelled using a simple model presented in Section 2.1.

2.1 Simulating Collisions with a Collision Cell

2.1.1 Control of Collision Frequency

Multiple collisions within the cell are highly undesirable as collisions beyond the first occur with energies that are not defined by or known by the user resulting in huge uncertainties. As the experiment seeks to probe the effect of vibrations on reactions between ions and neutrals at defined collision energies, transfer of internal or kinetic energy from secondary collisions would reduce the experiment’s accuracy, thus single collision conditions within the cell must be maximised.

Within simple kinetic gas theory, the frequency of collisions between a single ion passing

through a cell filled with a neutral gas (Z) is given by:

$$Z = \sigma \int_0^\infty c_{\text{rel}} dn(c) = \sigma \int_0^\infty c_{\text{rel}} n'(c) dc = \sigma n \left[\int_0^\infty c_{\text{rel}} f(c) dc \right] = \sigma n \bar{c}_{\text{rel}}. \quad (2.1)$$

where σ is the collision cross section for the averaged relative speeds of the ion and neutral molecules ($\bar{c}_{\text{rel}}$) and n is the number density of the neutral molecules. Equation 2.1 shows that the collision frequency is dependent upon three factors:

- The collision cross section (σ) at the collision energy (defined by the relative speeds of the collision partners).
- The mean relative velocity of the ions and neutral molecules.
- The number density of gas molecules within the ion path.

2.1.1.1 Collision Cross Section

Prediction of collision cross-sections of ion-neutral molecules is remarkably complex, and a wide range of theoretical models have been developed in order to predict them.^[381–383] The simplest of all models, the Langevin model, describes the collision cross-section of an ion-neutral collision in which the neutral has no permanent dipole. The Langevin collision cross-section (σ_L) is defined by:

$$\sigma_L = \frac{q}{2v\epsilon_0} \left(\frac{\alpha(M+m)}{mM} \right)^{\frac{1}{2}} \quad (2.2)$$

where q is the charge on the ion, v is the velocity of the ion, ϵ_0 is the permittivity of a vacuum (8.854×10^{-12} F m⁻¹), α is the polarisability of the neutral molecule, M is the mass of the ion and m is the mass of the neutral.^[384]

2.1.1.2 Relative Ion Neutral Speed

Ding^[385] and Tormachev^[386] both independently derived that the mean relative velocity between an ion passing through a (Maxwell-Boltzmann distributed) system of neutral

molecules can be determined through the relationship:

$$c = \bar{c}_{gas} \left((s + (2s)^{-1}) \frac{\sqrt{\pi}}{2} \operatorname{erf}(s) + \frac{1}{2} \exp\{-s^2\} \right) \quad (2.3)$$

where

$$s = \frac{c_{ion}}{c_{*gas}}, \quad \bar{c}_{gas} = \sqrt{\frac{8k_B T}{\pi m}}, \quad c_{*gas} = \sqrt{\frac{2k_B T}{m}},$$

m is the mass of the ion, T is the temperature of the gas, k_B is the Boltzmann constant, $\bar{c}_{gas}$ is the mean gas speed and c_{*gas} is the most probable gas speed.

2.1.1.3 Neutral Gas Number Density

If the neutral gas is assumed to behave as an ideal gas, its number density (ρ) can be calculated using Equation 2.4:

$$\rho = \frac{P}{k_B T} \quad (2.4)$$

where P is the pressure, k_B is the Boltzmann constant and T is the temperature of the gas.

2.1.1.4 Conclusions

Substituting all Equations 2.2, 2.3 and 2.4 into Equation 2.1 indicates that the collision frequency is dependent upon the following experimentally controllable parameters:

- The pressure and temperature of the neutral gas.
- The kinetic energy of the ion.
- The length of the collision cell.

Each of these experimentally controllable parameters has an impact on the design decisions surrounding the collision cell.

2.1.2 Controlling the Pressure of the Neutral Gas

Assuming all other conditions are fixed, raising the pressure of the neutral gas increases the number of collisions. Produced using a simple model based Equation 2.1, Figure 2.1

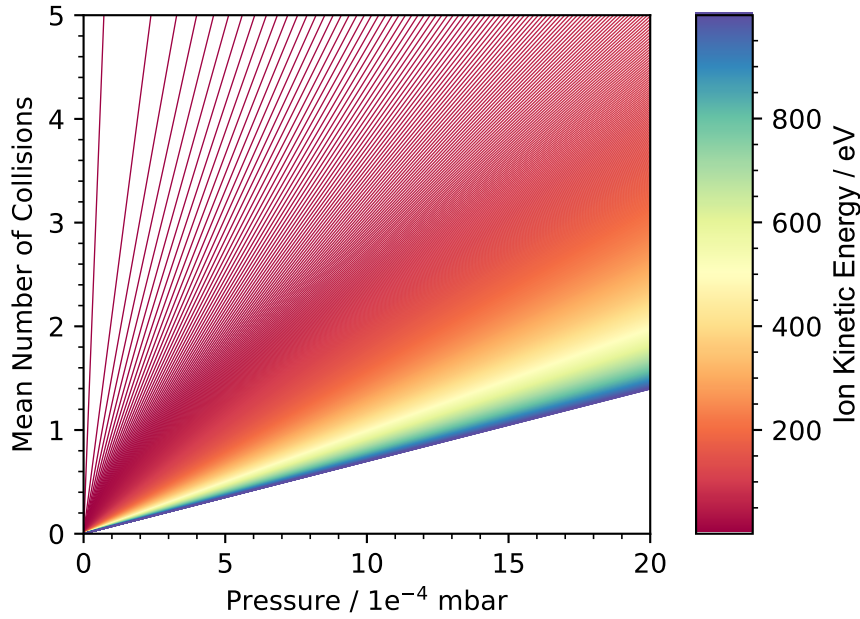


Figure 2.1: The mean calculated number of collisions that an Au^+ ion undergoes with CO_2 within a 100 mm long collision cell as a function of the pressure of CO_2 added to the collision cell over a range of Au^+ kinetic energies. The CO_2 was held at a fixed temperature of 297 K. The data was generated using a simple model based on Equations 2.2 through 2.4 substituted into Equation 2.1.

shows the mean number of collisions an Au^+ cation undergoes as it passes through a 100 mm collision cell filled with CO_2 as a function of the pressure of CO_2 at various Au^+ kinetic energies. As pressure of CO_2 is raised, the mean number of collisions that ions undergo increases. However, as the ion's kinetic energy increases, the mean number of collisions for a given pressure of gas within the cell, decreases. The kinetic energy of the ion has a heavy influence on the number of collisions it undergoes, meaning that the pressure of the neutral gas must be adjusted to account for the kinetic energy of the ion.

In terms of collision cell design considerations, assuming that Au^+/CO_2 is approximately representative of the behaviour of ion-neutral collisions of interest, the cell must be constructed such that it can maintain a constant pressure between approximately $1 \times 10^{-5} - 2 \times 10^{-3}$ mbar assuming Langevin limited collisions, to ensure that single ion-molecule collisions are the most common event within the cell based on the simple models presented above. Its ability to do this is dependent upon three factors:

- The rate at which gas is leaked into the cell.

- The collision cell's aperture size.
- The pumping speed of the pumps that maintain vacuum with the collision region.

A choked flow occurs when

$$P_{\text{downstream}} \leq P_{\text{upstream}} \left(\frac{2}{\gamma + 1} \right)^{\frac{\gamma}{\gamma - 1}}, \quad \text{where } \gamma = \frac{c_p}{c_v}, \quad (2.5)$$

$P_{\text{downstream}}$ is the pressure downstream of the orifice, P_{upstream} is the pressure upstream of the orifice, c_p is the heat capacity at constant pressure and c_v is the heat capacity at constant volume.

The vacuum within the collision region of the experiment is maintained by an Edwards STP 803C turbomolecular pump backed with a Leybold D40B rotary vane pump, giving a pumping speed of approximately 800 L s^{-1} (for N_2). An 800 L s^{-1} pumping speed vastly exceeds the amount of gas that can be leaked into the cell using a needle valve, making the assumption of a choked flow of gas out of the collision cell's apertures reasonable. The mass flow rate ($\dot{m}$, in kg s^{-1}) out of one of the collision cells apertures can be modelled by:

$$\dot{m} = C_d A \sqrt{\gamma \rho_0 P_{\text{upstream}} \left(\frac{2}{\gamma + 1} \right)^{\frac{\gamma}{\gamma - 1}}} \quad (2.6)$$

where C_d is the dimensionless discharge coefficient ($0 < C_d \leq 1$), A is the cross-sectional area of the orifice in m^2 , γ is the specific heat capacity as defined in Equation 2.5, ρ_0 is the density of the fluid in kg m^{-3} and P_{upstream} is the upstream pressure in bar.^[387]

If the mass flow rate out of the collision cell is modelled using the choked flow assumption with an ideal discharge coefficient, then the relationship between the pressure within the cell and the mass flow rate out of the cell as a function of both aperture diameter and the internal pressure of the cell for CO_2 (molar mass = 44 and $\gamma = 1.289$) is shown in Figure 2.2. Mass flow is positively correlated with both the internal pressure of the cell and the aperture size.

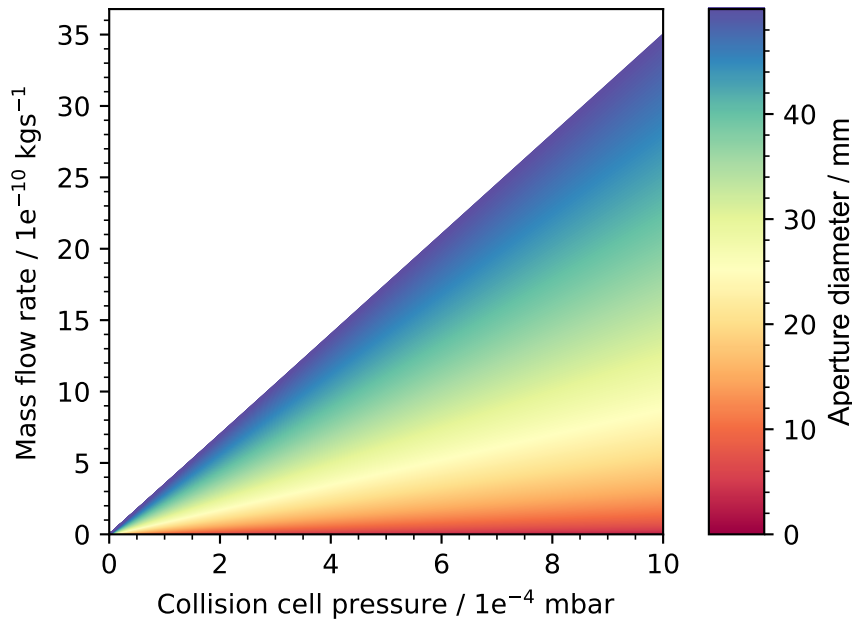


Figure 2.2: The mass flow rate out the collision cell as a function of the pressure within the cell using the choked flow approximation. The discharge coefficient was assumed to be 1 - i.e. ideal discharge conditions. The figure was generated using a simple model based on Equation 2.6 with appropriate physical constants.

2.1.3 Controlling the Kinetic Energy of the Ion and the Temperature of the Neutral Gas

Using the same conditions as presented in Figure 2.2 for Au^+ and CO_2 , the collision frequencies as a function of ion kinetic energy over a range of CO_2 temperatures are plotted (the pressure of CO_2 is held at 2×10^{-4} mbar) in Figure 2.3. The mean numbers of collisions drop with increasing temperature and ion kinetic energy as the faster the ions and neutral molecules approach one another, the smaller their collisions cross-section. Figure 2.1 indicates that both the neutral gas temperature and the ion kinetic energy need to be controlled not only for control over the collision energy but for control over the collision frequency.

The ion optics presented in Section 3 are responsible for the control of the ion kinetic energy, thus no further details are presented here. Cryo cooling and / or heating of the collision cell / neutral gas will in principle be possible, but initially the gas will be left at room temperature.

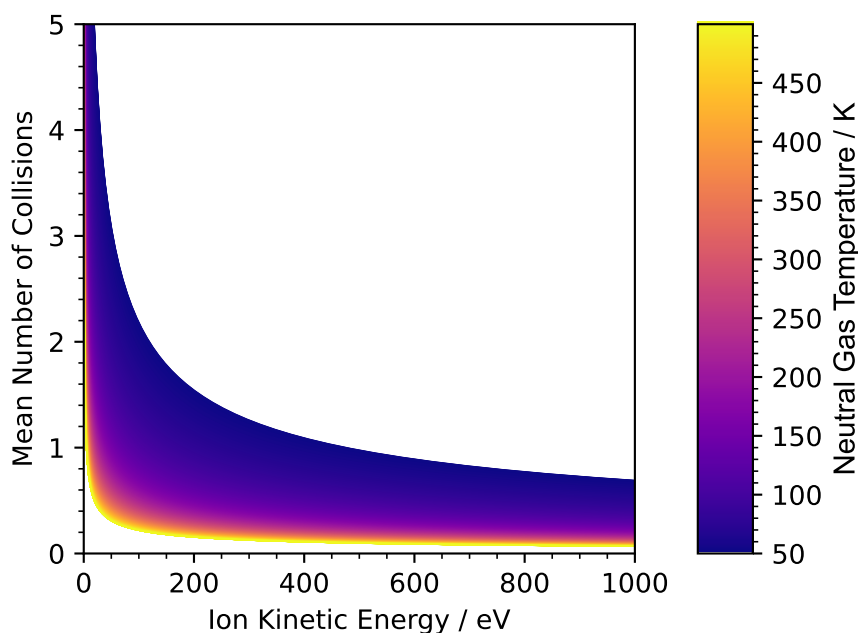


Figure 2.3: The predicted mean number of collisions that an Au^+ ion undergoes with CO_2 within a 100 mm long collision cell as a function of both the Au^+ kinetic energy over a range of CO_2 temperatures. The CO_2 pressure is set to 2×10^{-4} mbar. The data was generated using a simple model based on Equations 2.2 through 2.4 substituted into Equation 2.1.

2.1.4 Cell Length

The effect of changing the cell length is illustrated in Figure 2.4 using the same Au^+/CO_2 system used in the previous examples. The cell length is linearly related to the mean number of collisions, meaning that through the use of a longer cell, lower pressures of gas may be used to achieve the same number of collisions for a reaction. While beneficial to the longevity of the turbomolecular pumps, this does rely on being able to source a leak valve capable of leaking gas into the cell at a very low rate, so a balance must be struck between the two.

2.2 IR Excitation

The collision cell within this experiment has the additional complicating factor of needing to allow for vibrational excitation of the neutral molecules or the ionic metal species, and as such additional considerations associated with the IR light are required.

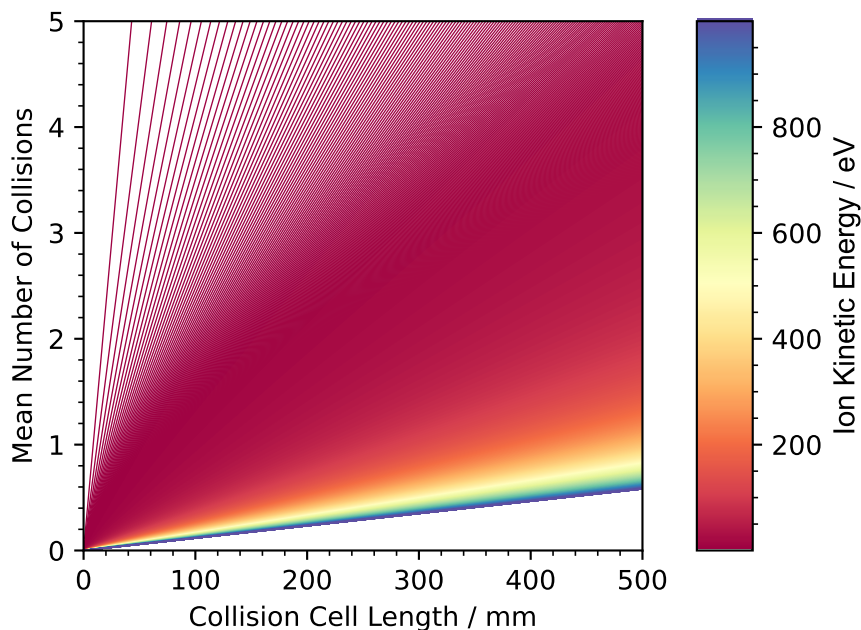


Figure 2.4: The mean number of collisions that an Au^+ ions undergo with CO_2 as a function of the collision cell length over a range of ion kinetic energies (0-1000 eV). The collision cell is filled with 2×10^{-4} mbar of CO_2 held at 297 K.

2.2.1 IR Beam Propagation Through Cell

The intended experiments with to be performed with the apparatus presented here involve vibrational excitation of the ions or the neutral molecules, thus an IR laser beam needs to be brought into (and out of) the cell. There are two ways in which the beam may be brought into the cell: either the beam may be counter-propagated along the ion's axis of travel through the cell; or the beam may be passed orthogonally through the cell. These are shown in Figures 2.5 a and b respectively.

While bringing the IR beam orthogonally does offer the opportunity to generate a multi-pass cell similar to the designs on Utz and co-workers [85], it prevents the IR beam from interacting with the ion beam as efficiently as it would in the counter-propagated setup. The ions are only ever able to collide with neutral molecules that occupy the volume the ion's collision cross-section carves out as it passes through the cell, so there is no need to excite neutral molecules outside of the path of the molecular beam. The addition of two extra apertures within the collision cell would increase gas leaking from the cell, both making the desired pressure within the cell harder to maintain but also increasing the gas

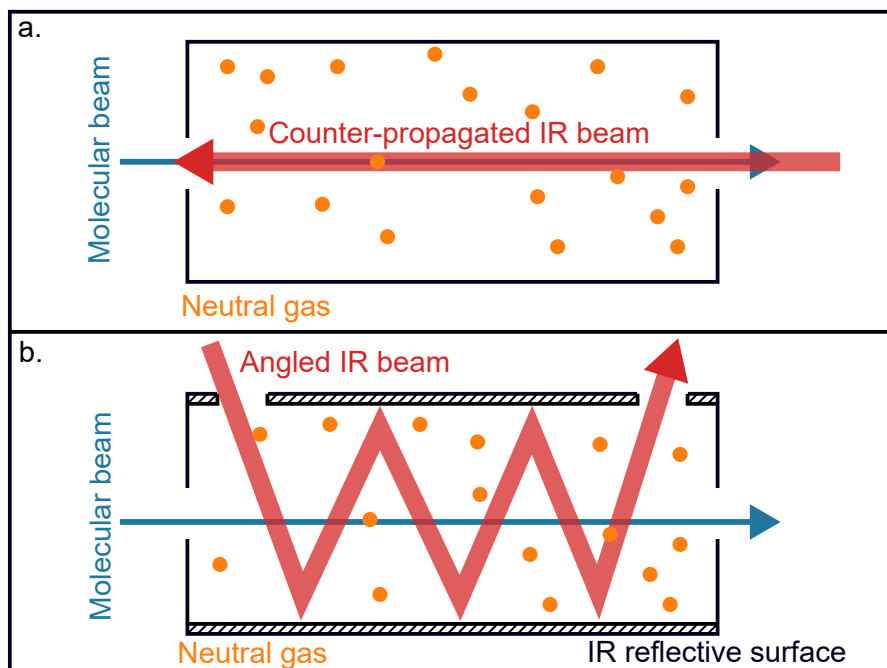


Figure 2.5: The two methods by which the infrared beam may be brought through the collision cell. a. The IR laser beam is counter-propagated through the cell along the axis of the molecular beam. b. The IR beam is brought in at an angle to the ion beam and collision cell. The interior of the cell is optically coated such that it is highly reflective of IR radiation and a multi-pass cell is formed.

load on the turbomolecular pumps used to maintain vacuum.

These three factors led to the decision to have the IR beam pass through the cell, allowing for the laser to enter and exit the cell via the same apertures that the ion beam enters and exits, meaning no modifications to the cell were required for infrared excitation.

2.2.2 Collisions With Vibrationally Excited States

Allowing the laser beam to propagate through the cell along the same axis as the ion beam allows for two kinds of experiments to be performed, as illustrated in Figure 2.6. Either the neutral molecule or ion/charged complex can be excited by the infrared beam, allowing for maximum flexibility in the search for mode-selective chemistry.

In cases where the neutral molecule is vibrationally excited, the probability of collision becomes dependent on the neutral molecule's motion to a much greater degree than when carrying out a collision with a vibrationally excited ion. The laser beam extrudes a volume through the collision cell, and any neutral molecules within the volume at t_0 when

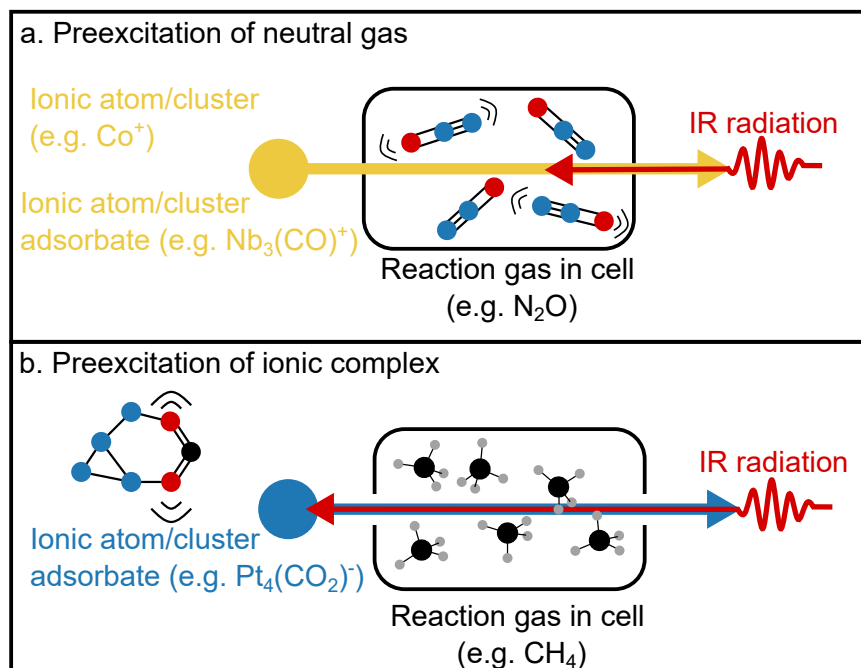


Figure 2.6: The two experimental operating modes that the collision cell may be run in when using the pass-through mode. (a) Pre-excitation of a neutral reaction gas - the neutral gas is vibrationally excited prior to interaction with an ionic atom/cluster or ionic atom/cluster complex. (b) Pre-excitation of an ionic atom/cluster complex - the ionic atom/cluster complex is vibrationally excited prior to interaction with a neutral gas.

the laser fires can be vibrationally excited. The photon fluence from the laser system is more than capable of vibrationally exciting all molecules within the volume that the laser beam extrudes within the collision cell. However, as time progresses and the ion progresses through the collision cell, excited states can be lost from the ion beam extruded volume through three key routes:

- Radiative loss of excited states
- Collisional deactivation.
- Excited state species random motion.

With no resonant photons present (after the excitation laser pulse), the excited state species may spontaneously transition back to the ground state, releasing a photon in the process. The rate of spontaneous emission, measured using the Einstein A coefficient, is

linked to the number of excited states ($N(t)$) at time t through the relationship:

$$\frac{\partial N(t)}{\partial t} = -A_{21}N(t) \quad (2.7)$$

Einstein A coefficients for spontaneous emission have been experimentally and theoretically calculated for various systems. For the first excited states of the CO₂ asymmetric stretch, the Einstein coefficient is 33.4 s⁻¹ for $v = 0 \leftarrow v = 1$.^[388] This means that the excited state lifetime of a vibrationally excited state is significantly longer than both the mean time between collisions and the transit time of the reactant ion through the cell (a 1 eV Au⁺ ion will pass through a 100 mm long cell in 1.01×10^{-4} s). Ions within the experiment will generally be travelling faster than this, and as such, the long radiative lifetimes of vibrationally excited molecules mean that losses due to spontaneous emission are of no concern on the timescales of interest.

The Maxwell-Boltzmann distributed system of neutral molecules undergoes Brownian motion, and as such, the molecules will occasionally collide with one another. Their mean collision rate is determined by:

$$Z = \rho\sigma\sqrt{\frac{8k_B T}{\pi\mu}}, \quad (2.8)$$

where ρ is the number density of gas molecules, σ is their collision cross-section, T is the temperature of the gas and μ is the reduced mass of a pair of molecules. By taking the reciprocal of the collision frequency, the average time between one collision and the next is obtained. Modelling CO₂ as a hard sphere with a collision cross-section of πr^2 (where r is the C=O bond length of 1.16 Å) the mean time between the collision of a single CO₂ molecule with another is 0.18 s when the CO₂ pressure is held at 1.0×10^{-4} mbar. This value vastly exceeds that of time it takes a 1 eV Au⁺ ion to pass through the 100 mm cell (1.01×10^{-4} s), meaning that, even assuming a 100% effective collisional deactivation success, on the timescale of the experiment, collisional deactivation is of no concern. The ion beam has a set route through which it can pass through the cell (i.e. from the entrance aperture through to the exit aperture). The laser beam should counterpropagate along exactly the same axis. Neutral molecules within the cell move randomly with speeds defined by a Maxwell-Boltzmann distribution, allowing the excited state neutral molecules to diffuse in and out of the ion beam path, which changes the

probability of a collision. The mean velocity of a molecule within a Maxwell-Boltzmann distribution is defined by:

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}} \quad (2.9)$$

where m is the mass of the molecule and T is the temperature of the molecules. In the 1.01×10^{-4} s it takes a 1 eV Au^+ ion to pass through the 100 mm cell, a neutral molecule will likely have moved an average distance of 38 mm. This is a significant distance, and results in the collision probability of the ion and neutral molecules decreasing rapidly with time after initial excitation.

To model collision probabilities effectively, the probability that a molecule remains within the ion beam volume at time t after the molecules have been excited needs to be determined. This was modelled by measuring the overlap of the probability sphere of a neutral molecule starting off within the volume extruded by the laser beam with the volume extruded by the ion beam. The cumulative distribution function of a Maxwell-Boltzmann distribution is given by:

$$\sum f(0 \rightarrow v) = \text{erf} \left(\frac{v}{\sqrt{2}a} \right) - \sqrt{\frac{2}{\pi}} \frac{v}{a} \exp \left(\frac{-v^2}{2a^2} \right), \quad \text{where } a = \sqrt{\frac{k_B T}{m}}, \quad (2.10)$$

m is the mass of the molecule and T is the temperature of the molecules. Equation 2.10 can be solved for various cumulative probabilities to determine the velocity below which $X\%$ of molecules within the distribution fall. Determination of this velocity allows the radius of the sphere within which 95% of molecules starting from a given position will be at time t after excitation. The overlap of this sphere with the cylindrical volume extruded by an ion beam provides an approximate estimate of the probability that the two will collide. Using this idea, a computational model using Monte Carlo integration was developed.

Figure 2.7 shows the probability of an ion colliding with an excited state of CO_2 (1.0×10^{-4} mbar at 297 K) as a function of time-based on a range of starting displacements of the excited state molecules within the ion beam. An exponential drop-off in collision probability occurs with time, and within 20 μs the probability drops to less than 0.1. Although the drop-off is fast, it is not so fast that an excited state collision is impossible.

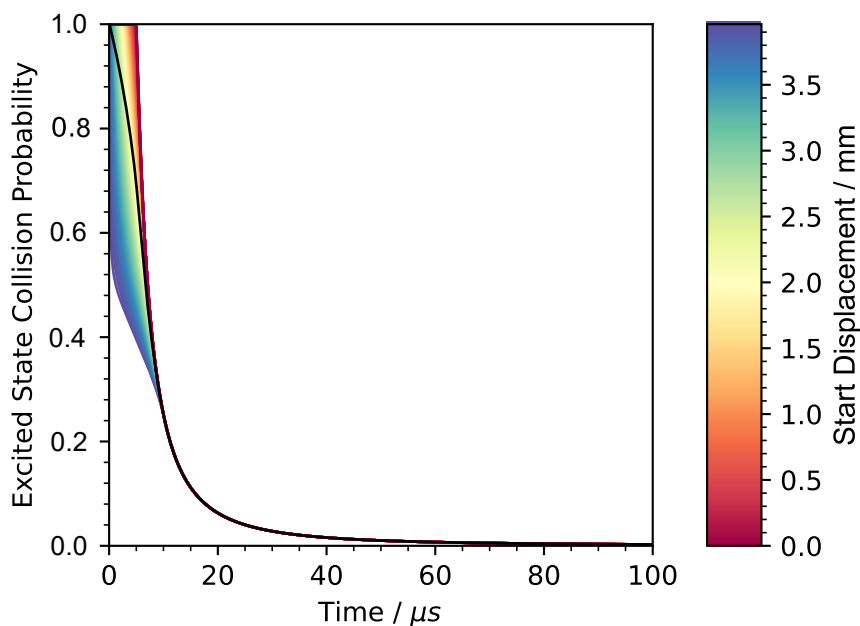


Figure 2.7: The probability that an ion will collide with an excited state CO_2 molecule as a function of time after the excitation via laser pulse for a variety of different starting displacements from the centre of the ion beam. The CO_2 gas is held at 297 K. Both the ion beam and laser beam are assumed to be perfectly overlapped each with a diameter of 4 mm. The black line indicates the mean collision probability.

To ensure the maximum chances of an excited state collision, the excitation pulse needs to be confined to within $\pm 5 \mu\text{s}$ of the ion entering the cell.

Vibrationally excited ions present much less of an issue as they travel on a predefined trajectory through the cell should consequently be "lost" to the experiment due to diffusion at a much lower rate. This presents more of an issue where the ions The long radiative lifetimes of vibrationally excited species, coupled with the fact that ions within molecular beams do not undergo collisions with one another, means that vibrationally excited ions are not lost due to spontaneous emission nor collisional deactivation. One major concern however, is the loss of vibrationally excited states due to IVR within the complexes. IVR is heavily dependant upon the the specific molecule and its exact calculation falls outside the scope of this thesis. However, when using the experiment, clusters and complexes should vibrationally excited when they are within the cell to minimise excited state losses due to IVR.

2.3 Collision Cell Design

Figure 2.8 shows a CAD render of the collision cell and a photograph of the cell prior to its addition to the experiment. Based on all of the factors above, the collision cell was designed to be 100 mm in length, with a 60 mm internal diameter tube. As the collision cell sits on the same optical rail as all other optics, it is supported at either end via 100 mm disks with the same 11 mm holes on the corners of a 60×60 mm square centred on the disk for support rods. The apertures at either end of the cell, responsible for the transmission of ions through the cell and allowing gas to flow out of the cell, are drilled into plates that can be screwed into either end of the collision cell with an o-ring to generate a gas seal (as opposed to drilling directly into a permanent face of the cell). This allows for plates with different aperture sizes to be swapped into the experiment with ease if required. The apertures initially selected were 10 mm in diameter. As the IR was to be brought in through the same apertures as the ions, no additional modifications were required in order to accommodate the IR laser beam. The collision cell is fitted with 1/4" Swagelok fittings on either side to allow gas to be brought in and measured from either side of the cell.

2.4 Gas Delivery and Pressure Measurement Within the Collision Cell

2.4.1 Gas Delivery

To leak gas into the cell at a constant rate, a computer-controlled needle valve (VAT 62.7) was purchased for use in the experiment. The needle valve is attached to the collision cell using a PTFE hose (thereby electrically isolating it) as illustrated in Figure 2.9. The valve is able to control pressures within the range 1×10^{-8} mbar Ls^{-1} to 2 mbar Ls^{-1} with fine control at all pressures. A schematic diagram of the valve both open and closed is shown in Figure A.4 within the Appendix.

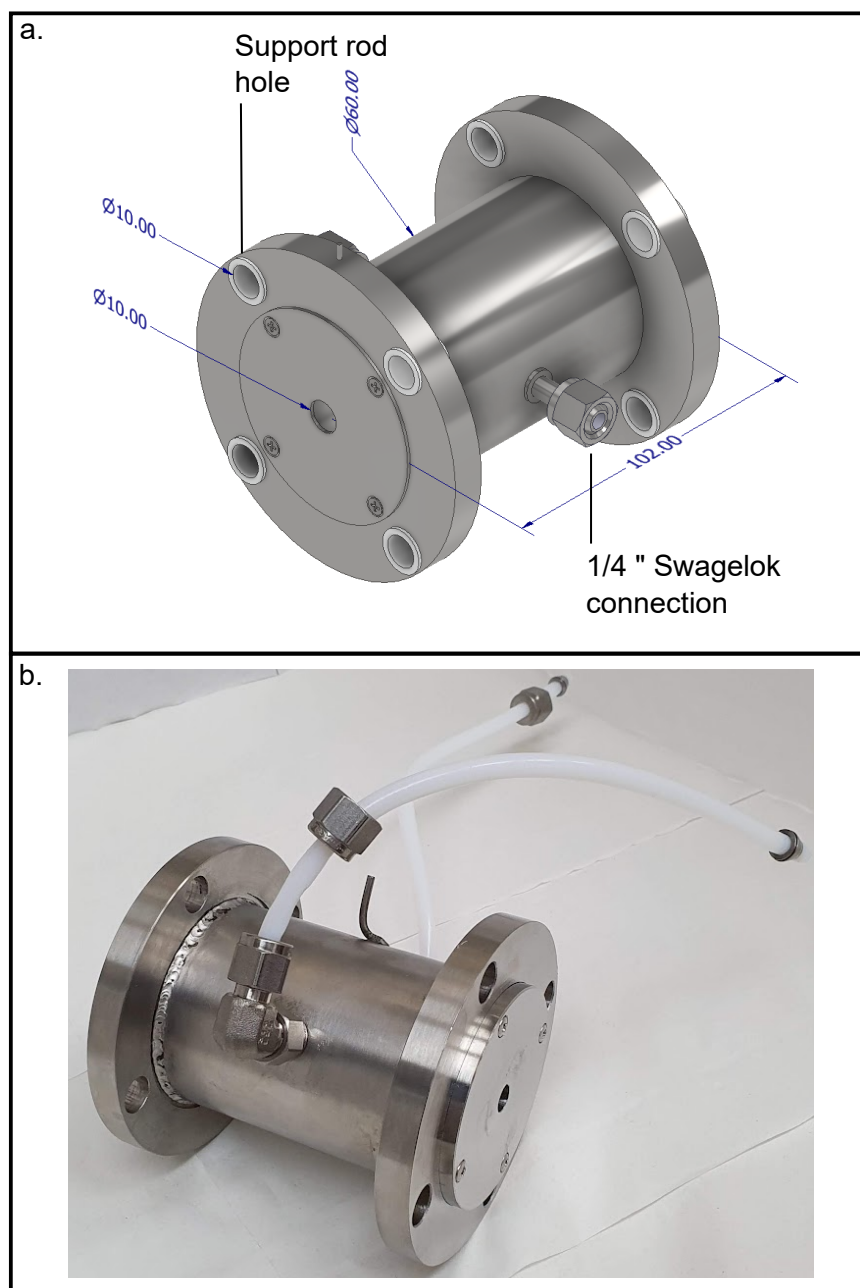


Figure 2.8: (a) CAD render of the collision cell with dimensions in mm. (b) Photograph of the collision cell prior to its addition to the experiment. The collision cell has 90° 1/4" Swagelok elbows with Polytetrafluoroethylene (PTFE) tube for gas delivery attached. See also Appendix B3.

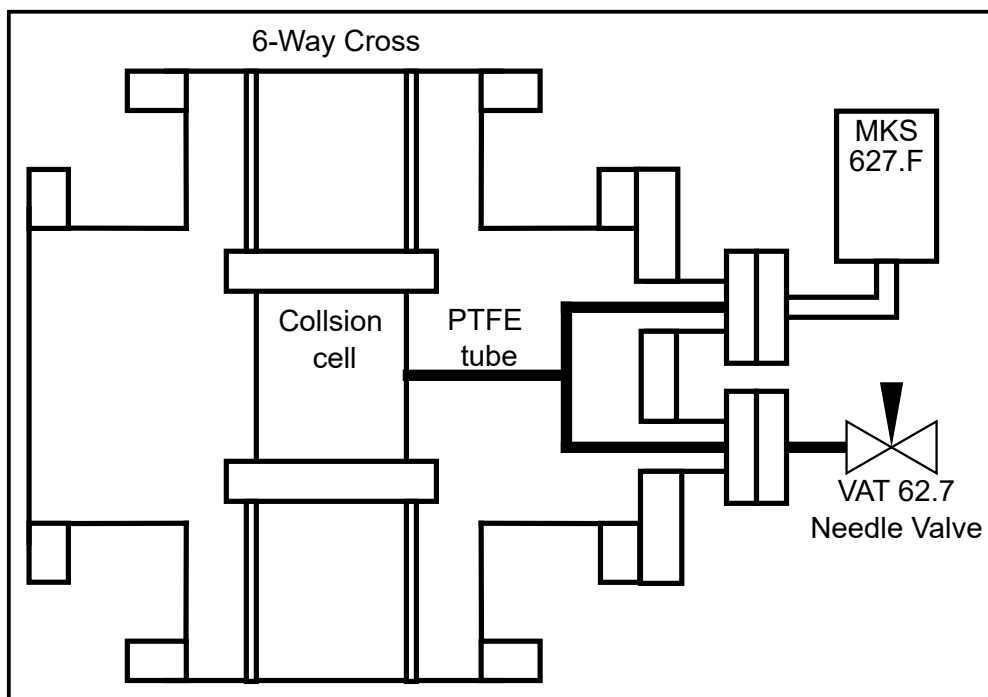


Figure 2.9: Delivery of reactant gas to the collision cell. Gas from the manifold in Figure A.3 is bled into the experiments by the VAT 62.7 needle valve. The line delivering the gas to the cell is split into a T junction. One arm of the T leads to the collision cell itself whereas the other loops back to a feedthrough for a connection the pressure gauge (MKS 627.F Baratron capacitance manometer gauge) which must remain outside the cell.

2.4.2 Pressure Measurement

As multiple different gases are to be used within the cell, the use of pressure gauges sensitive to the gas type is precluded. The only gauge type capable of measuring pressure over the range of interest with no gas-specificity are capacitance manometer gauges. Based on previous collision experiments, the MKS 627.F Baratron capacitance manometer was selected for use with the collision cell.^[389]

Accurate pressure reading within the cell is hampered by the fact that the pressure gauge has to be mounted externally to the experiment, meaning that the pressure gauge itself is located some distance away from the cell itself. In an attempt to gain a more accurate pressure measurement, the pressure gauge was attached (via PTFE hose) to the collision cell as shown in Figure 2.9. While there almost certainly is an error in the absolute pressure reading using this gauge, due to its distance from the collision cell, there are likely far greater errors within the experiment (e.g. collision energy), so this setup was

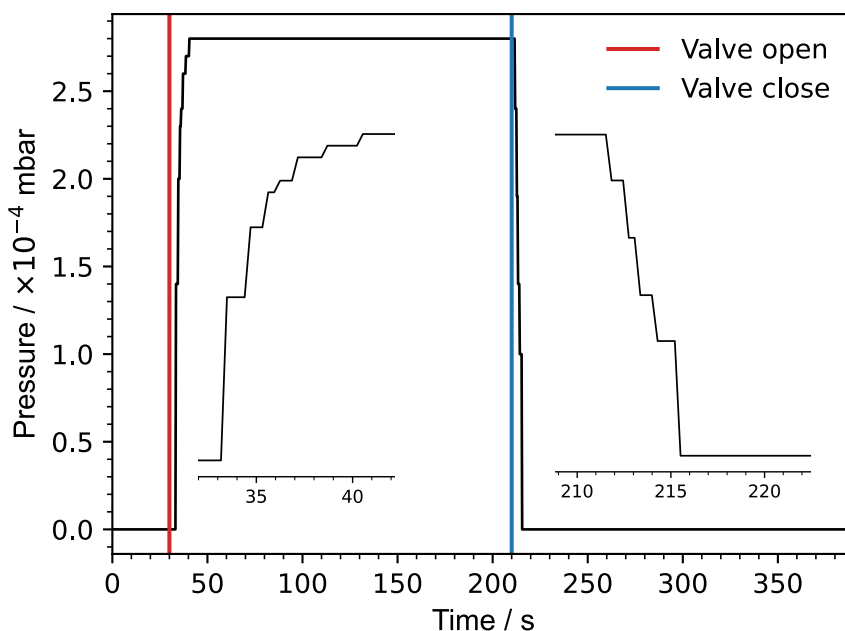


Figure 2.10: Relative pressure recorded within the collision cell when the flow rate is set to 2×10^{-5} mbar ls^{-1} . The valve is opened to the set flow rate at 30 s (indicated by the red line) and closed at 210 s (indicated by the blue line). A stable pressure of 2.8×10^{-4} mbar is achieved within 10 s of the valve opening. The N_2O at a 1.5 bar was held at 1.5 bar backing pressure. The inset figures illustrate the shape of the regions in which the pressure is increasing and decreasing with smaller timescale.

deemed acceptable and should, anyway, give a good relative measurement.

2.4.3 Performance and Control

Figure 2.10 shows the pressure of N_2O measured by the Baratron gauge within the cell as a function of time. The pressure is sampled approximately every 0.25 s. The needle valve is opened 30 s after the recording is started and closed after 180 s of being open. The recording is allowed to run for another 180 s before the recording is stopped. Within 10 s of the valve opening, a stable pressure of 2.8×10^{-4} mbar is achieved. When the valve is closed, it takes at least 6 seconds for pressure to return to "0" - i.e. all the gas bled into the cell to be removed.

If the measurements performed to generate the data shown in Figure 2.10 are repeated at a variety of different set flow rates on the needle valve, then a calibration between the set flow rate on the needle valve and the pressure achieved inside the cell can be produced.

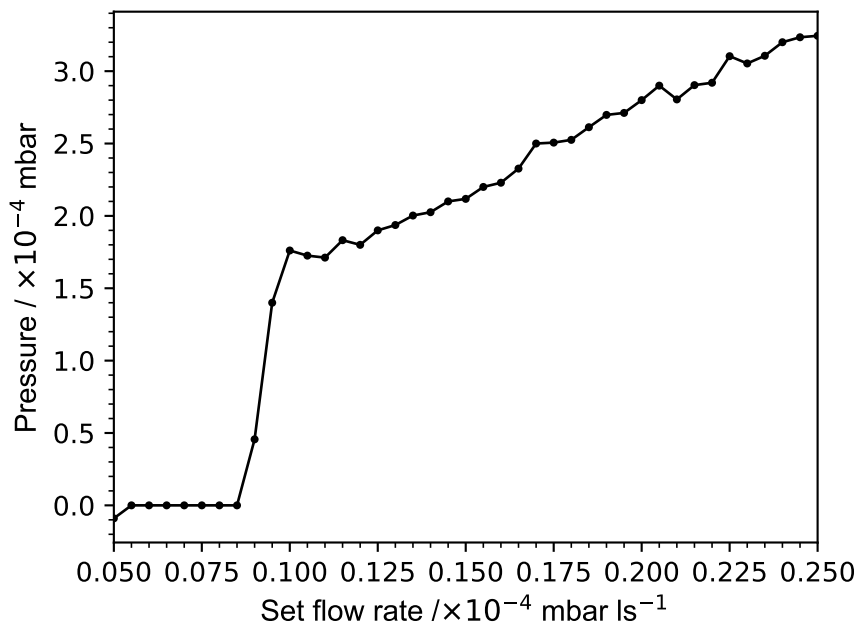


Figure 2.11: The measured pressure (using the MKS Baratron 627.F capacitance manometer) of N_2O within the collision cell as a function of the flow rate set on the VAT 62.7 variable leak rate valve. The backing pressure of N_2O was set to 1.5 bar.

An example of this pressure calibration is shown in Figure 2.11 for N_2O held at 1.5 bar backing pressure. Until a leak rate of more than 8.5×10^{-6} mbar ls $^{-1}$, no gas is admitted to the cell (that the pressure gauge can detect).

The generation of the calibration plot is handled within the custom LabVIEW software, and the calibration is stored such that the user may request a specific pressure within the cell without having to manually adjust the VAT 62.7 variable leak rate valve. The software is not described here for brevity, but is freely available on GitHub (see Appendix section F). The origin of the non-linear increase observed prior to 1×10^{-4} mbar is unclear however likely stems from non-linear steps within the motor that drives the needle valve within this range.

2.5 Conclusions

Based on simple physical modelling, a collision cell is capable of allowing ions to undergo single collisions with neutral molecules. Additional modelling of vibrational excitation and quenching demonstrates that a pulsed IR laser passing through the cell allows a

significant proportion of the neutral molecules to be excited and undergo a collision with an ion demonstrating the viability of the experiment using the collision cell design. Based on the physical constraints of the experiment, both a needle valve to leak gas into the collision cell (at a rate required to generate pressures needed for single collisions) and a pressure gauge to measure the pressure within the cell were also selected. Custom LabVIEW software to interface both the needle valve and pressure gauge was developed to allow the end user to set a desired pressure of neutral gas within the cell.

3 | Experiment Development

This chapter describes the design, construction and development of a major new instrument for the study of mode-selective ion-molecule chemistry based around the design of the collision cell presented within the previous chapter. Over the course of the instrument’s development, it has seen three major iterations in its design and each of these iterations is presented in this chapter along with some relevant characterisation of the issues that required further development and optimisation of the design.

3.1 Instrument Iteration I: Orthogonal Extraction with Mass Filtration

The instrument design presented within this section represents the initial concept design of the experiment and what was intended to be the end goal, rather than a stepping stone. Due to the issues surrounding the design (detailed in Section 3.1.3), several subsequent iterations of the experiment were developed. A description of the broad overview of the experiment is given before specific regions are explored in more detail.

3.1.1 Experimental Overview

The instrument was initially designed to generate a distribution of metal ions, spatially and energetically focus them such that they could be mass filtered with the narrowest possible energy distribution, collide them with a neutral molecule, and then detect the collision products. Vibrational excitation could be introduced to either the ionic metal species or the neutral species by means of excitation with a (pulsed) IR laser beam (as described in Section 2.2). Based on these objectives, mass-selected ions with well defined kinetic energies (minimal kinetic energy distributions) needed to be generated and directed through the collision cell described in Chapter 2 before being detected with a highly sensitive detection method. The experiment was designed with regards to these key concepts. All components beyond the ion source, based on a previous design within the Mackenzie group, each ion optic/component was developed using the SIMION 8.2 software

suite or in-house simulations developed as part of the work presented in this thesis (see Chapter 2). For brevity, the relevant data from SIMION simulations are confined to the Appendix.

The initial instrument design consisted of seven key parts: an ion source, in-line extraction, orthogonal extraction, free flight/mass filtration region, collision region, reflectron extraction region and finally the time of flight / detection region. Each is shown in Figure 3.1. Briefly, an ion / ionic cluster beam, produced via laser vaporisation of a metal target, is skimmed and passes into a differentially pumped chamber containing a series of Wiley-McLaren lenses in tandem. The first Wiley-McLaren lens spatially focuses the ion beam into the centre of the orthogonal Wiley-McLaren lens, which is then used to extract the ions along a new axis. Deflection plates are included to deflect the ion beam back onto the axis and compensate for the initial velocity of the ions along the original axis. An Einzel lens is used to focus the beam through the instrument. The ion beam is then allowed to undergo free flight before reaching a deflection-based mass filter which deflects all but the desired ions off-axis. The ions then pass through a collision cell that can be floated at a potential to decelerate the ions to a user-defined lab frame kinetic energy. Having passed through the collision cell and undergone a single collision with a neutral molecule (or not), the ions are then passed into another Wiley-McLaren lens that extracts them into a modified commercial reflectron time-of-flight (ReToF) mass spectrometer from the R.M. Jordan company where the ionic species (parent ions and ionic reaction products) are mass separated and detected.

3.1.2 Experimental Components

3.1.2.1 Ion Source

The ion source, common to all experiments within the Mackenzie cluster labs, is based on the designs of Smalley^[272] and Bondybey^[277], and is discussed in detail in Section 1.3 of the introduction. Briefly, the beam from a 532 nm Nd:YAG laser (Continuum Minilite II / Qunatel Ultra) is focused onto a rotating metal target generating an ablation plume which is entrained into a pulse of neutral (and inert) gas from a Parker-Hannifin General Series 9 Solenoid valve. The gas pulse is skimmed to generate a molecular (ion) beam.

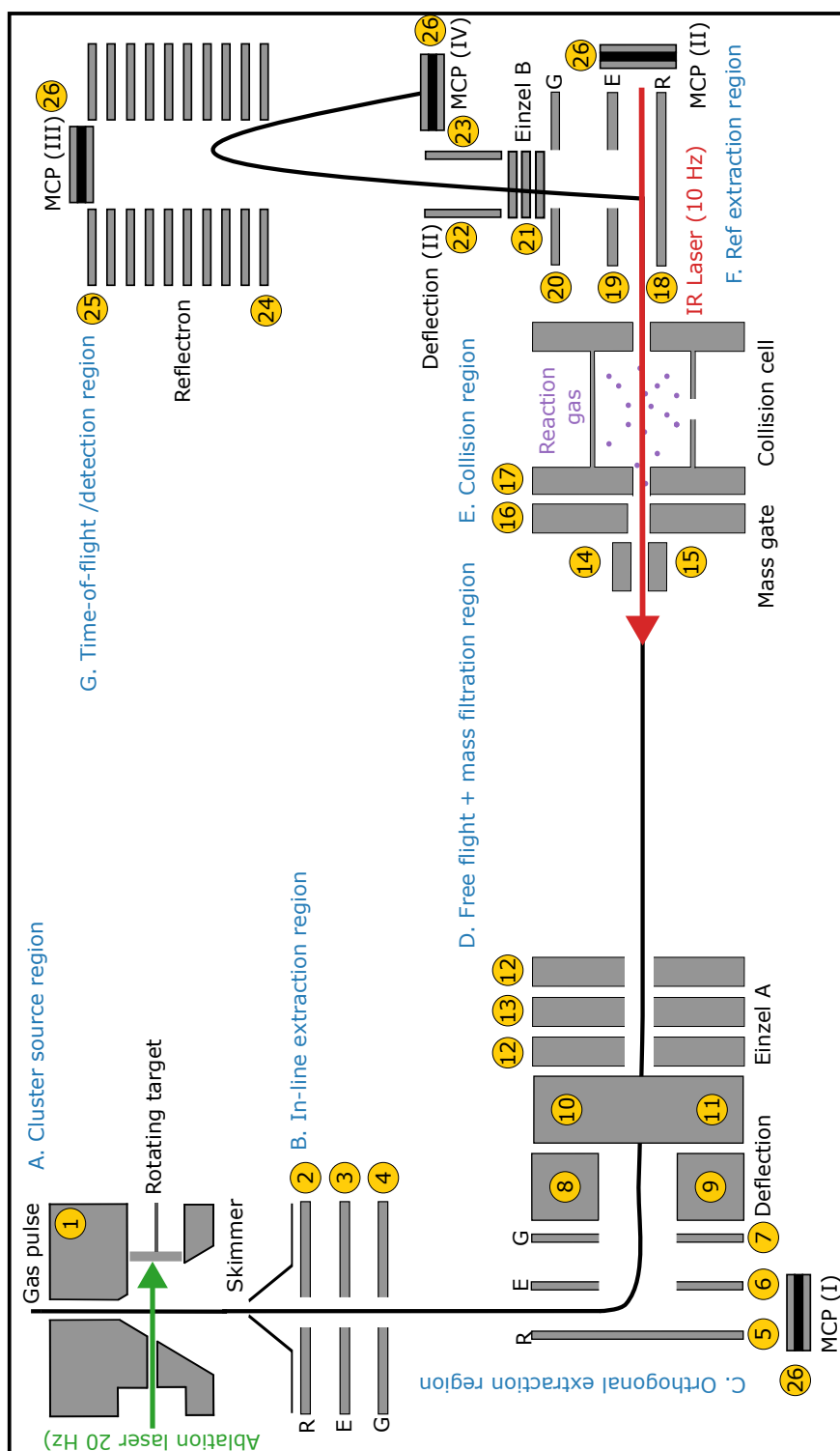


Figure 3.1: Schematic diagram illustrating the components of the initial iteration of the VEC (vibrationally enhanced collision) experiment. The black line illustrates the path of the molecular beam through the experiment. The red and green arrows represent the IR (tunable) and (532 nm) ablation lasers. The yellow circles represent controllable components applied and correspond to values given in Table 3.1.

Number	Control	Pulsed?
1	Source float	No
2	In-line WM repeller	Yes
3	In-line WM extractor	Yes
4	In-line WM ground	No
5	Orthogonal WM repeller	Yes
6	Orthogonal WM extractor	Yes
7	Orthogonal WM ground	No
8	Deflection left	No
9	Deflection right	No
10	Deflection top	No
11	Deflection bottom	No
12	Einzel A 1/3	No
13	Einzel A 2	No
14	Deflection Mass filter I	No
15	Deflection Mass filter II	Yes
16	Decel entrance float	No
17	Decel float	No
18	ReToF Repeller	Yes
19	ReToF Extractor	Yes
20	ReToF Ground	No
21	ReToF Focus	No
22	ReToF Deflection 1	No
23	ReToF Deflection 2	No
24	Reflectron Front	No
25	Reflectron Back	No
26	MCP	No

Table 3.1: The controlled potentials in the initial design of the collision experiment in Figure 3.1.

Ideally, the laser ablation source used within the experiment would produce a spatially and energetically well-resolved packet of ions that could be used directly within collision experiments. Figure 3.2 shows an example ToF spectrum of Au^+ ions, recorded 230 mm downstream of the skimmer of the laser ablation source used within these experiments (MCP I in Figure 3.1) with no potentials applied to any of the electrodes. Unlike the narrow distributions seen for the expansion of pure gases into a vacuum, the ions arrive (over) a very broad time window (between 600-1000 μs), indicating that the source produces very long packets of ions. The extremely intense signal at $t = 0$ is associated with the light from the ablation laser pulse, and is assigned to either photo-electrons or photons hitting the MCPs used to detect the ions.

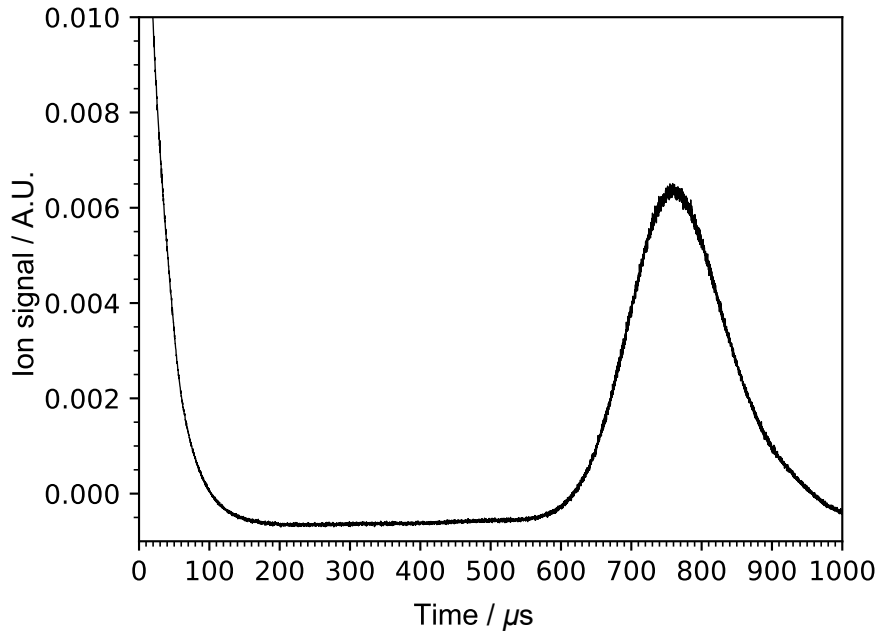


Figure 3.2: A representative ToF spectrum of Au^+ ablated in the presence of Ar (pulsed through a Parker-Hannifin General Series 9 Solenoid Valve at a backing pressure of 5 bar with a pulse duration of 400 μs).

The broad distribution of ions from this source can be assigned to two possible things: either the ions are widely distributed in space, or they have a large kinetic energy distribution. The solenoid valve used within the source opens for a minimum of approximately 400 μs , meaning that a long "slug" of gas is admitted to the source when the valve is open. Metal atoms / ions are generated during the 10 ns ablation pulse. The collisions with the gas molecules within the source distribute the ions over a wide area, as the number and frequency of collisions for each ion are not identical, meaning that they are entrained into the beam at different rates and thus become spatially spread out. The metal target is ablated orthogonally to the direction of the gas pulse, meaning that the ions must undergo many collisions with the gas before they are accelerated to the gas velocity. It is highly unlikely that all of the gas molecules are accelerated to the full beam velocity, resulting in a velocity distribution for the entrained ions. From ToF alone, it is difficult to assign which of these effects is more dominant without extensive theoretical modelling which is well beyond the scope of this thesis.

Regardless of their origin, the broad range of ToFs indicates that the ions produced from the source are inappropriate for attempting to carry out collision experiments. The

poor energy resolution induces a large uncertainty into the collision energies but also results in the ions generated within the source spread being out over an ever larger space, resulting in poor signal-to-noise ratios. Thus both the spatial and energy resolution must be addressed. Much of the rest of the work presented within this section of the thesis concerns the development of ion optics to control the ions generated in the source and make them suitable for collision experiments.

3.1.2.2 Orthogonal Extraction and Mass Filtration

Based on the ToF spectrum in Figure 3.2, the ions need to be both spatially focused and energetically focused. Orthogonal extraction with a Wiley-McLaren lens can uniquely do both of these simultaneously. The Wiley-McLaren lens was originally designed to spatially focus packets of ions with broad spatial distributions at the expense of energy resolution.^[307] The imparted energy distribution can be minimised by orthogonally extracting the ions as opposed to extracting them in-line as ion beams from laser vapourisation sources are more narrowly distributed orthogonal to the ion beams' direction of travel as compared to the ion beams length in its direction of travel. This concept is illustrated schematically in Figure 3.3. In addition to the spatial focusing of the ions, when orthogonally extracted, the velocity distribution of the ions in their original axis of travel is converted into a spatial distribution. This is easily rationalised through consideration of the vector sum of the orthogonally imparted velocity and the original ion velocity.

Two key disadvantages associated with orthogonal extraction were identified during SIMION simulations. Firstly, if extracting a broad packet of ions, the Wiley-McLaren lens would need enormous apertures to successfully extract large numbers of ions from the initial beam. With the small open aperture required in a Wiley-McLaren lens (with no mesh), many ions would be lost due to collision with the electrode. To avoid this, using an in-line Wiley-McLaren lens with low potentials pulsed onto the extractor and repeller electrodes, the ions from the source were gently spatially focused into the centre of the orthogonal extraction electrodes. Upon orthogonal extraction, the ions started from a much smaller spatial distribution resulting in a much higher transmission of ions. The second disadvantage of the orthogonal extraction with a Wiley-McLaren lens was that the lens itself had no means to deal with the residual radial velocity of the ions, which, while advanta-

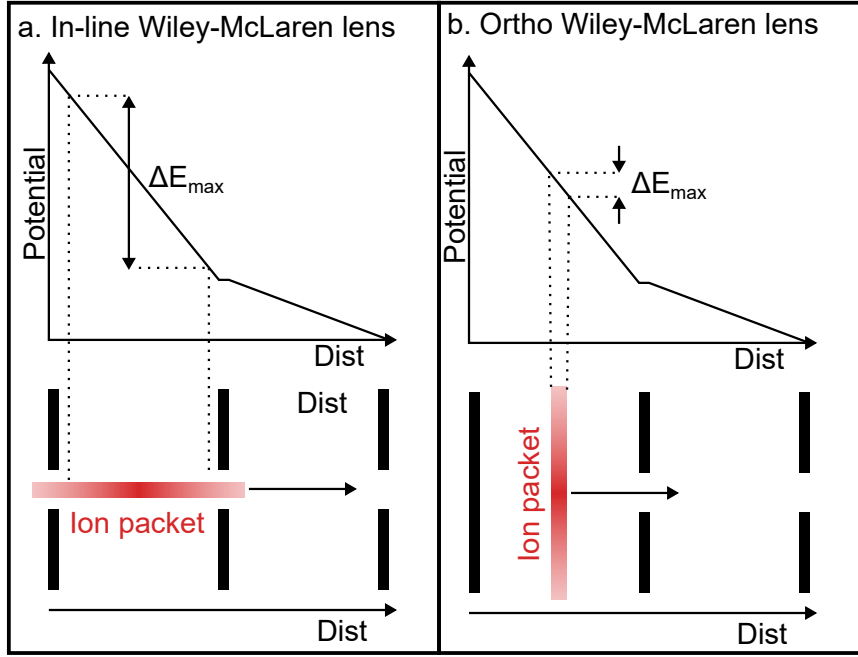


Figure 3.3: (a) The maximum difference in energy induced between ions in an in-line Wiley-McLaren lens. (b) The maximum energy difference induced between ions in an orthogonal extraction Wiley-McLaren lens.

geous for energy resolution, caused problems with ions walking off the main instrumental axis and being lost. This was avoided through the simple addition of deflection plates immediately after the orthogonal extraction region. To account for the additional focusing effects of the Wiley-McLaren lens, an Einzel lens is included immediately after the deflection plates.

Figure 3.4 (a) illustrates an example ToF spectrum recorded of Au^+ ions spatially focused with the in-line Wiley-McLaren lens. It illustrates the ability of the in-line Wiley-McLaren lens to spatially focus ions, reflected in the sharp time of flight signal at 254 μs . By adjusting the extractor/repeller ratio, the ions can be focused into the centre of the orthogonal extraction Wiley-McLaren lens. Figure 3.4 (a) also shows the broad packet of ions from Figure 3.2, indicating that only a small proportion of the ions in the originally generated packet are spatially focused.

Figure 3.4 (b) illustrates a ToF spectrum containing a single peak resulting from Au^+ ions striking MCP II in Figure 3.1. It illustrates that the Au^+ ions can be successfully orthogonally extracted, and spatially focused within the experiment thus showing that the combination of two Wiley-McLaren lenses, deflection plates and Einzel lenses were

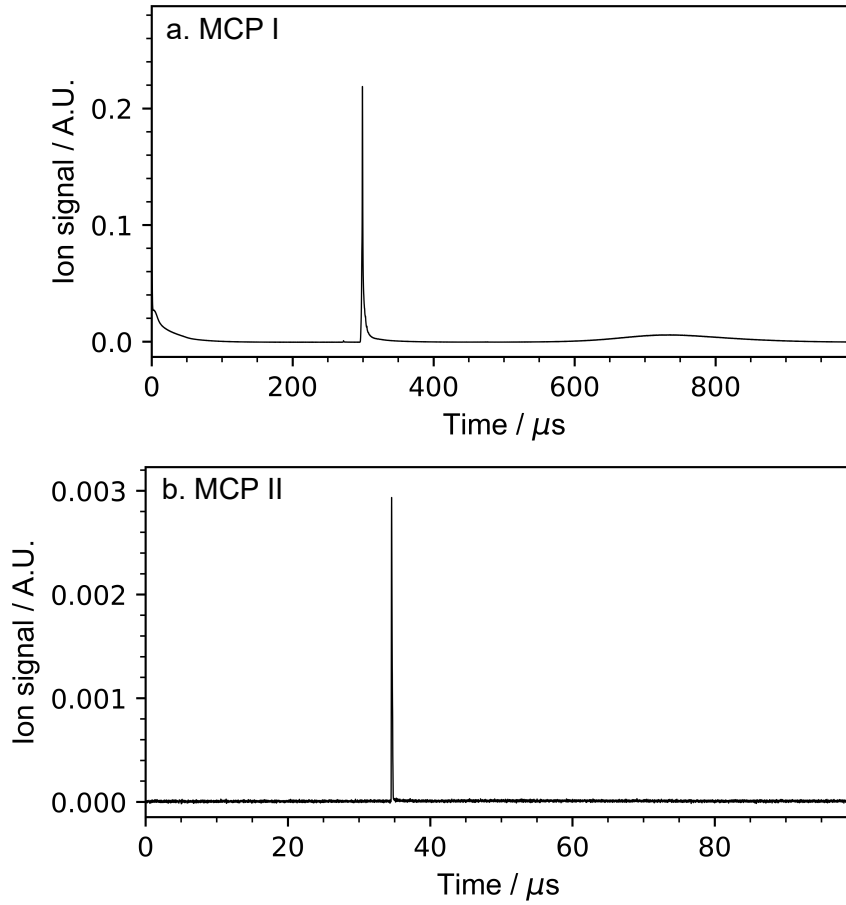


Figure 3.4: (a) Example ToF trace of Au^+ ions recorded at MCP I in Figure 3.1 using the in-line Wiley-McLaren lens to spatially focus the ions. The ToF is measured with respect to the ablation laser. (b) Example ToF trace of Au^+ ions recorded at MCP II in Figure 3.1 demonstrating successful orthogonal extraction of the ions. The ToF is measured with respect to the orthogonal extraction pulse.

successful in orthogonally extracting ions to generate a spatially resolved ion packet with minimal induced energy uncertainty. The ions presented in Figure 3.4 (b) were imparted with approximately 850 eV of kinetic energy during their extraction.

Figure 3.5 shows a series of ToF traces recorded as a function of the repeller potential whilst maintaining a good spatial focus of the ions with the extractor electrode. As the extraction energy is reduced, even with a correction from the deflection electrodes, the ion signal is lost due to the ions having a velocity that is too high in their original axis of travel. Figure 3.5 indicates that successful orthogonal extraction requires high kinetic energies to be imparted to the ions. As illustrated in the wealth of work from Armentrout and coworkers^[198–250], metal ion-neutral reactions typically require between 0–100 eV of

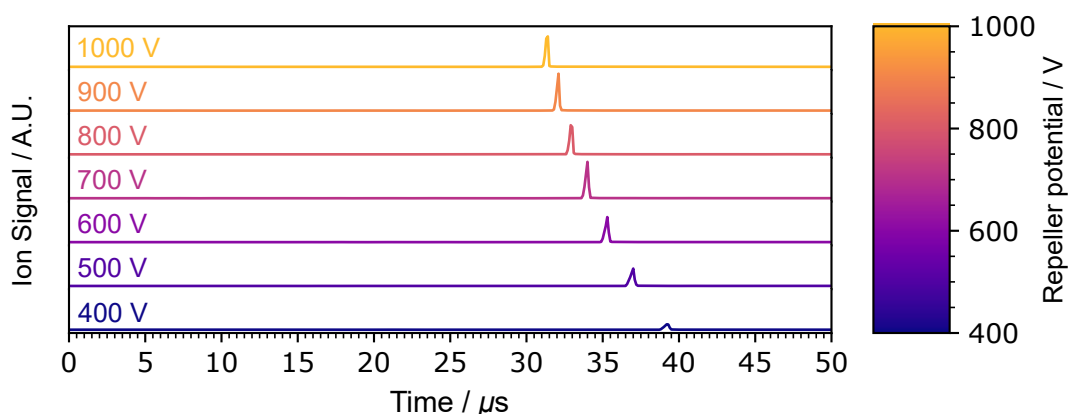


Figure 3.5: ToF traces of Au^+ ions recorded as a function of the repeller potential. The E/R ratio (0.0.8) is maintained through adjustments to the extractor potential concurrently with the repeller. No ToF traces below 400 V repeller potential are shown as there was no ion signal detected.

ion kinetic energy to generate collision energies (assuming a room temperature gas) that generate appreciable reaction cross-sections, meaning that the high orthogonal extraction energy becomes problematic for the experiment. To account for this the ions needed to be decelerated.

Having been extracted orthogonally, the ions are allowed to undergo free-flight for approximately 1 m before they pass through a deflection plate mass filter (based on a design of Duncan and co-workers).^[390] The deflection plates are held at a potential which deflects all of the ions off-axis. When the ion of interest arrives, the potentials on the deflection plates are removed (using a pulsed MOSFET switch) allowing the ions to fly on a straight trajectory through the rest of the instrument and thus be detected. As the mass filtration represented the least important aspect of the experiment, the mass filtration was relegated to simulations within SIMION only and has yet to be characterised experimentally and hence excluded from this thesis.

3.1.2.3 Ion Deceleration

Collisions within the experiment need to occur at low collision energies to (0-10 eV) within the COM frame to ensure a high excitation function for the reaction of interest (see Section 1.4.3) as well as to ensure that the effects of vibrational energy may be seen within the experiment. If the ion and neutral molecule are allowed to collide at very high

kinetic energies, the reaction will likely be driven over the barrier by the translational energy alone, partially if not completely obscuring any vibrationally mediated chemistry. Although the ionic metal species will likely be vastly heavier than the neutral molecule, meaning that most of the kinetic energy in the collision is located within the centre of mass (see Section 1.4), the ions require deceleration prior to collision to achieve the desired kinetic energy.

Prior to entering the collision cell, the ions can be decelerated between the (grounded) plate to which the mass filter deflection plates were mounted and the collision cell itself by floating the collision cell at a potential to generate a retarding electric field. Figure 3.6 shows a series of ToF traces of Au^+ ions recorded as a function of the applied decelerating potential (see Figure 3.1). As the deceleration potential was increased from 0 V through to 900 V, the ion signal can be seen to simultaneously broaden and decrease suggesting that the ions become spatially more spread out and a greater number of those ions fail to strike the detector. Based on the principles outlined by Allison and coworkers in their 1991 paper^[391], the Einzel lens was optimised to pre-focus the ions prior to passing them through the deceleration stage to minimise interaction with the curved electric field around the entrance aperture of collision cell.

The observed broadening is easily rationalised by considering the fact that the Wiley-McLaren lens ratios were optimised with no deceleration potential present within the system. The inclusion of the deceleration potential slows the ions down - essentially increasing their ToF, meaning that the Wiley-McLaren ratio no longer focuses the ions spatially at the detector. The deceleration only acts axially and has no effect on the radial velocity of the ions; thus, when decelerated, the radial components of the ion's velocity vector contribute more and cause the ion to "walk off" the axis. While insignificant with small deceleration potentials, the radial velocity becomes a significant proportion of the ion's velocity vector when decelerated significantly. The radial velocity of the ions comes from three sources: the energy of the ion in the original axis of travel (prior to orthogonal extraction), the deflection plates, and the Einzel lens, and if these do not perfectly balance out, then the ions will have radial velocity in addition to their axial velocity.

Converting the ToFs shown in Figure 3.6 to ion energies (based on a simple linear accel-

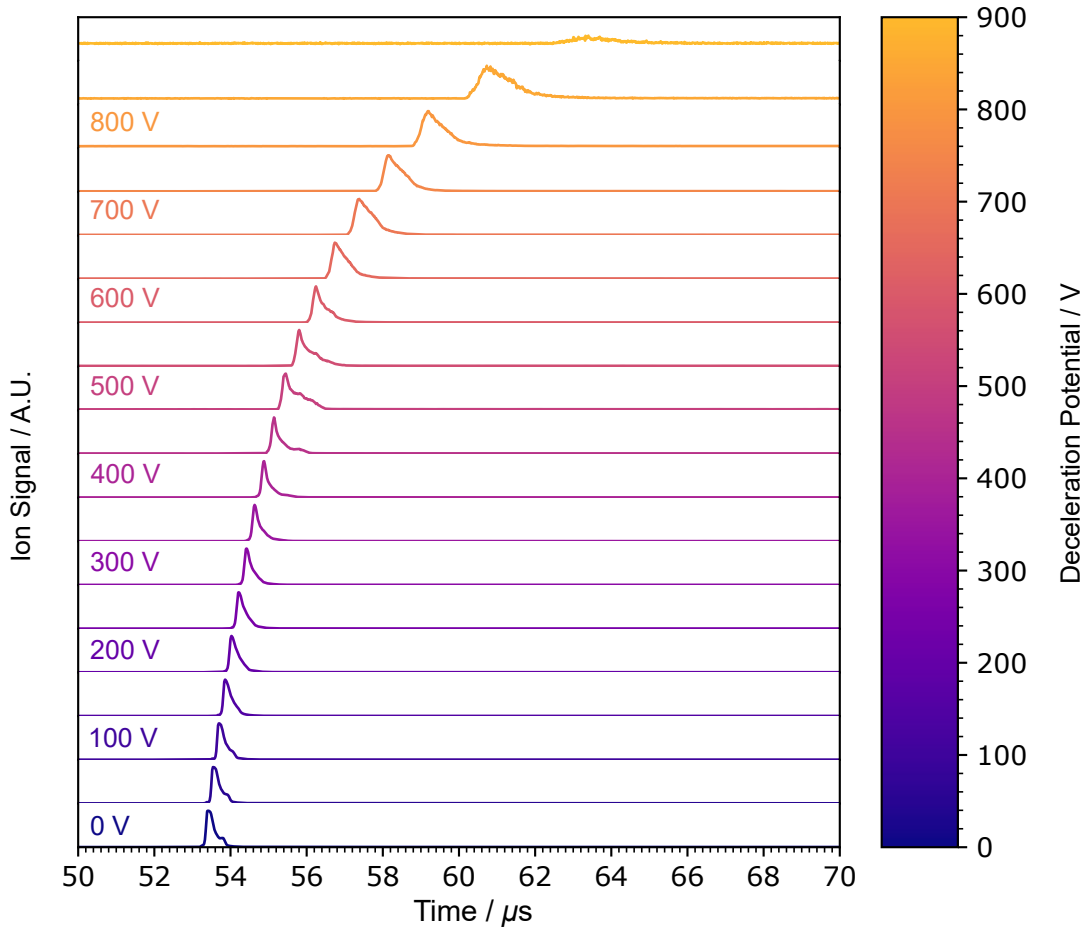


Figure 3.6: ToF traces of Au^+ ions recorded as a function of the deceleration potential applied. The ions were orthogonally extracted using potentials of 1000 V on the repeller, 887 V on the extractor and 0 V on the ground electrode. Both the Einzel lens and deflection plate potentials were varied with the deceleration potentials to achieve maximum ion signal. The recorded ToFs here (given relative to the orthogonal extraction pulse) differ significantly from those recorded in Figure 3.5 due to differing MCP positions.

eration model) illustrates that the accessible range of kinetic energies within the collision cell whilst maintaining appreciable signal spans from the ion's extraction energy down to 150 eV. In order to achieve lower lab-frame energies, and hence COM collision energies an alternative iteration was subsequently developed (see Section 3.2).

3.1.2.4 Collision Cell For Single Collisions

The design and construction of the collision cell, already presented in Chapter 2, formed the basis around which the rest of the experiment was designed. Rendered in Figure B.7 in Appendix Section B.3, the collisions cell consist of a 60 mm diameter and 100 mm long

hollow steel tube with apertures at either end (10 mm). Apertures (mounted onto plates for easy alteration of aperture size) are placed at either end to allow ions to pass through as well as gas out of the cell. The two 1/4" Swagelok connections on either side of the cell facilitate gas being bled into the cell and pressure measurements within the cell to be taken. Gas is admitted into the cell using an electronically actuated needle valve (VAT 62.2), and the pressure of the gas within the cell is measured using an MKS Baratron 627.F pressure gauge. The pressure gauge and needle valve are interfaced with custom LabVIEW software that, based on an (automatically generated) calibration curve, allows the user to set a known pressure of gas ($1 \times 10^{-5} - 1 \times 10^{-1}$ mbar). Gas is delivered to the needle valve via a custom-built manifold shown in Figure A.3 in Appendix Section B. The pressure within the cell is set such that based on the ion kinetic energy and the neutral gas temperature, the most likely outcomes are either a single collision between an ion and neutral or no collisions at all based on Poisson statistics (see Chapter 2). The method through which this is determined is outlined in Chapter 2.

To electrically isolate the cell from the grounded vacuum chambers and gas delivery system, gas is delivered to the cell via PTFE tubes with 1/4" Swagelok fittings.

The ToF spectrum presented in Figure 3.4 (b) was recorded with the ions passing through the collision cell with no deceleration potential applied, indicating that the deflection blocks and Einzel lens were capable of both steering and focusing the ion beam through the collision cell.

3.1.2.5 Ion Detection

Within the experiment, ions are detected using microchannel plates (MCPs). Four are placed throughout the instrument for ion detection at various points. The first two MCPs (MCPs I and II in Figure 3.1) are used to detect the properties of ions that are steered through the first two parts of the experiment and, as such, are not used for accurate mass-resolved product detection. MCP set I (Kore-35691 25mm MCP assembly mounted to a DN100CF flange), situated in-line with the source, is used to ensure that the source conditions produce ions and to optimise the in-line Wiley McLaren conditions, whereas MCP set II (Kore-35691 25mm MCP assembly mounted to a translation stage) is used

to optimise orthogonal extraction conditions as well as deceleration conditions. MCP set II is mounted on a translation stage to allow the IR beam to propagate through the experiment once the ions have been successfully optimised.

Collision product detection is carried out using either MCP set III or IV situated within a commercial reflectron time-of-flight (ReToF) mass spectrometer from the R.M. Jordan company. A schematic diagram adapted from the R.M. Jordan website is presented in Figure E.1 within the appendix. The ReToF mass spectrometer consisted of a set of orthogonal extraction optics (made up of a Wiley-McLaren lens, Einzel lens and deflection plates), a flight tube and a reflectron (consisting of 22 plates).^[392] Detection of ions on MCP set III (Kore-35691 25mm MCP assembly mounted to a DN100CF flange) enables the ReToF mass spectrometer to be run in a linear mode (i.e. with the reflectron inactive), whereas detection of ions (Kore-31594 MCP stack situated in custom mountings shown in Figure E.2 in the Appendix) allows detection of ions with the ReToF mass spectrometer in reflectron mode.

As discussed above, the extraction optics for the ReToF mass spectrometer were designed to extract the ions orthogonally as opposed to inline (such as those used previously in experiments similar to this^[393]). While advantageous in terms of mass resolution of the ReToF, the second orthogonal extraction presents a major problem. The extraction optics associated with the R.M. Jordan ReToF mass spectrometer are rated to a maximum of 5 kV, meaning that the repeller plate may pulse up to a maximum of 5 kV also. High ion kinetic energies (200-1000 eV) prior to orthogonal extraction into the ReToF result in large signal losses (even with steering), making ion deceleration a necessary requirement for the experiment to function in its intended fashion. As the deceleration presented in this section allowed the ions to re-accelerate as they exit the collision cell, detecting ions within the reflectron was impossible so no data concerning the ReToF is presented here.

3.1.2.6 Experimental Control

Control of the experiment can be broadly broken down into three key regimes:

- DC potential control
- Pulse control

- (Collision cell) Gas control

To simplify the end-user experience, the experiment presented here was designed with the goal of being able to control each of the categories presented above from a single lab PC, and to this end, these aspects of the experiment are controlled from a single custom LabVIEW program. Although not discussed in detail here, it is freely available to download from GitHub (see Appendix Section F).

The experiment requires a large number of potentials to be controlled simultaneously, as illustrated by Table 3.1. To allow control of all of these potentials from a single control PC, the electronics workshops in the Department of Physical and Theoretical Chemistry at the University of Oxford (specifically Robert Howcroft) developed a series of DC electronic control units. Each voltage control unit, comprising of a series of DC high-voltage power supplies (from Spellman), are interfaced with a PC via FTDI D2XX chips allowing text-based commands to be sent to the unit to select a potential. Custom LabVIEW drivers were developed for communication with these control units so as they could be easily integrated into the already existent experimental controls. Although these drivers are not discussed in detail here, they are freely available on GitHub (see Appendix Section F).

Pulse generation is achieved using two Quantum Composers 9520 delay generators, each interfaced with LabVIEW via drivers available from National Instruments (see Appendix Section G for the link to these). The lab PC initialises these and can adjust the pulse durations and delays as well as the synchronisation of each of the channels. Pulses from the Quantum Composers 9520 delay generators are used to drive both the laser systems as well as the pulsed voltages. Potentials are pulsed with using fast MOSFET switches (Behlke) which accept TTL pulses from the pulse generators as inputs to control both the time and duration for which the potential is applied to the electrodes.

In addition to the pulse and potential control, a needle valve and pressure gauge that leak gas into the collision cell are controlled with the same LabVIEW program. The pumps maintaining vacuum within the experiment (TMP and backing (rotary vane) pumps) are all controlled externally to the PC.

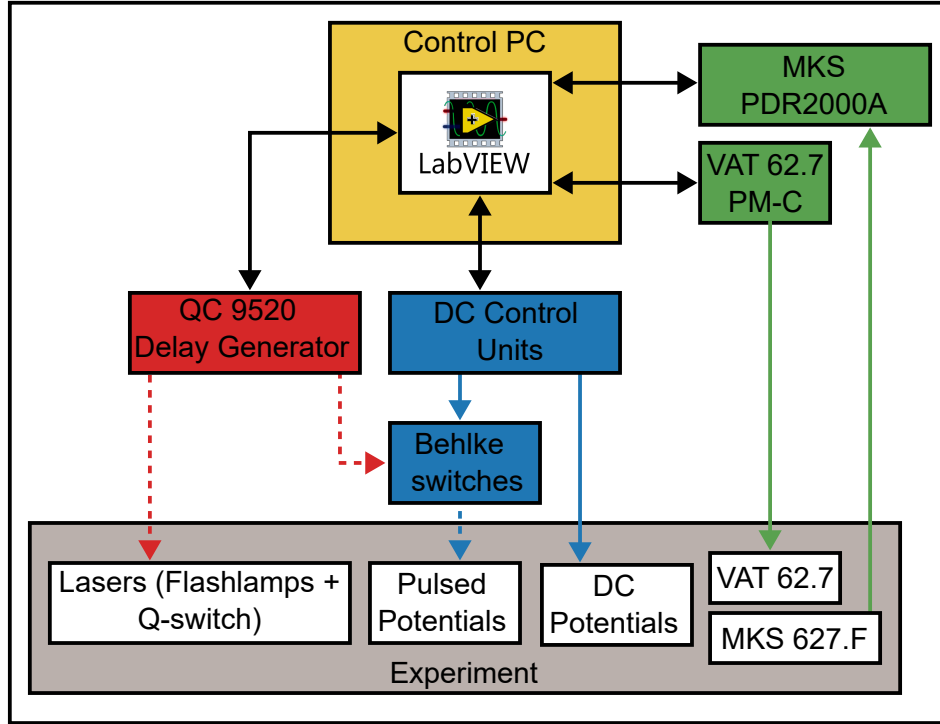


Figure 3.7: Schematic diagram illustrating the arrangement of experiment controls and how they are interfaced with the main control PC/LabVIEW. The black lines indicate USB communications, red dashed lines indicate TTL pulses, blue lines indicate potentials whereas green lines indicate other communications. The VAT PM-C and VAT 62.7 are the controllers and electronically actuated needle valves respectively. The MKS 627.F and MKS PDR2000A are the pressure gauge and its transducer for the collision cell respectively.

3.1.2.7 Data acquisition and analysis

Ion signal may be detected on any of the four sets of MCPs placed throughout the experiment (see Figure 3.1). These MCPs are strategically placed to enable users to generate ion signals at a series of points to allow for optimisation of ions passing through the experiment. The signal from the MCPs is processed using the oscilloscope and processing PC system illustrated schematically in Figure 3.8.

The pulse generator, controlled through the LabVIEW software, sends a pulse to the PXIe 5160 oscilloscope, initiating an acquisition of the time-dependent voltages on the MCP. Aspects of the oscilloscope's acquisition, e.g. sample rate or vertical resolution, are both controlled from the LabVIEW software. Having completed the acquisition, the data is then sent via the PXIe-8381 data transfer card and a PCI express port on the PC to the LabVIEW program. The LabVIEW software processes the data outside of other control

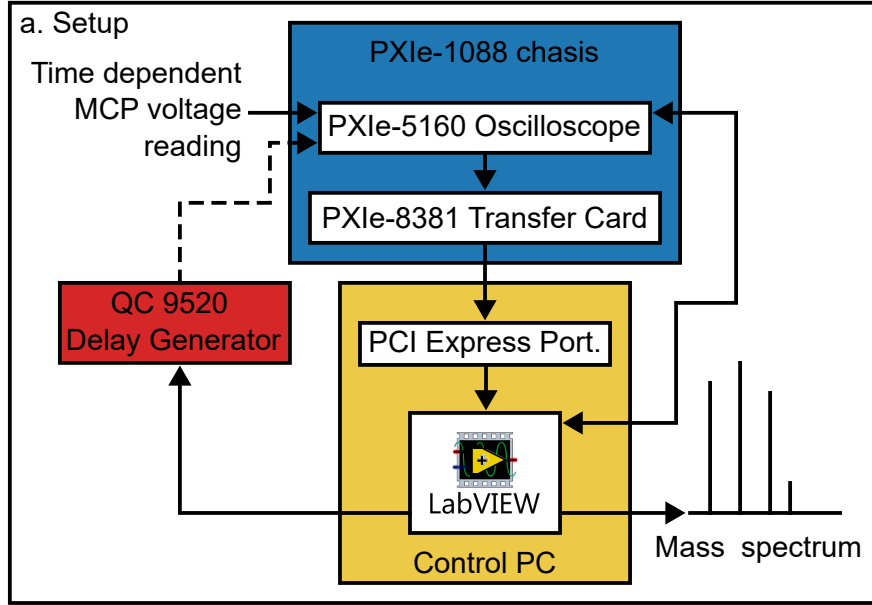


Figure 3.8: (a) Schematic diagram illustrating the arrangement of electronics used to generate ToF traces with the experiment.

loops (to ensure fast processing of the data) to generate a ToF spectrum (within the time domain) and presents it to the user. The data acquisition software is also freely available on GitHub (see Appendix Section F).

3.1.3 Experimental Problems

The initial design of the experiment presented two major issues, which together, prevented this iteration of the experiment from functioning in its intended manner.

1. Upon deceleration many ions were lost from the beam.
2. Ions with axial kinetic energies more than 150 eV were extremely difficult to orthogonally extract and detect in the ReToF mass spectrometer.

Ions must be extracted at high potentials in order to successfully pass them around the corner and direct them along the instrumental axis onto a detector. These high ion kinetic energies are themselves problematic in two senses: firstly, we wish to perform low centre of mass collision energy experiments; and secondly, the high energy ions are impossible to orthogonally extract into the ReToF mass spectrometer. The deceleration, while successful in slowing the ions down, also resulted in significant ion signal losses.

The source of this loss was initially postulated to be the heavy radial focus of the ions during deceleration from field curvature associated with the deceleration field around the apertures.^[394, 395] Even if the deceleration was successful, when exiting the collision cell, the ions would re-accelerate, resulting in the ions gaining back all of their kinetic energy prior to orthogonal extraction - preventing them from being detected within the ReToF if they were originally extracted with high kinetic energy.

In order to circumvent these issues, the experiment was reconfigured with additional ion optics to help with deceleration to produce the second iteration of the experiment, presented in Section 3.2 below.

3.2 Instrument Iteration II: Orthogonal Extraction with No Mass Filtration

3.2.1 Experimental Modifications

Based on the issues encountered in the first iteration of the instrument, several modifications were simulated using SIMION prior to their introduction to form the second iteration of the instrument, shown schematically in Figure 3.9. To reduce the difficulty of steering the ions over long distances without radially confining them, the extended free-flight region and mass filter were removed. Removing each of these allowed the deceleration stage to be placed immediately after Einzel lens A, providing much finer control over to focus of the ions as they enter the deceleration stage. Whilst the SIMION simulations clearly demonstrated that the focusing effect of the Einzel lens placed directly before the deceleration stage increases transmission of ions undergoing deceleration, this effect has already been demonstrated in a very similar system of electrodes by Allison and coworkers^[394, 395] hence the simulations are not included within this thesis for brevity. The focus of Einzel lens A causes the beam to diverge after passing the focal point of the lens, hence to avoid signal loss, a second Einzel lens (Einzel lens B) was included immediately after the collision cell. While Einzel lens B was simulated, its behaviour was extremely similar to that of Einzel lens A so its simulated ion trajectories are not presented as part of this work. Finally, to prevent the ions from accelerating back to their original beam

velocity, an ion re-referencing tube was added to the experiment to re-reference the ions back to a 0 V potential after the ions were decelerated, allowing them to be orthogonally extracted into the ReToF mass spectrometer.

Number	Control	Pulsed?
1	Source float	No
2	In-line WM repeller	Yes
3	In-line WM extractor	Yes
4	In-line WM ground	No
5	Orthogonal WM repeller	Yes
6	Orthogonal WM extractor	Yes
7	Orthogonal WM ground	No
8	Deflection left	No
9	Deflection right	No
10	Deflection top	No
11	Deflection bottom	No
12	Einzel A 1/3	No
13	Einzel A 2	No
14	Deceleration float	No
15	Einzel B 2	No
16	Re-referencing tube	Yes
17	ReToF Repeller	Yes
18	ReToF Extractor	Yes
19	ReToF Ground	No
20	ReToF Focus	No
21	ReToF Deflection 1	No
22	ReToF Deflection 2	No
23	Reflectron Front	No
24	Reflectron Back	No
25	MCP	No

Table 3.2: The controlled potentials in the initial design of the collision experiment in Figure 3.9.

3.2.1.1 Ion Re-referencing

As shown in the previous sections, the ions are decelerated prior to passing through the collision cell. After the collision cell, the ions were originally simply allowed to re-accelerate back up to their original orthogonal extraction velocity. The Angular Reflectron D-850 from the R.M. Jordan company relies upon the ions being orthogonally extracted from their original trajectory. If the ions are allowed to re-accelerate after exiting the collision cell, extracting them into the reflectron with the maximum 5 kV pulses that the

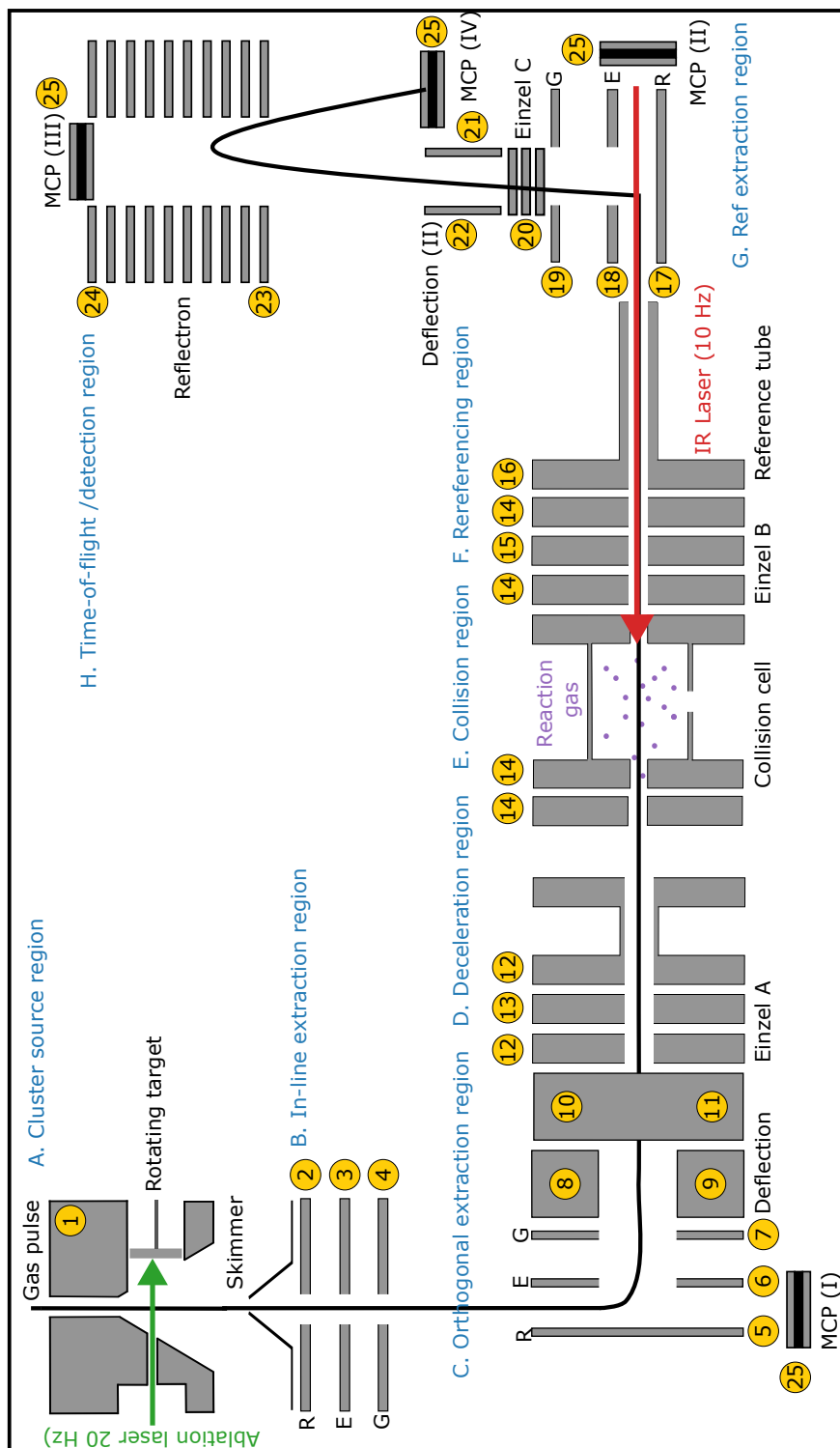


Figure 3.9: Schematic diagram illustrating the components of the second iteration of the VEC (vibrationally enhanced collision) experiment. The black line illustrates the path of the molecular beam through the experiment. The red and green arrows represent the IR (tunable) and (532 nm) ablation lasers. The yellow circles represent voltages applied to the ion optics/electrodes and correspond to values given in Table 3.2.

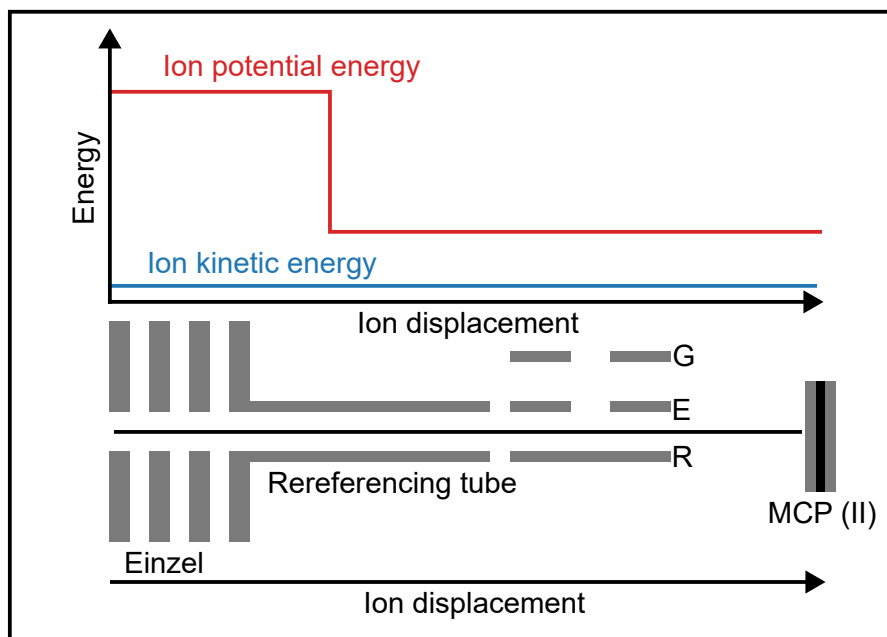


Figure 3.10: The principle of operation of the referencing tube. Ions enter the re-referencing tube floated at the deceleration potential. Whilst the ions are in the tube, the potential is dropped to 0 V preventing the ions from accelerating as they exit. This removed their potential energy without converting it to kinetic energy.

reflectron optics are rated to proved almost impossible. Based on this, the ions must be prevented from re-accelerating after exiting the collision cell. This can be achieved in two ways: either the reflectron extraction optics must be floated at the collision potential and pulsed from the float potential, or the ions can be referenced to ground. Pulsing potentials from a floated base was deemed undesirable due to the required modifications to the existing circuitry (Behlke switches) used to pulse the potentials as well as the poorly defined electric fields generated by floating the extraction optics. Ion re-referencing was, therefore, required to prevent re-acceleration to allow for orthogonal extraction into the Jordan ToF mass spectrometer.

The ions are passed into a re-referencing tube floated at the deceleration potential when they initially enter, and whilst they are passing through, the potential is dropped to 0 V. The symmetric shape of the tube generated as this occurs results in no significant net electric field being generated, preventing the ions from re-accelerating down a field gradient as they exit the floated optics towards the ReToF extraction region. Figure 3.10 illustrates this process schematically.

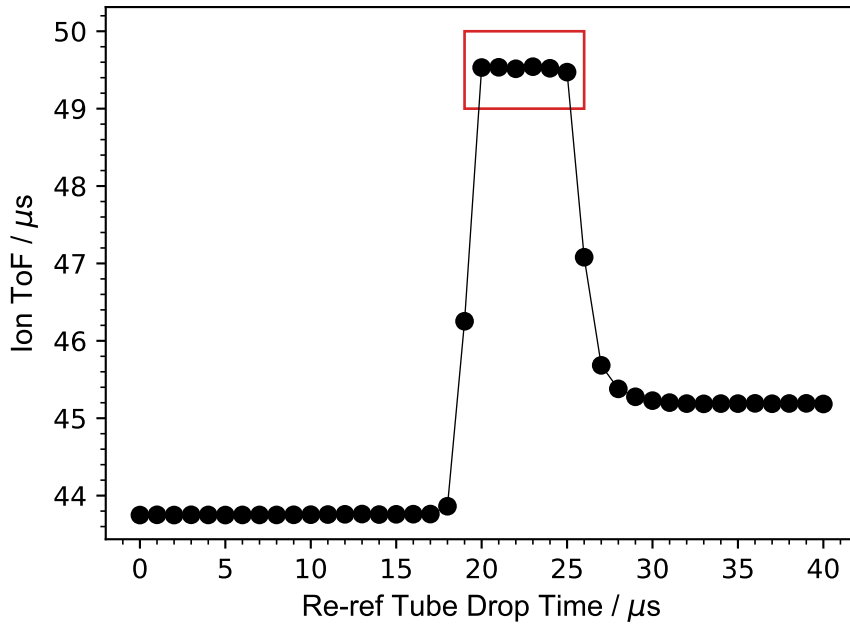


Figure 3.11: Recorded Au^+ ToFs as a function of the time at which the re-referencing tube is dropped to 0 V from the deceleration potential of 300 V. The red box indicates the range of times that the potential is dropped whilst the ions are within the tube (i.e. the successful "drop window").

For correct operation, the potential of the tube must be dropped to 0V when the (bulk of the) ion packet is within the tube, meaning its successful operation has a strong dependence upon the time at which the drop occurs relative to orthogonal extraction. Figure 3.11 illustrates the ToF of Au^+ ions passing through the instrument with a decelerating potential of 300 V applied as a function of the time at which the re-referencing tube drops to 0 V. Between 0 μs and 17 μs the potential drops too early (i.e. before the ions enter the tube) and the ions accelerate due to the field generated between the final electrode of the second Einzel lens and the re-referencing tube, resulting in the shortest ToF observed. As the drop time is delayed further, the ions are able to enter the tube and are successfully re-referenced. As this means they remain at their decelerated kinetic energy, this results in the longest ToF observed. Beyond 25 μs , the ions exit the tube before the potential is dropped and they re-accelerate as they exit the tube, resulting in a reduced ToF. Their ToF is still greater than ions that accelerated earlier, as they travel a greater distance at the lower (decelerated) velocity. In order to re-reference the ions, the drop must occur within the "drop window" indicated by the red box in Figure 3.11.

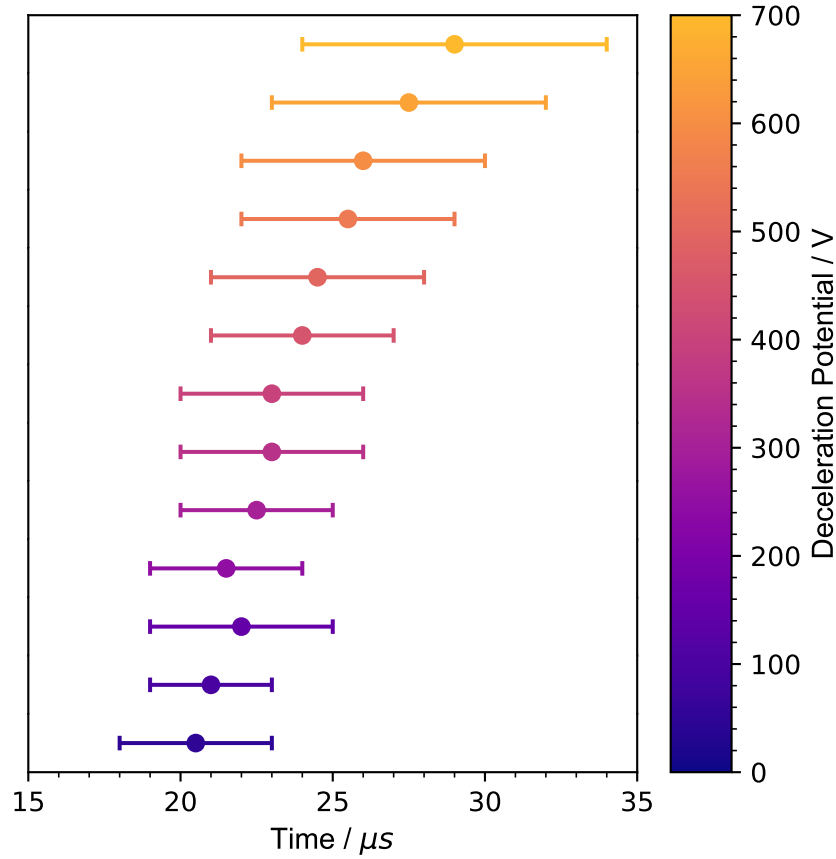


Figure 3.12: Successful "drop windows" (times at which the potential in the re-referencing tube can be dropped ensuring ions are within the tube when it occurs) for Au^+ as a function of the deceleration potentials.

The drop window is dependent upon the decelerating potential applied to the ions - higher decelerating potentials result in slower ions, requiring the drop window to be delayed. Figure 3.12 shows the potential drop window as a function of the deceleration potential. The deceleration potential is plotted up to 700 V only, as with higher decelerating potentials, all signal is lost on the detector as discussed previously. The windows can clearly be seen to increase with the decelerating potential. A clear broadening of the windows can be seen which results from the ion packet spreading out in space due to the deceleration. While Figure 3.12 illustrates the dependence of the drop window on decelerating potential, it is dependent on many other conditions within the experiment not illustrated here. Thus once ideal operating conditions for a given experiment are found, the drop window should be optimised by taking ToF traces as a function of drop time and selecting a drop time that appears within the ideal "drop window" shown in Figure 3.11.

Neither Figure 3.11 nor Figure 3.12 show the effect of ion referencing on the amount of signal that reaches the detector. Figure 3.13 shows a series of ToF traces of Au^+ ions decelerated and re-referenced after orthogonal extraction. When the ions are successfully re-referenced, broadening of the peaks becomes worse when compared to the previous deceleration ToF traces in Figure 3.6. The increased broadening can be ascribed to the increased distance the ions have to travel at the reduced velocity. Where the ions are allowed to accelerate before or after the drop tube, their residual radial velocity causes less of an issue as it makes up a smaller component of their travel vector, however, when they remain decelerated they are able to walk off the central axis to a much greater degree. The broadening of the peaks resulted from increased de-focusing of the ion packet from the spatially focused packet generated from the orthogonal extraction Wiley-McLaren lens when no decelerating potential was present. In addition to the worse performance of deceleration, the peak shapes were markedly different when decelerated - the origin of this was unclear.

While the re-referencing of the ions themselves was successful, the deceleration performance was made markedly worse through the inclusion of the re-referencing tube, with it increasing signal loss, broadening the peaks more, and introducing strange features into the mass signal shape.

3.2.2 Conclusions

As illustrated in the previous section, significant signal losses are incurred when axially decelerating the ions and re-referencing them principally due to excess radial velocity. The simplest solution to this issue is to radially confine the ions, once they are decelerated, with an octupole ion guide in a similar fashion to that used by Armentrout and co-workers and several other groups.^[232, 393] The octupole ion guide prevents the radially divergent ions from drifting too far off axis, ensuring a much higher proportion of ions are transmitted. While an octupole ion guide for this experiment is under active development (by Dr Peter Watson) at the time of writing of this thesis, the complex nature and long development time of this infrastructure required a short term "stop-gap" solution.

Vibrationally enhanced chemistry has been previously observed to occur within the source

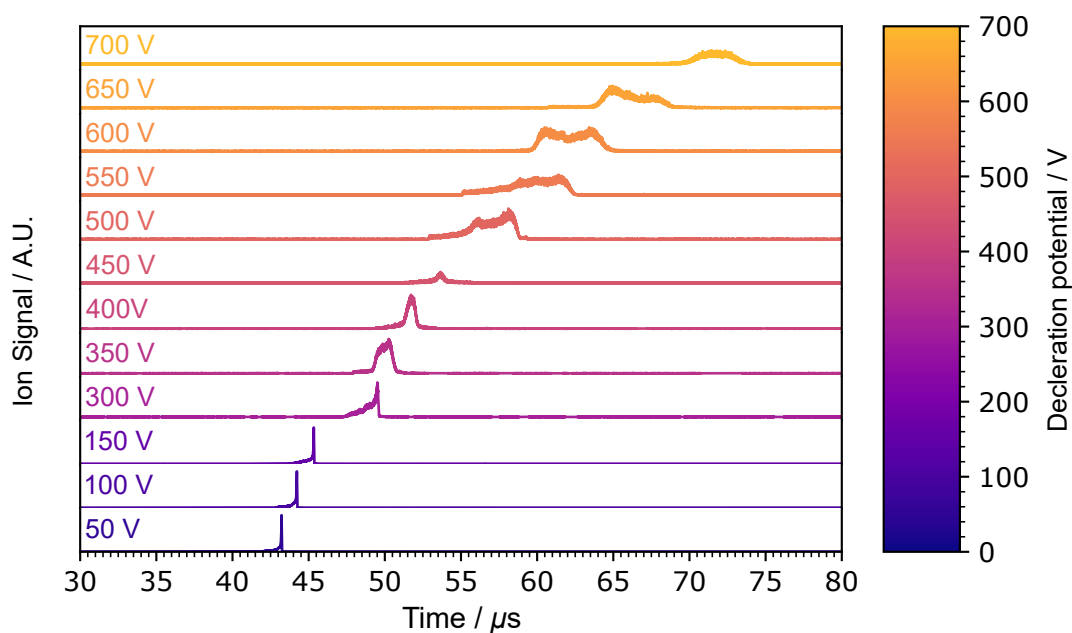


Figure 3.13: ToF traces of Au^+ ions recorded as a function of the deceleration potential applied. The re-referencing tube was used to ensure the ions were prevented from re-accelerating. The ions were orthogonally extracted using potentials of 1000 V on the repeller, 887 V on the extractor and 0 V on the ground electrode. Both the Einzel lens and deflection plate potentials were varied with the deceleration potentials to achieve maximum ion signal. The ToF appears differently from the ToF traces presented in Figure 3.6 due to the modified experiment length and slightly different conditions. Data for 200/250 V deceleration potentials is omitted as these experiments failed for unknown reasons. There are significant fluctuations in the integrated intensity due to fluctuations in conditions required to maintain signal day-to-day.

region of the experiment.^[75] The collision energies and rates within a laser ablation source are poorly defined and likely have a wide range of collision energies. In theory, the collisions within the collision cell could be markedly less well defined in terms of the collision energy and still allow vibrationally mediated chemistry to be observed. If true, this would allow the experiment to be linearised and avoid orthogonal extraction altogether. This would be advantageous in several aspects. Firstly it would allow for the ions to be spatially focused with much lower energies negating the need for deceleration, but more importantly, the radial velocity of the ions is minimised as they are accelerated in one axis only (until they are orthogonally extracted for detection in the ReToF). The linear variant of the collision experiment is presented in Section 3.3.

3.3 Instrument Iteration III: Linear Extraction with No Mass Filtration

3.3.1 Experimental Modification

As an interim solution to ion signal loss due to the ion's "off-axis" velocity while the octupole ion guide is developed, the experiment was reconfigured into its current form presented in Figure 3.14. This iteration contains identical optics to the second iteration of the experiment presented in Section 3.2, save for the removal of the orthogonal extraction Wiley-McLaren lens. As explored in detail in Section 3.2.2, the removal of the orthogonal extraction allows for a much gentler spatial focusing of ions negating the need for (harsh) deceleration as well as removing a large source of the ion's radial velocity. Although it does come at the expense of some energy resolution, this was deemed acceptable for the temporary instrument that this setup represents. While the deceleration optics still within the instrument are somewhat superfluous, they were left in to allow for testing if required.

As all of the optics, aside from the ReToF, have been characterised in other chapters or in previous sections, no further details are given here.

3.3.1.1 Ion Detection in ReToF

This iteration of the instrument was the only iteration that successfully orthogonally extracted ions into the ReToF mass spectrometer. All of the previous ion optics were characterised extensively previously; thus for brevity, only the ReToF mass spectrometer is characterised here. Figure 3.15 shows a ToF trace of Au^+ ions recorded in the reflectron. The Au^+ ions were extracted from the source with 100 eV of kinetic energy and passed through the collision cell prior to being orthogonally extracted into the reflectron to generate the ToF spectrum shown in Figure 3.15. The performance of the ReToF system was also evaluated using $\text{Ta}_n(\text{CO}_2)^+$ clusters and the data is shown in Appendix Section D.3.

The single peak within Figure 3.15 illustrates that ions can be passed through the ex-



Figure 3.14: Schematic diagram illustrating the components of the linear iteration of the VEC (vibrationally enhanced collision) experiment. The black line illustrates the path of the molecular beam through the experiment. The red and green arrows represent the IR (tunable) and (532 nm) ablation lasers. The yellow circles represent voltages applied to the ion optics/electrodes and correspond to values given in Table 3.3.

Number	Control	Pulsed?
1	Source float	No
2	In-line WM repeller	Yes
3	In-line WM extractor	Yes
4	In-line WM ground	No
5	Deflection left	No
6	Deflection right	No
7	Deflection top	No
8	Deflection bottom	No
9	Einzels A 1/3	No
10	Einzels A 2	No
11	Deceleration float	No
12	Einzels B 2	No
13	Re-referencing tube	Yes
14	ReToF Repeller	Yes
15	ReToF Extractor	Yes
16	ReToF Ground	No
17	ReToF Focus	No
18	ReToF Deflection 1	No
19	ReToF Deflection 2	No
20	Reflectron Front	No
21	Reflectron Back	No
22	MCP	No

Table 3.3: The controlled potentials in the linear collision experiment in Figure 3.14.

periment successfully with a defined energy and be detected on the reflectron. This ToF spectrum indicates that the experiment is essentially ready to be used in collision experiments, as ions can be passed with controlled energy through all of the ion optics and detected in the reflectron.

3.4 Conclusions

An initial design for a collision experiment to measure vibrationally mediated reactions between ionic metal species and neutral molecules in the gas phase was developed from scratch. The design used the concept of orthogonal extraction to spatially focus the ions with minimal induced energy differences. Although successful in its intended role, the ion kinetic energies required for successful orthogonal extraction meant that ion deceleration was required not only to achieve collision energies appropriate for ion-neutral reactions

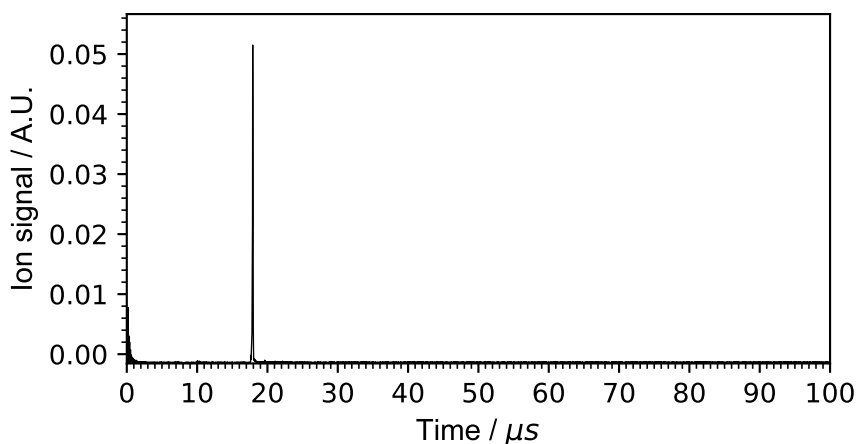


Figure 3.15: ToF spectrum of Au^+ ions passed through the collision cell at 100 eV prior to being orthogonally extracted into the reflectron.

but also for the second orthogonal extraction into the ReToF mass spectrometer used for product detection.

Ion deceleration proved extremely difficult resulting in the initial experimental design being superseded by a linear design. Although the linear variant of the experiment incurs reduced energy resolution (see Figure 3.3), it eliminates the requirement for high orthogonal extraction energies and deceleration as well as removing the largest source of radial ion velocity. Ions have been successfully passed through the entire linear instrument and detected in the ReToF mass spectrometer. Coupled with the completed infrastructure for the rest of the instrument (including electronic controls, vacuum systems and gas delivery systems), the detection of ions within the ReToF illustrate that the instrument is now ready to measure the outcomes of reactive collisions.

The linear instrument represents a temporary "stepping stone" variant of the instrument. An octupole ion guide will be added to the post-deceleration region of the experiment to radially confine the ions after they have been decelerated, preventing the high ion losses seen previously. With the addition of the octupole ion guide, the variant of the experiment presented in Section 3.1 of this chapter can be easily rebuilt (thanks to the modular design of the ion optics) with the octupole ion guide installed to help guide the ions through the post deceleration region. A schematic diagram of the intended experimental setup including the octupole ion guide is included in Figure 3.16.

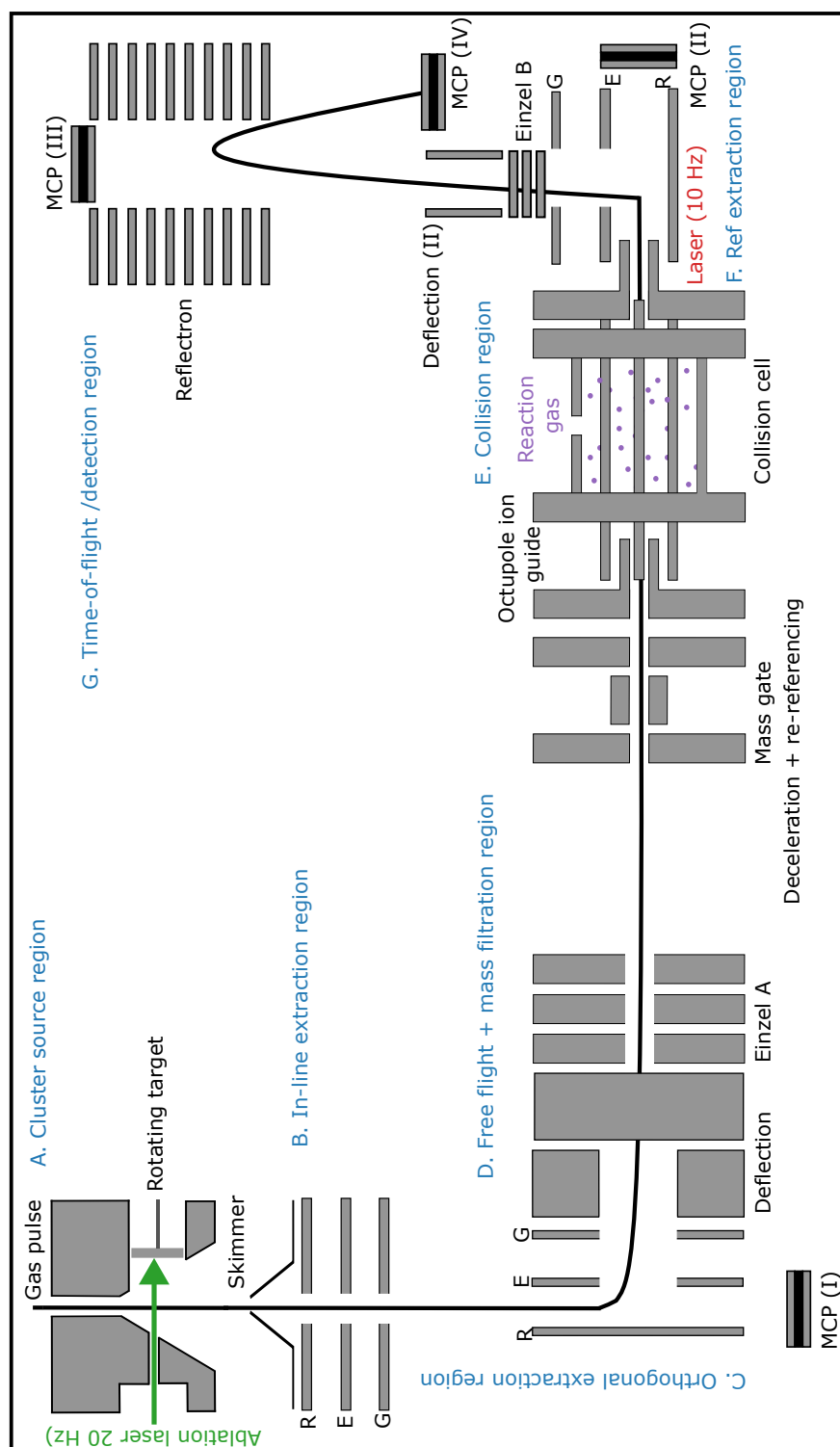


Figure 3.16: Schematic diagram illustrating the components of the bent, mass filtered (with an octupole ion guide installed) variant of the VEC (vibrationally enhanced collision) experiment. The black line illustrates the path of the molecular beam through the experiment. The red and green arrows represent the IR (tunable) and (532 nm) ablation lasers.

4 | Summary of Developmental Work

While the experimental development work is still ongoing, the foundations for a working experiment have been fully developed as part of the work presented within this section of the thesis. This Chapter of the thesis outlines the completed work thus far and reiterates the challenges encountered during the development, as well as outlining the future work.

4.1 Completed Development Work

Starting from scratch, and during a global pandemic, a completely novel experiment has been developed to study the effects of vibrational energy on the outcomes of reactive collisions between metal ions and neutral species in the gas phase. Based on the mass spectrometric investigations, the ions generated from a laser vaporisation source were deemed to be inappropriate for collision experiments due to their spatial distribution. Although the origin of the spatial distribution was unclear, a novel method for focusing the ions spatially with minimal induction of energy distributions to the ion packet was postulated, simulated and developed into a real experimental piece of apparatus. Due to high orthogonal extraction energies, an ion decelerator based on an Einzel lens was developed to slow the ions prior to undergoing reactive collisions. The collision cell, designed based on custom-built collision models, was developed, simulated and constructed. For collision product detection, an old (defunct) reflectron ToF mass spectrometer from the R.M. Jordan company was modified and incorporated into the experiment.

The complete set of work carried out as part of this project is illustrated in Table 4.1, and cumulatively, it has led to the construction of an instrument that will allow for collisions of ionic metal species with neutral gas molecules to be investigated, both in terms of their translational energy dependence and vibrational energy dependence.

Aspect	Major Milestones Completed
Experimental design	• CAD designs of all optics and mounting systems. • CAD designs of all vacuum chamber configurations. • CAD design of the experimental mounting frames. • CAD design of all laser optical systems and shielding. • SIMION simulations of all optics as well as many other candidate ion optics. • Custom simulations of collisions. • Custom simulations of vacuum pumping required.
Experimental construction	• 3 major iterations of the instrument have been successfully constructed and used to generate data: - Iteration I: Orthogonal extraction with mass filtration. - Iteration II: Orthogonal extraction with no mass filtration. - Iteration III: Linear instrument with in-line extraction. • All control software has been completely written in LabVIEW NXG and LabVIEW classic. The software, optimised for maximum performance. The software enables control of: - All ion optic potentials (DC or pulsed) - All instrumental timings and delays. - All data acquisition. • All major gas delivery systems have been constructed and are fully operational. • Installation (and characterisation) of Quantel Ultra laser to replace the original Minilite II system used for ablation.
Experimental characterisation	• Each of the three major iterations of the instrument have been characterised allowing for design adjustments to be made in the subsequent versions. Characterisation has included: - How the ion signal (detected on micro-channel plates (MCPs) placed throughout the experiment) changed as a function of potential applied to ion optics. - How the ion signal changed as a function of various times and delays.

Table 4.1: The work completed as part of the instrumental development divided into the three key areas: design, construction and characterisation.

4.2 Challenges

Chapter 3 illustrates that several issues were encountered through out the developmental process. The most important issue located was the observed loss in ion signal as the deceleration potential was raised. Ion deceleration, an integral aspect of the experiment, was required to reduce the ion kinetic energies such that collisions between the ions and the neutral molecules could take place at low COM frame kinetic energies (< 10 eV) and allow for successful extraction into the ReToF mass spectrometer for (mass resolved) ion detection.

The ion signal loss was initially assigned to poor deceleration behaviour associated with the two plate system used. However, improvement of the the decelerator through the addition of an Einzel lens immediately prior to the deceleration stage did not improve the behaviour to a satisfactory degree. Based on this finding, it was concluded that the residual velocity of the ions associated with their motion in their original axis of travel caused the ion beam to walk off axis, preventing the ions from reaching the detectors. Spatial defocusing of the ions that occurs when the ions are decelerated further exacerbates this issue.

Based on the work presented in Chapter 3, a temporary solution was developed in the form of a linearised version of the experiment described in Section 3.3. This removes the orthogonal extraction element of the experiment and instead uses linear extraction, allowing for much smaller extraction potentials to be used, negating the need for large decelerating potentials and removing the residual velocity component. Initial testing (see Section 3.3) demonstrated that the linearised iteration of the experiment was able to pass ions through the experiment with 100 eV of energy and successfully orthogonally extract them into the reflectron indicating that collision experiments can now be performed.

4.3 Future Work

With the experiment ready to carry out collisions, initial characterisations of the single collision reactions can now be carried out. Previously investigated reactions of ionic

metal species with neutral gas phase molecules, such as those previously characterised by Armentrout and co-workers^[198–250] should be undertaken within the newly developed experimental apparatus. This will allow for comparison to be made between the two to ensure that ion molecule collisions of the correct energies can be achieved, as well as simultaneously calibrating the experiment. With these experiments successfully completed, IR radiation can then be introduced into the ionic metal species or neutral molecules undergoing collisions and the effects of vibrational excitation on the outcomes of reactions under single collision conditions investigated.

The change from orthogonal extraction to linear extraction comes at the expense of energy resolution of the ion packet (see Figure 1.12). If the energy resolution of the linear variant of the experiment is found to be unacceptable, the experiment can be returned to its design including orthogonal extraction, with the addition of an octupole ion guide allowing for the ions to be radially confined to the centre of the instrument and preventing them from walking off when decelerated to the desired kinetic energy. An octupole ion guide has been previously used in a similar experiment to great effect^[393], hence should prove helpful if the decision is taken to return to the orthogonal extraction variants of the instrument.

Part II: Infrared Spectroscopy of Ho^+ Ion Complexes With CO_2 and OCS

5.1 Introduction

This chapter details the apparatus used to record infrared photodissociation spectra of the $\text{HoO}_x(\text{CO}_2)_y^+$ and $\text{HoO}_x(\text{OCS})_y^+$ clusters. Over the course of the work presented within this thesis, the experiment has undergone several changes, most notably the addition of a quadrupole mass filter, the addition of a wavelength extension crystal to the laser system, the replacement of a 10 Hz ablation laser with a 20 Hz ablation laser, and the development of new control software. All of the work listed here, aside from the addition of the quadrupole mass filter, was undertaken as part of this PhD project. Each distinct iteration of the experiment, along with the upgrades (and their characterisation) made, are described in this chapter.

5.2 Experiment Overview

The infrared photodissociation experiment has had two key iterations over the course of the work carried out in the thesis. Both iterations of the apparatus were able to carry out IR-PD experiments albeit in slightly different ways. The original iteration, version A (see Section 5.2.1), allowed the recording of IR-PD spectra of a wide range of different parent ion masses simultaneously, whereas the addition of the quadrupole mass filter permits the recording of IR-PD spectra of single species. Both sets of apparatus have unique properties that come with both advantages and disadvantages. The OPO/OPA system used to generate IR light for the experiments is also described in this section.

5.2.1 Stage A: Reflectron time-of-flight IRPD experiment

This experimental apparatus was constructed around 2014 by previous group members.^[396] Figure 5.1 shows this iteration of the experiment, consisting of two differentially pumped stages - the ion source and the detection stage.

The ion source is identical to the source used in the collision experiment discussed in

Section 1.3, so it is not described in detail here. Briefly, a 532 nm laser beam (from a Continuum Minilite II) is passed through an aperture within a cutaway source block such that it strikes a rotating metal target. The ablation plume generated from the laser beam striking the metal surface is entrained in a gas pulse (He/Ar) from a Parker-Hannifin General Series 9 solenoid valve. The expansion is directed along the main axis of the instrument. The ligand of interest can be seeded into the Ar/He backing gas, allowing it to complex with the metal ions generated in the ablation plume. Prior to the supersonic shock-wave generating turbulence within the beam, the beam is passed through a skimmer, generating a collimated molecular beam.

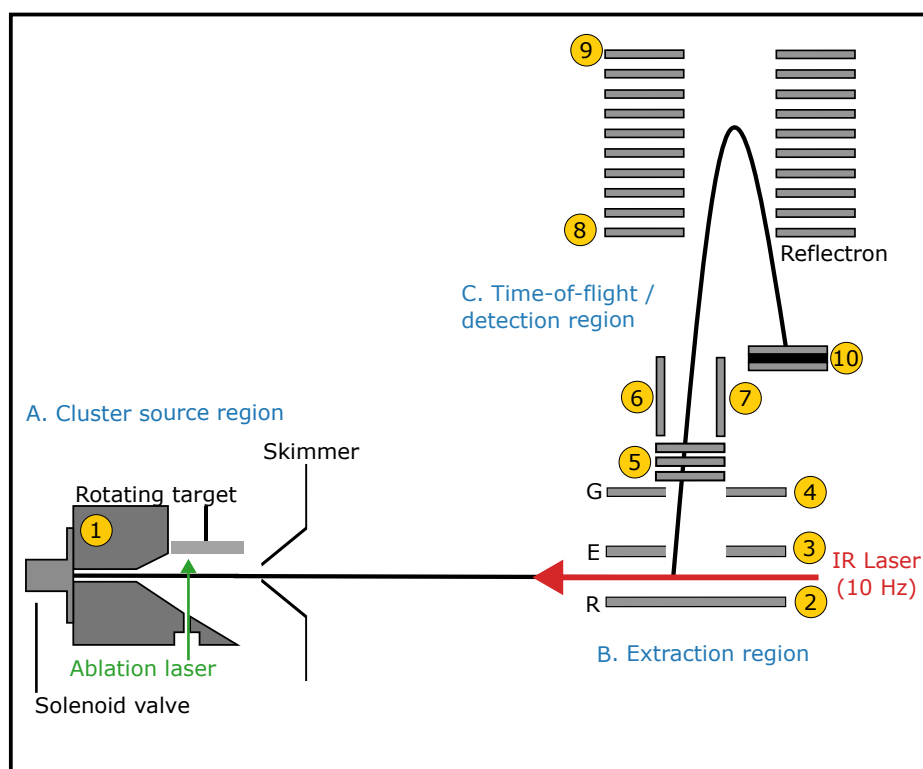


Figure 5.1: A schematic diagram of the non mass-selected variant of the IRPD experiment. The black line illustrates the path of the molecular beam through the experiment. The IR (tuneable) and (532 nm) ablation lasers are represented by the red and green arrows respectively. The yellow circles represent voltages applied to the ion optics/electrodes and correspond to values given in Table 5.1.

The molecular beam generated within the source then passes into the extraction optics (a three-plate Wiley-McLaren lens) of the commercial (R.M. Jordan) reflectron time-of-flight mass spectrometer in which the ions are detected, shown schematically in Figure 5.1. The theory and operational details of these exact reflectron time-of-flight mass spectrometers

Number	Control	Pulsed?
1	Source float	No
2	Repeller	Yes
3	Extractor	Yes
4	Ground	No
5	Focus	No
6	Deflection 1	No
7	Deflection 2	No
8	Reflectron Front	No
9	Reflectron Back	No
10	MCP	No

Table 5.1: The control elements used in the IRPD experiment corresponding to yellow numbers in Figure 5.1.

have previously been covered, as the exact same reflectron is used in the collision experiment described in the first half of this thesis. The reflectron allows a ToF mass spectrum of ions produced in every cycle of the experiment to be recorded. A tuneable infrared laser beam generated from an OPO/OPA system (Laservision) pumped by a Powerlite II Nd:YAG laser (Continuum) is counter-propagated down the axis extruded by the molecular beam. The laser pulse is timed such that the IR photons interact with the molecular beam prior to the extraction of ions into the reflectron, allowing photo-fragmentation to occur prior to measurement of the ToF mass spectrum. ToF mass spectra are then recorded as a function of the IR wavelength, and the depletion of the parent ion is measured as a function of IR wavelength allowing for the generation of IR spectra. In this iteration of the experiment, IR-PD spectra of a wide range of different ion masses are recorded simultaneously, as any ions generated in the source will (in theory) reach the reflectron extraction optics. While recording the depletion in this in-line arrangement had the advantage that spectra of all species could be recorded simultaneously, it suffered from the fact that the measured depletion was small in the comparatively large parent signal. Further to this, where several parent ions absorb at the same frequency, simultaneous depletion of all parents results in enhancements in other channels in a process called cascading.

5.2.2 IRPD Stage B: Quadrupole mass selected IRPD experiment

In 2018 a commercial quadrupole mass filter and quadrupole bender (Extrel QMS 150) were added to the experiment, as illustrated in Figure 5.2.^[397] The experiment now consists of three differentially pumped stages: the source region, mass filtration and bending region, and finally the detection region. The source and detection regions were identical to those in the original apparatus shown in Figure 5.1, and were operated in exactly the same way.

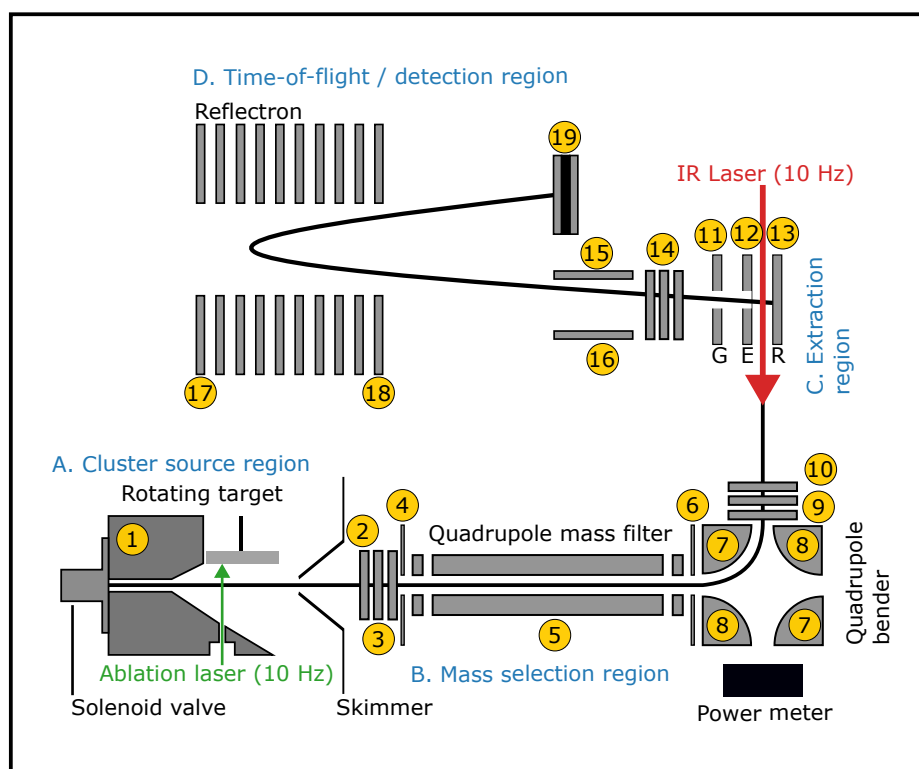


Figure 5.2: The mass-selected variant of the IRPD experiment not to scale. The black line illustrates the path of the molecular beam through the experiment. The red and green arrows represent the IR (tuneable) and (532 nm) ablation lasers respectively. The yellow circles represent control elements given in Table 5.2.

The addition of the mass filter to the experiment allowed for single parent ions to be selected from the range of ions generated in the source, allowing for spectroscopy to be carried out on single masses of ions. The quadrupole bender was added to prevent the IR laser from entering the source region of the experiment, and helped to reduce the

experiment's physical footprint within the lab.

The addition of the quadrupole mass filter and bender was advantageous compared to the linear mode described in the previous section, as the IR spectra can now be recorded in the enhancement channel of daughter ions (when they previously had to be recorded in the depletion of parent ions), leading to significantly improved signal-to-noise ratios within the spectrum. However, quadrupole mass filters usually incur large transmission losses, making experiments, in general, more challenging due to low ion signals. These challenges become particularly apparent for species produced in low number densities, such as Ar-tagged species, as the experiment simply cannot generate enough of the species of interest to transmit a detectable number of them to the detector compared to the linear version of the instrument, described in Subsection 5.2.1.

Number	Control	Pulsed?
1	Source float	No
2	Einzel A 1/3	No
3	Einzel A 2	No
4	Entrance lens	No
5	Pole bias	No
6	Exit lens	No
7	Inner poles	No
8	Outer poles	No
9	Einzel B 1/3	No
10	Einzel B 2	No
11	Repeller	Yes
12	Extractor	Yes
13	Ground	No
14	Focus	No
15	Deflection 1	No
16	Deflection 2	No
17	Reflectron Front	No
18	Reflectron Back	No
19	MCP	No

Table 5.2: The potentials used in the quadrupole mass selected variant of the IRPD experiment corresponding to yellow numbers in Figure 5.2.

5.3 LaserVision OPO/OPA System

The tuneable infrared light used within the IR-PD experiments presented within this thesis, is generated in a commercial OPO/OPA system from LaserVision pumped by 1064 nm light from an Nd:YAG laser (Continuum Powerlite II). Figure 5.3 shows the arrangement of optics along with the non-linear optical crystals used to tune the wavelength of light within the system. While the theory of the OPO/OPAs is presented in Section 1.8.2, the practical operation of the LaserVision OPO/OPA is described here.

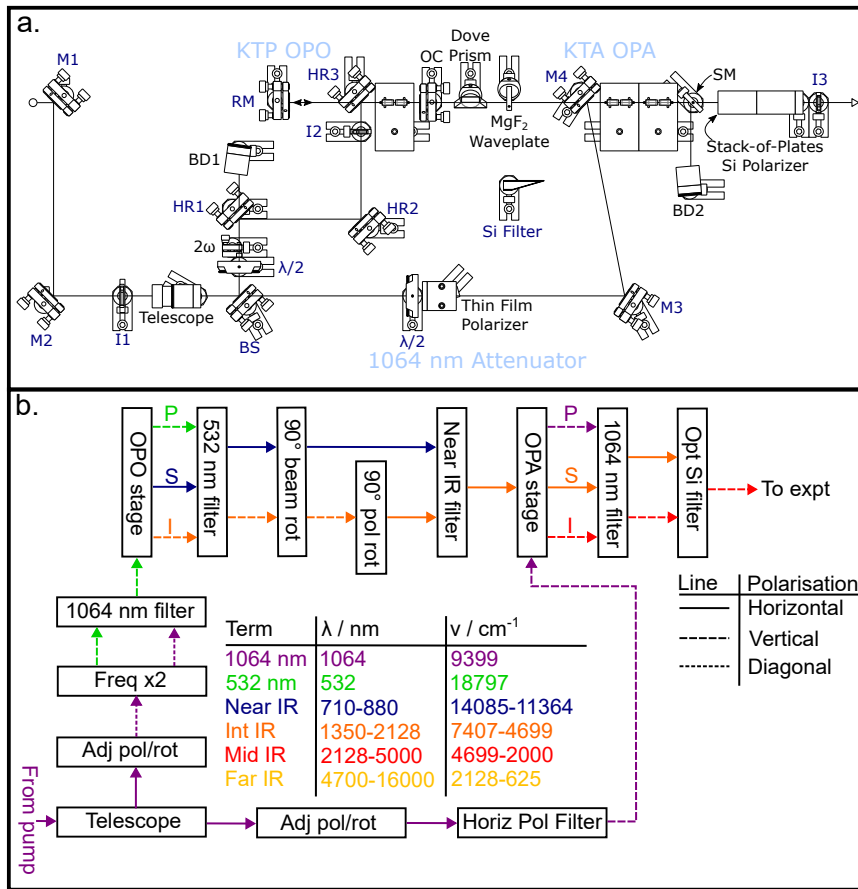


Figure 5.3: (a) The optical bench of the OPO/OPA system from LaserVision. (b) A schematic diagram of the OPO/OPA system illustrating the energies and polarisation of the beams as they pass through the system.

Briefly, a 1064 nm beam from the pump laser is split in two using beamsplitter B1 in Figure 5.3. Half of the beam is sent to the OPO stage whereas the other half is sent directly to the OPA stage. Prior to entering the OPO stage, the 1064 nm beam is frequency doubled using KTP (potassium titanyl phosphate/ $\text{K}(\text{O}_5\text{PTi})$) crystal to generate 532 nm

light which is then passed to the OPO.

The OPO consists of two KTP crystals which are type II phase-matched for parametric oscillation. Two crystals are used to account for beam walkoff.^[398–401] The 532 nm pump beam (P) generates two new beams - the signal (S) and the idler (I) - which are in the near IR region ($11364\text{--}14085\text{ cm}^{-1}$) and intermediate IR region ($4699\text{--}7407\text{ cm}^{-1}$), respectively. The frequencies of the signal and idler beams are tuned by counter-rotating the crystals due to their uniaxially birefringent nature.^[340] Only the idler beam is allowed to pass into the OPA, as the others are filtered out.

In addition to the idler beam from the OPO (which now acts as the signal beam in the OPA), the 1064 nm beam is also passed into the OPA. The OPA stage consists of two pairs of KTA (potassium titanyl arsenate/ KTiOAsO_4) crystals which are all type II phase-matched for difference frequency generation (DFG).^[340, 402] Just like the OPO, the OPA may also be tuned by rotating the crystals.^[340] Via DFG, an additional beam (the idler/I) is generated within the mid-IR region ($2000\text{--}4699\text{ cm}^{-1}$). An optional, stack-of-plates Si polariser can be added to remove the signal beam if working with the mid-IR beam only.

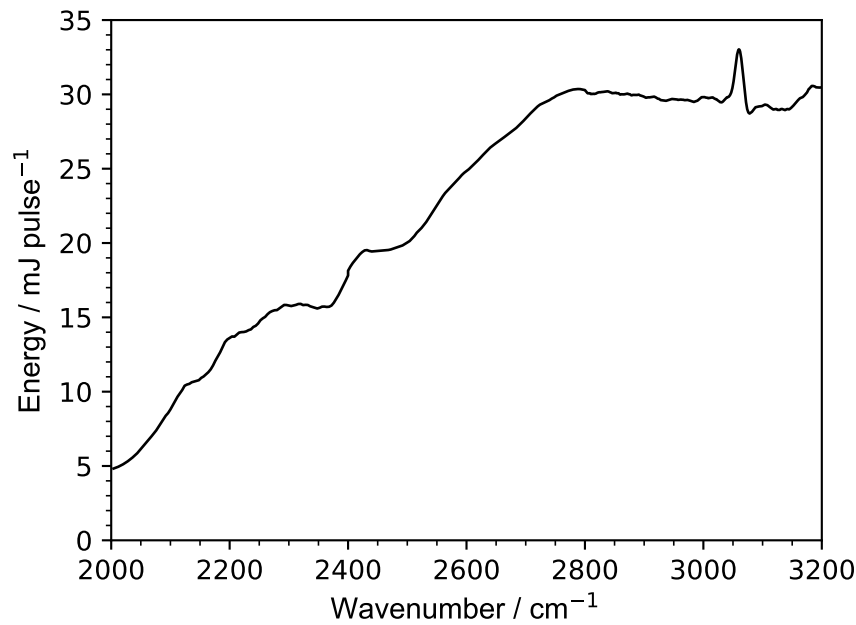


Figure 5.4: The energy-per-shot dependence on the wavelength ($2200\text{--}3200\text{ cm}^{-1}$) generated from the LaserVision OPO/OPA system in the mid-IR range.

Figure 5.4 illustrates the energy-per-shot generated by the LaserVision OPO/OPA system as a function of wavelength between 2200-3200 cm^{-1} . While the OPO/OPA system is pumped with the same energy every shot (approximately 600 mJ pulse^{-1}), it can clearly be seen that the conversion efficiency, across the spectral range shown, is far from constant. The peak seen at around 3108 cm^{-1} results from the fact that this is the position at which all of the crystals within the system are aligned perfectly parallel with one another, resulting in minimal back reflection and maximum conversion efficiency. However, the energy-per-shot demonstrated in Figure 5.4 means there are more than enough photons present to carry out IR-PD experiments, as demonstrated by the wealth of work from the group previously. [75, 396, 397, 403–409]

5.4 Experimental modifications

Throughout the course of the work presented in this thesis, multiple upgrades to the IR-PD experiments have been made. The most notable of these are detailed here to act as a reference for future group members. These consist of (in chronological order): (i) upgrading the experiment with a power meter and LabVIEW sub-VIs that were integrated into the original software to measure IR laser power in real-time, thereby allowing calculation of absorption cross sections; (ii) the introduction of two new wavelength extension crystals to the OPO/OPA system, which allows the generation of IR light between 600-2000 cm^{-1} ; and finally, (iii) the inclusion of a 20 Hz ablation laser (which also triggered the need to rewrite the entire LabVIEW data acquisition software suite).

5.4.1 Measuring IR power in real time

As Figure 5.4 shows, there are significant variations in the OPO/OPA conversion efficiency over the accessible spectral range. The result of this is a variation in energy-per-shot and photon flux produced at each wavenumber. The IR intensities within spectra generated by this experiment depend heavily on photon flux, as this determines how many species are able to absorb enough photons to overcome the dissociation threshold. Simply put, a high photon flux will generally result in higher fragmentation yields for a given IR transition within a molecule.

In order to account for this, and to avoid photon flux variations generating artefacts within spectra recorded on the experiment, ideally spectra should be measured in terms of each species' absorption cross-section (rather than in terms of raw enhancement/depletion intensities as they were previously). The relationship between a species' absorption cross section (σ), the photon flux (ϕ), the parent ions intensity prior to depletion (N_0), the daughter ion intensity after depletion (N_f) and the proportion of the molecular beam overlapped with the IR beam (α , nominally taken to be 1) is:

$$\sigma = \frac{1}{\phi} \ln \left(1 - \frac{N_f}{\alpha N_0} \right). \quad (5.1)$$

The photon flux (ϕ) is the measure of photons passing a unit area per unit of time, and is related to the pulse energy of the IR laser (E_{shot}), the photon frequency (ν), the area of the laser beam (A) and the pulse duration (t) by:

$$\phi = \frac{n_{\text{photon}}}{At} = \frac{E_{\text{shot}}}{E_{\text{photon}}At} = \frac{E_{\text{shot}}}{h\nu At}. \quad (5.2)$$

Based on Equations 5.1 and 5.2, in order to be able to generate IR spectra in terms of σ , three measurements are thus required: N_0 , N_f and E_{shot} at each wavenumber the IR spectrum is recorded at. The experimental apparatus and software already allowed for the determination of both N_0 and N_f easily. In order to record pulse energy, two alterations were made: firstly, a power head was included in the experimental apparatus (as illustrated in Figure 5.2); and secondly, new software was written such that pulse energies and mass spectra could be recorded simultaneously.

5.4.1.1 Addition of a Power Meter

A power meter (Ophir Vega) was added at the exit window as shown in Figure 5.2 was added to the experiment.

5.4.1.2 LabVIEW Software to Measure Power in Real-time

New LabVIEW software was written using binary communications, to enable recording of shot-by-shot pulse energies in real time from the power meter. For brevity, details are

not given here. However, the complete set of drivers, documentation and an example are all provided in a repository on GitHub (see Appendix section F for the URL links).

5.4.2 OPO/OPA wavelength extension

The OPO/OPA system available from LaserVision in its original form is shown in Figure 5.3 and generates wavelengths of IR light in the int-IR and mid-IR regions ($7407\text{--}4699\text{ cm}^{-1}$ and $4699\text{--}2000\text{ cm}^{-1}$ respectively). In order to generate light below 2000 cm^{-1} , an additional crystal placed beyond the OPA was required. During the time frame in which the work presented in this thesis was performed, two different wavelength extension crystals; AgGaSe₂ followed by ZnGeP₂, were added to the system, tested and used. As these crystals had not been previously used within the group, their addition to the experiments and characterisation is detailed here.

5.4.2.1 AgGaSe₂ wavelength extension crystal

AgGaSe₂ is a crystalline solid in the I-42d space group with tetragonal symmetry.^[410] An image of the crystal used in the experiment is shown in Figure 5.5 b (it is coated in a proprietary anti-reflection coating) and its crystalline structure is shown in Figure 5.5 c. It is an optically negative uniaxial crystal that has good transmittance between $0.7\text{ }\mu\text{m}$ and $18\text{ }\mu\text{m}$ along with a strong non-linear polarisation response to applied (IR) light. As a result of these properties, it can be used in parametric down-conversion via difference frequency generation.^[411] It is available to purchase from LaserVision and can be integrated directly into the OPO/OPA system so that IR light between $2128\text{--}625\text{ cm}^{-1}$ can be generated.

A schematic diagram of the optical setup of the OPO/OPA/extension crystal system is illustrated in Figure 5.6. The beam polarisations are much the same as illustrated in Figure 5.3 b save for the removal of the stack-of-plates Si polariser to allow both the signal and idler beams to exit the OPA stage. Due to the AgGaSe₂ crystal's relatively low damage threshold, it is placed approximately 2 m downstream of the exit from the OPA. The signal and idler beams from the OPA act as the pump and idler beams in the AgGaSe₂ crystal, resulting in a newly generated (signal) beam in the far-IR region

(625–2128 cm^{-1}).

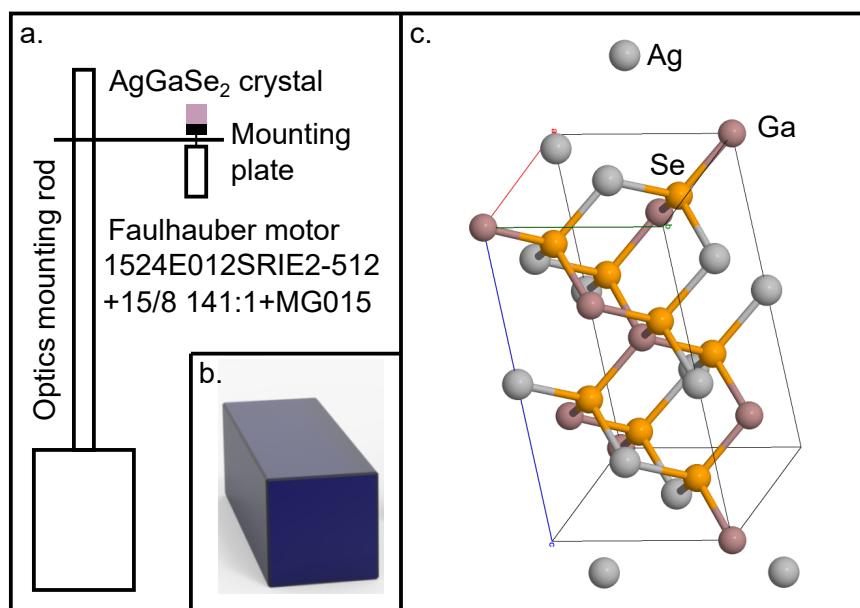


Figure 5.5: a. The optical support and motor used to mount the AgGaSe_2 crystal. The axis of its rotation is from left to right within the plane of the page. b. An image of the AgGaSe_2 crystal used. c. The unit cell crystal structure of AgGaSe_2 with atoms labelled (adapted directly from Springer^[410]).

As shown in Figure 5.5 a, the crystal is mounted on an optical mount via a Faulhaber 1524E012SR1E2-512+15/8 141:1+MG015 motor, which allows the crystal to rotate. As this crystal is Type II phase matched, just as all of the crystals in the original OPO/OPA system, it may also be rotated in the horizontal plane to generate different wavelengths of IR light in the far IR region. It is critical that good overlap of the signal and idler beams is maintained at the crystal to maximise the difference frequency generation efficiency. The rotation of the crystal governs the wavelength produced and is controlled via the motor controls program (the additional tuning table for this crystal is provided by LaserVision). All three beams (P,S and I) are then passed through a ZnSe/Si filter placed at 45° to the beam which transmits the far IR but reflects the idler and pump beams into a beam dump (see Figure 5.5). Finally, the far IR beam is passed to the experiment.

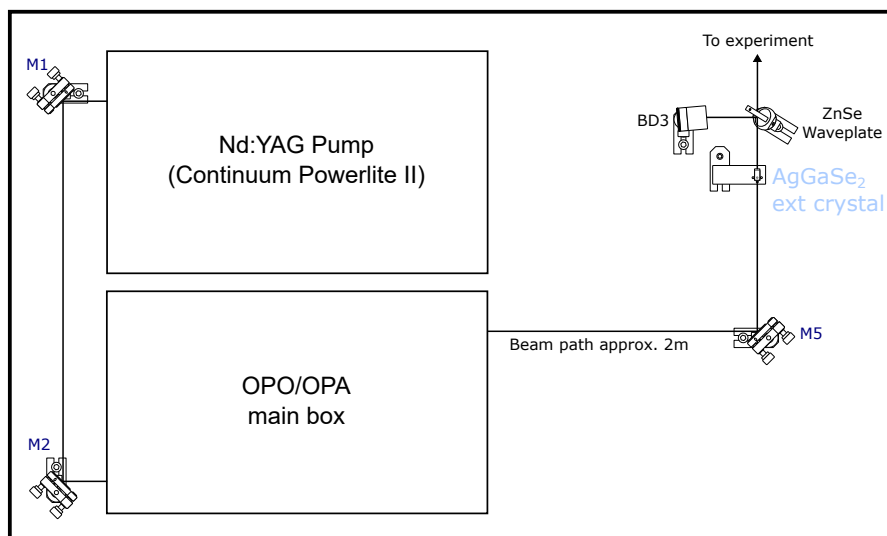


Figure 5.6: The optical bench of the AgGaSe_2 wavelength extension crystal system. For a diagram of the interior of the OPO/OPA system, see Figure 5.3.

Prior to any experiments or power dependence investigations, the laser needed to be calibrated correctly to ensure that it was able to produce the wavelength that was set within the motor controls software. To do this, a simple photo-acoustic IR spectrum of NO was recorded. The predicted spectrum (generated within the PGOPHER software from Bristol) and the photo-acoustic spectrum of NO are shown in Figures 5.7 a and b respectively.^[412] Three bands within the experimental spectrum can be seen. The central peak centred around 1872 cm^{-1} was assigned to be the Q-branch of NO and the other two (from left to right) are assigned to be the P and R branches resulting from $v' \leftarrow v''$ rovibrational transitions in NO. The experimentally measured Q-branch position of 1872 cm^{-1} is shifted from the previously predicted value of 1876 cm^{-1} but is within laser linewidth.^[413]

To ascertain the performance of the crystal over the accessible range of wavelengths, the energy-per-shot dependence of the laser as a function of wavelength was measured and is shown in Figure 5.8. There is a significant variation in the energy-per-shot produced by this system due to the conversion efficiencies within each crystal of the system varying with wavelength. The power generated by the laser system in the far IR region is much lower than that generated in the mid-IR. This is not surprising given that the signal and idler beams from the main OPO/OPA were used in the extension crystal which was

suggested to have a conversion efficiency (at a maximum) of only 30%. However, it was deemed that this performance is acceptable.

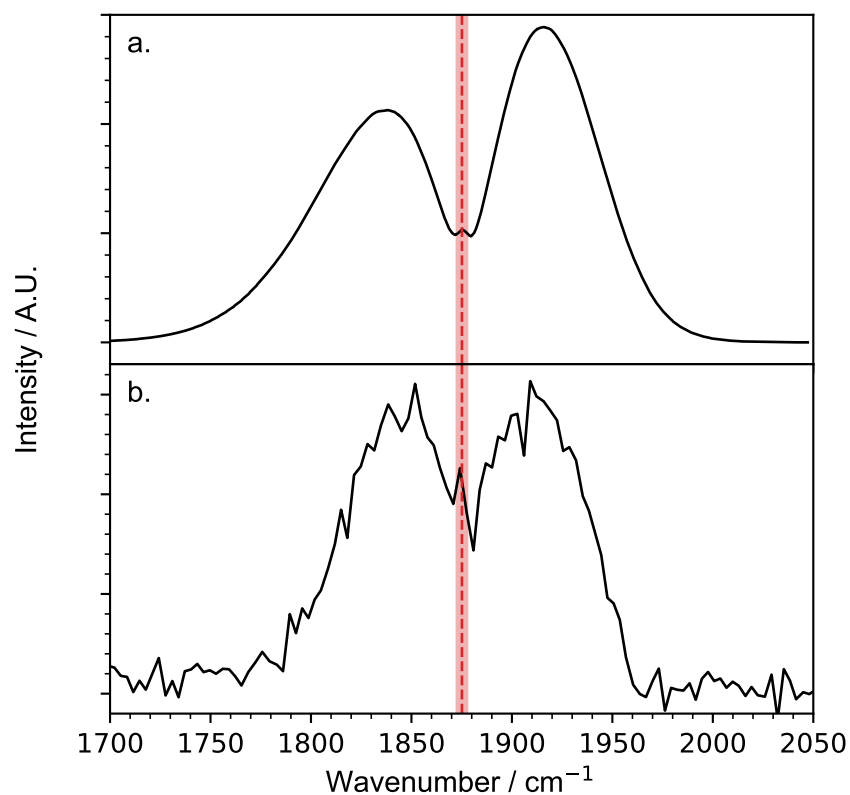


Figure 5.7: a. The predicted rovibrational spectrum of NO generated in the PGOPHER software at 300 K (Lorentzian line-width of 10 cm⁻¹).^[412] b. The photo-acoustic spectrum of 1 bar of NO at 298 K was recorded with the OPO/OPA system with the installed AgGaSe₂ wavelength extension crystal. Both spectra contain a line centred around the origin of the Q branch of NO (red dashed line) that extends 5 cm⁻¹ (indicating the line-width of the laser system).

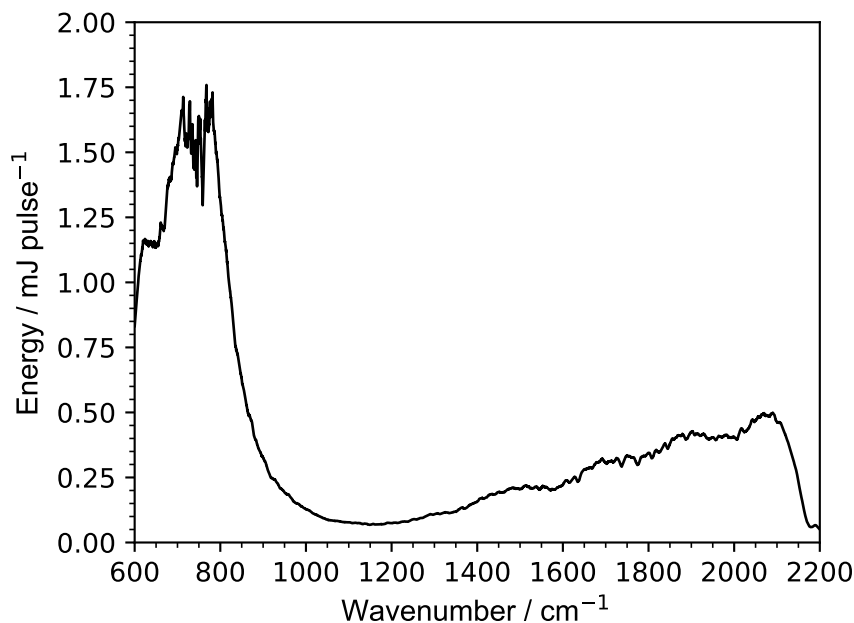


Figure 5.8: The wavenumber dependence (600-2200 cm^{-1}) of the pulse energy generated from the LaserVision OPO/OPA system with the AgGaSe_2 wavelength extension crystal installed.

5.4.2.2 ZnGeP_2 wavelength extension crystal

ZnGeP_2 is a similar crystal to AgGaSe_2 in that it also adopts the I-42d space group with tetragonal symmetry as can be seen from its crystal structure shown in Figure 5.9 c. While both compounds form uniaxially birefringent crystals, AgGaSe_2 has negative birefringence whereas ZnGeP_2 has positive birefringence. ZnGeP_2 also has a markedly smaller transmission range (0.75-12.0 μm) when compared to AgGaSe_2 (0.7-18 μm). However, ZnGeP_2 has a much higher damage threshold (60 MW cm^{-2}) relative to that of the AgGaSe_2 (10-20 MW cm^{-2}), meaning that it can be pumped with much higher photon fluxes.^[414, 415]

If ZnGeP_2 is used in place of AgGaSe_2 as a wavelength extension crystal within the LaserVision OPO/OPA system, ZnGeP_2 should be able to produce much higher photon fluxes in the far-IR yielding higher energies-per-shot. Increasing the photon fluxes within the experiment is extremely advantageous in that it means dissociation thresholds are more likely to be overcome allowing for spectra of more species with more tightly bound ligands (etc.) to be recorded. Given that the shot-to-shot energy of the AgGaSe_2 was quite

low, the ZnGeP_2 crystal offered a distinct advantage over the AgGaSe_2 crystal although at the cost of being unable to record spectra below 1000 cm^{-1} . Hence in 2022, a ZnGeP_2 crystal was purchased from Deintech.

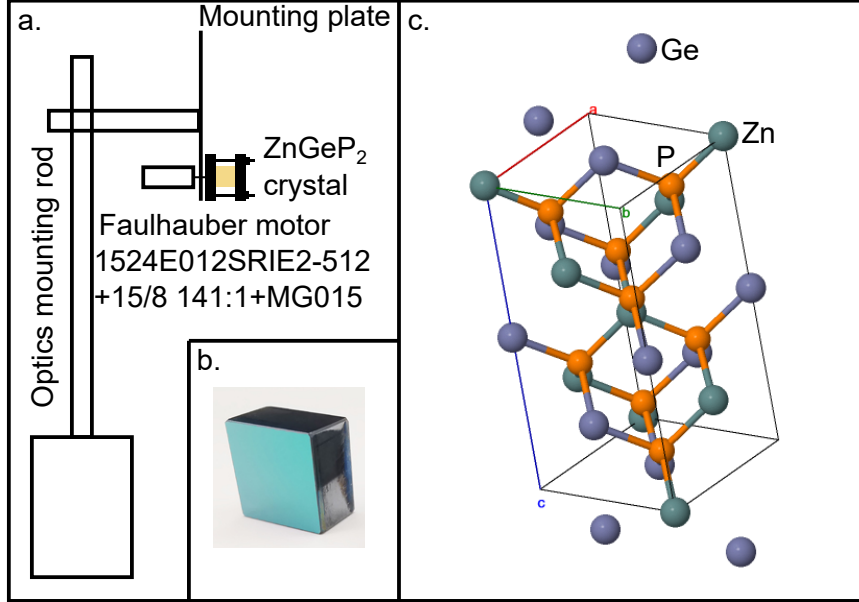


Figure 5.9: a. The optical support and motor used to mount the ZnGeP_2 crystal. The axis of its rotation is from top to bottom within the plane of the page. b. An image of the ZnGeP_2 crystal was used. c. The crystal structure of ZnGeP_2 with atoms labelled (adapted directly from Springer^[416]).

Addition of the ZnGeP_2 to the OPO/OPA system was non-trivial due to the fact that the entire OPO/OPA prior to the extension crystals were Type II phase matched, the ZnGeP_2 crystal was Type I phase-matched. Practically, this means that the axis of rotation of the ZnGeP_2 crystal required to modulate DFG is orthogonal to the axis in which all other Type II phase-matched crystals were rotated. There were two possible solutions to this issue; either the mechanism for rotating the crystal could be, itself, rotated by 90° such that the crystal would rotate in the correct axis, or the polarisation plane of the IR beams from the OPA could be rotated by 90° .

In order to minimise power losses and complex optical setups required to rotate the polarisation plane of the beam, it was decided that the crystal rotation axis would be rotated by 90° . The crystals within the LaserVision system are attached to blocks that then mount to the rotating spindle of a motor using double-sided tape. While acceptable when the crystal is supported underneath by the block and motor, it is not acceptable

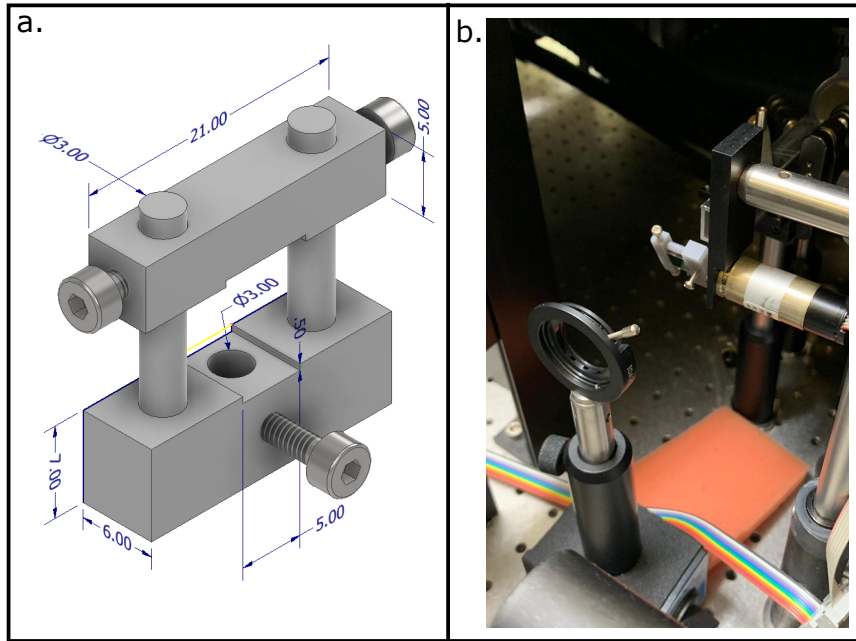


Figure 5.10: a. Annotated CAD render of the crystal mount designed to hold the ZnGeP_2 crystal. b. Photograph of the whole assembly in situ (taken by Peter Watson).

when the whole arrangement is rotated by 90° as it exposes the crystal to gravity, acting in an axis orthogonal to the axis in which it is supported. To ensure the ZnGeP_2 crystal was secure, a new crystal mount, shown in Figures 5.10 a and b, was designed and 3D printed so that the crystal could be clamped as well as glued to the rotating block. The crystal is clamped on either side and has a small groove that aids in centring the crystal on the mount. It also provides a small amount of support in the axis in which gravity acts. The mount is much shorter than the length of the crystal to avoid pump beams that strike the surface of the mount from ablating material from the mount and depositing it onto the front face of the crystal.

The optical setup for the system ZnGeP_2 crystal is shown schematically in Figures 5.11 a and b. It is extremely similar to the setup used for the AgGaSe_2 with only minor differences. Due to the damage threshold of the ZnGeP_2 crystal being much higher than the AgGaSe_2 crystal, it was placed much closer to the exit aperture of the OPO/OPA crystal (it can be placed up to 0.25 m away from the aperture). As Figure 5.11 also shows, the optical setup was also changed to allow for easier switching between the mid-IR mode and the far-IR mode through the addition of a new beam path and flip-mounted mirrors. Previously, the motor mount for the crystal needed to be moved out of the way

when switching which (along with the beam alignment required when doing this) was an extremely time-consuming process. Aside from the change in crystal and moving the other crystal closer, the beam energies and polarisation remained the same between the AgGaSe₂ setup and the ZnGeP₂ setup.

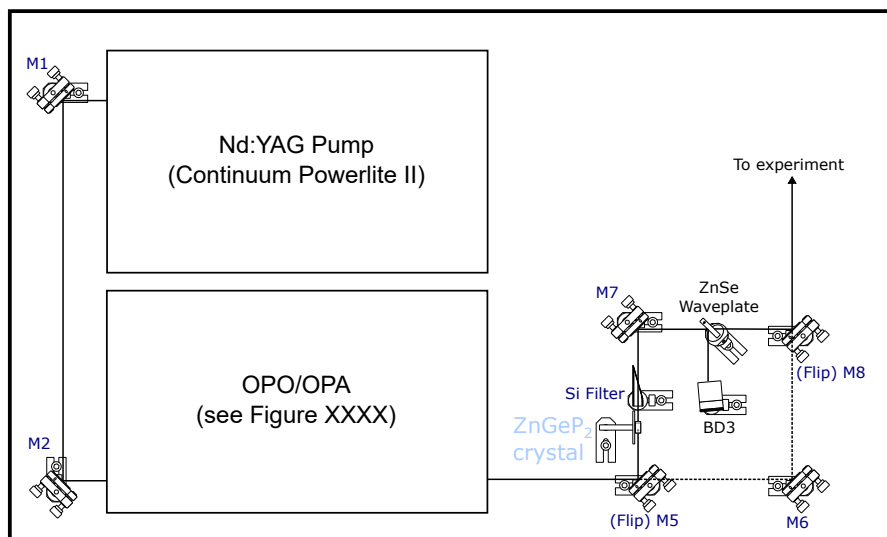


Figure 5.11: The optical bench of the ZnGeP₂ wavelength extension crystal system. For a diagram of the interior of the OPO/OPA system, see Figure 5.3.

With the ZnGeP₂ crystal installed, its performance relative the AgGaSe₂ crystal was then evaluated. Figure 5.12 shows the pulse energy dependence on the wavenumber (1200-2200 cm⁻¹) of the ZnGeP₂ as well as a comparison with AgGaSe₂. The ZnGeP₂ energy-per-shot (red) is at least two times higher than the AgGaSe₂ energy per shot (black) which illustrates the significant improvement in energy performance. The loss of the ability to record spectra below 1200 cm⁻¹ was not especially problematic, as the group had never previously recorded a spectrum in that region. The improved pulse energy allowed, in theory, for the generation of spectra with improved signal-to-noise ratios and the study of species with higher binding energies. While it would have been nice to compare spectra recorded with each crystal, variations in experimental conditions (due to variables beyond the crystal) would have resulted in unfair comparisons, so these studies were not performed.

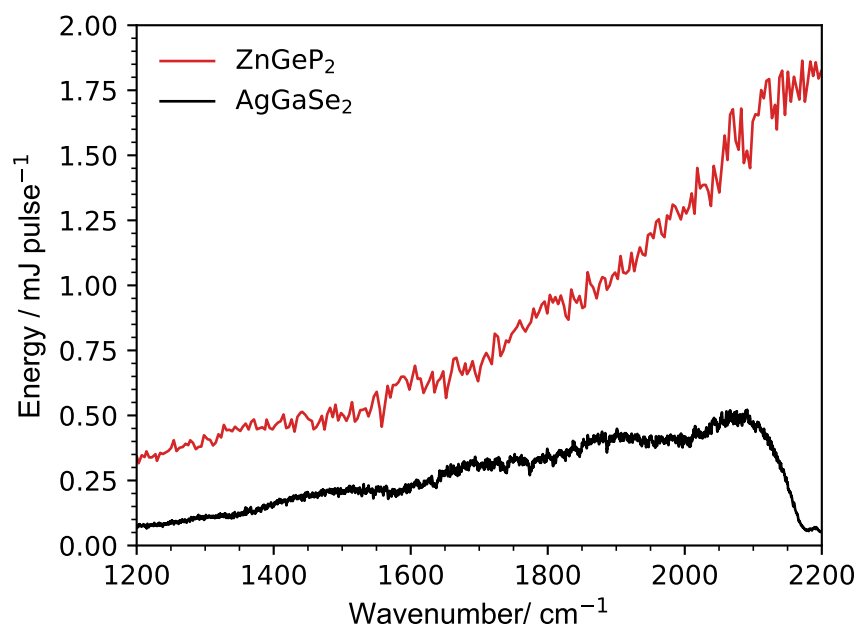


Figure 5.12: The energy-per-shot dependence on the wavelength (12000-2200 cm^{-1}) generated from the LaserVision OPO/OPA system with the AgGaSe₂ (black) and ZnGeP₂ (red) wavelength extension crystals installed.

5.4.3 20 Hz ablation laser

The final upgrade made to the IR-PD experiment undertaken during this study was the replacement of the 10 Hz ablation lasers (Continuum Minilite II) with 20 Hz ablation lasers (Quantel Ultra). The faster ablation laser doubled the possible repetition rate of the experiment, making data acquisition twice as fast. The addition of the 20 Hz laser system did require a major modification to the IR-PD experiment in terms of data acquisition. The experiment relies upon being able to record a whole mass spectrum with the IR laser on and off in order to generate difference mass spectra, thus the experiment needed a way to differentiate what the IR laser was doing (firing or not) when a mass spectrum was recorded.

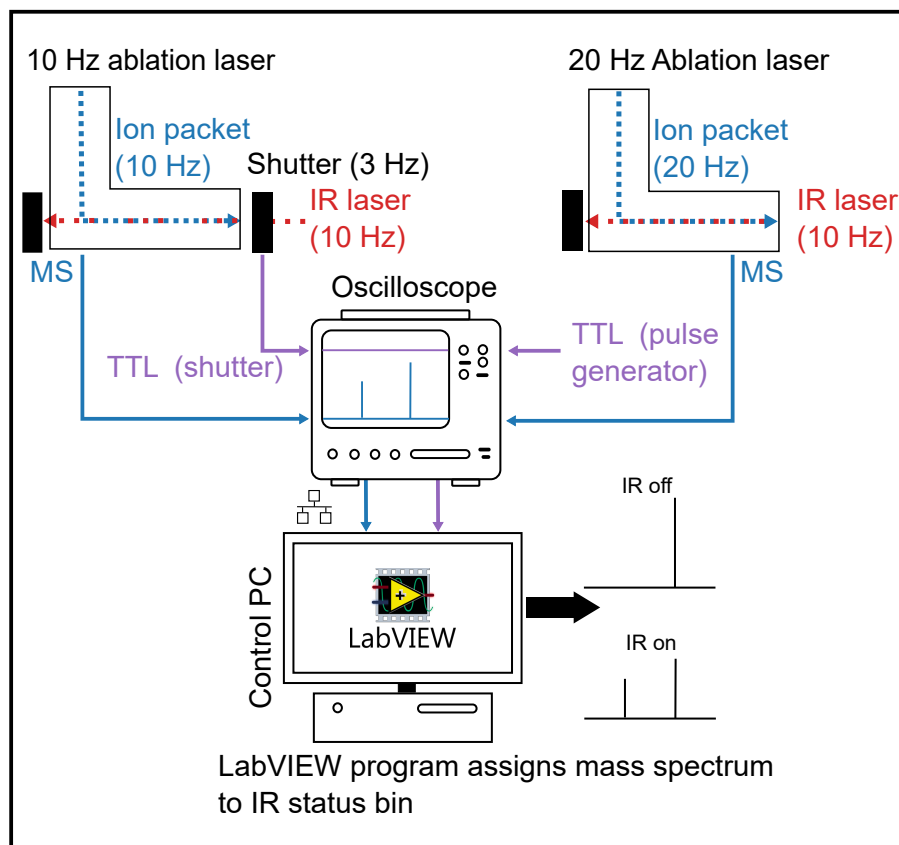


Figure 5.13: Schematic diagram illustrating how the binding of IR on/off mass spectra works in both the 10 Hz and 20 Hz repetition rate variants of the experiment.

Both the ablation laser and IR laser ran at 10 Hz, meaning that a shutter was needed to block the IR laser beam so that "IR off" mass spectra could be generated. The shutter was run at 3 Hz meaning that it remained open for 0.33 s allowing three shots of light from the IR laser to pass through the experiment while the experiment completed three cycles before closing for 0.33 s and preventing the IR laser from passing through the experiment for three additional experimental cycles. Based on this, the experiment was able to generate the so-called "IR on" and "IR off" mass spectra. In-house data acquisition software (LabVIEW) binned mass spectra based on the shutter status. The shutter outputs a TTL pulse (low when closed, high when open) which was monitored using the oscilloscope (Teledyne-Lecroy Waverunner 64Xi) that was also used to acquire the experimental mass spectra. The control software could then acquire the traces (from both the mass spectrum channel and shutter status channel) from the oscilloscope and then assign the mass spectra

to the correct bin based on the average value of the shutter trace (IR off when the average shutter trace value was below a user-defined threshold and open when the value was above the threshold). The diagram on the left of Figure 5.13 shows this process schematically.

With the introduction of the 20 Hz ablation laser, the mass spectra could be recorded at twice the repetition rate of the IR laser, meaning that no shutter was required as the IR laser would fire every other experimental cycle. With the loss of the shutter, binning was achieved through the use of TTL pulse from a single channel of the pulse generator (Berkeley Nucleonics Model 575) instead. This channel was synchronised with the channels providing the fire flashlamp and q-switch pulses to the main IR pump laser. The TTL pulse from the generator supplied to the scope would only read high when the IR laser fired in that experimental cycle (and equivalently would read low when it didn't). Then an identical method to that used in the 10 Hz setup, could be used in the LabVIEW control software to bin the data in the new 20 Hz setup. The experiment on the right-hand side of Figure 5.13 illustrates this schematically.

5.4.4 New Software

The original experimental architecture proved incapable of the increased transfer rates necessary to operate at 20 Hz and so an entire re-write of the acquisition software was required.

Figure 5.14 shows a schematic diagram of the architecture of the new software.

The major difference between the original software and the new software was the segmentation of the various components of the code into their own while or for loops. This architecture takes advantage of modern multi-core CPUs and passes each process onto its own core so that the time-sensitive aspects of the experiment (such as the acquisition of mass spectra) are able to run independently of other parts of the code (which could slow them down). Each data acquisition while loop was set to gather data at 20 Hz. Other components of the code, such as the user interface event monitoring, were also separated into their own loops to ensure that the graphical user interface remained responsive to user inputs even while other components of the code ran. In addition to the main VI developed to control the experiment, numerous sub-VIs and libraries were developed for

the various other aspects of the experiment, including sub-VIs to control the OPO/OPA system, sub-VIs for analysing the traces, and those already detailed for power measurement. While these are not detailed in the main body of this thesis, they are freely available to download from GitHub (see Appendix Section F). The main VI, all sub-VIs and documentation are all provided in repositories on GitHub (see Appendix section F for the URL links).

The re-written software allowed for the experiment to operate at almost its full 20 Hz repetition rate (not accounting for crystal tuning times) and produced data in a much cleaner and more straightforward way. Due to its segmentation into both sub-VIs and into specific loops, it is also much more readable and accessible to students and postdoctoral researchers who are not familiar with LabVIEW when compared with the previously implemented software. Unfortunately, due to data transfer performance issues with the Teledyne-Lecroy Waverunner 64Xi oscilloscope, data acquisition at 20 Hz was still not possible and without improvements from Teledyne-Lecroy remains impossible to fix whilst using this oscilloscope. However, by switching out the Waverunner 64Xi for a much newer and better performing National Instruments 5160 oscilloscope (identical to that used in the collision experiment presented previously) in combination with the new software developed here, the 20 Hz data acquisition rate was made possible.

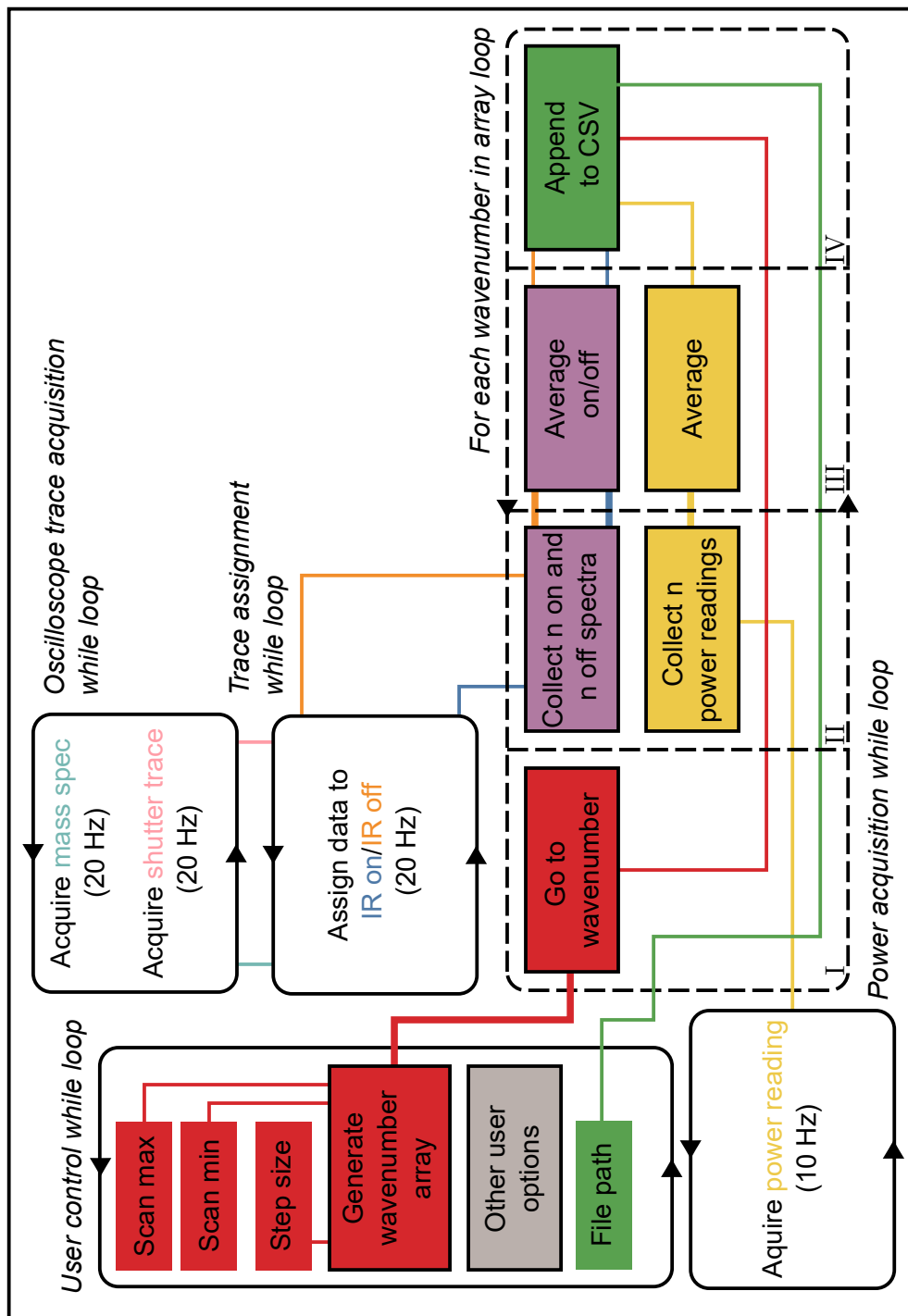


Figure 5.14: A schematic diagram showing the operation of the new IRPD experimental software. Variables are shown as a block with no border, sub-functions as blocks with black borders, while loops as solid black lines, for loops as dashed lines and wires as lines.

6 | An infrared study of CO₂ activation by Holmium ions, Ho⁺ and HoO⁺

This chapter presents the results of a spectroscopic study of the complexes of Ho(CO₂)_n⁺ and Ho[O(CO₂)_n]⁺ obtained when Ho is ablated in the presence of CO₂ seeded into Ar. Spectra were recorded in two spectral ranges: 1650-1950 cm⁻¹ and 2300-2450 cm⁻¹, and assigned using predicted structures (generated from potential energy surface searches) using DFT. CO₂ binds in a molecular/end-on fashion to Ho⁺ in Ho(CO₂)_n⁺ complexes, and showed little evidence of activation. Ho[O(CO₂)_n]⁺ complexes in which $n \geq 3$, by contrast, show clear spectroscopic evidence of the formation of a carbonate radical anion moiety ($\{\text{CO}_3\}^{\cdot\delta-}$). The characteristic vibrational band of this structure red-shifts with increasing CO₂ coordination, displaying clear evidence of charge transfer between ligands mediated by a metal centre.

This work was undertaken partly with Dr. Alice Green, whose contributions are clearly labelled. These results were published in Issue 37 (October 2022) of Physical Chemistry Chemical Physics as Brewer *et. al.*^[417]

6.1 Introduction

6.1.1 CO₂

CO₂ as a molecule of interest needs almost no introduction. As one of the most abundant greenhouse gases within the atmosphere, its physical and chemical properties have been an area of intense investigation for many years.^[418]

CO₂ can be used as a feedstock for a wide variety of different industrial reactions, although these reactions typically require harsh conditions and high concentrations of CO₂, which are not present in the atmosphere.^[419, 420] Metals (particularly transition metals) have been shown to be able to act as catalysts in many of these reactions, or even to act as materials that can capture CO₂ from the atmosphere.^[421–424] It is the behaviour of CO₂ when adsorbed to metals (specifically Ho⁺ ions) that forms the basis of this chapter.

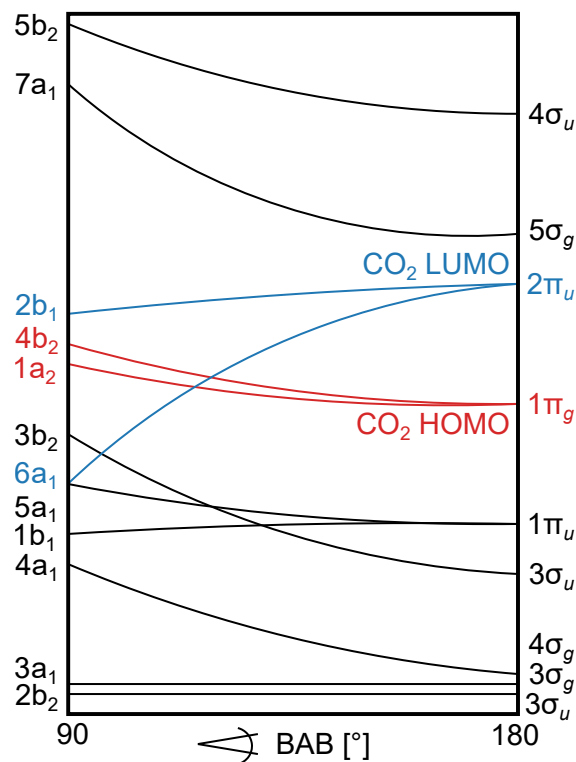


Figure 6.1: The Walsh diagram of BAB molecule. The diagram is also valid for BAC molecules if the *u/g* labels of the orbitals are removed (due to symmetry breaking). The HOMO and LUMO orbitals of CO₂ are shown in red and blue respectively. This diagram is adapted from the original paper by Walsh.^[425]

Linear ($D_{\infty h}$) in its ground state, CO₂ has equal C=O bond lengths of 1.16 Å.^[426] The Walsh diagram of a BAB triatomic molecule is shown in Figure 6.1, and the HOMO ($1\pi_g$) and LUMO ($2\pi_u$) of CO₂ are shown in red and blue respectively. Electron donation into the strongly antibonding LUMO results in weakening of the C–O bond. In addition to this, activation is accompanied by the O–C–O bond angle reducing towards 90° to reduce the energy of the $2\pi_u$ orbitals and stabilise the additional electron density. As such, bends away from a 180° O–C–O bond angle signify activation. Equally, any electron density withdrawn from the HOMO ($1\pi_g$), which has strong bonding character, will also result in activation.^[407]

CO₂ has been shown to bind to different metal ions in a variety of motifs including $M(\eta^1\text{-OCO})$, $M(\eta^1\text{-CO}_2)$, $M(\eta^2\text{-(C,O)O})$, $M(\eta^2\text{-(O,O)C})$, and even dissociatively ($M(\eta^1\text{-(CO, O)})$). Anionic metal centres have been typically shown to activate CO₂ to a much greater degree than cations, as they are much more capable of donating electron density into the

$2\pi_u$ orbitals of CO₂ than a cation (which binds its electrons much more tightly). As such, the chemistry of anionic metal atoms and clusters is richer than that of cations, with a large variety of binding motifs observed.

Cations typically bind in an M(η^1 -OCO) fashion to CO₂ via weak charge-quadrupole interactions that do little to activate or perturb the structure of the CO₂.^[396, 427–433] CO₂ bound in this fashion usually exhibits an asymmetric stretch that is weakly (10–20 cm^{−1}) blue-shifted from the free CO₂ asymmetric stretch at 2349 cm^{−1}.^[434] Duncan and coworkers suggest that the origin of the blue-shift lies in the fact that the oxygen atoms in the CO₂ molecules encounter a "repulsive wall" of the metal cation during the course of the vibration, shifting the vibration to higher energy.^[428] There are however exceptions to this behaviour. V⁺, Cr⁺, and Mn⁺ cations have all been observed to bind CO₂ molecules in an M(η^2 -(C,O)O) fashion and even "oxalate-like" structures when large numbers of CO₂ ligands coordinate to the ion.^[428, 435] Based on previous work on mixed ligand [Mg(CO₂)(H₂O)_{*n*}]⁺ complexes, this behaviour is thought to arise from the additional ligands providing enough electron density to the cation to alter the binding mode.^[436] ICP-SIFT experiments have shown some early transition metal cations capable of dissociatively binding CO₂. Additional spectroscopic evidence for the dissociative binding of CO₂ has also been obtained for Ti⁺, V⁺ and Ni⁺ cations.^[428, 431, 437, 438] Work with cationic metal clusters has been extremely limited, with only a single study showing size-dependent reactivity of Ta_{*n*} clusters towards CO₂.^[439]

Metal oxide species have shown a much greater reactivity towards CO₂, as the oxide O provides an atom with which the metal cation can react. However, CO₂ has been observed to bind in mostly a molecular fashion to metal oxide species.^[406, 438, 440] A notable exception to this was found by Jiang and coworkers when they found that CO₂ formed a {CO₃} moiety adsorbed in YO(CO₂)_{*n*}⁺ complexes.^[441] The work of Jiang inspired the group to look at other lanthanide metals to examine their interactions with CO₂.

6.1.2 Holmium

Holmium (Ho) is a mono-isotopic Lanthanide metal of atomic number 67 (and atomic mass 165) first discovered in 1878 by Jacques-Louis Soret and Marc Delafontaine.^[442, 443]

Despite its low abundance (1.4 ppm of the Earth’s crust), it has found uses in strong magnets, nuclear reactors and medical lasers.^[444–450] There are estimated to be approximately 400,000 tonnes of Ho within the Earth (most concentrated in China, the US and Australia), although only 10 (as of 2011) tonnes are produced a year, highlighting the fact that it is not well-utilised metal.^[451]

Being a lanthanide metal, the chemistry of Ho is dominated by the +3 oxidation state (Ho(III)), although some work has been able to generate Ho(II) complexes.^[452] Holmium, just as many other lanthanides, struggles to undergo any π back bonding due to the lanthanide contraction reducing orbital overlap. This limits its interactions to those with more ionic character.^[453]

Many metal cations bind to CO₂ via a weak charge quadrupole interaction, resulting in little activation or perturbation of the CO₂ and leading to virtually no catalytic properties. Based on the fact that Holmium cations preferentially adopt a +3 oxidation state, it was theorised that singly charged Ho⁺ cations might be able to donate electron density towards (CO₂) ligands and thus activate them, making a better candidate for activation or carbon capture applications.

6.2 Experimental details

The IR action spectra presented within this section were recorded on two different iterations of the infrared photo-dissociation experiment presented in Section 5.2. Initially, the in-line arrangement (shown in Figure 5.2.1) was used (by Dr. Alice Green) to record IR action spectra, via parent ion depletion, of a wide range of Ar-tagged parent complexes between 2300–2450 cm^{−1}. This process is shown in Reaction 2;



The species highlighted in blue indicates the parent ion species, the depletion of which was used to generate the IR spectra. These spectra are denoted as [-Ar] within the text and are shown in blue in all experimental spectra. While this method generates a consistent

Colour code	Pathway
Red	$\text{HoO}_n(\text{CO}_2)_m^+ \rightarrow \text{HoO}_n(\text{CO}_2)_{m-1}^+ + \text{CO}_2$
Green	$\text{HoO}_n(\text{CO}_2)_m\text{Ar}^+ \rightarrow \text{HoO}_n(\text{CO}_2)_m^+ + \text{Ar}$
Blue	$\text{HoO}_n(\text{CO}_2)_m\text{Ar}^+ \rightarrow \text{HoO}_n(\text{CO}_2)_m^+ + \text{Ar}$

Table 6.1: The colours assigned to each method by which IR spectra were generated. The species highlighted indicates the species used to measure the IR spectrum.

series of spectra for all complexes simultaneously, the signal-to-noise ratio is often poor due to fluctuations in parent ion intensity.

More recently, a QMF (quadrupole mass filter) was added to the experiment (see Section 5.2.2), allowing the measurement of a single complex size at a time in both depletion and enhancement channels. With this updated apparatus, action spectra of the $\text{Ho}(\text{CO}_2)_n^+$ and $\text{Ho}[\text{O}(\text{CO}_2)_n]^+$ complexes are recorded via the loss of a CO₂ ligand in the enhancement channel. Reaction 3 shows the process by which the IR spectra in the enhancement channel were generated;



The IR spectrum is recorded in the enhancement of the daughter channel rather than the depletion of the parents; hence the daughter ion is highlighted in this case. These spectra are denoted as -CO₂ within the text, and are shown in red in all experimental spectra. Due to concerns surrounding the high binding strength of CO₂ to the Ho⁺ ion, spectra were also recorded via the loss of Ar from an Ar-tagged parent in the enhancement channel, as shown in Reaction 4;



These spectra are denoted as -Ar within the text, and are shown in green in all experimental spectra.

DFT calculations at the UB3P86/Def2-TZVP level of theory were used in conjunction with the Kick³ algorithm to search the potential energy surfaces for each complex size. Although other basis-set and functional combinations were investigated (SDD and

ω B97XD), only minimal differences in energy ordering were found, so only calculations at the UB3P86/Def2-TZVP level of theory are presented. While all of the theoretical data are presented based on the Russell-Saunders nomenclature, Ho is a large atom and so experiences a high degree of spin-orbit coupling which Russell-Saunders coupling does not capture accurately. Vibrational frequencies were scaled by a factor of 0.96 to better match with the experiment based on the differences between the experimentally measured and calculated free CO₂ asymmetric stretch (2349 cm⁻¹ and 2441 cm⁻¹ respectively). Line spectra were convoluted with a Lorentzian function with a full width at half-maximum (FWHM) of 8 cm⁻¹ to aid comparison with experimental spectra.

6.3 Mass spectra of HoO_n(CO₂)_m⁺

The mass spectrum of Ho ablated in the presence of 2.5% CO₂ seeded into Ar is shown in Figure 6.2. Two key species are observed: Ho(CO₂)_n⁺ and Ho[O(CO₂)_n]⁺ (square brackets indicate that multiple isomeric structures are possible and no structural information is necessarily assumed) along with Ar-tagged analogues (marked with asterisks). The intensity of the Ho(CO₂)_n⁺ signal falls away with increasing complex size such that by $n \geq 4$, no significant intensity in any complex size can be seen. On the other hand, the Ho[O(CO₂)_n]⁺ species show intensity up to higher complex sizes, species up to $n = 15$ were observed.

The origin of the oxide peaks was initially unclear, as there are at least two possible routes by which the oxides can form. Many metals contain surface oxides, which can generate oxide complexes. However, it is also possible that the CO₂ can react to form complexes in which the CO₂ dissociates to form HoO and CO. Figure 6.3 shows the Ho metal target ablated under similar conditions used to generate Figure 6.2, with the major difference being that the CO₂ was removed from the backing gas mixture. No peaks other than the Ho⁺ signal can be seen within this mass spectrum. Based on this, it may be concluded that the surface oxides provide a negligible contribution to the generation of HoO in this case. Instead, the HoO likely results from a gas-phase reactive pathway that enables the generation of the Ho[O(CO₂)_n]⁺ species from CO₂ directly.

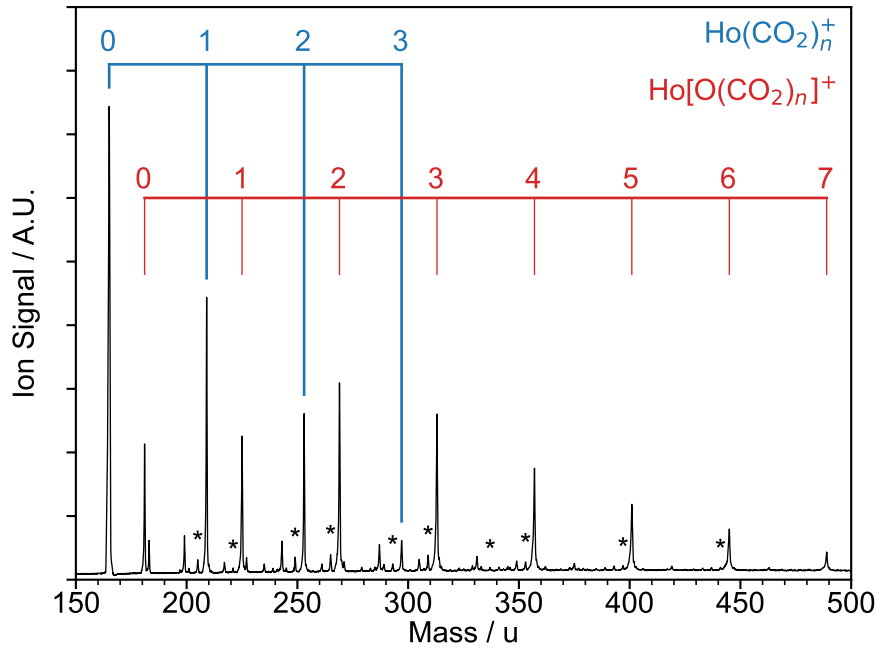


Figure 6.2: Representative time-of-flight mass spectrum obtained following the laser ablation of a Ho target in the presence of a backing gas mixture of ca. 2.5% CO_2 in Ar. $\text{Ho}(\text{CO}_2)_n^+$ and $\text{Ho}[\text{O}(\text{CO}_2)_n]^+$ complexes are formed in high number density, together with Ar-tagged species (marked with asterisks). Other, unmarked peaks result from background H_2O adsorption to the clusters. Adapted directly from the corresponding paper associated with this work.^[417]

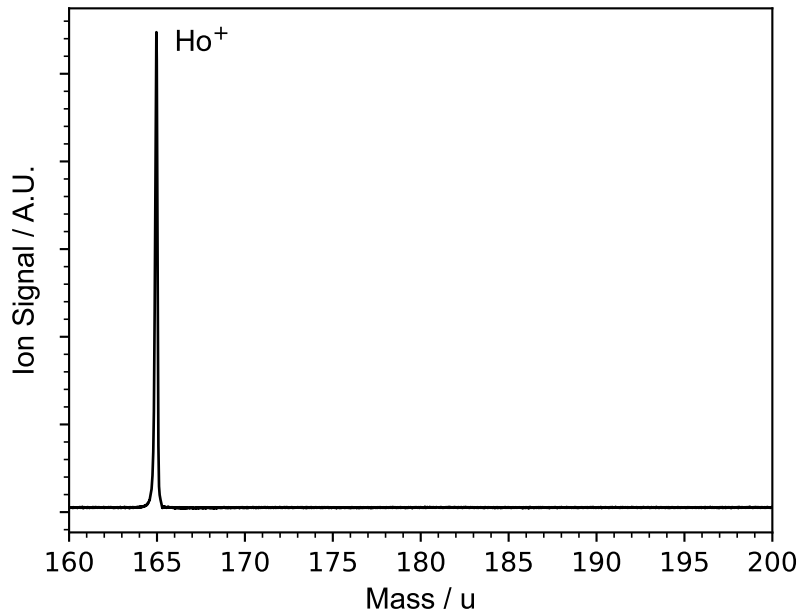


Figure 6.3: Representative time-of-flight mass spectrum obtained following the laser ablation of a Ho target in the presence of an Ar backing gas. Only Ho^+ ions are generated.

6.4 IR(M)PD spectra of HoO_n(CO₂)_m⁺

6.4.1 Ho(CO₂)_n⁺ (*n*=1-3)

Figure 6.4 shows the infrared action spectra for Ho(CO₂)_n⁺ complexes. Each spectrum shows a single feature between 2350-2450 cm⁻¹ that is assigned to a CO₂ asymmetric stretch. Each of the features is slightly blue-shifted from the free CO₂ asymmetric stretch, which is indicative of a CO₂ that is O-bound to the Ho⁺ via a charge-quadrupole interaction (M(η_1 -OCO)). The features recorded in the -CO₂ enhancement channel are broadened relative to those recorded in the [-Ar] depletion channel, as well as being blue-shifted to a greater degree relative to the free CO₂ asymmetric stretch. This is a commonly observed phenomenon and arises from the fact that the Ar binds much more weakly to the Ho⁺ relative to the CO₂ ligands. This means that fewer IR photons are needed to reach the dissociation threshold of Ar relative to CO₂, and Ar tagging preferentially selects cooler complexes. The Duncan group has discussed this phenomenon in detail previously for Mg(H₂O)_n⁺ complexes.^[454]

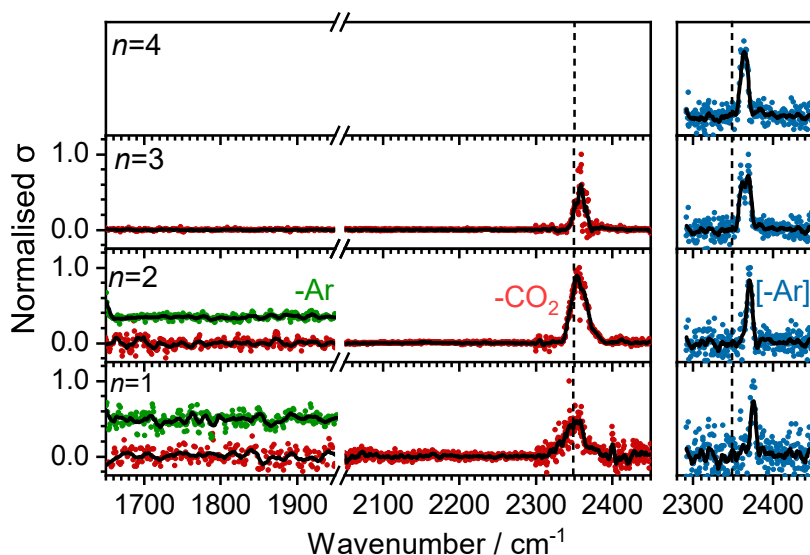


Figure 6.4: Infrared action spectra of Ho(CO₂)_n⁺ (*n* = 1 – 4) complexes with and without Ar-tagging. Spectra were recorded in the daughter fragment channels of Ho(CO₂)_n⁺ (*n* = 1 – 4, red data points) and Ho(CO₂)_n⁺-Ar (*n* = 2 – 3, green) as well as the parent ion depletion of Ho(CO₂)_n⁺-Ar (*n* = 1 – 4, blue, right panel). The vertical dashed line indicates the *v*₃ band of free CO₂ at 2349 cm⁻¹. Adapted directly from the corresponding paper associated with this work.^[417]

A potential energy surface search was carried out at each complex size. Three key structural motifs were found for the Ho(CO₂)_n⁺ complexes. The first structural motif involved every CO₂ binding to the central Ho⁺ in a M(η_1 -OCO) fashion (see isomer M in Figure 6.5). The second motif resulted from one of the CO₂ ligands binding in a dissociative fashion to the central Ho⁺ to form HoO with a CO bound in an M(η_1 -CO) fashion. All other CO₂ ligands bound via the M(η_1 -OCO) mode as seen for the previous isomer. An example of this motif is denoted by isomer "Dis" in Figure 6.5. The final motif observed resulted from two of the CO₂ ligands forming a dimerised/"oxalate-like" structure. Any additional CO₂ ligands are then bound via the now familiar M(η_1 -OCO) mode. As two CO₂ ligands are required to form the oxalate structure, these motifs are only seen where $n \geq 2$. This structural motif is illustrated by isomer Dim in Figure 6.5.

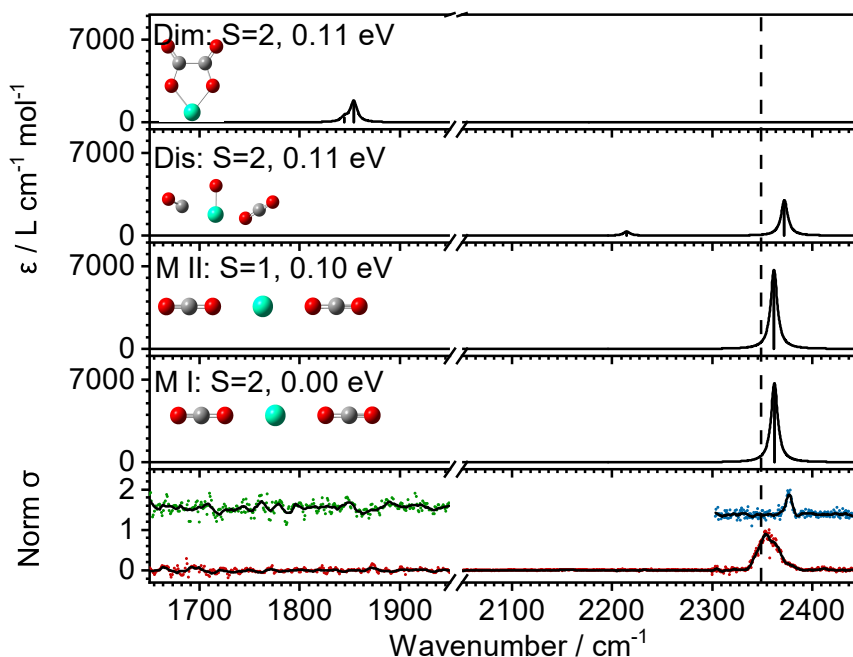


Figure 6.5: Comparison of experimental and simulated spectra of energetically low-lying structures (UB3P86/Def2-TZVP) for Ho(CO₂)_n⁺. The vertical dashed line indicates the asymmetric stretch (v_3) fundamental of free CO₂ at 2349 cm⁻¹. Ho blue, C grey and O red. Adapted directly from the corresponding paper associated with this work.^[417]

Inspection of Figures 6.4 and 6.5 indicates that CO₂ binds to the bare Ho⁺ cation through the simple M(η_1 -OCO) binding motif (the global minimum structures for $n = 1$ and $n = 2$). Although the Dis and Dim isomers are relatively low in energy (and the Dim isomer

for $n = 1$ is the global minimum structure) their formation is likely kinetically hindered given that a significant rearrangement of atoms would be required.

6.4.2 HoO(CO₂)_{*n*}⁺ (*n*=1-11)

Figure 6.6 shows the IR spectra of Ho[O(CO₂)_{*n*}]⁺ for complex sizes ranging from $n = 1 - 11$. All complex sizes show a peak in the 2350-2400 cm⁻¹ region indicative of an asymmetric CO₂ stretch. These peaks, as seen for the Ho(CO₂)_{*n*}⁺ structures, imply the presence of CO₂ bound via a weak charge-quadrupole interaction. The better-resolved spectra (recorded in the [-Ar] depletion channel between 2300-2450 cm⁻¹), shown in blue, demonstrate clear spectral structure suggesting either multiple isomers or multiple binding motifs of CO₂. They are also blue-shifted relative to the peaks recorded in the -CO₂ enhancement channel. For complexes in which at least three CO₂ molecules are bound, features between 1850-1760 cm⁻¹ are observed in addition to those between 2300-2450 cm⁻¹. These peaks were assigned to {CO₃}^{δ-} moieties bound in an M(η²-O, O(CO)) fashion based on computationally generated structures and the previous work of Jiang and coworkers which found similar features in the 1850-1760 cm⁻¹ region in their spectra of YO(CO₂)_{*n*}⁺, which they also assigned to {CO₃}^{δ-} moieties.^[441]

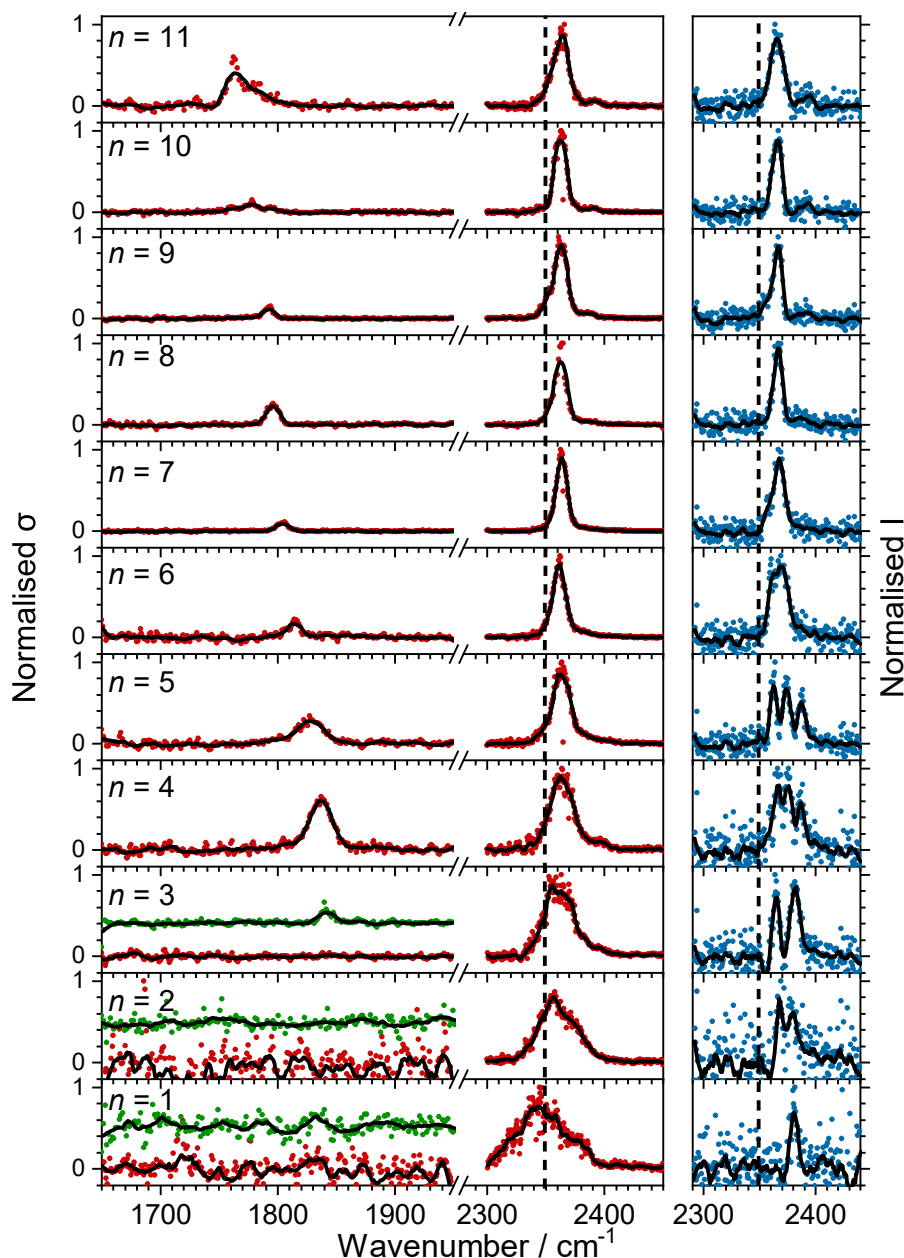


Figure 6.6: Infrared action spectra of $[\text{HoO}(\text{CO}_2)_n]^+$ complexes. The spectra were recorded in the $-\text{CO}_2$ and $-\text{Ar}$ daughter fragment channels of $[\text{HoO}(\text{CO}_2)_n]^+$ ($n = 1 - 11$, red) and $[\text{HoO}(\text{CO}_2)_2^+-\text{Ar}]$ ($n = 1 - 3$, green), respectively (left-hand panel) as well as the depletion of $[\text{HoO}(\text{CO}_2)_2^+-\text{Ar}]$ ($n = 1 - 11$, blue), right-hand panel. The vertical dashed lines indicates the fundamental (ν_3) band in free CO_2 at 2349 cm^{-1} . Adapted directly from the corresponding paper associated with this work.^[417]

Computational potential energy surface searches for $\text{Ho}[\text{O}(\text{CO}_2)_n]^+$ yielded two structural motifs. Examples of each can be seen for $\text{Ho}[\text{O}(\text{CO}_2)_2]^+$ in Figures 6.7 and 6.8. The first structural motif which will be henceforth referred to as a "carbonate structure" contained a motif resulting from the reaction of a single CO_2 ligand with the oxide to form the

$\{\text{CO}_3\}^{\delta-}$ moiety discussed in the previous paragraph. The additional CO_2 ligands (if any) remain molecularly bound to the Ho^+ . While this isomer is referred to as carbonate (or C-isomer), it is important to establish that it is not a true carbonate, as Hirshfeld charge analysis shows that, at most, the $\{\text{CO}_3\}^{\delta-}$ moiety carries a -1 charge. Carbonates carry a formal -2 charge, meaning that this species is not a true carbonate despite being referred to as such by Jiang and co-workers.^[441]

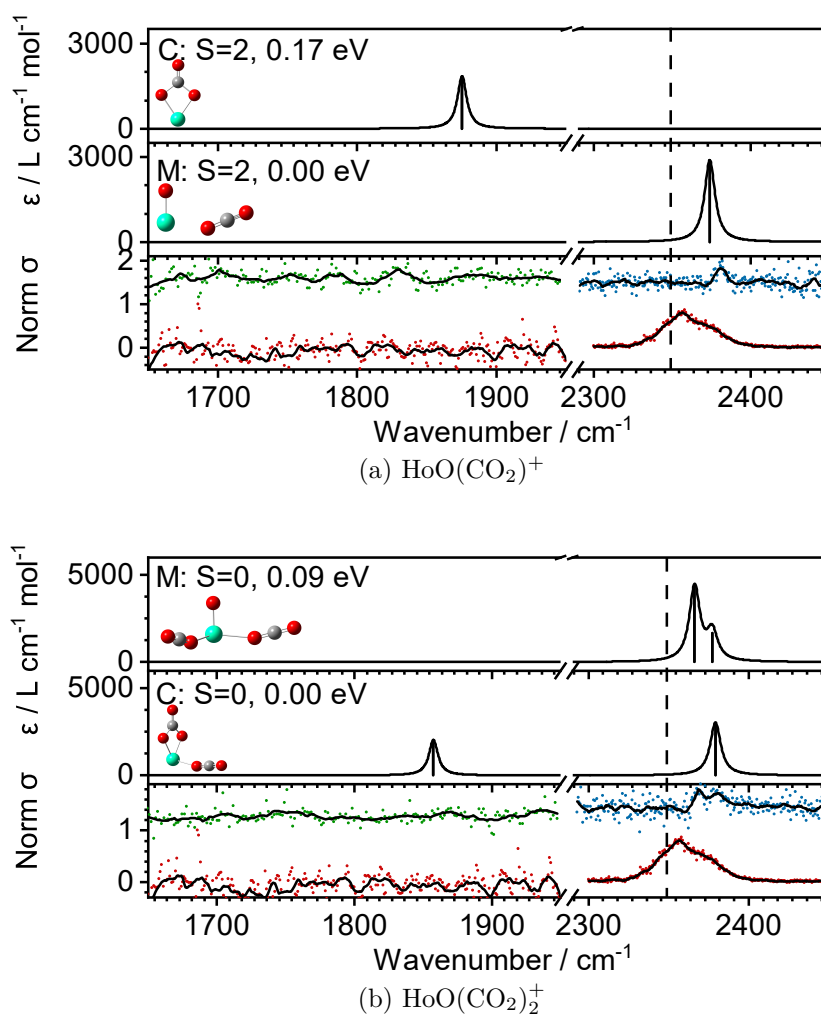


Figure 6.7: Comparisons between simulated (UB3P86/Def2-TZVP) experimental spectra of $\text{HoO}(\text{CO}_2)_n^+$ ($n = 1 - 2$). Red and green data points represent spectra recorded in - CO_2 and -Ar daughter channels, respectively. Blue data was recorded in [-Ar] depletion. The dashed line indicates the vibrational frequency of the asymmetric stretch (ν_3) of free CO_2 at 2349 cm^{-1} . Adapted directly from the corresponding paper associated with this work.^[417]

The other structural motif observed contained only CO_2 ligands molecularly bound to a

central Ho-O motif. This motif is referred to as the M-isomer. Both structural motifs contain molecularly bound CO₂, meaning that the asymmetric CO₂ stretch (in the 2300-2450 cm⁻¹ region) is not spectroscopically unique to a particular structure and thus is not structurally diagnostic. The carbonate structure generates an additional IR feature resulting from a C-O stretch within the {CO₃}^{δ-} moiety between 1800-1850 cm⁻¹. This feature is unique to the C-isomer, making it structurally diagnostic.

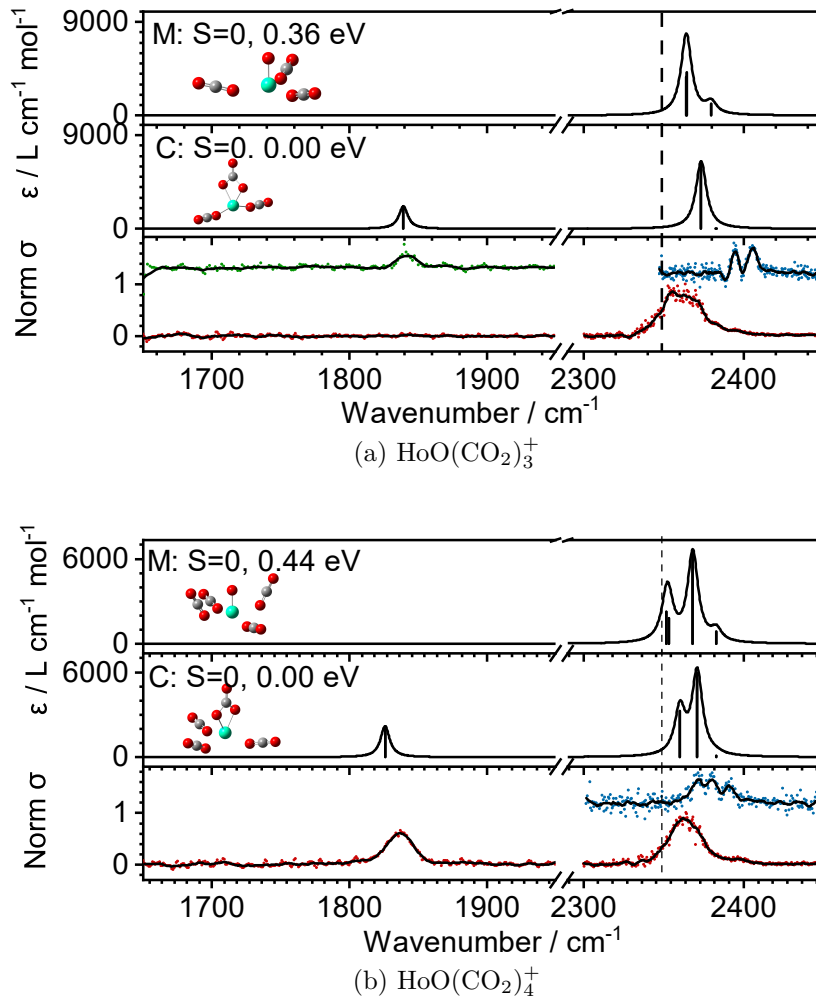


Figure 6.8: Comparisons between simulated (UB3P86/Def2-TZVP) experimental spectra of $\text{HoO}(\text{CO}_2)_n^+$ ($n = 3 - 4$). Red and green data points represent spectra recorded in -CO₂ and -Ar daughter channels, respectively. Blue data was recorded in [-Ar] depletion. The dashed line indicates the vibrational frequency of the asymmetric stretch (ν_3) of free CO₂ at 2349 cm⁻¹. Adapted directly from the corresponding paper associated with this work.^[417]

6.5 Potential Energy Surfaces of Ho[O(CO₂)_n]⁺

Based on the experimental spectra shown in Figure 6.6, Ho[O(CO₂)_n]⁺ species with $n \geq 3$ contain the {CO₃}^{δ-} moiety. Figure 6.9 shows potential energy surfaces for Ho[O(CO₂)_n]⁺ species ($n = 1 - 4$), including the entrance channels to their formation and the interconversion between the isomeric forms. It should be noted that in the $n = 4$ case, the barrier is an approximated barrier rather than a fully optimised barrier due to difficulty in locating the exact form of the transition state. In every case, both isomeric forms of Ho[O(CO₂)_n]⁺ lie below the entrance channel and are separated by a transition state that is also sunken, meaning that either isomeric form could be adopted. As such, the argument for why this behaviour occurs is rationalised not on the sole presence of isomers, but on the nature of the experiment carried out and the energies required to lose ligands.

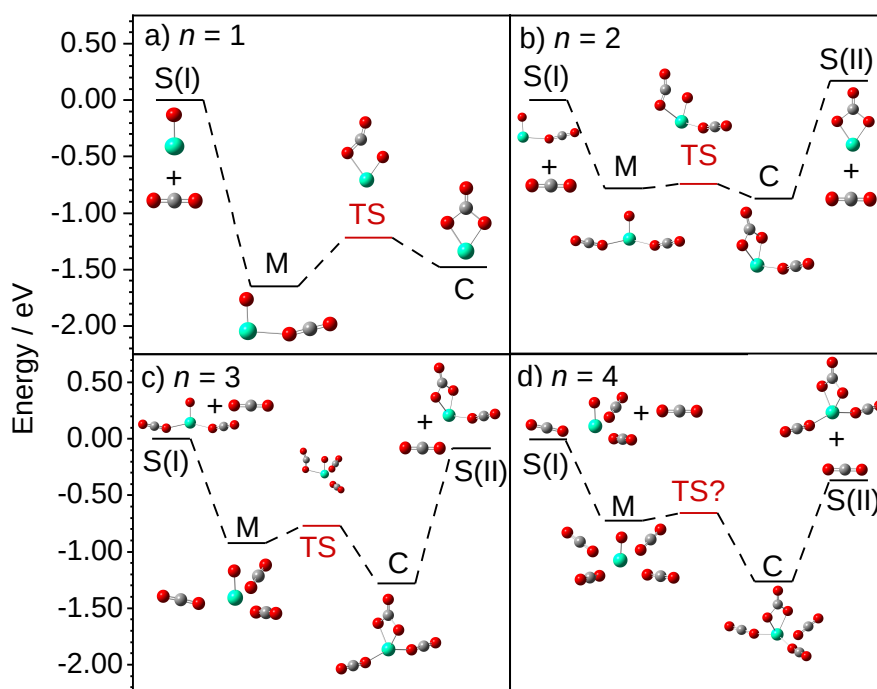


Figure 6.9: Potential energy surfaces for HoO(CO₂)_n⁺ ($n = 1 - 4$) generated at the UB3P86/Def2-TZVP level of theory showing the relative energies HoCO₃(CO₂)_n⁺ (labelled C-isomers) and HoO(CO₂)_n⁺ (M-isomer) structures. The surfaces show the transformation between species. S(I) represents HoO(CO₂)_{n-1}⁺ isomer and free CO₂ and S(II) represents the HoCO₃(CO₂)_n⁺ isomer with free CO₂. Adapted directly from the corresponding paper associated with this work.^[417]

Figure 6.10 shows a generic potential energy surface for a Ho[O(CO₂)]_n⁺ complex size. IRPD spectra rely on IR photon absorption to break apart the complex of interest to generate parent ion depletion and daughter ion enhancement. Of the non-Ar-tagged species, only loss of CO₂ was observed.

Based on the potential energy surfaces in Figure 6.10, the only possible exit channels resulted in CO₂ loss from either the molecularly bound or C-isomers. CO₃ loss is so energetically unfavourable (≥ 5 eV) that it was not observed. An infrared photon at 2450 cm⁻¹ has energy ca. 0.30 eV meaning that CO₂ loss requires multiple photon absorption. If the frequency of photon absorption is assumed to be low relative to the rate of IVR, then conceivably either route for CO₂ loss could occur as the barriers to conversion lie markedly lower in energy than CO₂ loss (see Figures 6.9 and 6.10). If it is assumed that the C-isomer is indeed present for each size, there are two dissociation routes possible: direct loss of CO₂ from the C-isomer (energy shown in blue in Figure 6.10) or conversion to the molecularly bound form followed by CO₂ loss (energy shown in yellow in Figure 6.10).

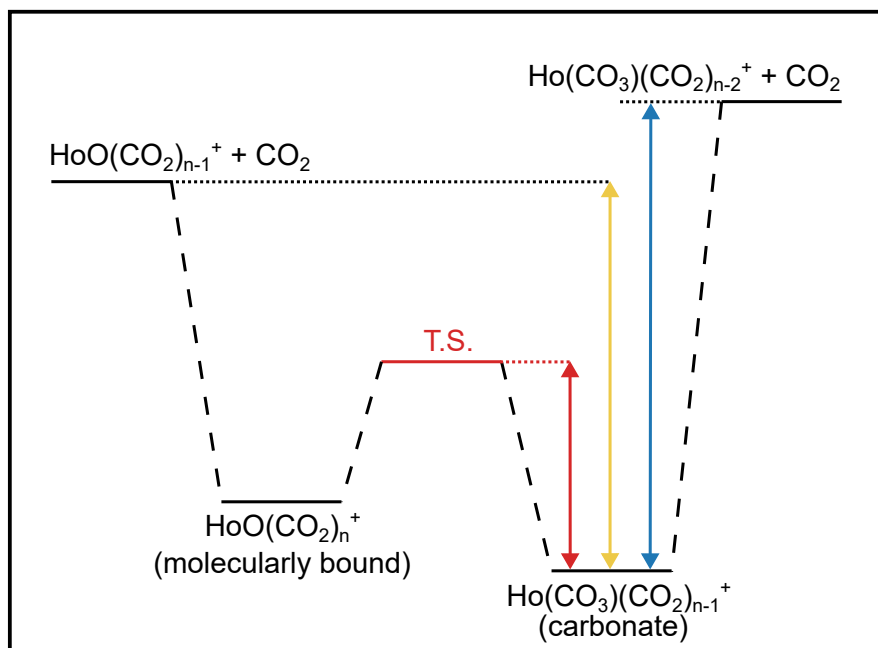


Figure 6.10: An example PES illustrating the various entrance/exit channels and isomers for $\text{Ho}[\text{O}(\text{CO}_2)]^+$. The coloured lines illustrate the various energy barriers for $\text{Ho}[\text{O}(\text{CO}_2)]^+$ ions. The blue line illustrates the barrier to direct CO_2 loss, the red line the barrier to interconversion to the molecularly bound form and the yellow line the barrier to interconversion to the molecularly bound form followed by CO_2 loss. Adapted directly from the corresponding paper associated with this work.^[417]

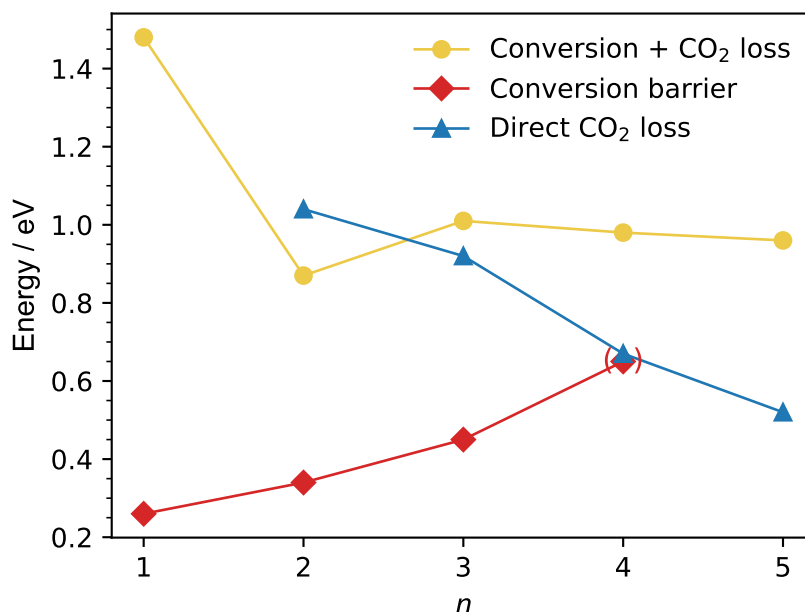


Figure 6.11: The barriers to CO₂ loss from the C-isomer. The blue points indicate the barrier to direct loss of CO₂ from the C-isomer, the yellow points indicate the barrier to conversion the M-isomer followed by CO₂ loss and the red line indicates the barrier to conversion from the C-isomer to the M-isomer. The barrier to interconversion at $n = 4$ is estimated.

The $\{\text{CO}_3\}^{\delta-}$ moiety is spectroscopically visible, for complexes sizes $n \geq 4$, in the direct CO₂ loss channels as it is energetically favourable compared to other loss routes (i.e. conversion to the molecularly bound form followed by CO₂ loss). Figure 6.11 illustrates the energy required for loss of CO₂ from the C-isomer from each pathway along with the $\text{M} \longleftrightarrow \text{C}$ conversion barrier. For complex sizes of $n = 1 - 3$, the barrier to conversion sits much lower in energy than the barrier to direct CO₂ loss, meaning that conversion happens well before CO₂ is lost, preventing further photon absorption due to the loss of the chromophore. At $n = 4$, the barrier to conversion and barrier to direct CO₂ loss are both approximately the same. Direct CO₂ loss becomes a viable pathway, hence the $\{\text{CO}_3\}^{\delta-}$ moiety's vibrational band becomes visible in CO₂ loss channel. Ar tagging the $n = 3$ complex allowed the $\{\text{CO}_3\}^{\delta-}$ moiety's vibrational band to be seen as the barrier to Ar loss is much lower than CO₂ loss. Ar tagging experiments carried out on the $n = 1 - 2$ species show no spectral evidence for $\{\text{CO}_3\}^{\delta-}$ moieties, suggesting that for these complex sizes, the $\{\text{CO}_3\}^{\delta-}$ moieties really are not present or the Ar binds too tightly.

6.6 Trends in the {CO₃}^{δ-} moiety

There is a strong red-shift in the bands associated with the {CO₃}^{δ-} moiety with increasing numbers of CO₂ ligands. Figure 6.12 (a) shows the vibrational frequency of the CO stretch in {CO₃}^{δ-} as a function of ligand number, along with the calculated Hirshfeld charges associated with each significant component of the complex. The red-shift within the {CO₃}^{δ-} moiety, which reflects the weakening of the C-O bonding within this structure, does not result from charge donation by Ho⁺ but rather from charge donation from the additional CO₂ ligands (most likely via σ donation). This illustrates that the vibrational frequency (and therefore bond strength) of the C-O within the {CO₃}^{δ-} moiety can be tuned through the choice of ligands and the number of them. It also demonstrates that Ho⁺ acts simply as a conduit to pass electron density from one ligand to another rather than as an electron donor itself.

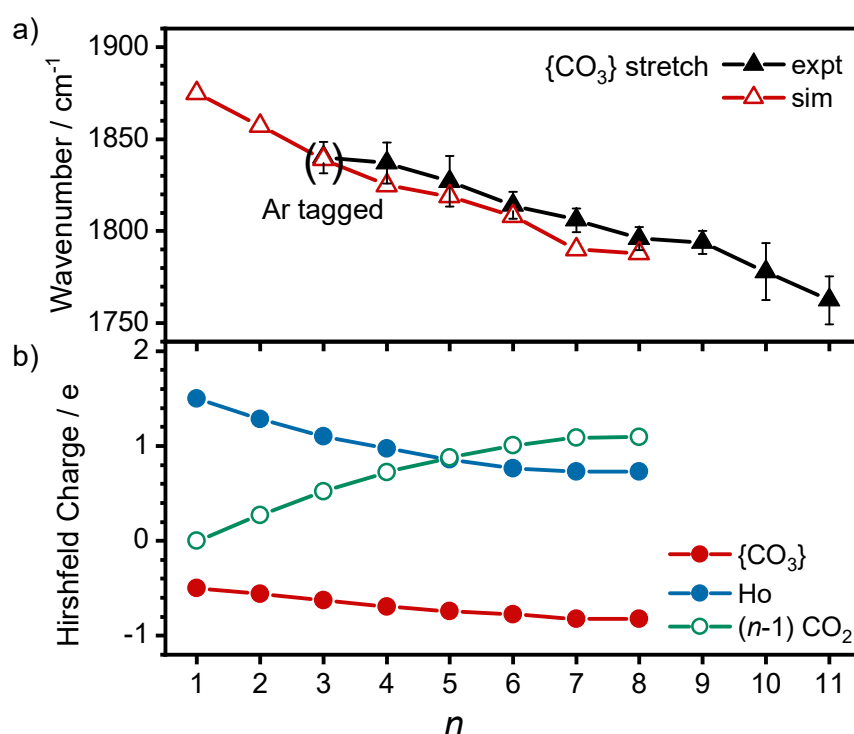


Figure 6.12: (a) Observed and calculated wavenumber of the C=O stretch in the {CO₃}^{δ-} moiety of C-isomers as a function of complex size. Uncertainties represent the half-width at half maximum of the experimental peaks. (b) Trends in the Hirshfeld charges on the {CO₃}^{δ-} moiety (red), Ho atom (blue, solid) and the CO₂ ligands (green) with increasing complex size. Adapted directly from the corresponding paper associated with this work.^[417]

6.7 Conclusions and outlook

Ho⁺ cations are able to react with multiple CO₂ molecules to produce two species: Ho(CO₂)_n⁺ and Ho[O(CO₂)_n]⁺. The CO₂ ligands bind weakly to the central Ho⁺ in an M(η₁-OCO) fashion via a weak charge-quadrupole interaction that results in little perturbation of the CO₂ ligand structure. The σ donation towards the Ho⁺ makes subsequent CO₂ binding less favourable so only complex sizes of $n \leq 4$ were observed.

Ho[O(CO₂)_n]⁺ complexes are thought to result from a reaction of CO₂ with Ho⁺. Ho[O(CO₂)_n]⁺ ions adopt two isomeric forms, one in which the CO₂ binds in the M(η₁-OCO) fashion to HoO and one in which {CO₃}^{δ-} is formed, with the latter being more stable for $n \geq 2$. σ donation from the CO₂ ligands within Ho[O(CO₂)_n]⁺ is localised onto the oxide, making it susceptible to attack via the electrophilic carbon in the CO₂ ligands. Once the {CO₃}^{δ-} moiety forms, electron density localises here, weakening the CO bonds. In this sense, the degree of activation is controllable and, in this regard, complexes behave very similarly to the YO(CO₂)_n⁺ complexes reported by Jiang and coworkers.^[441]

The work presented within this chapter has already had an impact on the development of a novel catalyst. The dry reformation of methane using CO₂ has proved to be an attractive route for the production of hydrogen due the low hazards associated with the precursor materials as well as potentially chemically useful intermediates.^[455] Although dry reformation of methane may be carried out on a variety of different late transition metals (including: Pd, Pt, Rh, and Ru), the expense associated with these metals has driven research towards cheaper metals such as Ni and Fe. Bagabas and co-workers doped holmium oxide (Ho₂O₃) into nickel-based catalysts supported on yttria-stabilised zirconia and were able to demonstrate that the addition of Ho₂O₃ into the catalyst promoted the conversion of methane.^[455] They rationalised the observed behaviour based on the work presented in Chapter 6 illustrating the broader impact on catalysis that this work has already had.

The work performed on CO₂ inspired the work with Ho and OCS described in the next chapter. OCS is an analogue of CO₂ in which one of the oxygen atoms is replaced by a sulphur atom. This introduces a permanent dipole and reduces the symmetry to produce

a richer structural distribution. In terms of work beyond the scope of this thesis, it would be interesting to investigate more strongly donating ligands and the behaviour of CO₂ bound to Ho⁺ to see how weak the C-O bonds within the {CO₃}^{δ-} moiety can be made, or maybe even if the CO₂ can be forced into adopting the oxalate like structure in the case of Ho on the bare Ho⁺ ions. Work within the group is now being carried out using mixed ligand systems to attempt to promote reactions between the species generated by CO₂ and other small gas phase molecules such as NO. Beyond this, studies into the effects of changing the lanthanide cation would be useful in better understanding the role that the metal cation plays in the transfer of charge between various ligands.

7 | An infrared study of $\text{Ho}[(\text{OCS})_n]^+$ ion molecule complexes

This chapter presents the spectroscopic study of the $\text{Ho}[(\text{OCS})_n]^+$, $\text{Ho}[\text{S}(\text{OCS})_n]^+$ and $\text{Ho}[\text{O}(\text{OCS})_n]^+$ complexes generated when Ho is ablated in the presence of OCS seeded into He. Spectra of each molecule were recorded between 1200-2400 cm^{-1} and assigned based on DFT calculations. OCS was found to react with Ho^+ ions to form both $\text{HoO}^+ + \text{CS}$ and $\text{HoS}^+ + \text{CO}$ as well as bind in a molecular fashion analogous to CO_2 . Both HoO^+ and HoS^+ were observed to produce $\{\text{CO}_2\text{S}\}^{\delta-}$ and $\{\text{COS}_2\}^{\delta-}$ respectively that preferentially bound to the Ho^+ via sulphur atoms. The COS_2 C=O bond stretch is observed to red-shift with increasing complex size, illustrating that additional OCS ligands donate electron density to stabilise the thiocarbonate in an identical fashion to the behaviour seen in $\text{Ho}[\text{O}(\text{CO}_2)_n]^+$ species.

These results are in preparation for publication. The work presented here was undertaken with a Part II student Jonathan Mason.

7.1 Introduction

Based on the previous work carried out with CO_2 and Ho^+ ions, replacing CO_2 with OCS was seen as the next logical stepping stone. As the chemistry and behaviour of both Ho and CO_2 are discussed previously in Chapter 6, only OCS is discussed here.

7.1.1 OCS

OCS is a valence isoelectronic analogue of CO_2 in which an oxygen atom is replaced by a sulphur atom. While much less abundant in the atmosphere than CO_2 , OCS plays an extremely important role within the global sulphur cycle. It acts as a reactant for many reactions in the atmosphere, producing sulphuric acid, which then falls as acid rain. There are many anthropogenic sources of OCS, including CS_2 production, coal-fired power stations, and the manufacture of synthetic fibres. These produce around 1×10^6 tonnes of OCS a year.^[456] As such, OCS capture and subsequent reactions to generate other useful

products (e.g. thiocarbamate pesticides) are of interest. OCS is a sulphur-transfer reagent in the hydrodesulphurisation of natural gas, and as such its reactions and interactions with metals have also been investigated.^[457–459]

OCS is a linear triatomic molecule with $\text{C}_{\infty\text{v}}$ symmetry. It consists of a central carbon atom with an oxygen and carbon atom on either side of it. The C=O bond length is 1.15 Å, whereas the C=S bond length is 1.56 Å. Like CO_2 , OCS can be activated by having electrons withdrawn from its (strongly bonding) HOMO or donated into its (strongly antibonding) LUMO. Equally, OCS will bend away from its linear ground state structure as it becomes activated (see the Walsh diagram in Figure 6.1 in the previous chapter).

Armentrout and co-workers have studied the reactions of OCS with a range of metal cations, and found that many metal cations react with OCS to form MS^+ (and also CO).^[460–464] ICP-SIFT experiments, however, showed only molecular binding to Au^+ cations.^[465] The Mackenzie group has previously demonstrated size-selective reactivity of Au_n^+ towards OCS.^[407] However, beyond the studies listed above, the reactions and behaviour of OCS towards metal ions and clusters have been poorly studied.

The rationale behind using OCS for the work presented in this chapter was to investigate how the introduction of asymmetry and a larger more diffuse atom to CO_2 would change the reactivity and behaviour observed when Ho^+ ions and CO_2 react.

7.2 Experimental Details

All of the experimental data presented within this section of the thesis were recorded on the iteration of the instrument containing the quadrupole mass filter elaborated on in Section 5.2.2. In all cases where not explicitly mentioned, the spectra were recorded in the enhancement channel (shown in red) from OCS loss from the parent ion (shown in Reaction 5);



DFT calculations at the UB3P86/Def2-TZVP level of theory were used in conjunction with the Kick³ algorithm to search the potential energy surfaces for each complex size. The UB3P86/Def2-TZVP level of theory was selected to ensure comparisons with the work with Ho^+ and CO_2 could be made - although this incurred the issues surrounding the method of coupling discussed previously in Section 6.2. Vibrational frequencies were scaled by a factor of 0.96 to better match with the experiment based on the differences between the experimentally measured and calculated free OCS asymmetric stretch (2062 cm^{-1} and 2140 cm^{-1} respectively). Line spectra have been convoluted with a Lorentzian function with a full width at half-maximum (FWHM) of 8 cm^{-1} to aid comparison with experimental spectra.

7.3 Mass spectra

The mass spectra presented here were recorded with two different gas mixes. The first, shown in Figure 7.1, was recorded while ablating Ho metal in the presence of OCS seeded into He. The second mass spectrum, shown in Figure 7.3, was recorded while ablating Ho into a mixture of OCS and CO_2 seeded into He. The latter experiment was carried out in order to help with the generation of species of interest within the experiment. Each mass spectrum is discussed in detail within this section.

7.3.1 Ho and OCS in He

Figure 7.1 shows the mass spectrum of Ho ablated in the presence of 1% OCS seeded into He. Three distinct species can be seen: $\text{Ho}[(\text{OCS})_n]^+$, $\text{Ho}[\text{S}(\text{OCS})_n]^+$ and $\text{Ho}[\text{O}(\text{OCS})_n]^+$. Once again, the square brackets denote the potential for multiple indistinguishable isomeric structures. The intensity of all species falls away with complex size, although it falls away most sharply in the oxide species ($\text{Ho}[\text{O}(\text{OCS})_n]^+$), which produces appreciable intensity for $n = 1$ only. $\text{Ho}[(\text{OCS})_n]^+$ produced experimentally observable intensity up to $n = 4$, whilst the $\text{Ho}[\text{S}(\text{OCS})_n]^+$ peaks were observed to be the most intense and fell away in intensity the slowest, with peaks being observed up to $n = 5$ (and beyond with different conditions). By comparison to CO_2 , OCS shows a richer variety of products due to the presence of sulphur. The dominance of the $\text{Ho}[\text{S}(\text{OCS})_n]^+$ complexes within the

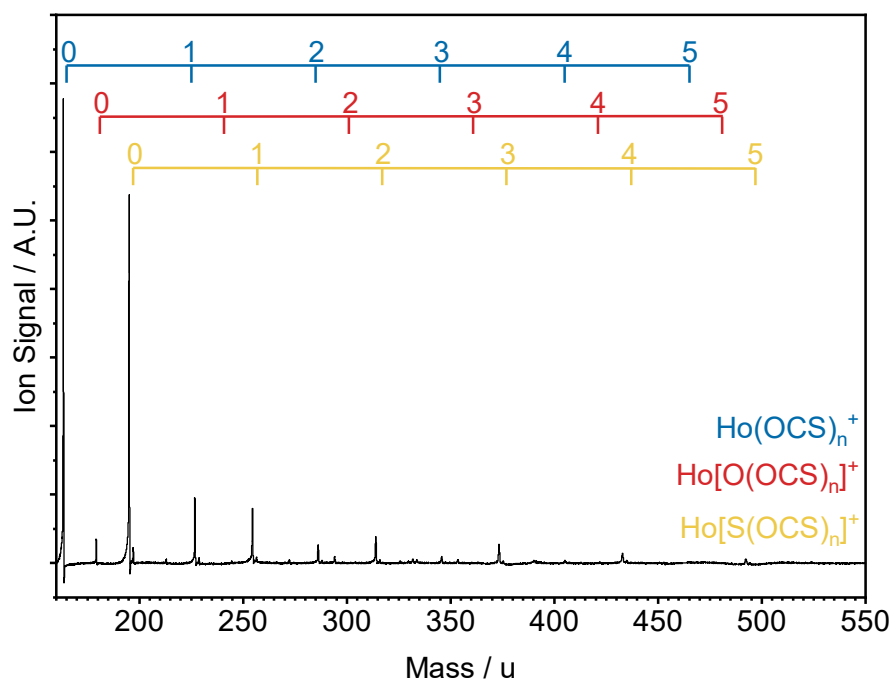


Figure 7.1: Representative time-of-flight mass spectrum obtained following the laser ablation of a Ho target in the presence of a backing gas mixture of ca. 1% OCS in He. $\text{Ho}[(\text{OCS})_n]^+$, $\text{HoS}(\text{OCS})_n^+$ and $\text{HoO}[(\text{OCS})_n]^+$ complexes are all formed up to at least $n = 2$.

spectrum suggests that the OCS is considerably more reactive towards dissociation on Ho^+ than CO_2 . No evidence for further reactions of HoS^+ or HoO^+ is seen within the spectrum.

Figure 6.3 in Chapter 6 shows the mass spectrum of Ho ablated in He only under similar conditions used to generate the mass spectrum in Figure 7.1, and neither HoS nor HoO are produced. Metals rarely generate sulphide surface structures in the way that they do oxide structures from exposure to air, meaning that the most plausible explanation for the presence of the sulphide species is the direct reaction of Ho^+ ions with OCS to produce CO and HoS. Equally, the lack of HoO also suggests that Ho also reacts with OCS to form HoO.

Figure 7.2 shows the PES for the $\text{Ho}^+ + \text{OCS}$ reactions. The PES shows a variety of different species produced. However, most notably, it shows the routes by which HoS^+ and HoO^+ can be produced from a linearly molecularly-bound form as well as a variety of different intermediates in which the OCS is strongly activated by the Ho^+ . Most

of the potential energy surface (aside from two exit channels and a transition state) is submerged by more than 0.5 eV below the energy of the entrance channel ($\text{Ho}^+ + \text{OCS}$) which, in theory, makes most of the surface readily accessible. Notably, the $\text{HoO}^+ + \text{CS}$ exit channel sits considerably higher in energy than the $\text{HoS}^+ + \text{CO}$ exit channel. The difference in energy between the two exit channels explains the increased number density of the sulphide species relative to the oxide species.

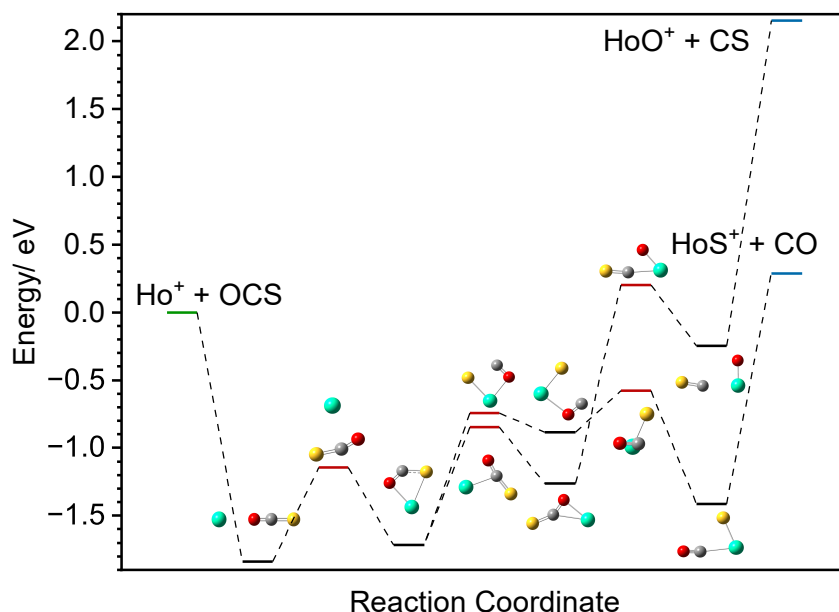


Figure 7.2: Potential energy surface for $\text{Ho}(\text{OCS})^+$ generated at the UB3P86/Def2-TZVP level of theory showing the relative energies of the major isomers and transition states located within the potential energy landscape.

7.3.2 Ho, CO_2 and OCS in He

Figure 7.3 shows a representative mass spectrum generated when Ho is ablated in the presence of a mixture of 2.5% OCS and 2.5% CO_2 seeded into He. Surprisingly, very few $\text{Ho}(\text{CO}_2)_n^+$ or mixed-ligand $\text{Ho}[(\text{CO}_2)_n(\text{OCS})_m]^+$ species are generated, suggesting that the presence of OCS inhibits CO_2 binding to the Ho^+ ions. It is highly likely that while $\text{Ho}(\text{CO}_2)_n^+$ complexes form (see Chapter 6), the higher binding energy of OCS relative to CO_2 results in CO_2 ligands being displaced. The addition of CO_2 however, can clearly be seen to promote the formation of $\text{Ho}[\text{O}(\text{OCS})_n]^+$ species when compared to the mass

spectrum generated using only OCS (see Figure 7.1).

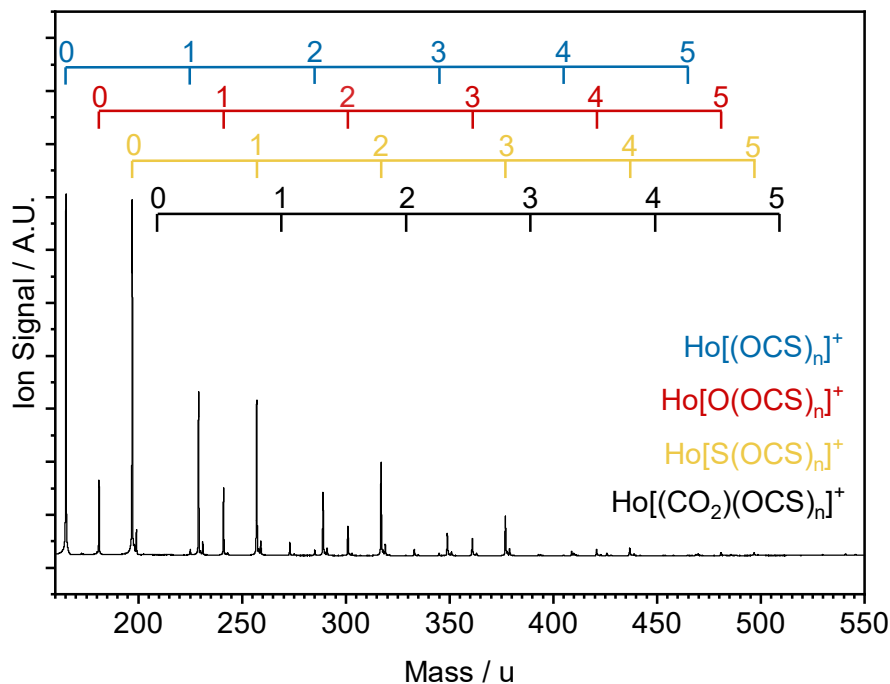


Figure 7.3: Representative time-of-flight mass spectrum obtained following the laser ablation of a Ho target in the presence of a backing gas mixture of ca. 2.5% OCS and 2.5% CO_2 in He. $\text{Ho}[(\text{OCS})_n]^+$, $\text{HoS}(\text{OCS})_n^+$ and $\text{Ho}[\text{O}(\text{OCS})_n]^+$ complexes are all formed up to at least $n = 3$.

With CO_2 and OCS added to the system, there are two possible oxide formation routes. Either the CO_2 reacts with the Ho^+ to form HoO^+ before OCS displaces any CO_2 ligands or the HoO^+ is produced directly from a reaction with OCS. While it is clear how direct HoO^+ production from CO_2 would increase the number of $\text{Ho}[\text{O}(\text{OCS})_n]^+$ species, the reason as to why the addition of CO_2 changes the reactions of HoO^+ and OCS is less clear.

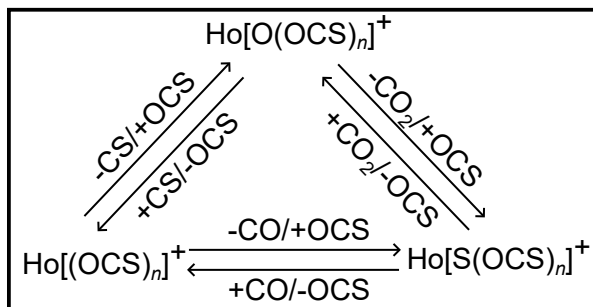


Figure 7.4: The reactions by which Ho^+ ions and n OCS molecules may produce $\text{Ho}[\text{O}(\text{OCS})_n]^+$ and $\text{Ho}[\text{S}(\text{OCS})_n]^+$.

Figure 7.4 illustrates a postulated reactive cycle that shows how $\text{Ho}[\text{S}(\text{OCS})_n]^+$ and $\text{Ho}[\text{O}(\text{OCS})_n]^+$ can be formed from $\text{Ho}[(\text{OCS})_n]^+$. The reactions within the source are governed by the frequency of collisions of the metal species (Ho^+) with the required reactants ($\text{CO}_2 + \text{OCS}$), as well as the energy barriers, hence reaction rates and product distributions can be strongly influenced by the amount of a given species present. Oxide formation proceeds via one of two routes, either via direct loss of CS or via the formation of an oxide followed by loss of an OCS and gain of a CO_2 . Seeding of CO_2 to the ($\text{He} + \text{OCS}$) mixture helps promote the conversion of the sulphide species (already produced in high abundance in the presence of OCS) to the oxide. While these explanations do offer a qualitative explanation as to why the CO_2 helps oxide formation, it is hard to deconvolute the intracluster reaction from the growth or complexes on HoO^+ and HoS^+ formed in the initial reactive step.

7.4 $\text{Ho}[(\text{OCS})_n]^+$

Due to the high OCS binding energies, $\text{Ho}[(\text{OCS})_n]^+$ complex sizes smaller than $n = 4$ proved difficult to record with satisfactory signal-to-noise (if possible to record at all), hence they are not shown or discussed here. $n = 4$ was the smallest complex size to show efficient fragmentation. Complex sizes of $n > 4$ were recorded, however they show almost identical spectra to $n = 4$ and add little to the scientific picture. For brevity, they are not included in the discussion here.

7.4.1 $\text{Ho}[(\text{OCS})_4]^+$ IR-PD Spectrum

Figure 7.5 shows the experimental spectrum of $\text{Ho}[(\text{OCS})_4]^+$ (in the final panel) along with a series of low lying isomers located during a potential energy landscape search. The experimental spectrum shows the three bands between 1900 and 2000 cm^{-1} (1931 , 1960 and 1988 cm^{-1}) along with an additional band at 2102 cm^{-1} . The potential energy landscape search revealed four key isomeric structures including (in order of relative energy) a dissociatively-bound structure ("dis"), a dimerised structure ("dimer"), a molecularly bound but bent structure ("bent") and a linearly molecularly-bound structure ("mol").

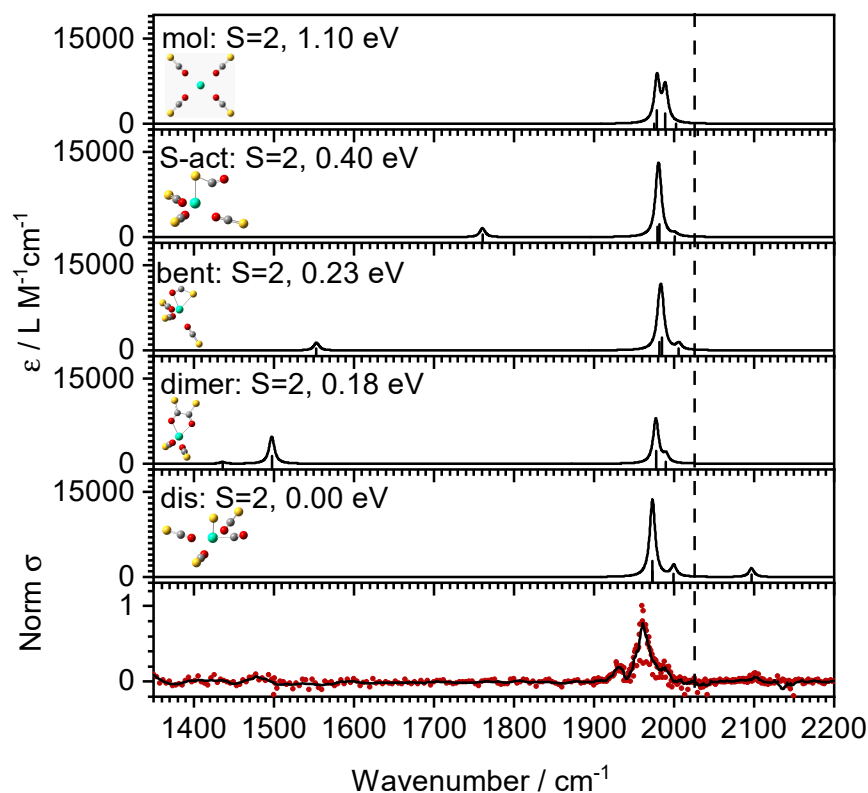


Figure 7.5: Comparison of experimental and simulated spectra of energetically low-lying structures (UB3P86/Def2-TZVP) for $\text{Ho}[(\text{OCS})_4]^+$. The vertical dashed line indicates the asymmetric stretch (ν_3) fundamental of free OCS at 2062 cm^{-1} . Ho blue, C grey, O red and S yellow.

The three bands at 1931 , 1960 and 1988 cm^{-1} within the experimental spectrum are assigned to asymmetric OCS stretches from OCS bound to Ho^+ via the oxygen atom. They are red-shifted from the free OCS asymmetric stretch (on average) by 102 cm^{-1} .

Compared to the CO_2 complexes presented in Chapter 6, which show little evidence of activation when molecularly bound (the CO_2 asymmetric stretch blue-shifts by 10-20 cm^{-1}), the red-shifted OCS asymmetric stretch shows that they are strongly activated - even when bound molecularly. Rather than resulting from donation of electron density into the LUMO, this activation comes from the withdrawal of electron density from the HOMO of OCS. The electron density within OCS is localised onto the oxygen atoms, generating the dipole moment. O-bound OCS localises this electron density closer to the Ho^+ , which offers an explanation as to why the OCS is activated more than CO_2 . An additional argument could be that the more diffuse orbitals of OCS allow for a greater overlap with the Ho^+ orbitals compared to CO_2 . Each predicted structure in Figure 7.5 contains OCS molecules bound in the o-bound, linear, and molecular fashion, making the OCS asymmetric stretch a non-diagnostic of an isomer.

Each isomer, aside from the linearly molecularly-bound form, shows a spectroscopically distinct feature in addition to the OCS asymmetric stretch. These features are summarised in Table 7.1. The band at 2102 cm^{-1} within the experimental spectrum matches perfectly with the C=O stretch of CO produced from the dissociatively-bound isomer (dis) in Figure 7.5, confirming the presence of the dis isomer. No evidence of dissociative binding of CO_2 to Ho^+ was obtained (see Chapter 6), providing direct evidence of the increased reactivity of OCS towards Ho^+ relative to CO_2 . The increased reactivity results from the C-S bond being weaker than the C-O bond. The presence of the dissociatively-bound isomer provides a route through which the sulphide species is produced as the dissociatively-bound bound isomer can simply lose CO upon collision with an additional OCS, as shown in Reaction 6;



While the dimerised isomer ("dim") and activated isomer in Figure 7.5 can be ruled out based on the lack of diagnostic peaks within the experimental spectrum, the molecularly-bound isomer ("mol") could not (as it contains no unique structures), meaning that it could also have been present. The only structure definitively confirmed was the dissociatively-bound isomer ("dis").

Isomer	Feature position / cm^{-1}	Associated structural motifs
mol	NA	NA
S-act	1761	S-bound bent OCS
bent	1553	O/S-bound bent OCS
dimer	1436 and 1498	O-bound thio-oxalate
dis	2102	C-bound CO

Table 7.1: The (calculated) positions of spectroscopically distinct structural motifs associated with isomers found for $\text{Ho}(\text{OCS})_4^+$ during the potential energy landscape search.

7.4.2 Thermodynamic stability of the dissociatively bound isomers of $\text{Ho}[(\text{CO}_2)_n]^+$

Figure 7.6 a shows the energies of each isomer (relative to the molecularly bound isomer) as a function of complex size. For $n = 1 - 2$, the putative global minimum structures contain an activated/bent OCS (see isomer "bent" in Figure 7.5). For $n \geq 3$, it changes to become the dissociatively-bound isomer (see isomer "dis" in Figure 7.5). This suggests that the addition of OCS ligands stabilises the dissociatively-bound isomer relative to the other isomers.

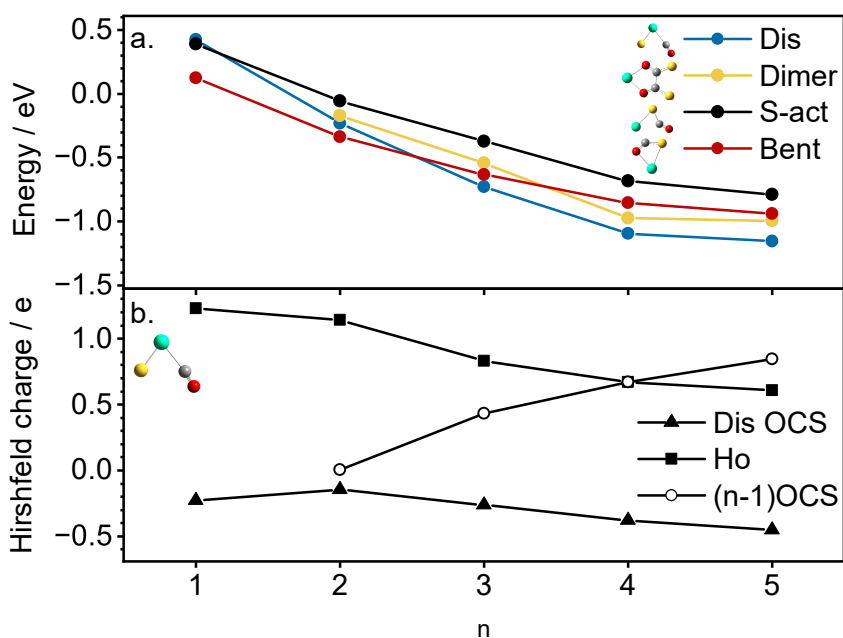


Figure 7.6: (a) The relative energy of the computationally generated isomers at each size from $n = 1 - 5$. (b) The Hirshfeld charges in each complex's components as a cluster size function.

Figure 7.6 illustrates the Hirshfeld charge distributed around the dissociative isomer at each complex size. When the dissociatively bound isomer forms, a $\text{Ho}-\text{OCS}$ and $\text{OC}=\text{S}$ bond are broken and a $\text{Ho}-\text{S}$ and $\text{Ho}-\text{CO}$ bond formed. The $\text{Ho}-\text{S}$ bond is weak due to the electronegativity of both Ho^+ and S (both stabilised through the accumulation of electron density), which results in the dissociatively bound isomer being less thermodynamically stable at smaller sizes. O-bound OCS molecules bound in a molecular and linear fashion are able to donate electron density (as evidenced by their red-shifts relative to free OCS shown in Figure 7.5). Thus, as the complex size increases and more OCS binds to the Ho^+ ion in a molecular and linear fashion, the additional electron density from the molecularly bound OCS is localised onto both the Ho^+ and S stabilising the $\text{Ho}-\text{S}$ bond.

7.5 $\text{Ho}[\text{S}(\text{OCS})_n]^+$

Due to the high OCS binding energies, $\text{Ho}[\text{S}(\text{OCS})_n]^+$ complex sizes smaller than $n = 4$ proved difficult to record with satisfactory signal-to-noise (if possible to record at all), hence they are not shown or discussed here. $n = 4$ was the smallest complex size to show efficient fragmentation. Complex sizes of $n > 4$ were recorded, however they show almost identical spectra to $n = 4$ and add little to the scientific picture. For brevity, they are not included in the discussion here.

7.5.1 $\text{Ho}[\text{S}(\text{OCS})_4]^+$ IR-PD Spectrum

Figure 7.7 shows the experimental spectrum of $\text{Ho}[\text{S}(\text{OCS})_4]^+$ (final panel) along with energetically low-lying isomers (and their spectra) located during a potential energy landscape search. The experimental spectrum shows three bands between 1900-2000 cm^{-1} (1934, 1959, 1982 cm^{-1}) and an additional, low-intensity band, at 1724 cm^{-1} . The potential energy landscape search revealed three key isomeric structures including (in order of energy): a structure in which one of the OCS molecules reacts with the sulphide S to form a $\{\text{COS}_2\}^{\delta-}$ moiety bound to the Ho^+ by both S atoms (see isomer "S, S-bound TC" in Figure 7.7), a structure in which the same $\{\text{COS}_2\}^{\delta-}$ moiety forms but bind to the Ho^+ by S and O (see isomer "S, O-bound TC" in Figure 7.7) and finally a structure

in which the OCS molecules bind in a linear and molecular fashion to the Ho^+ via O (see isomer "M" in Figure 7.7).

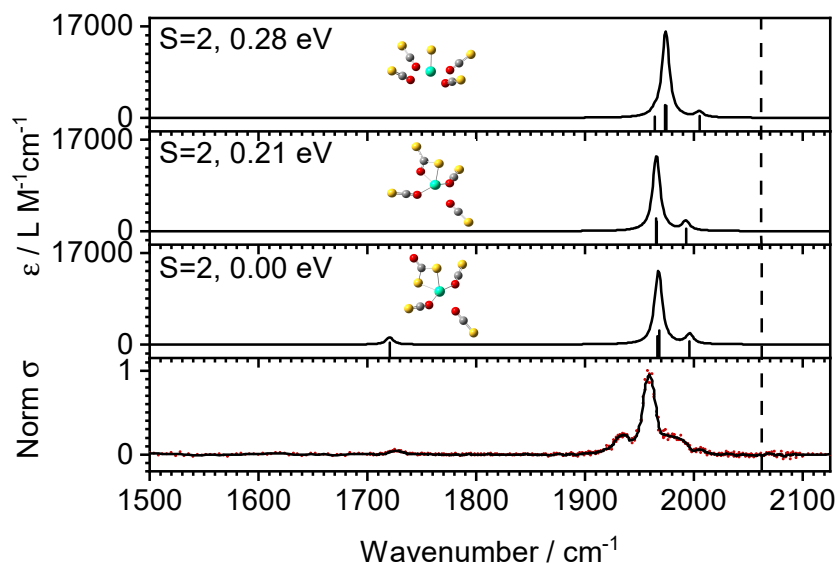


Figure 7.7: Comparison of experimental and simulated spectra of energetically low-lying structures (UB3P86/Def2-TZVP) for $\text{Ho}[\text{S}(\text{OCS})_4]^+$. The vertical dashed line indicates the asymmetric stretch (v_3) fundamental of free OCS at 2062 cm^{-1} . Ho blue, C grey, O red and S yellow.

The three bands between $1900\text{--}2000 \text{ cm}^{-1}$ ($1934, 1959, 1982 \text{ cm}^{-1}$) are assigned to OCS asymmetric stretches. In an identical fashion to that seen for $\text{Ho}[(\text{OCS})_4]^+$, the asymmetric stretches were red-shifted relative to the free OCS stretch by an average of 104 cm^{-1} , indicating that the molecularly bound OCS molecules are significantly activated via the loss of electron density from their HOMO. As all isomers within the potential energy landscape search contained these molecularly bound OCS molecules, the asymmetric stretches are not structurally diagnostic.

The low-intensity band, at 1724 cm^{-1} within the experimental spectrum is assigned to the CO stretch within the S, S-bound $\{\text{COS}_2\}^{\delta-}$ moiety, based on the good match in the band position in both the experimental and calculated spectrum of the "S, S-bound TC" isomer. It should be noted that there was a remarkably good match between the experimental data and theoretical data for this isomer. The formation of $\{\text{COS}_2\}^{\delta-}$ moiety was analogous to the $\{\text{CO}_3\}^{\delta-}$ moiety seen in $\text{Ho}[\text{O}(\text{CO}_2)]_n^+$ ($n \geq 3$) complexes in Chapter 6.

Aside from the putative global minimum structure ("S, S-bound TC" in Figure 7.7), none of the isomers located within the potential energy landscape search produced spectroscopically unique bands within the accessible wavelength range of the laser system, meaning that no structure could be ruled out.

7.5.2 $\{\text{COS}_2\}^{\delta-}$ Formation

Formation of the molecularly bound isomer through reaction 7:



is established in Section 7.5. Formation of the $\{\text{COS}_2\}^{\delta-}$ moiety occurs via a $2 + 2$ cycloaddition transition state.^[441] Localisation of electron density onto the S atom within the complex promotes nucleophilic attack of OCS onto the S atom and facilitates the $2 + 2$ cycloaddition reaction. Figure 7.9 (c) shows a clear increase of the Hirshfeld charge on the S and Ho^+ atoms with increasing complex size suggesting that the electron donation by the additional molecularly-bound OCS ligands promotes the formation of the $\{\text{COS}_2\}^{\delta-}$ moiety.

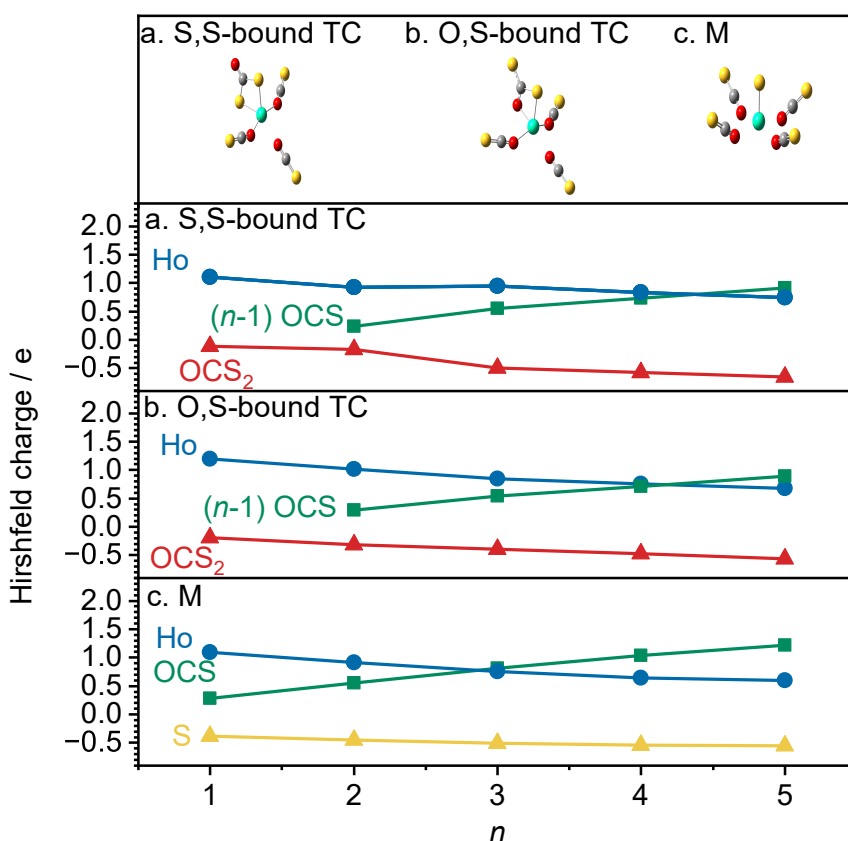


Figure 7.8: (a) Trends in the Hirshfeld charges on the $\{\text{COS}_2\}^{\delta-}$ moiety (red triangles), Ho atom (blue, circles) and the CO₂ ligands (green, squares) with increasing complex size for the S, S-bound TC isomer. (b) Trends in the Hirshfeld charges on the $\{\text{COS}_2\}^{\delta-}$ moiety (red triangles), Ho atom (blue, circles) and the CO₂ ligands (green, squares) with increasing complex size for the O, S-bound TC isomer. (c) Trends in the Hirshfeld charges on the s atom (yellow triangles), Ho atom (blue, circles) and the CO₂ ligands (green, squares) with increasing complex size for the molecularly bound isomer.

The Hirshfeld charge for the S, S-bound and O, S-bound $\{\text{COS}_2\}^{\delta-}$ moieties are shown in Figure 7.9 (a) and (b) respectively. The distributions of charge with complex size are similar and do not offer an explanation for the stability of the S, S-bound isomer compared to the O, S-bound isomer. There is a possibility that the asymmetry of the O, S-binding motif introduces ring strain that is not present in the symmetric S, S-binding motif.

7.5.3 Thiocarbonate Red-Shift

The characteristic stretch associated with the C=O bond in the CS₂O moiety red-shifts as more OCS ligands are added to the complex (see Figure 7.9). This red-shift results from

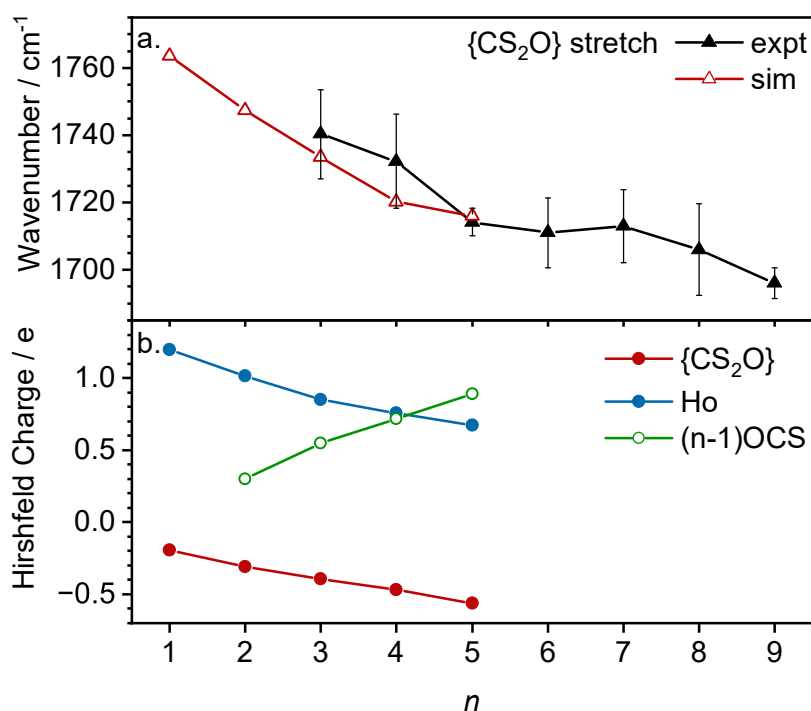


Figure 7.9: (a) Observed and calculated wavenumber of the C=O stretch in the CS_2O moiety of TC-isomers as a function of complex size. Uncertainties represent the half-width at half maximum of the experimental peaks. (b) Trends in the Hirshfeld charges on the CS_2O moiety (red), Ho atom (blue, solid) and the CO_2 ligands (green) with increasing complex size.

the donated electron density from successive molecularly-bound OCS molecules weakening the C=O bond within the $\{\text{COS}_2\}^{\delta-}$ moiety. This is similar behaviour to that observed in the CO_2 (see Figure 6.12).^[417]

The red-shifting behaviour seen in the $\text{HoS}(\text{OCS})_n^+$ species is compared with the red-shifts seen in $\text{HoO}(\text{CO}_2)_n^+$ species in Figure 7.10. The first and most apparent difference between the two species is that the $\text{O}_2\text{C}=\text{O}$ vibrational frequency in $\text{HoO}(\text{CO}_2)_n^+$ C-isomer is higher than the $\text{S}_2\text{C}=\text{O}$ vibrational frequency in $\text{HoS}(\text{OCS})_n^+$ TC-isomers. This most likely results from the reduced mass effect of the S atoms in $\text{S}_2\text{C}=\text{O}$ compared to the O in $\text{O}_2\text{C}=\text{O}$.

Despite, on average, OCS donating (0.05 e) more charge than a CO_2 ligand, the average red-shift per additional CO_2 is measured to be -8.6 cm^{-1} , whereas for OCS the shift is only -7.3 cm^{-1} , showing that the $\{\text{COS}_2\}^{\delta-}$ moiety was less sensitive to additional electron

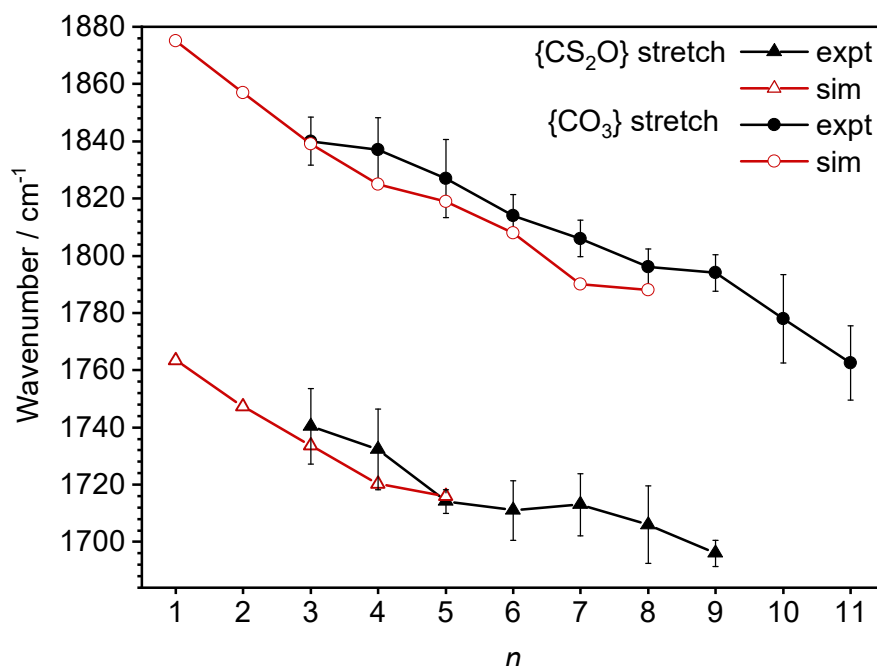


Figure 7.10: The observed and calculated wavenumber of the $\text{O}_2\text{C}=\text{O}$ stretch in the $\{\text{COS}_2\}^{\delta-}$ moiety in $\text{Ho}(\text{CO}_3)(\text{CO}_2)_{n-1}^+$ isomers and the $\text{S}_2\text{C}=\text{O}$ stretch in the $\{\text{COS}_2\}^{\delta-}$ moiety of $\text{Ho}(\text{CS}_2\text{O})(\text{OCS})_{n-1}^+$ isomers as a function of complex size. Uncertainties represent the half-width at half maximum of the experimental peaks.

density than the $\{\text{CO}_3\}^{\delta-}$ moiety. A possible explanation is that the diffuse sulphur atoms within the CS_2O moiety are able to distribute the electron density over a larger volume of space, resulting in a lower susceptibility to the additional electron density.

7.6 $\text{HoO}[(\text{OCS})_n]^+$

Due to the high OCS binding energies, $\text{Ho}[\text{O}(\text{OCS})_n]^+$ complex sizes smaller than $n = 4$ proved difficult to record with satisfactory signal-to-noise (if possible to record at all), hence they are not shown or discussed here. $n = 4$ was the smallest complex size to show efficient fragmentation. Complex sizes of $n > 4$ were recorded, however they show almost identical spectra to $n = 4$ and add little to the scientific picture. For brevity, they are not included in the discussion here.

7.6.1 $\text{HoO}[(\text{OCS})_4]^+$ IR-PD Spectrum

Figure 7.11 shows IR spectra of $\text{HoO}[(\text{OCS})_4]^+$ recorded in two different enhancement channels resulting from the depletion of $\text{HoO}[(\text{OCS})_4]^+$. One is recorded in the enhancement channel (yellow) of OCS loss in Reaction 8:



and the other is recorded in the enhancement channel (red) resulting from CO_2 loss in Reaction 9:



The OCS loss enhancement spectral channel shows a single feature at 1978 cm^{-1} , whereas the CO_2 loss enhancement channel shows three bands at 1932 , 1960 and 1975 cm^{-1} . Both channels also show a single band at 1774 cm^{-1} and 1770 cm^{-1} in the OCS loss and CO_2 loss channels respectively.

In addition to the experimental spectrum, a series of four key energetically low-lying isomers generated from a potential energy landscape search are shown in Figure 7.11. These isomers include (in order of energy): (i) a structure in which one of the OCS molecules reacts with the oxide O to form a $\{\text{CO}_2\text{S}\}^{\delta-}$ moiety bound to the Ho^+ by an S and O atom (see isomer "S, O-bound TC" in Figure 7.11); (ii) a structure in which OCS reacts with the oxide to form the sulphide species (see Section 7.5), and a molecularly bound CO_2 (see isomer "CO₂ mol" in Figure 7.11); (iii) a structure in which one of the OCS molecules reacts with the oxide O to form a $\{\text{CO}_2\text{S}\}^{\delta-}$ moiety bound to the Ho^+ by both O atoms (see isomer "O, O-bound TC" in Figure 7.11); and finally, (iv) a structure in which all OCS molecules are molecularly-bound in a linear fashion (see isomer "mol" in Figure 7.11).

Despite the differences between the OCS loss and CO_2 loss spectral channels (addressed in Section 7.6.2), all of the bands between 1900 - 2000 cm^{-1} in both spectra are assigned to asymmetric stretches of OCS bound in a molecular fashion. The peaks are red-shifted by

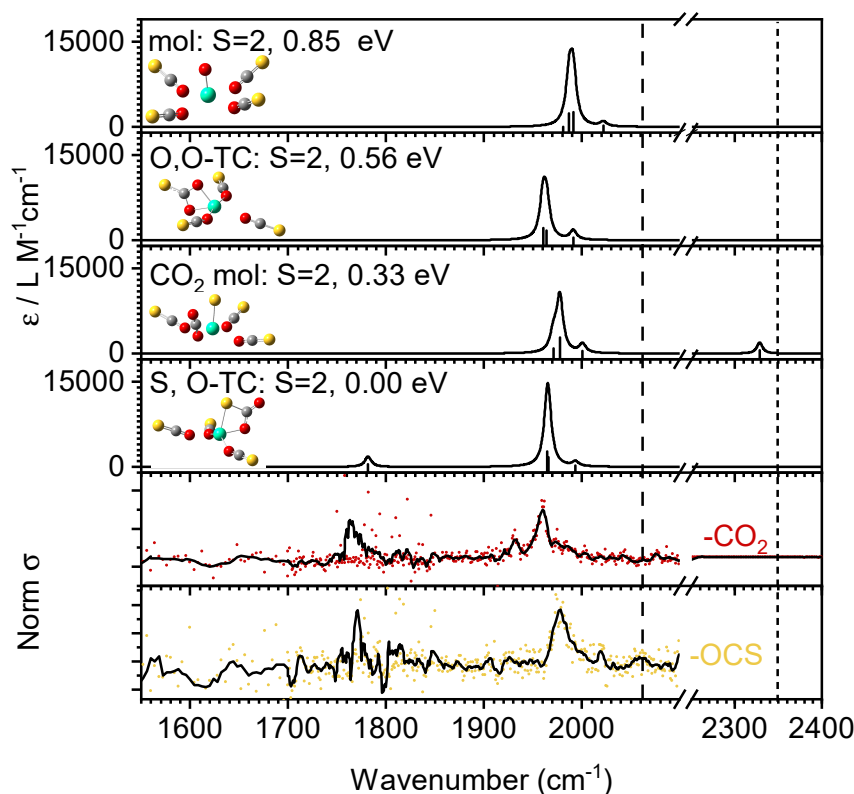


Figure 7.11: Comparisons between simulated (UB3P86/Def2-TZVP) experimental spectra of $\text{HoO}[(\text{OCS})_4]^+$. The black dashed line indicates the vibrational frequency of the asymmetric stretch (ν_3) of free OCS at 2062 cm^{-1} and the black dotted line indicates the vibrational frequency of the asymmetric stretch (ν_3) of free CO_2 at 2349 cm^{-1} .

an average of 101 cm^{-1} from the free OCS asymmetric stretch, meaning that the molecularly bound OCS molecules were significantly activated in the $\text{Ho}[\text{O}(\text{OCS})_n]^+$ complexes (as well as in $\text{Ho}[(\text{OCS})_n]^+$ and $\text{Ho}[\text{S}(\text{OCS})_n]^+$ species).

The additional feature centred at 1774 cm^{-1} and 1770 cm^{-1} in the OCS loss and CO_2 loss channels respectively is assigned to the $\text{SOC}=\text{O}$ stretch within the S, O-bound $\{\text{CO}_2\text{S}\}^{\delta-}$, based on its similarity to the band position seen in the "S, O-bound TC" isomer in Figure 7.11, confirming the "S, O-bound TC" isomer's presence.

No CO_2 asymmetric stretch within the $2300\text{--}2400\text{ cm}^{-1}$ (in the CO_2 loss channel) is observed, ruling out the presence of the " CO_2 "mol" isomer. The lack of spectral evidence for molecularly bound CO_2 , coupled with the presence of a CO_2 loss channel, suggests that absorption of IR photons promotes intra-cluster chemistry. Figure 7.12 shows the PES for low lying isomers of $\text{Ho}[(\text{OCS})_2]^+$, and illustrates the routes by which CO_2 may

be lost: conversion to the isomer containing molecularly bound CO_2 (labelled I CO_2) followed by loss of the CO_2 .

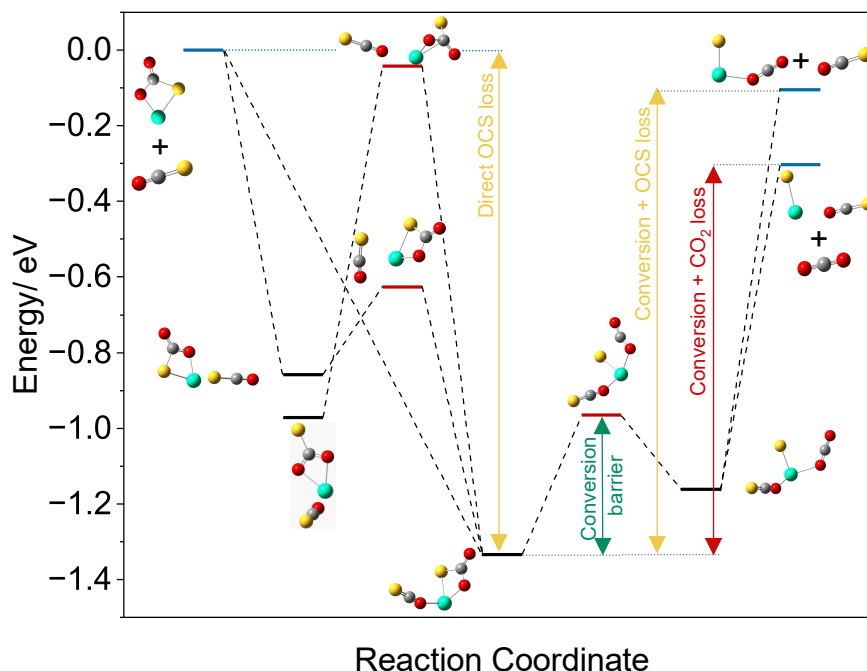


Figure 7.12: Potential energy surface for low lying isomers of $\text{Ho}[\text{O}(\text{OCS})_2]^+$ generated at the UB3P86/Def2-TZVP level of theory showing the relative energies of the major isomers located within the potential energy landscape search.

Also shown within Figure 7.12 are the relative energies for OCS or CO_2 loss from the putative global minimum isomer which are given by way of example. For all complex sizes, including $n = 4$, the conversion followed by OCS or CO_2 is more favourable than direct OCS loss. While when $n = 2$, conversion followed by CO_2 loss is energetically favourable relative to conversion followed by OCS loss, the energy ordering swaps at $n = 2$ and conversion followed by OCS loss becomes more favourable.

The final isomers ("O, O-bound TC" and "mol") contain no unique spectroscopic features within the accessible wavelength range of the laser system, making them impossible to rule out (although they are markedly higher in energy than the putative global minimum structure).

7.6.2 Rationalising spectral differences between OCS loss verses CO_2 loss

Figure 7.13 (a) shows the "IR-on" mass spectrum produced when the quadrupole mass filter is set up to allow only $\text{Ho}[\text{O}(\text{OCS})_4]^+$ through and the IR laser is set to 1970 cm^{-1} . In order to obtain an appreciable signal from $\text{Ho}[\text{O}(\text{OCS})_4]^+$, the quadrupole's mass resolution must be reduced to the point where a small amount of $\text{Ho}[\text{S}(\text{OCS})_4]^+$ bleeds through.

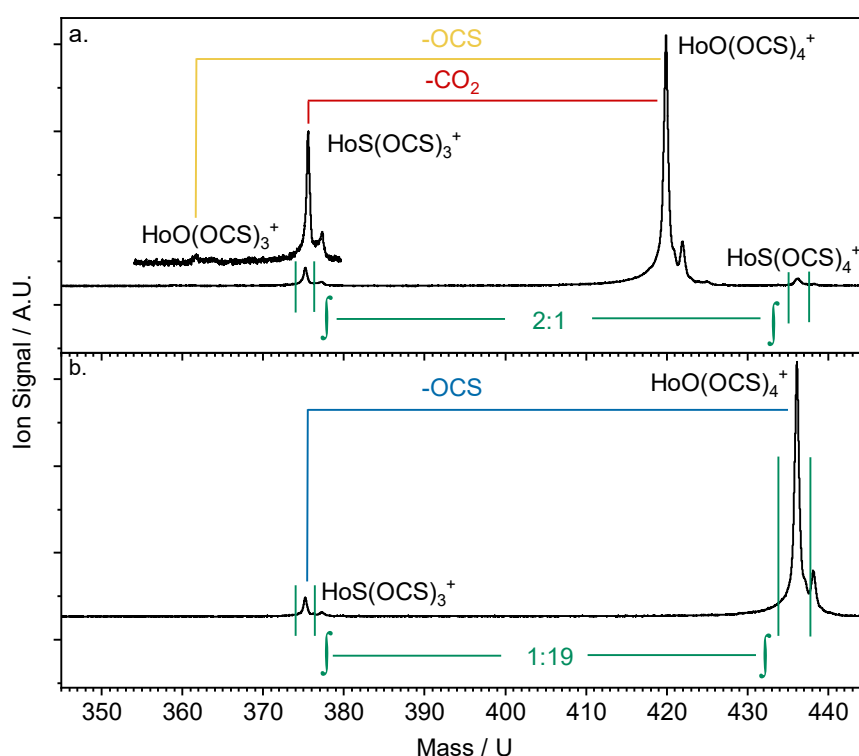


Figure 7.13: (a) A mass spectrum recorded with IR laser at 1970 cm^{-1} with the quadrupole mass filter set to favour $\text{Ho}[\text{O}(\text{OCS})_4]^+$. Both $\text{Ho}[\text{O}(\text{OCS})_4]^+$ and $\text{Ho}[\text{S}(\text{OCS})_4]^+$ complexes pass through the mass filter. Both have resonances at 1970 cm^{-1} and consequently both may lose OCS to form $\text{Ho}[\text{O}(\text{OCS})_3]^+$ and $\text{Ho}[\text{S}(\text{OCS})_3]^+$ daughter complexes, respectively. However, as illustrated by the red line, the $\text{Ho}[\text{O}(\text{OCS})_4]^+$ may also lose a CO_2 molecule to produce $\text{Ho}[\text{S}(\text{OCS})_3]^+$ daughter complexes. The relative integrated intensity of both $\text{Ho}[\text{S}(\text{OCS})_4]^+$ and $\text{Ho}[\text{O}(\text{OCS})_3]^+$ complexes is shown in green. (b) A mass spectrum recorded with IR laser at 1970 cm^{-1} with the quadrupole mass filter set to favour $\text{Ho}[\text{O}(\text{OCS})_4]^+$. Only $\text{Ho}[\text{O}(\text{OCS})_4]^+$, and its corresponding $\text{Ho}[\text{S}(\text{OCS})_3]^+$ daughter complex, are observed. The relative integrated intensity of both $\text{Ho}[\text{S}(\text{OCS})_4]^+$ and $\text{Ho}[\text{S}(\text{OCS})_3]^+$ complexes is shown in green.

Within Figure 7.13 (a), three possible photofragmentation reactions occur: Reaction 8, Reaction 9 and finally,



Because the daughter channel ($\text{Ho}[\text{S}(\text{OCS})_3]^+$) common to both CO_2 loss from $\text{Ho}[\text{O}(\text{OCS})_4]^+$ as well as OCS from $\text{Ho}[\text{S}(\text{OCS})_4]^+$, the origin of the spectrum from the $\text{Ho}[\text{S}(\text{OCS})_3]^+$ daughter complex channel could result from either/both $\text{Ho}[\text{O}(\text{OCS})_4]^+$ and $\text{Ho}[\text{S}(\text{OCS})_4]^+$. The resulting infrared spectrum recorded in this channel, could contain features from both species. Only Reaction 10 can occur in Figure 7.13 (b) as no $\text{Ho}[\text{O}(\text{OCS})_4]^+$ is present. The integrated intensities presented in Figure 7.13 (b), shows that around only 5% of the $\text{Ho}[\text{S}(\text{OCS})_4]^+$ complex is depleted at 1970 cm^{-1} , thus the bulk of the $\text{Ho}[\text{S}(\text{OCS})_3]^+$ daughter complex seen in Figure 7.13 (a) must necessarily come from CO_2 loss from $\text{Ho}[\text{O}(\text{OCS})_4]^+$ complexes as much less $\text{Ho}[\text{S}(\text{OCS})_4]^+$ is present in this spectrum. This suggests that while features that associated with OCS loss from $\text{Ho}[\text{O}(\text{OCS})_4]^+$ complexes are likely to be present in the spectrum, the spectrum should be dominated by features from CO_2 loss from $\text{Ho}[\text{O}(\text{OCS})_4]^+$ complexes.

Figure 7.14, shows the infrared spectra resulting from measuring the integrated absorption intensity as a function of wavelength of $\text{Ho}[\text{O}(\text{OCS})_3]^+$ (yellow) and $\text{Ho}[\text{S}(\text{OCS})_3]^+$ (red) using the quadrupole conditions presented in Figure 7.13 (a) along with the $\text{Ho}[\text{S}(\text{OCS})_3]^+$ spectrum using the quadrupole conditions used in Figure 7.13 (b). All three spectra show feature(s) between $1900\text{-}2000 \text{ cm}^{-1}$ resulting from molecularly bound OCS . The spectra recorded in the $\text{Ho}[\text{S}(\text{OCS})_3]^+$ daughter channels show marked similarity, suggesting that the spectrum is dominated by the feature associated with $\text{Ho}[\text{S}(\text{OCS})_4]^+$, contrary to what was predicted based on the spectral integration discussed previously. The spectrum recorded in the $\text{Ho}[\text{O}(\text{OCS})_3]^+$ channel is blue shifted to a higher intensity than the most intense peaks seen within the other spectra. Its position and intensity match well with the shoulder features seen within the previous spectra.

Both spectra from mainly $\text{Ho}[\text{O}(\text{OCS})_4]^+$ complex fragmentation channels (red and yellow spectra) show a single feature at 1770 cm^{-1} resulting from the $\{\text{CO}_2\text{S}\}^{\delta-}$ moiety. This

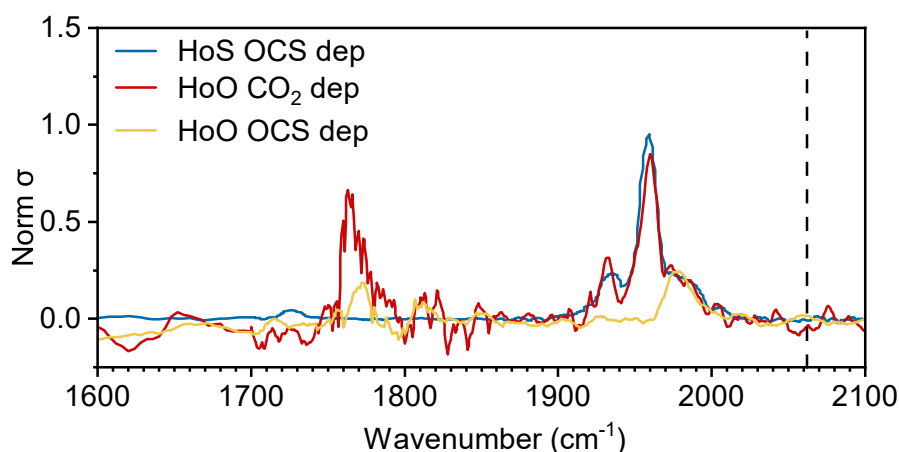


Figure 7.14: Overlaid IR spectra recorded in the enhancement channel of OCS loss from $\text{Ho}[\text{S}(\text{OCS})_4]^+$ (blue), the enhancement channel of OCS loss from $\text{Ho}[\text{O}(\text{OCS})_4]^+$ (yellow) and the enhancement channel of CO_2 loss from $\text{Ho}[\text{O}(\text{OCS})_4]^+$ (red). The black dashed line indicates the vibrational frequency of the asymmetric stretch (ν_3) of free OCS at 2062 cm^{-1} .

feature is not present in the blue spectrum recorded in the $\text{Ho}[\text{S}(\text{OCS})_3]^+$ channel resulting from OCS loss from $\text{Ho}[\text{S}(\text{OCS})_4]^+$, confirming that this feature resulted from the oxide only. Equally the feature seen at 1724 cm^{-1} in the blue spectrum isn't present in the red or yellow spectra.

The interpretation of these results is unclear as within the $1900\text{--}2000\text{ cm}^{-1}$ region spectral features associated with $\text{Ho}[\text{S}(\text{OCS})_4]^+$ appear to dominate whilst the region between $1700\text{--}1800\text{ cm}^{-1}$ shows no features associated with this molecule. One possible explanation comes from the fragmentation efficiency. Direct loss of OCS is likely to be more efficient in cases where the OCS is directly excited by the incident radiation as compared to cases where another part of the complex is excited and IVR transfers energy to OCS resulting in cleavage of the $\text{Ho}\text{--}\text{OCS}$ bond. Hence when excited between $1900\text{--}2000\text{ cm}^{-1}$, the small amount of $\text{Ho}[\text{S}(\text{OCS})_4]^+$ leaking through the quadrupole dominates the spectrum but in the $1700\text{--}1800\text{ cm}^{-1}$ region produces no features. This argument fails to address the issue with the fact that $\text{Ho}[\text{O}(\text{OCS})_4]^+$ also contains a large number of molecularly bound OCS molecules and is more abundant than $\text{Ho}[\text{S}(\text{OCS})_4]^+$ under the conditions presented in Figure 7.13 (a). This could potentially result from the lowered absorption cross sections or higher binding energies of OCS in the $\text{Ho}[\text{O}(\text{OCS})_4]^+$ versus $\text{Ho}[\text{S}(\text{OCS})_4]^+$.

7.7 Conclusions and outlook

Ablation of Ho metal in the presence of OCS yields a wide variety of species including $\text{Ho}[(\text{OCS})_n]^+$, $\text{Ho}[\text{S}(\text{OCS})_n]^+$ and $\text{Ho}[\text{O}(\text{OCS})_n]^+$, although the oxide species were only produced in appreciable number densities when additional CO_2 was added to the OCS gas mix.

Many of the IR spectra are ambiguous due to common spectral features between isomeric forms. However, Ho^+ ions were shown to be able to bind n OCS molecules in a dissociative fashion (to form $\text{HoS}(\text{CO})(\text{OCS})_{n-1}^+$) and bind to it a molecular fashion analogous to the charge-quadrupole binding frequently seen in metal cation CO_2 complexes.^[396, 427, 429–433] Unlike CO_2 , which shows no evidence of activation, the molecularly bound OCS asymmetric stretches are red-shifted by 100 cm^{-1} , suggesting significant activation resulting from electron withdrawal from the OCS HOMO.

While both HoS^+ and HoO^+ bind OCS in a molecular fashion, they are also able to react with OCS to form $\{\text{COS}_2\}^{\delta-}$ and $\{\text{CO}_2\text{S}\}^{\delta-}$ moieties, respectively, in an analogous fashion to the $\{\text{CO}_3\}^{\delta-}$ formed from HoO^+ and CO_2 (see Chapter 6).^[417] The formation of these species is driven by electron density withdrawn from the molecularly bound OCS molecules. The characteristic spectral band associated with $\{\text{COS}_2\}^{\delta-}$ moieties is observed to red-shift in exactly the same way as the CO_3 moieties in their CO_2 analogues resulting from charge donation from additional ligands. The behaviour shown by Ho^+ ions within this Chapter, as well as Chapter 6, readily illustrate holmium and its oxides ability to activate molecules suggesting that they could act as excellent catalysts with tuneable properties.

Completing a similar study with CS_2 would also prove interesting, allowing for a full examination of how replacing each of the oxygen atoms with sulphur in CO_2 changes the observed chemistry. An investigation into mixed ligand Holmium complexes is planned within the group with the idea that the activating power of Ho^+ ions towards CO_2 and OCS could make them reactive towards other ligands such as N_2O or even NO . In addition to altering the ligands, alterations to the metal centre should also prove interesting. For example, Ho clusters could well have a different set of reactivity towards OCS, as size

effects in clusters can often radically alter their reactivity. When investigating Ho clusters, it would also prove useful to begin to investigate the effects of doping other metals into the clusters.^[466] Given their propensity to activate OCS (and CO_2), other lanthanide metals could also prove interesting.

8 | Conclusions and Future Work

This thesis is divided into two distinct sections: the first details the development of a new instrument to study the effects of vibrational energy on the outcomes of reactive collisions between metal ions and neutral species in the gas phase; the second section details two infrared photodissociation spectroscopic studies of Ho^+ cations with CO_2 and OCS in the gas phase, along with upgrades to the existing infrared photodissociation spectrometer within the group.

8.1 Part I: Vibrationally Mediated Collision Experiment

8.1.1 Part I: Conclusions

While there has been extensive work carried out on the effects of the addition of vibrational energy to reactions, these have been limited to simple systems such as HF exchanging its H atom with Cl or to the dissociative chemisorption of methane on extended metal surfaces. Armentrout and co-workers have extensively characterised the translational energy dependence of the reactions of many different ionic metal clusters and complexes with small neutral molecules in the gas phase however they never investigated reaction dependence upon the internal energy of the reacting species. When vibrationally enhanced dissociative chemisorption of methane on Au^+ ions within the Mackenzie group, the gap within previous literature was identified and the decision to develop a new instrument was undertaken.

From an idea through to a physical instrument, a completely novel experiment has been developed to study the effects of vibrational energy on the outcomes of reactive collisions between metal ions and neutral species in the gas phase. Based on the mass spectrometric investigations, the ions generated from a laser vaporisation source were deemed to be inappropriate for collision experiments due to their spatial distribution. Although the origin of the spatial distribution was unclear, a novel method for focusing the ions spatially with minimal induction of energy distributions to the ion packet was postulated,

simulated and developed into a real experimental piece of apparatus. Due to high orthogonal extraction energies, an ion decelerator based on an Einzel lens was developed to slow the ions prior to undergoing reactive collisions. The collision cell, designed based on custom built collision models was developed, simulated and constructed. For collision product detection, an reflectron ToF mass spectrometer from the R.M. Jordan company was modified and incorporated into the experiment.

The ion signal loss was initially assigned to poor deceleration behaviour associated with the two plate system used. However, improvement of the decelerator through the addition of an Einzel lens, immediately prior to the deceleration stage, did not improve the behaviour to a satisfactory degree. Based on this finding, it was concluded that the residual velocity of the ions associated with their motion in their original axis of travel caused the ion beam to walk off axis, preventing the ions from reaching the detectors. Spatial defocusing of the ions that occurs when the ions are decelerated further exacerbates this issue.

Based on the work presented in Chapter 3, a temporary solution was developed in the form of a linearised version of the experiment described in Section 3.3. This removes the orthogonal extraction element of the experiment and instead uses linear extraction allowing for much smaller extraction potentials to be used negating the need for large decelerating potentials. This also removes the residual velocity component. Initial testing (see Section 3.3) demonstrated that the linearised iteration of the experiment was able to pass ions through the experiment with an energy of 100 eV and successfully orthogonally extract them into the reflectron, indicating that collision experiments can now be performed.

8.1.2 Part I: Future Work

With the linear variant of the experiment operational to the point where ions can be passed through the collision cell with controlled energy and detected within the reflectron, work can commence on achieving successful reactive collisions between ions and neutrals. The system selected to do this is Au^+ and N_2O , based on several different factors: firstly, the collisional energy dependence has already been characterised by Ar-

mentrout, and coworkers^[467]; and secondly, the Mackenzie group has previous experience of N₂O-ion complexes and vibrationally exciting N₂O.^[408] The Au⁺ and N₂O reaction is particularly facile for study within the collision experiment as it produces three different products: AuO⁺, AuNO⁺ and AuN₂⁺, all of which are significantly separated in mass, making them easily detectable within the ReToF mass spectrometer (as opposed to the reactions of methane). Au⁺ is also attractive as it is mono-isotopic, which simplifies the interpretation of the mass spectra still further as well as increasing signal. Having measured the product distributions as a function of collision energy and compared the results to those of Armentrout, vibrational energy may be added to the N₂O by means of a laser pulse from the OPO/OPA system, allowing the effect of the addition of vibrational energy to the collision pair to be measured at different collision energies.

Beyond the initial study indicated above, there are a variety of different reactions that can be investigated, and the reactions possible are only limited by the number density of ions that can be generated. Some particular systems of interest would be reactions of Pt₄(CO₂)⁻ anions with vibrationally excited neutral partners, as the highly activated CO₂ bound to the Pt₄⁻ makes reaction highly likely.^[405] Equally, the activated CO₂ itself could be vibrationally excited prior to collision, perhaps leading to different reactive outcomes.

The change from orthogonal extraction to linear extraction comes at the expense of energy resolution of the ion packet (see Figure 1.12). If the energy resolution of the linear variant of the experiment is found to be unacceptable, the experiment can be returned to its design including orthogonal extraction with the addition of an octupole ion guide. This addition allows for the ions to be radially confined to the centre of the instrument, and prevents them from walking off when decelerated to the desired kinetic energy. An octupole ion guide has been used previously in a similar experiment to great effect^[393]; it should prove helpful if the decision is taken to return to the orthogonal extraction variants of the instrument.

8.2 Part II: Infrared Photodissociation Studies of Gas Phase Ho^+ Complexes

The spectral range accessible to the IRPD experiment and the vibrationally altered collision experiment was enhanced through the addition of two new non-linear optical crystal(s). The new crystals extended the wavelength range of the OPO/OPA system from LaserVision down to 1000 cm^{-1} , enabling the spectroscopic studies of the highly activated CO_2 and OCS species presented in Chapters 6 and 7, respectively. In addition to the upgrades to the IR laser system, the custom LabVIEW data acquisition software was completely rewritten. This was prompted by the upgrade of the ablation laser from a 10 Hz (Continuum Minilite II) to a 20 Hz system (Quantel Ultra), which overwhelmed the previous acquisition software.

8.2.1 Part II: Conclusions

Ablating Ho metal in the presence of CO_2 seeded in Argon generated two types of species: $\text{Ho}(\text{CO}_2)_n^+$ and $\text{Ho}[\text{O}(\text{CO}_2)_n]^+$ (postulated to result from a reaction of CO_2 with Ho^+). While CO_2 was observed to bind to both Ho^+ and HoO^+ in an $\text{M}(\eta_1\text{-OCO})$ fashion via a weak charge quadrupole interaction, the $\text{Ho}[\text{O}(\text{CO}_2)_n]^+$ was seen to generate an additional structure: the $\{\text{CO}_3\}^{\delta-}$ moiety bound in an $\text{M}(\eta_2\text{-(OO)CO})$ fashion that arises from the electrophilic attack of a carbon within a molecularly bound CO_2 . The $\{\text{CO}_3\}^{\delta-}$ moieties were observed in $\text{Ho}[\text{O}(\text{CO}_2)_n]^+$ complexes with three or more CO_2 ligands. σ donation from the CO_2 ligands within $\text{Ho}[\text{O}(\text{CO}_2)_n]^+$ is localised onto the oxide, making it susceptible to attack via the electrophilic carbon in the CO_2 ligands. Once the $\{\text{CO}_3\}^{\delta-}$ moiety forms, electron density localises here, weakening the CO bonds. In this sense, the degree of activation is controllable and, in this regard, complexes behave very similarly to the $\text{YO}(\text{CO}_2)_n^+$ complexes reported by Jiang and coworkers.^[441]

Inspired by the work carried out with CO_2 , the structures produced when Ho metal reacts with OCS seeded into argon were then investigated using IRPD spectroscopy. Three different species are generated: $\text{Ho}[(\text{OCS})_n]^+$, $\text{Ho}[\text{S}(\text{OCS})_n]^+$ and $\text{Ho}[\text{O}(\text{OCS})_n]^+$ (although the oxide species were only produced in appreciable number densities when additional

CO₂ was added to the OCS gas mix). Although many of the IR spectra are ambiguous due to common spectral features between isomeric forms, Ho⁺ ions were shown to be able to bind n OCS molecules in a dissociative fashion (to form Ho[S(CO)(OCS) _{$n-1$}]⁺) and bind to it a molecular fashion analogous to the charge-quadrupole binding frequently seen in metal cation CO₂ complexes.^[396, 427, 429–433] Unlike CO₂, which shows no evidence of activation, the molecularly bound OCS asymmetric stretches are red-shifted by 100 cm⁻¹, suggesting significant activation resulting from electron withdrawal from the OCS HOMO. While both HoS⁺ and HoO⁺ bind OCS in a molecular fashion, they are also able to react with OCS to form {COS₂}^{δ-} and {CO₂S}^{δ-} moieties respectively in an analogous fashion to the {CO₃}^{δ-} formed from HoO⁺ and CO₂ (see Chapter 6).^[417] The formation of these species is driven by the electron density withdrawn from the molecularly bound OCS molecules. The characteristic spectral band associated with {COS₂}^{δ-} moieties is observed to red-shift in exactly the same way as the CO₃ moieties in their CO₂ analogues resulting from charge donation from additional ligands.

8.2.2 Part II: Future Work

The work presented within this thesis has illustrated that Ho⁺ cations exhibit a wide range of interesting chemistry when they complex with other gas phase molecules due to their ability to transfer electron density between their ligands. The addition of different ligands forms the primary avenue of interest concerning Ho⁺ complexes. CS₂ is the first ligand of interest as it can be directly compared to both CO₂ and OCS and will give insights into sulphur-specific chemistry on Ho⁺ ions. Beyond completing studies into the sulphur analogues of CO₂, mixed-ligand complexes could prove especially fruitful to study, as the Ho⁺ would allow electrons from electron-rich ligands such as NO or N₂O to be passed onto other ligands, thus activating them. In addition to altering the ligands, alterations to the metal centre could also prove interesting. Theoretical studies of Ho clusters and their reactivity to different ligands is now underway within the group. Given their propensity to activate OCS (and CO₂), other lanthanide metals could also prove fruitful.

8.3 Broader Impacts

While the results presented in this thesis are interesting within their own right, this work has also contributed to the wider understanding of metals and their role in catalysis as well as how vibrational energy can affect the outcomes of the reactions of ionic metal clusters with neutral gas molecules. This section of the conclusion examines how the work performed as part of this thesis has contributed to these concepts.

In Section 1.1.2 of the introduction, the concepts surrounding reaction control on the molecular level, including mode selective chemistry, were introduced. The new instrument detailed in Chapters 2 through 4 sought to extend the field of mode selective chemistry into the reactions of small neutral gas molecules on ionic metal clusters. As the instrument still remains incomplete at the time of writing this thesis, the impacts on the broader community remain unclear. However, once the instrument is complete, it will offer the possibility of performing collision experiments on the reactions of ionic metal clusters with neutral gas molecules with a high degree of collisional energy control and the ability to vibrationally excite either species in the collision. This will dramatically extend the capabilities of existing experiments which: (i) are limited to collisions between extremely simple non-metallic species^[144–147]; (ii) are limited to reactions on metal surfaces^[76–78, 80–101]; or, (iii) have no ability to control the vibrational energy of the collision partners.^[198–250]

The work presented in Part II of the thesis (Chapters 6 and 7) clearly demonstrated the power of Ho^+ cations to activate and promote the reaction of both CO_2 and OCS , hence illustrating Holmium’s potential as a catalytically active material. The dry reformation of methane using CO_2 has proved to be an attractive route for the production of hydrogen due the low hazards associated with the precursor materials as well as potentially chemically useful intermediates.^[455] Although dry reformation of methane may be carried out on a variety of different late transition metals (including Pd, Pt, Rh, and Ru), the expense associated with these metals has driven research towards cheaper metals such as Ni and Fe. Bagabas and co-workers doped holmium oxide (Ho_2O_3) into nickel-based catalysts supported on yttria-stabilised zirconia and were able to demonstrate that the

addition of Ho_2O_3 into the catalyst promoted the conversion of methane.^[455] They rationalised the observed behaviour based on the work presented in Chapter 6 illustrating the broader impact on catalysis that this work has already had. In contrast to the work on $\text{HoO}_n(\text{CO}_2)_m^+$ complexes in Chapter 6, the work on $\text{HoS}_x\text{O}_y(\text{CO}_2)_z^+$ complexes has yet to be published so has had limited impact beyond the Mackenzie group. However, the similar behaviour seen, when compared to CO_2 , further reinforces the potential of Ho as a catalytically active material. In addition to this, another group used the results presented within Chapter 6 as part of a model designed to predict the effects of bond angles on the stretching frequencies of C=O carboxylato complexes.^[468] Finally, Zhou and co-workers used the data presented in Chapter 6 to help rationalise similar trends seen in $\text{Ta}[\text{O}_3(\text{CO}_2)_n]^+$ complexes.^[469]

Beyond the novel use of Ho_2O_3 as a dopant in the Nickel catalyst associated with dry reformation previously discussed, holmium has seen little use as a catalyst. With the work presented within this thesis, holmium has been shown to be able to successfully activate CO_2 and OCS illustrating its potential, as well as other f-block metals, as potential catalytic materials, and it is hoped that other researchers will utilise holmium in additional catalysts.

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A.1 Vacuum Systems

Throughout the experimental interactions, the vacuum systems have remained the same and are illustrated in Figure A.1.

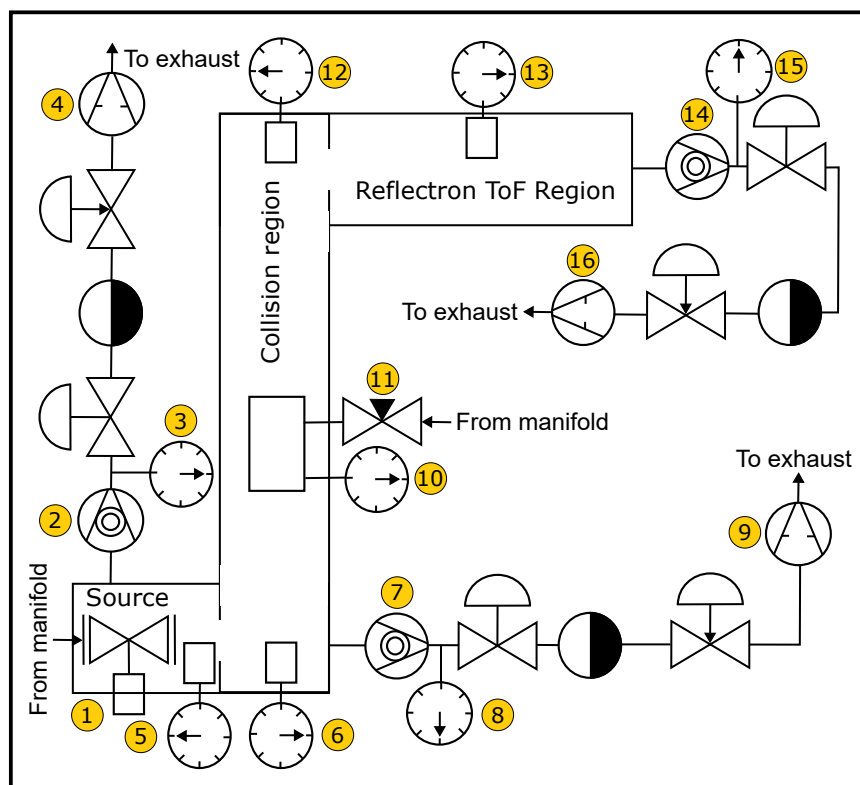


Figure A.1: Schematic diagram of the vacuum systems (as well as gas injection systems) used with the collision experiment. The experiment is divided into three regions - the source, collision region and ToF region and each is pumped with a separate turbomolecular pump. Pressure gauges are also included in each region such that the pressure can be measured in each region. Each numbered pump and gauge is indicated in Table A.1.

Number	Type
1	Parker-Hannifin General Series 9 Valve
2	Edwards STP-A1303 TMP
3	Leybold TTR 91 N
4	Edwards E2M40 Rotary Vane Pump
5	Leybold PENNINGVAC PTR 225 N
6	Leybold IONIVAC ITR 90
7	Edwards STP-A1303 TMP
8	Leybold IONIVAC ITR 90
9	Leybold TRIVAC D40B Rotary Vane Pump
10	MKS 627.F Baratron Capacitance Manometer
11	VAT 62.7 Needle Valve
12	Leybold IONIVAC ITR 90
13	Leybold PTR 90 N
14	Oerlikon Leybold TMP 151
15	Leybold TTR 91 N
16	Leybold TRIVAC D25B Rotary Vane Pump

Table A.1: Vacuum components illustrated in Figure A.1

A.2 Gas Manifolds

A.2.1 Source Manifold

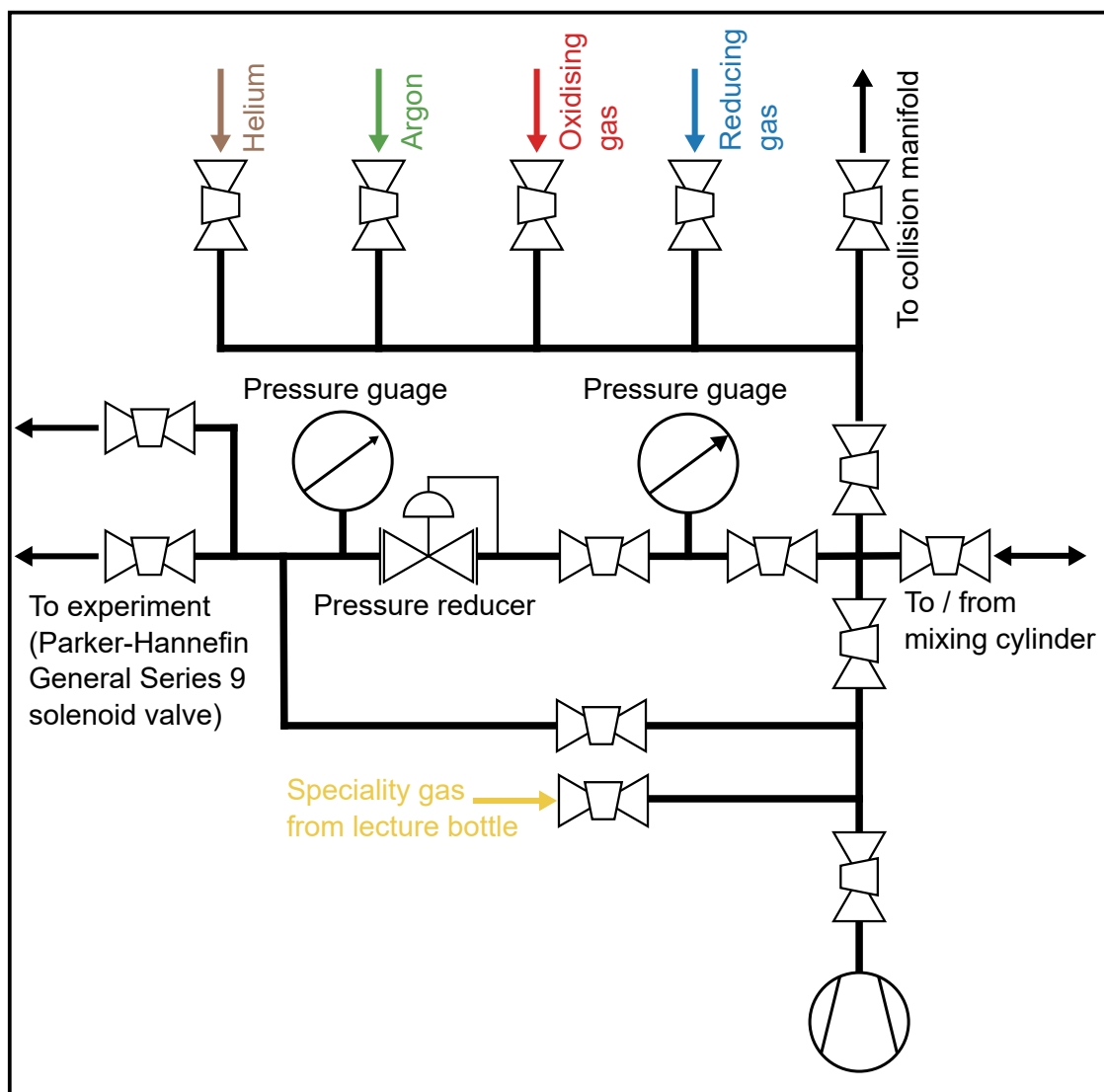


Figure A.2: Schematic diagram illustrating the gas manifold use to deliver gas the solenoid valve (Parker Hannifin General Series 9) in the source. A route to deliver gas to the collision cell gas control manifold (shown in Figure A.3) is also present allowing gas to be delivered to the collision cell via this manifold. The plug valves used are Swagelok SS-4P4T-BK fittings, the pressure gauges are Swagelok PGC-50-PC100-C-4FSF-BF gauges and the pressure regulator is a KBP1F0A4A5A20000 regulator. The system is evacuated using a Leybold Trivac-D25B rotary vane pump.

A.2.2 Collision Cell Manifold

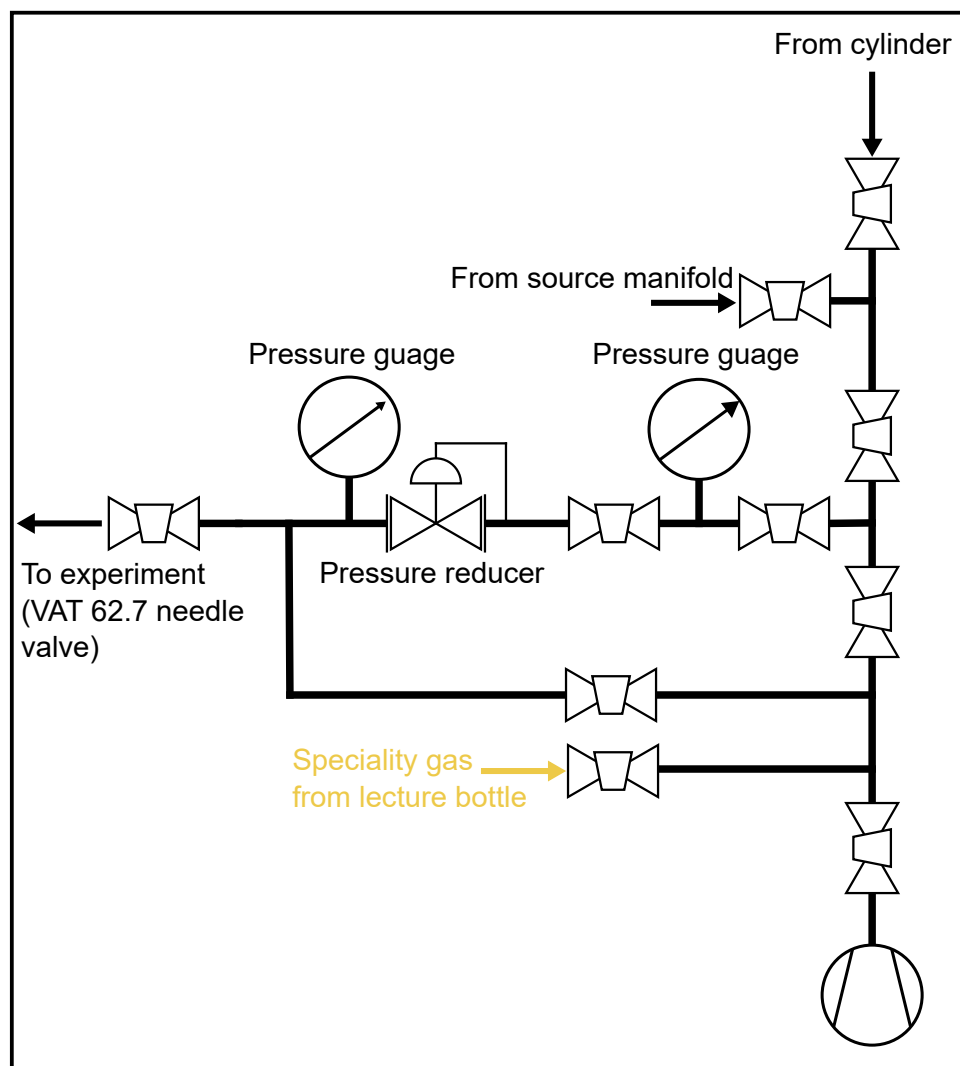


Figure A.3: Schematic diagram illustrating the gas manifold use to deliver gas to the collision cell. Gas may be delivered from three sources, the source manifold, a large cylinder or a small lecture bottle. The plug valves used are Swagelok SS-4P4T-BK fittings, the pressure gauges are Swagelok PGC-50-PC100-C-4FSF-BF gauges and the pressure regulator is a KBP1F0A4A5A20000 regulator. The system is evacuated using a Leybold Trivac-D25B rotary vane pump.

A.3 VAT Valve Operation

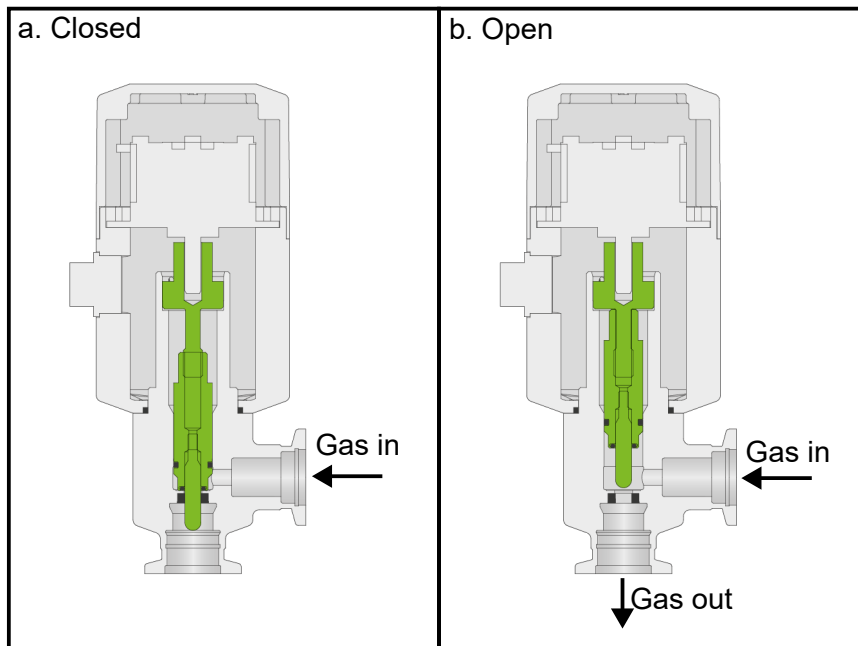


Figure A.4: Schematic diagram illustrating the operation of the VAT 62.7 needle valve.
(a) Closed valve. (b) Open Valve

B.1 Orthogonal Extraction

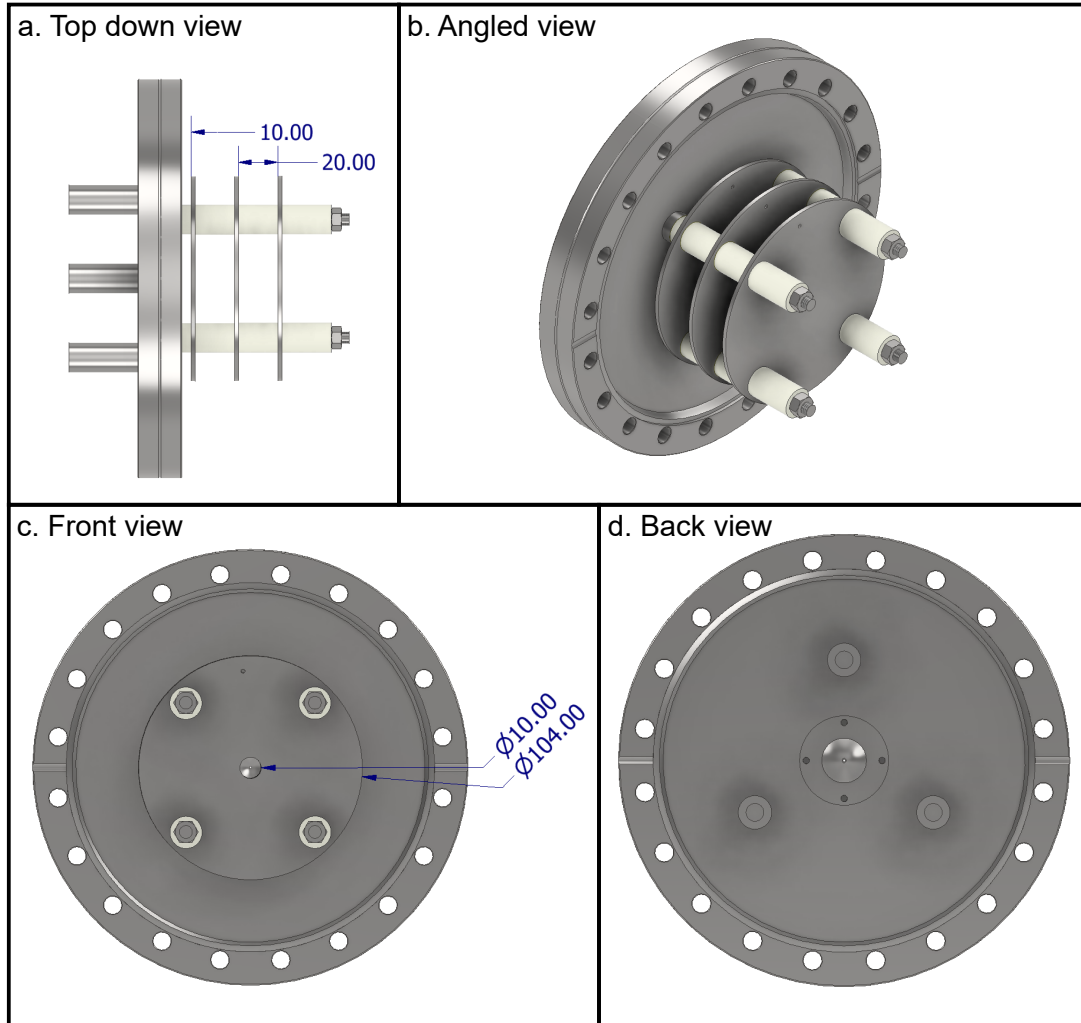


Figure B.1: CAD renders of ion optics with dimensions in mm. (a) Top down view. (b) Angled view. (c) Front view. (d) Back view. This design was adapted from previous experiment.

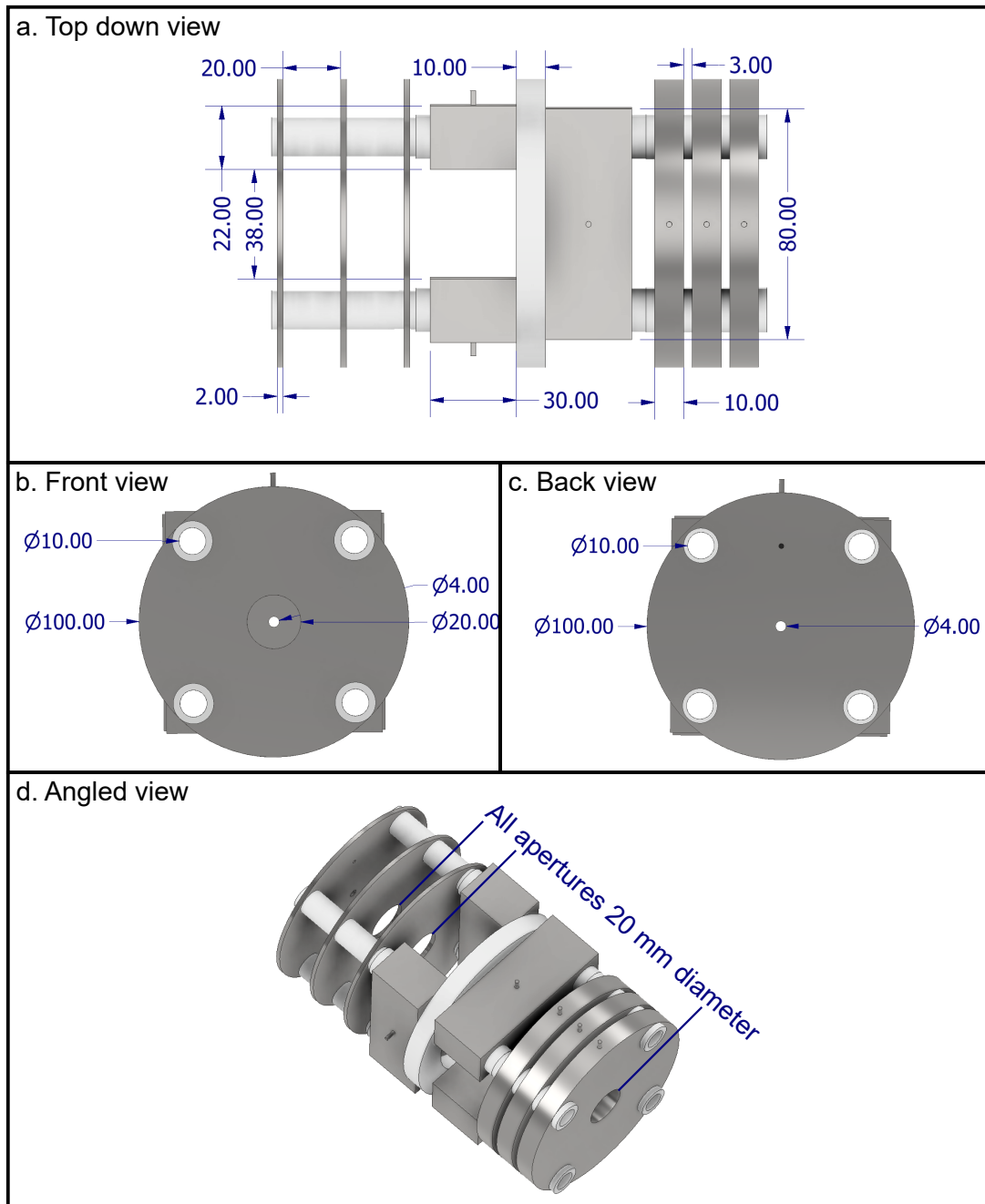


Figure B.2: CAD renders of ion optics with dimensions in mm. (a) Top down view. (b) Front view. (c) Back down view. (d) Angled view.

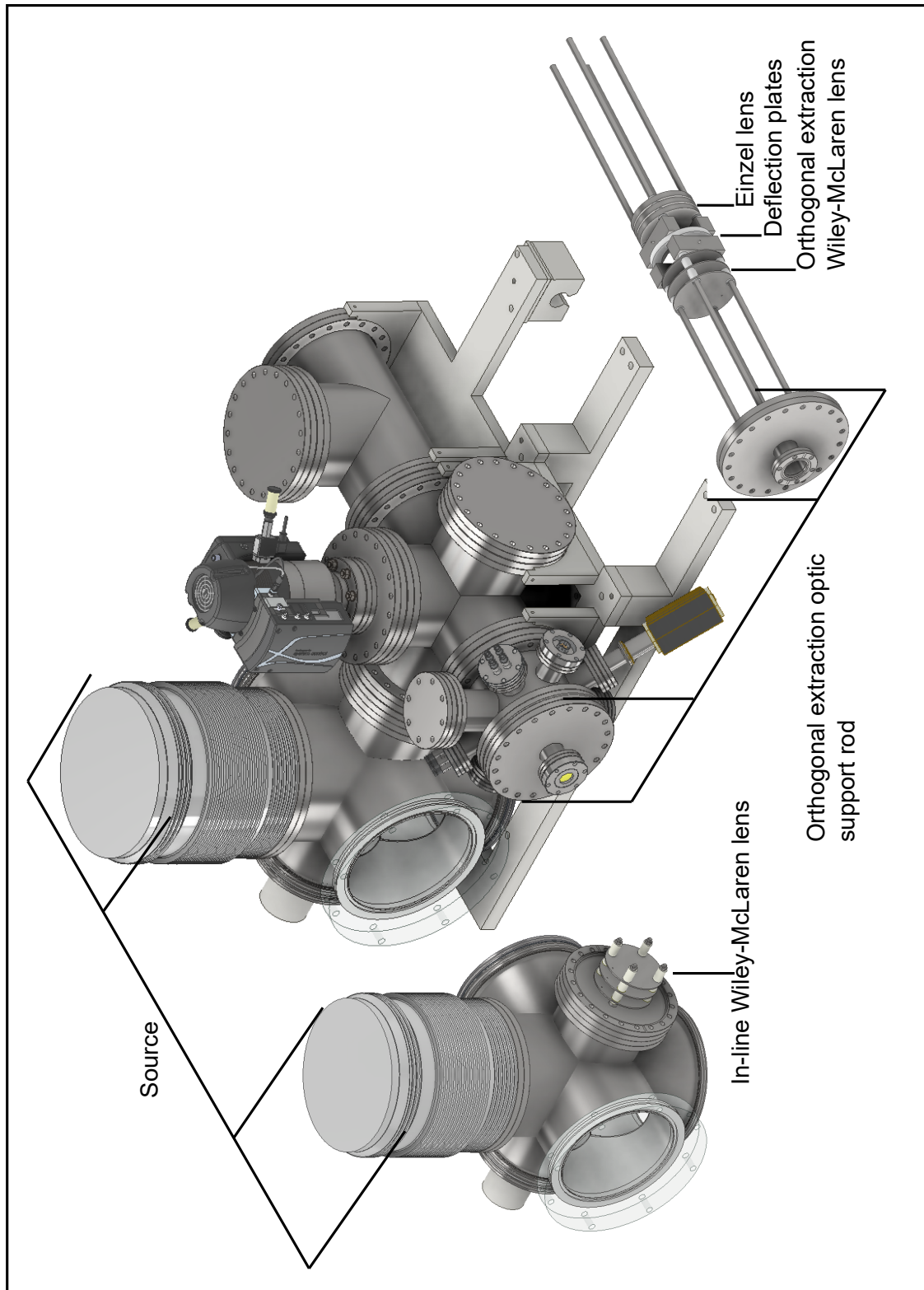


Figure B.3: A CAD render of the source and DN160CF 6WX/tee used to support the orthogonal extraction optics. Components carrying ion optics are shown outside of the main vacuum chambers to illustrate how they are supported.

B.2 Ion Deceleration

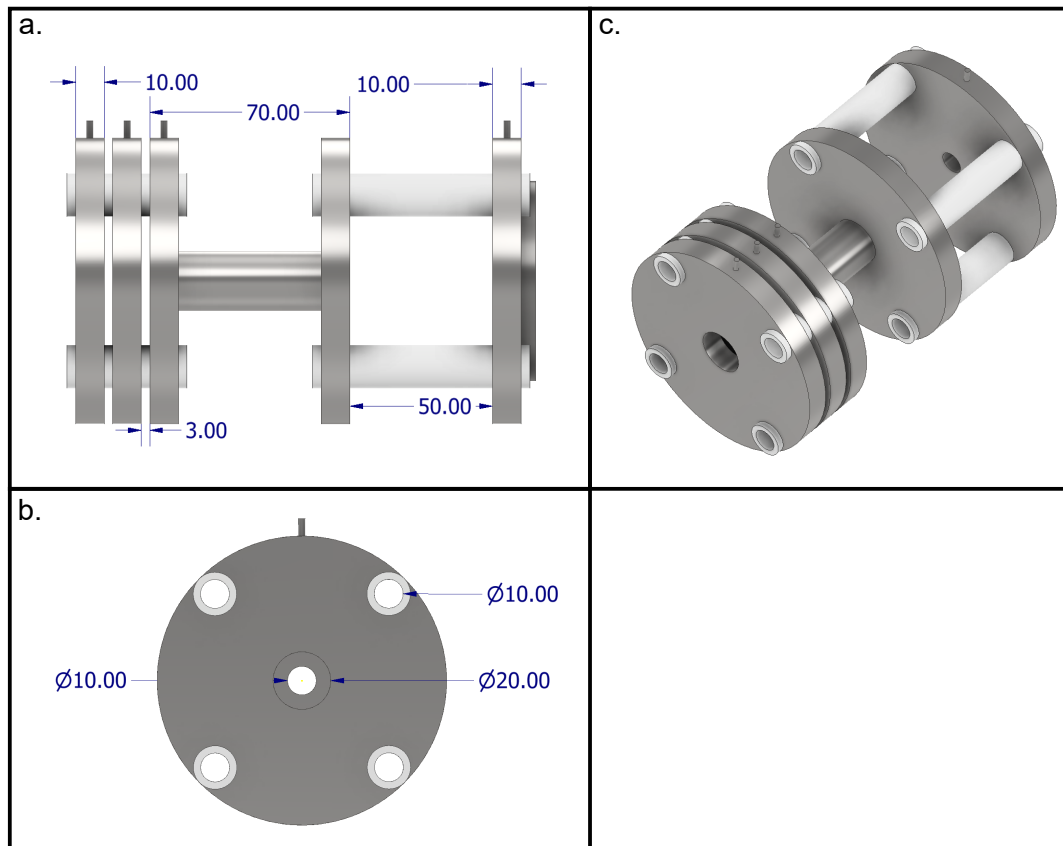


Figure B.4: CAD renders of ion optics with dimensions in mm. (a) Side on view. (b) Front view. (c) Angled view. (d) Back view.

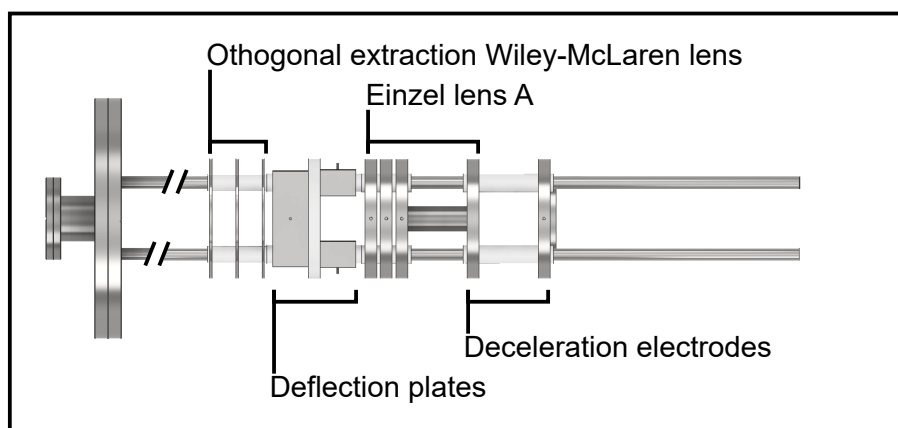


Figure B.5: The deceleration optics mounted to the support rods shown in Figure B.3 in addition to the orthogonal extraction Wiley-McLaren lens.

B.3 Collision Cell

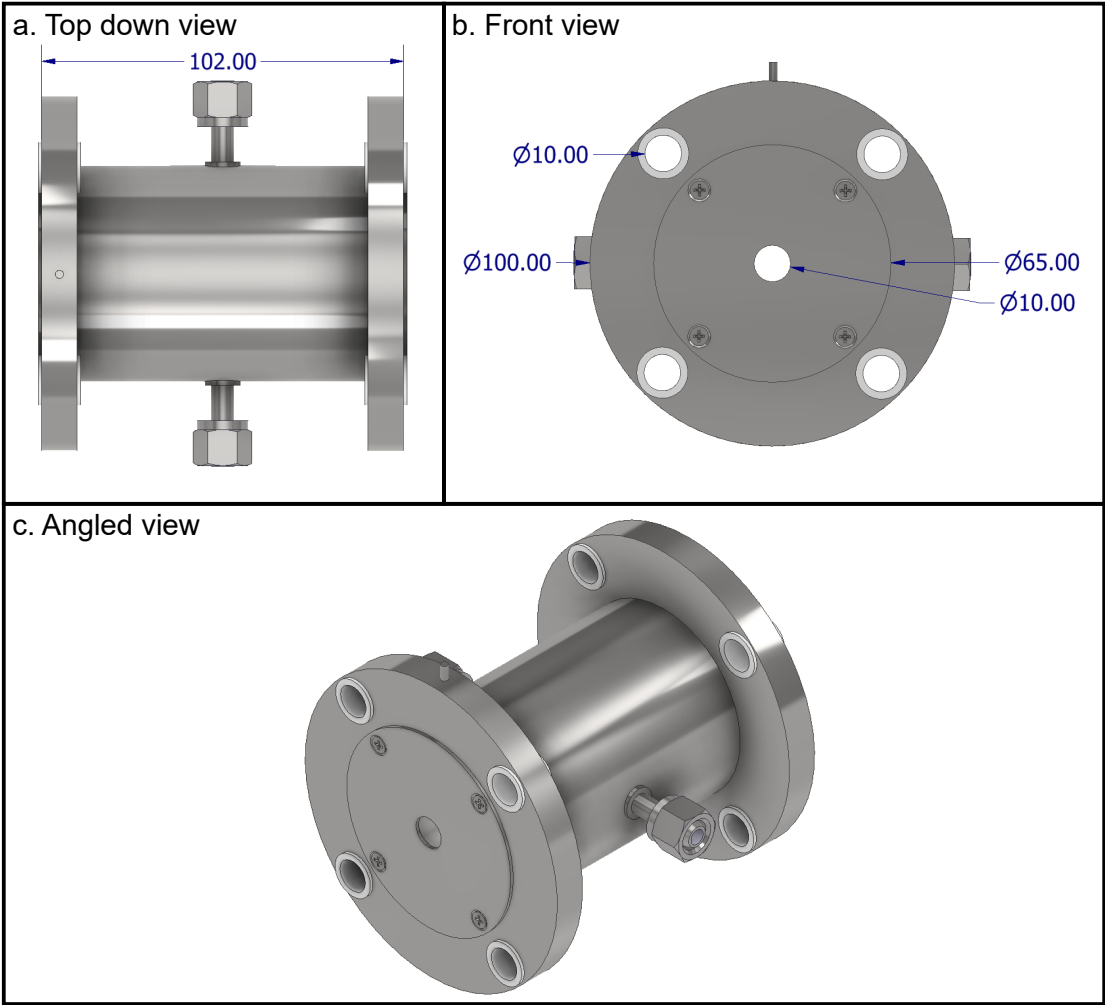


Figure B.6: CAD renders of of the collision cell. (a) Top down view. (b) Front view. (c) Angled view.

B.4 Re-Referencing Tube

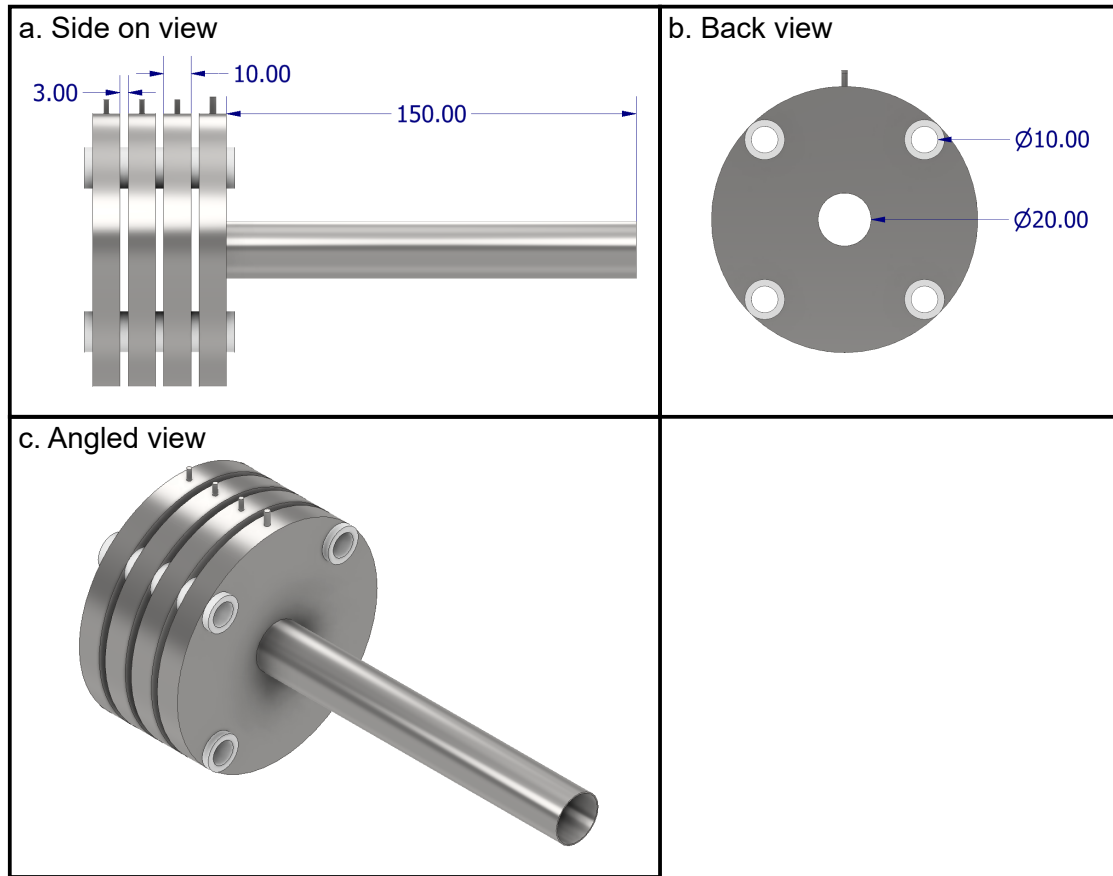


Figure B.7: CAD renders of Einzel lens B and the re-referencing tube. (a) Side on view. (b) Back view. (c) Angled view.

C | Ion Optics Simulations

The ion trajectories and data derived from these were all generated using the SIMION 8.2 software package. All plotting of data and trajectories was carried out using custom built software which is available upon request.

C.1 In-Line Wiley McLaren Lens

C.1.1 Extractor/Repeller Ratio

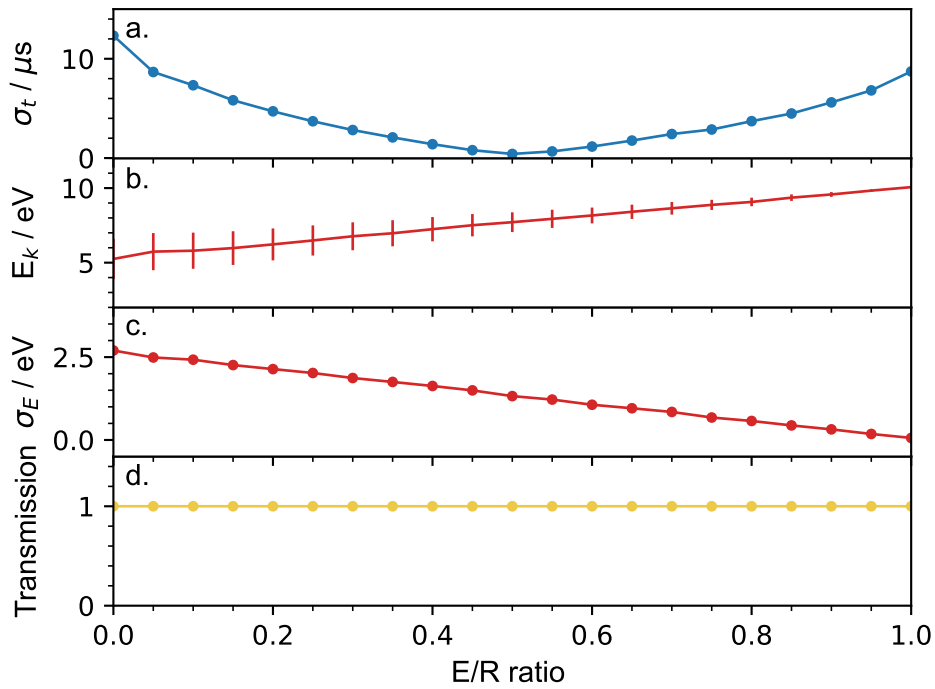


Figure C.1: The dependence of a series of parameters measured when 1000 0.32 eV Au^+ ions in a 20 long mm cylinder distribution with a 1 mm radius between the extractor and repeller electrodes are extracted using the in line Wiley-McLaren lens. The repeller electrode is maintained at 10 V and the ground electrode is maintained at 0 V. The extractor electrode is varied in potential to generate the different E/R ratios. (a) shows the dependence of the standard deviation of the ions ToF as they pass through the plane 105 mm beyond the ground plate on the E/R ratio. (b) shows the dependence of the mean energy as they pass through the plane 105 mm beyond the ground plate on the E/R ratio. (c) shows the dependence of the standard deviation in energy as they pass through the plane 105 mm beyond the ground plate on the E/R ratio. (d) shows the dependence of the ions transmission as they pass through the plane 105 mm beyond the ground plate on the E/R ratio.

C.2 Orthogonal Extraction

C.2.1 Orthogonal Extraction Wiley-McLaren Lens

C.2.1.1 Extractor/Repeller Ratio

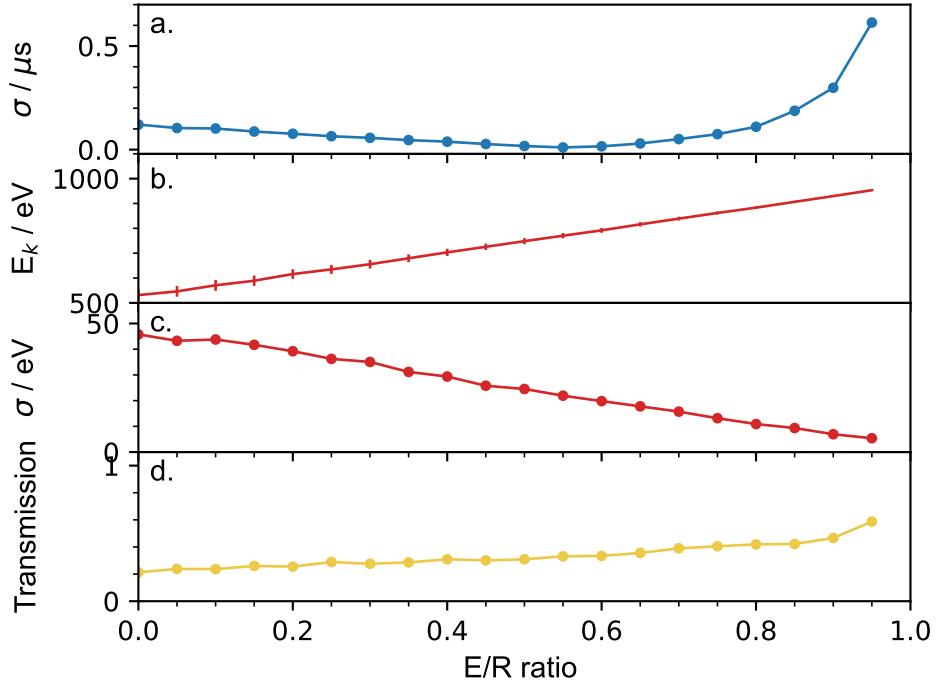


Figure C.2: The dependence of a series of parameters measured when 1000 10 eV Au^+ ions in a 50 mm cylinder distribution with a 2 mm radius between the extractor and repeller electrodes are extracted. The repeller is held at 1000 V and the extractor potential is varied to achieve the desired E/R ratio. (a) shows the dependence of the standard deviation in ToF on the E/R ratio. (b) shows the dependence of the mean energy on E/R ratio. (c) shows the dependence of the standard deviation in energy on the E/R ratio. (d) shows the dependence of the ions transmission on the E/R ratio.

C.2.1.2 Repeller Magnitude

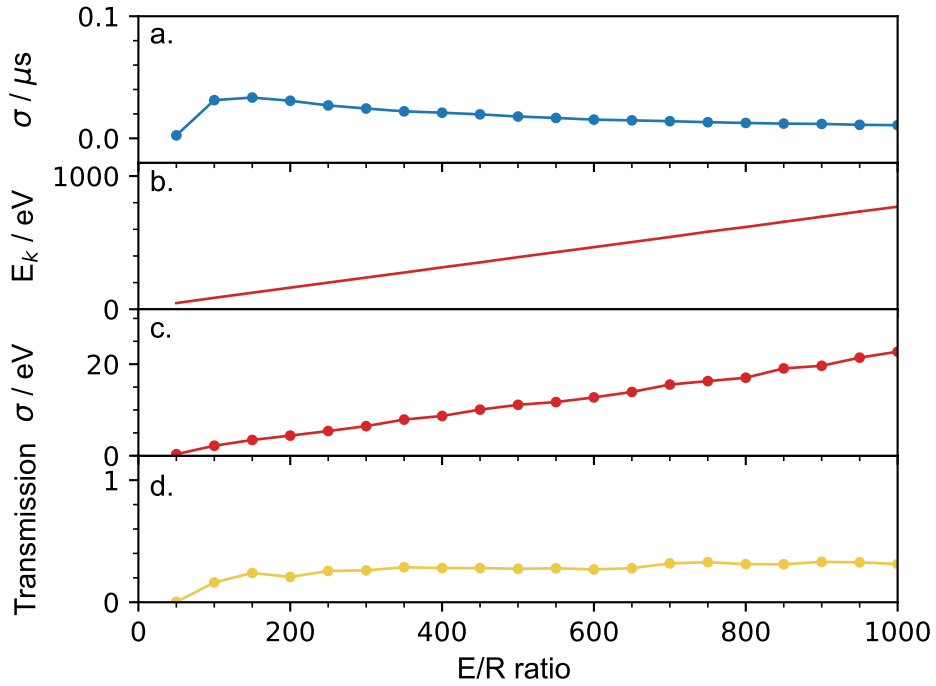


Figure C.3: The dependence of a series of parameters measured when 1000 10 eV Au^+ ions in a 50 mm cylinder distribution with a 2 mm radius between the extractor and repeller electrodes are extracted using a Wiley-McLaren lens. Both the extractor and repeller are changed simultaneously to maintain the E/R ratio at 0.55. (a) shows the dependence of the standard deviation in ToF on the magnitude of E and R. (b) shows the dependence of the mean energy on the magnitude of E and R. (c) shows the dependence of the standard deviation in energy on the magnitude of E and R. (d) shows the dependence of the ions transmission on the magnitude of E and R.

C.2.2 Orthogonal Extraction Deflection Plates

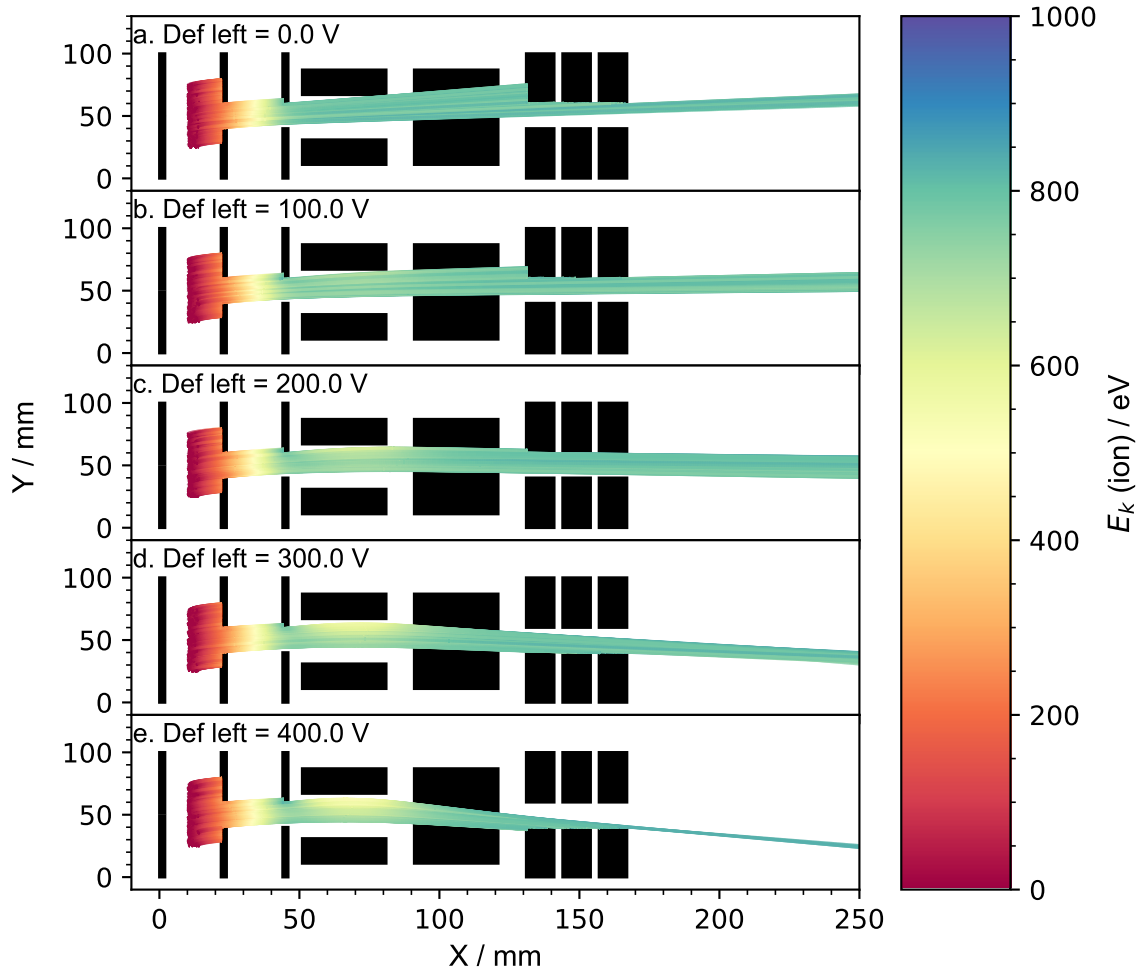


Figure C.4: A series of trajectories of 1000, 10 eV Au^+ ions recorded as a function of the deflection potential applied to the left deflector (looking down the extraction axis). The repeller is pulsed to 1000 V, the extractor is pulsed to 550 V and the ground electrode was held at 0 V. The deflection electrode immediately after the Wiley-McLaren lens and above the beam is swept through a series of (positive) potentials.

C.2.3 Orthogonal Extraction Einzel Lens

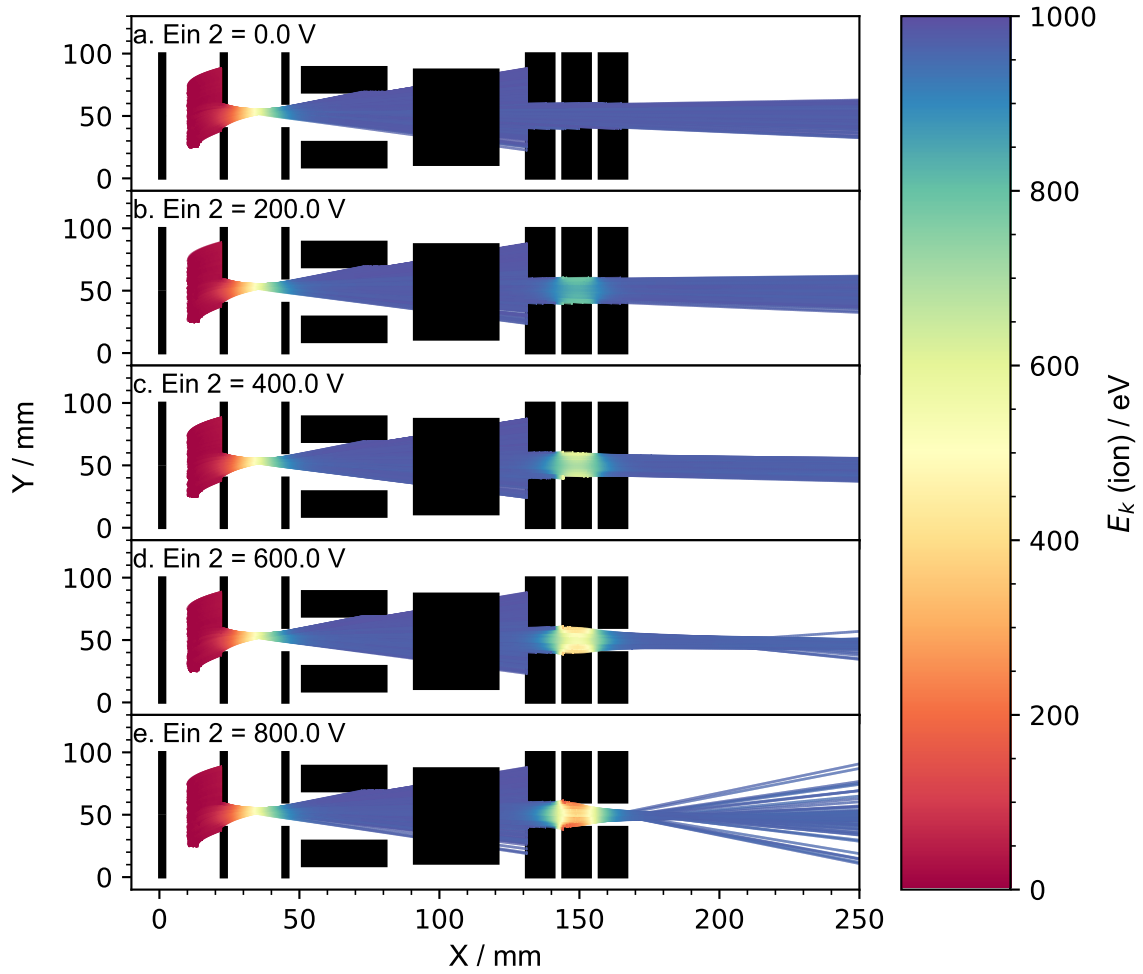


Figure C.5: A series of trajectories of 1000, 10 eV Au^+ ions recorded as a function of the potential applied to the second Einzel lens electrode. The repeller is pulsed to 1000 V, the extractor is pulsed to 950 V and the ground electrode was held at 0 V. This pulse pattern on the orthogonal extraction Wiley-McLaren lens induces a large radial focus into the ions.

D | Ion Optic Characterisation

D.1 In-Line Wiley McLaren Lens

D.1.1 Extractor/Repeller Ratio

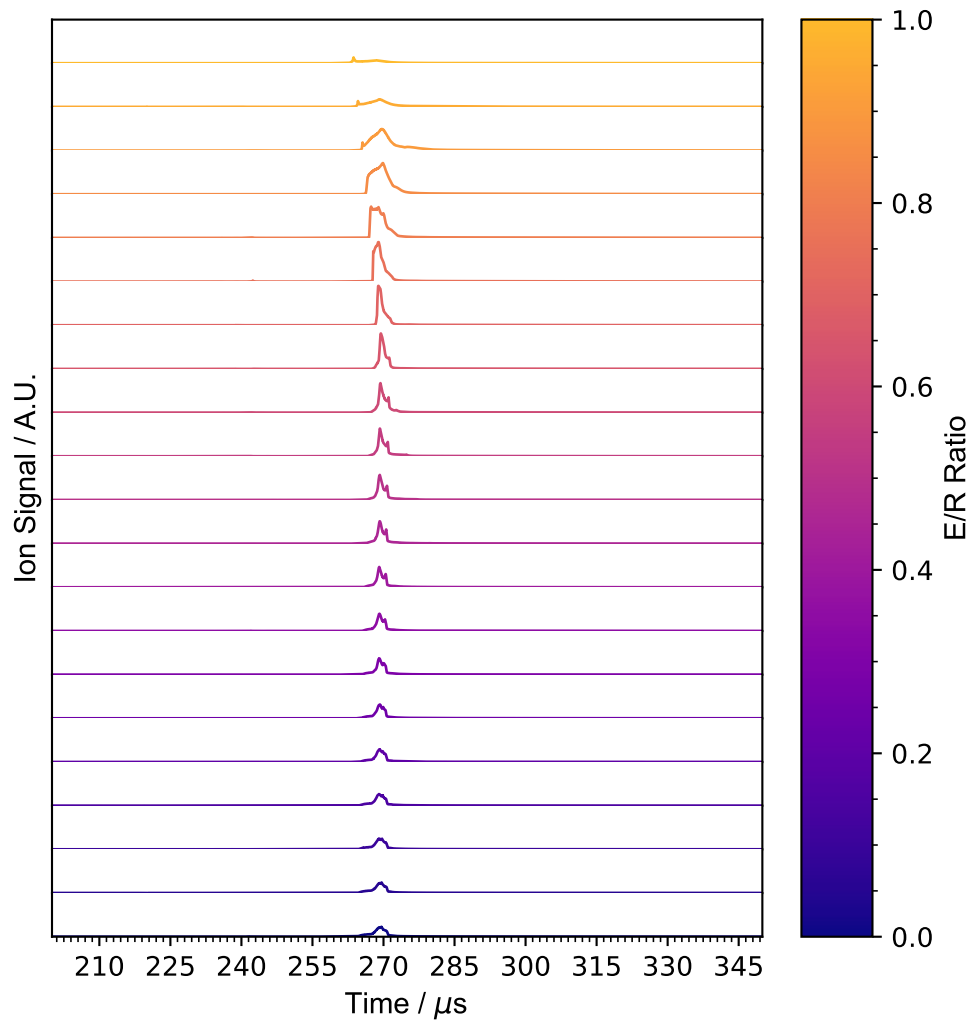


Figure D.1: A series of ToF mass spectra of Au^+ ions plotted as a function of the E/R ratio applied to the in-line Wiley-McLaren lens. The repeller electrode was held at 100 V and the extractor was varied to alter the E/R ratio.

D.1.2 Repeller Magnitude

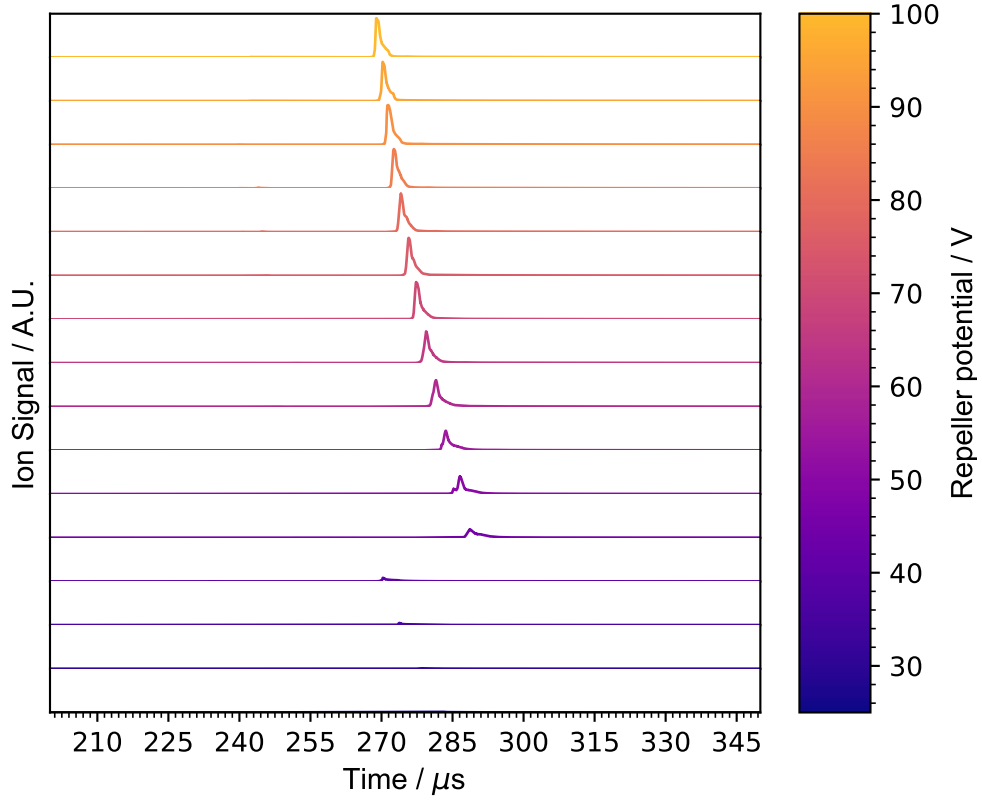


Figure D.2: A series of ToF mass spectra of Au^+ ions plotted as a function of the repeller potential magnitude applied to the in-line Wiley-McLaren lens. The E/R ratio was fixed at 0.7 and the repeller and extractor potentials were both varied.

D.1.3 Pulse Delay (re. to ablation laser)

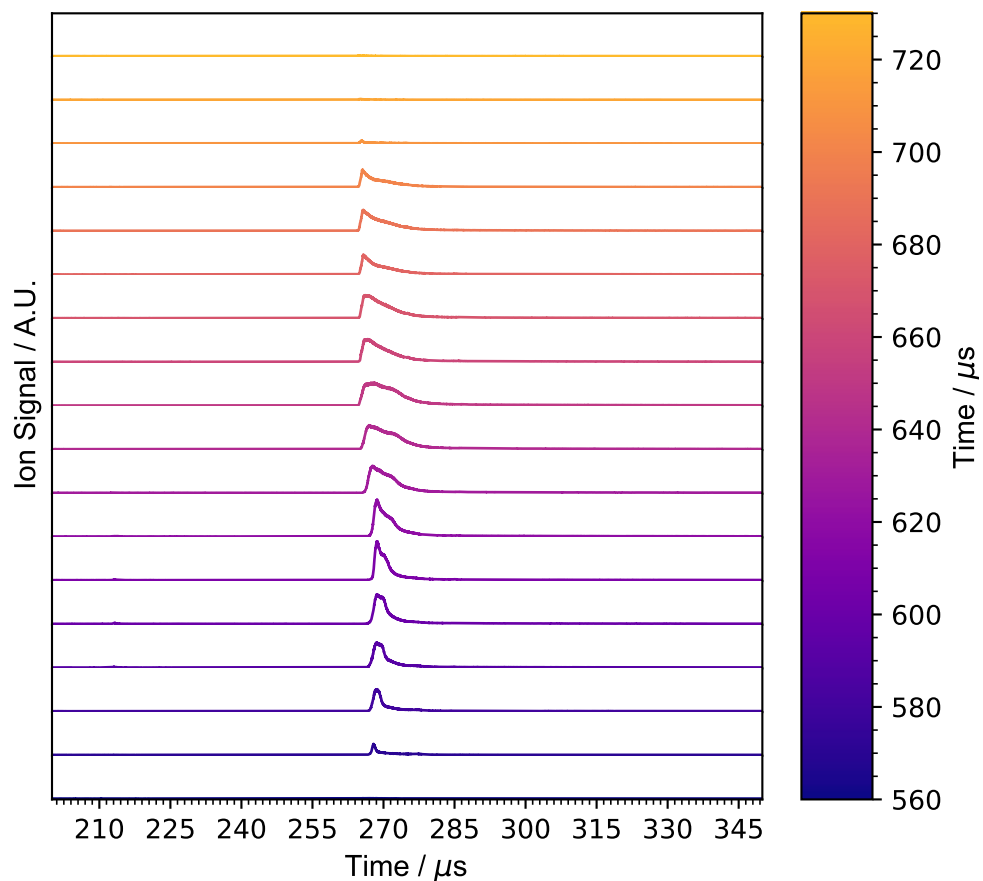


Figure D.3: A series of ToF mass spectra of Au^+ ions plotted as a function of when the the in-line Wiley-McLaren electrodes were pulsed relative to the ablation laser. The repeller was held at 100V and the extractor at 70 V.

D.2 Orthogonal Extraction Optics

D.2.1 Orthogonal Extraction Wiley-McLaren Lens

D.2.1.1 Extractor/Repeller Ratio

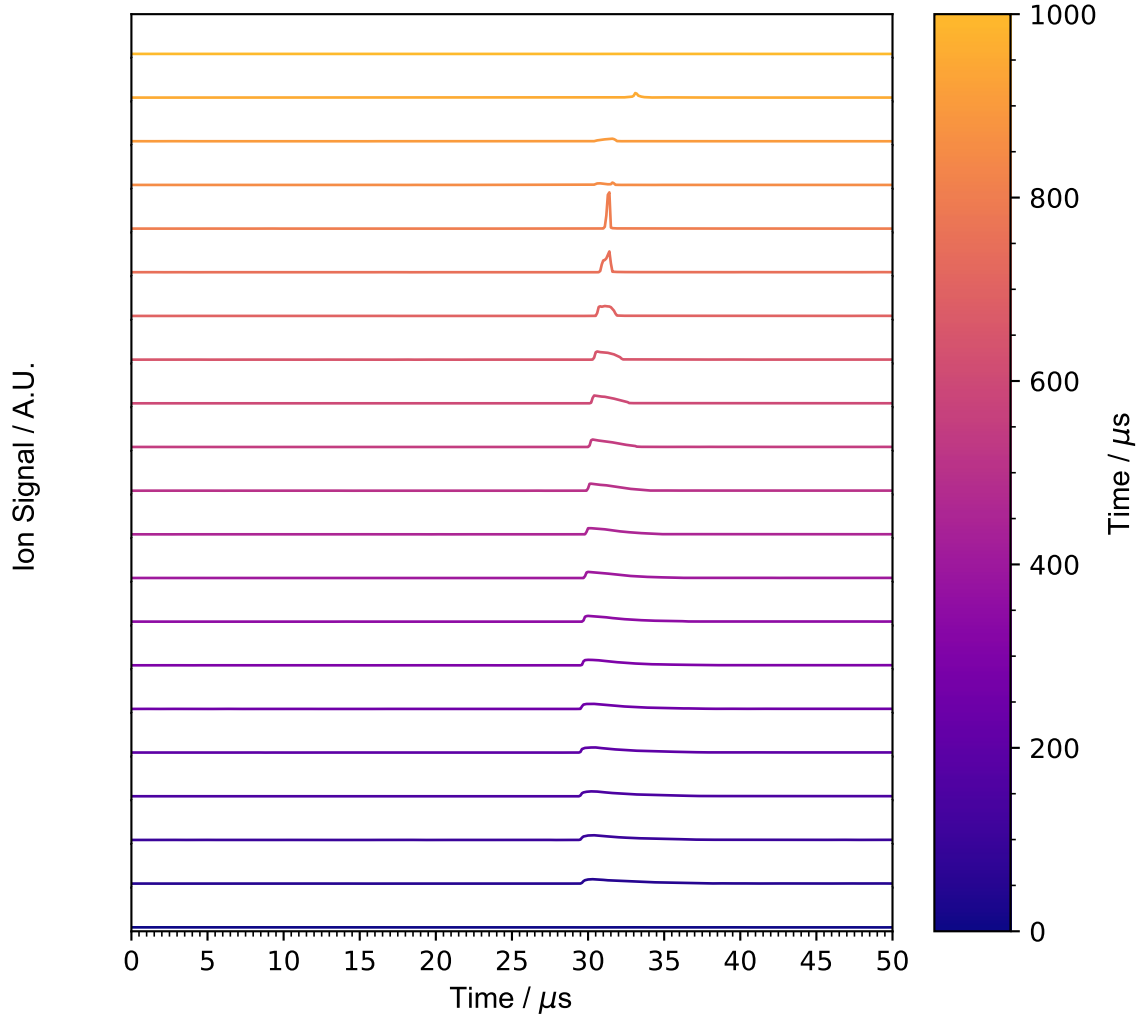


Figure D.4: ToF spectra of Au^+ recorded as a function of the orthogonal extraction Wiley-McLaren lens extractor/repeller ratio. The repeller potential is fixed at 1000V and the extractor is altered to change the extractor/repeller ratio.

D.2.1.2 Repeller Magnitude

The characterisation of the repeller magnitude is presented in the main body of the thesis in Figure 3.5 so is not presented here.

D.2.1.3 Pulse Delay

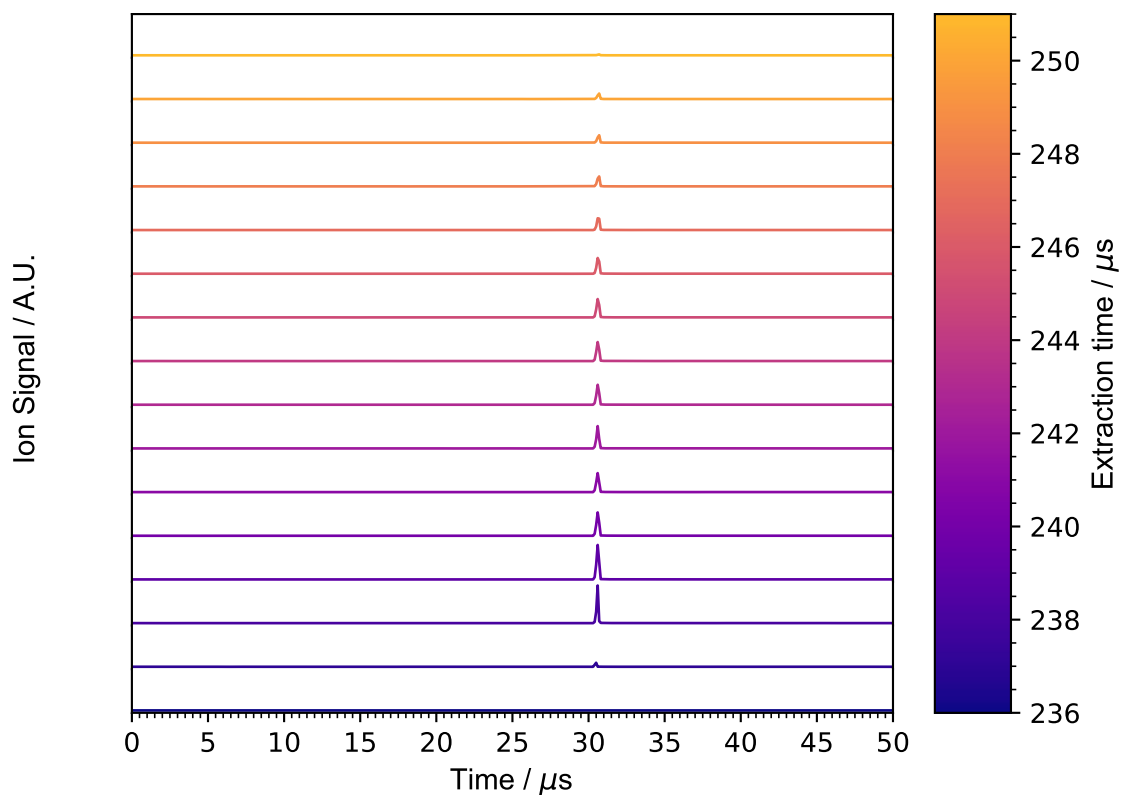


Figure D.5: ToF spectra of Au^+ recorded as a function of the time at which the orthogonal extraction Wiley-McLaren plates were pulsed relative to the ablation laser. The in-line Wiley-McLaren lens was not active when these ToF spectra were recorded.

D.2.2 Orthogonal Extraction Deflection Plates

D.2.2.1 Left

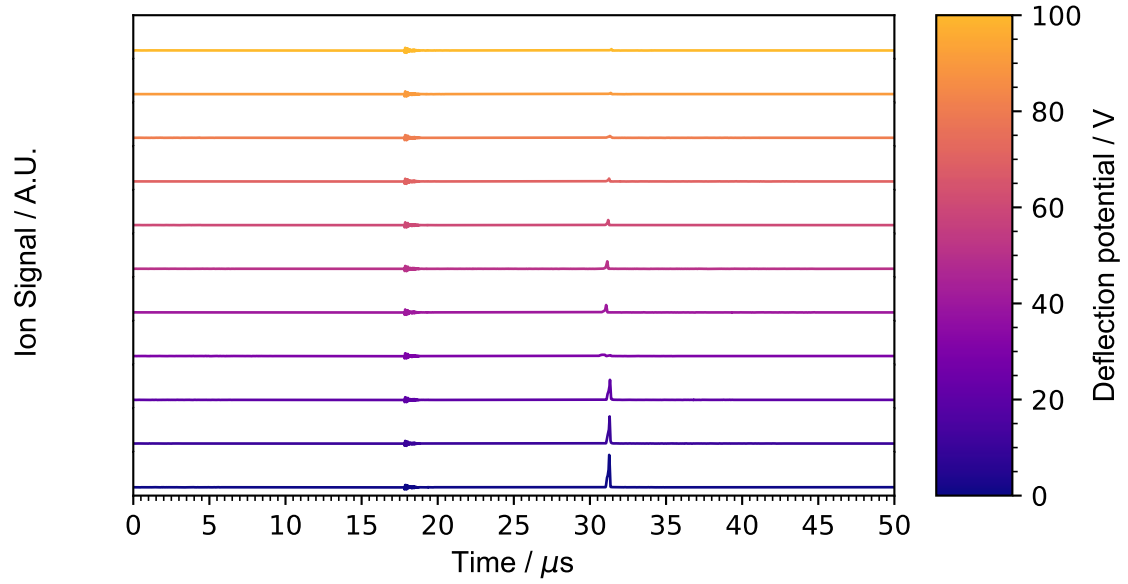


Figure D.6: A series of ToF spectra of Au^+ ions recorded as a function of the deflection potential applied to the left deflection plate (looking down the extraction axis).

D.2.2.2 Right

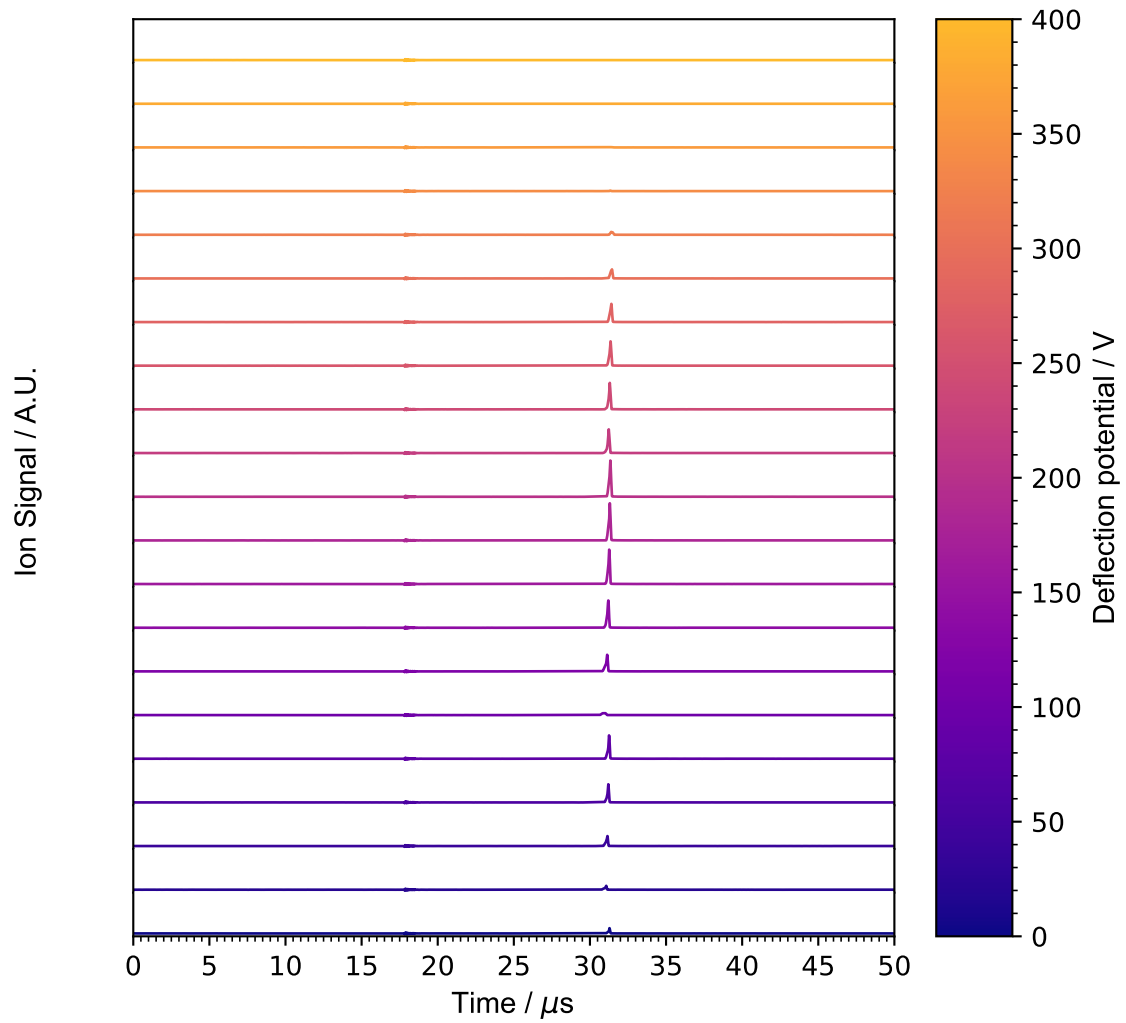


Figure D.7: A series of ToF spectra of Au^+ ions recorded as a function of the deflection potential applied to the right deflection plate (looking down the extraction axis).

D.2.2.3 Top

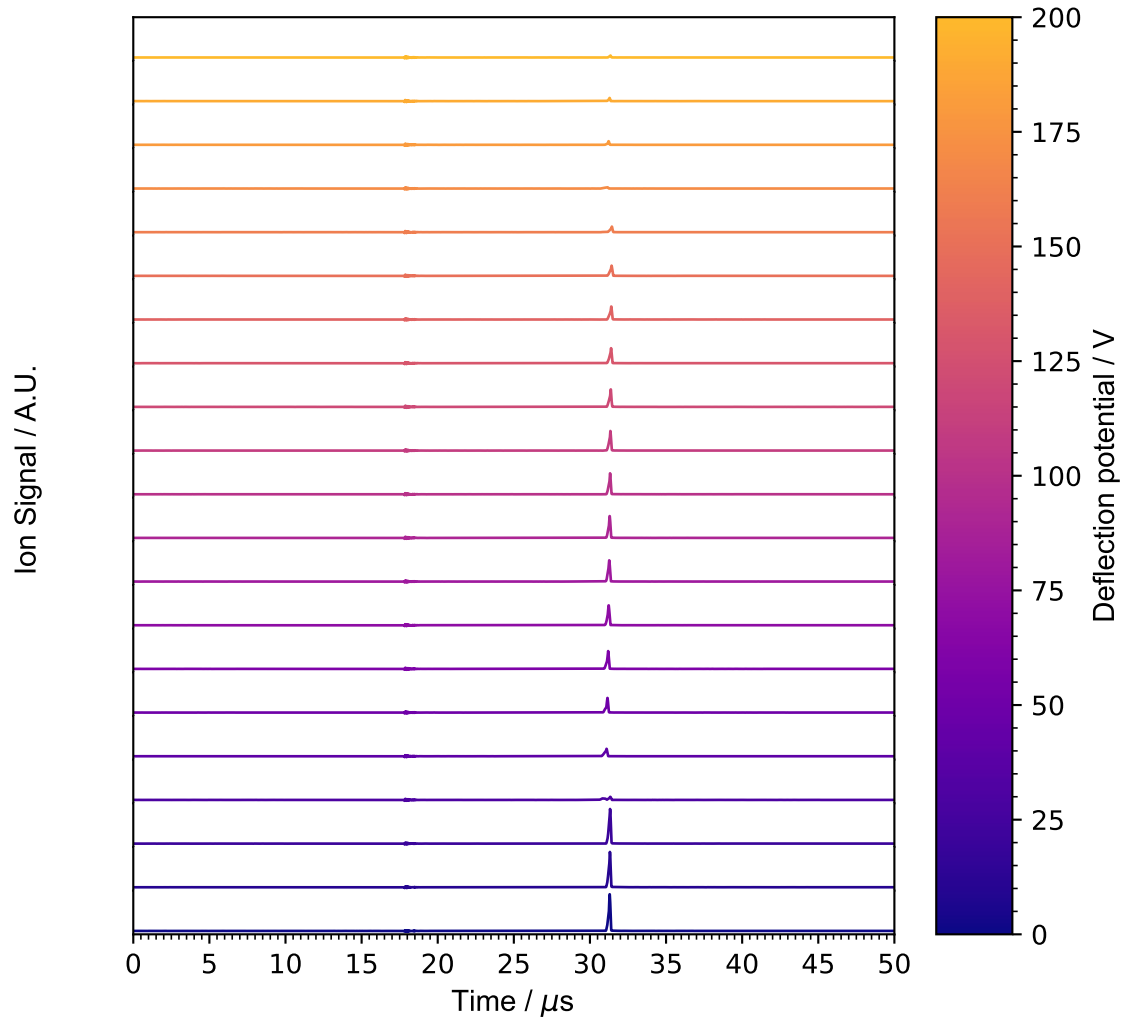


Figure D.8: A series of mass spectra of Au^+ ions recorded as a function of the deflection potential applied to the top deflection plate (looking down the extraction axis).

D.2.2.4 Bottom

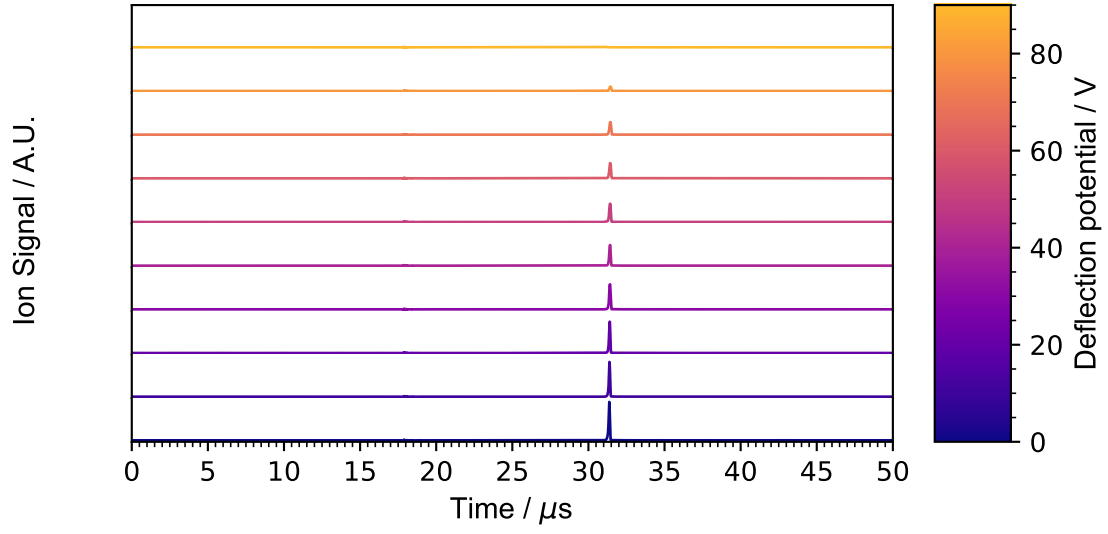


Figure D.9: A series of ToF spectra of Au^+ ions recorded as a function of the deflection potential applied to the bottom deflection plate (looking down the extraction axis).

D.2.3 Einzel Lens A

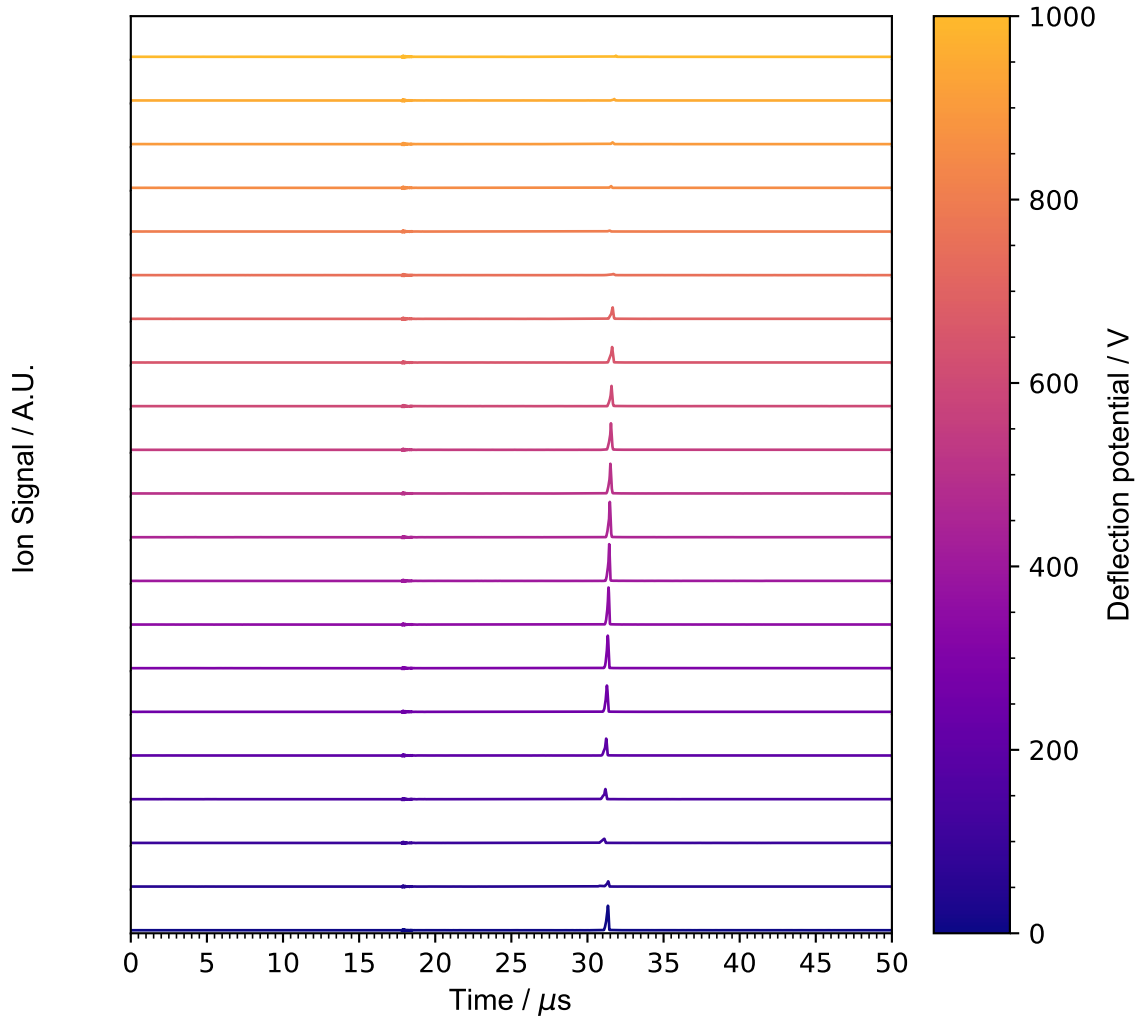


Figure D.10: A series of ToF spectra of Au^+ ions recorded as a function of the deflection potential applied to the central lens of Einzel lens A.

D.3 ReToF Mass Spectrometer

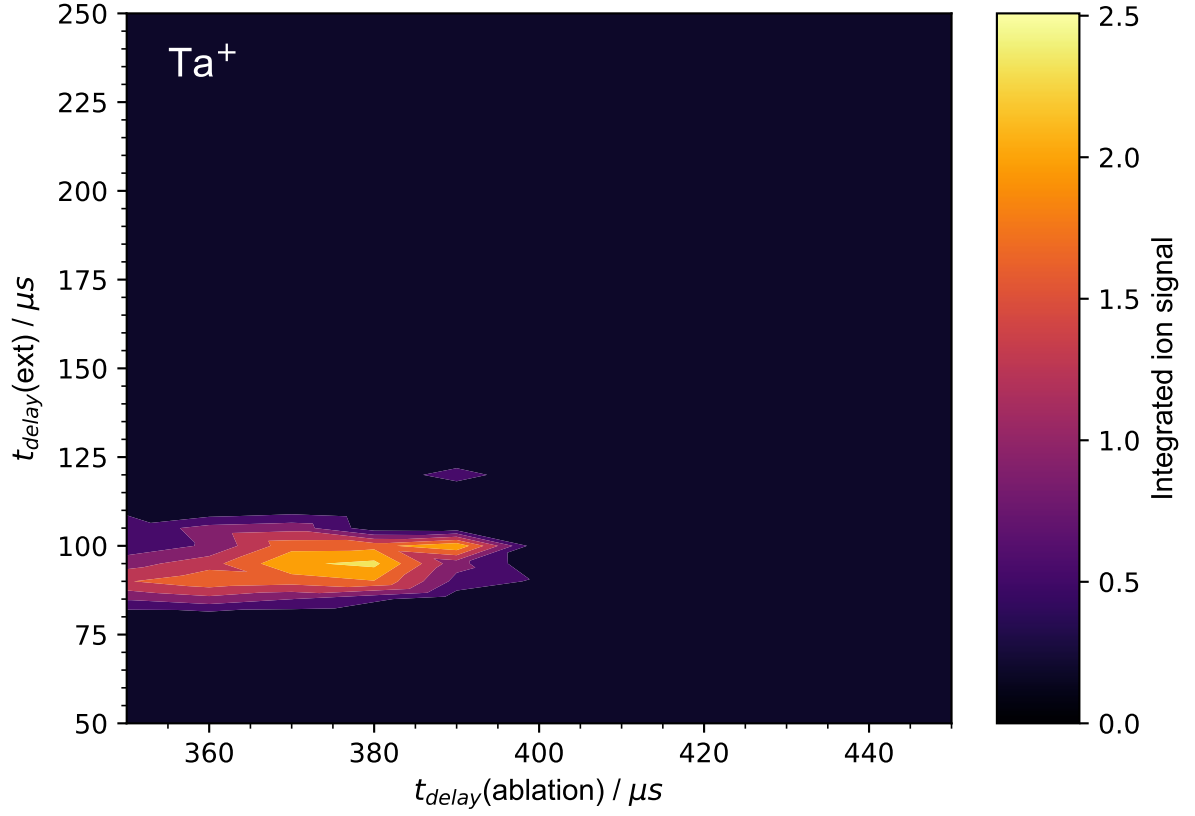


Figure D.11: A heat maps illustrating the conditions under which Ta^+ cations are generated and detected within the reflectron. All Ta^+ cations were extracted linearly with 100 eV of energy.

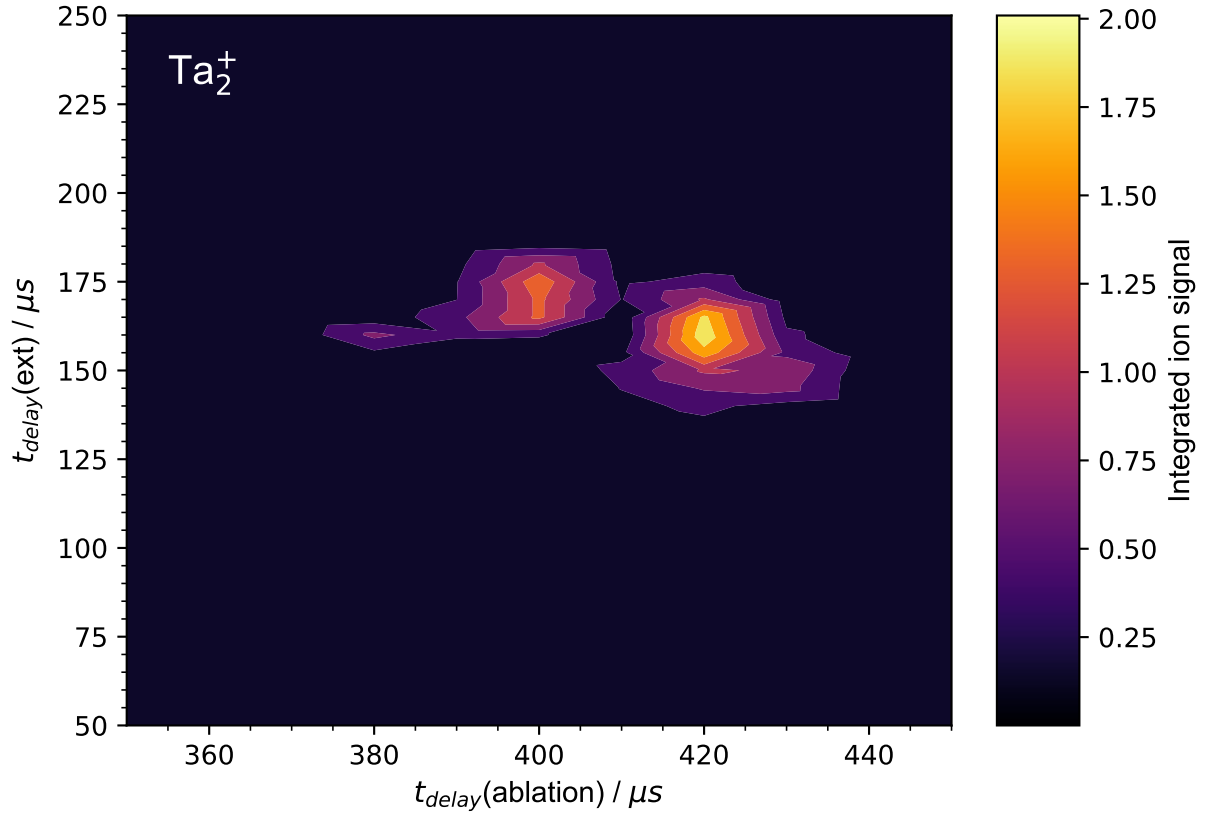


Figure D.12: A heat maps illustrating the conditions under which Ta_2^+ cations are generated and detected within the reflectron. All Ta_2^+ cations were extracted linearly with 100 eV of energy.

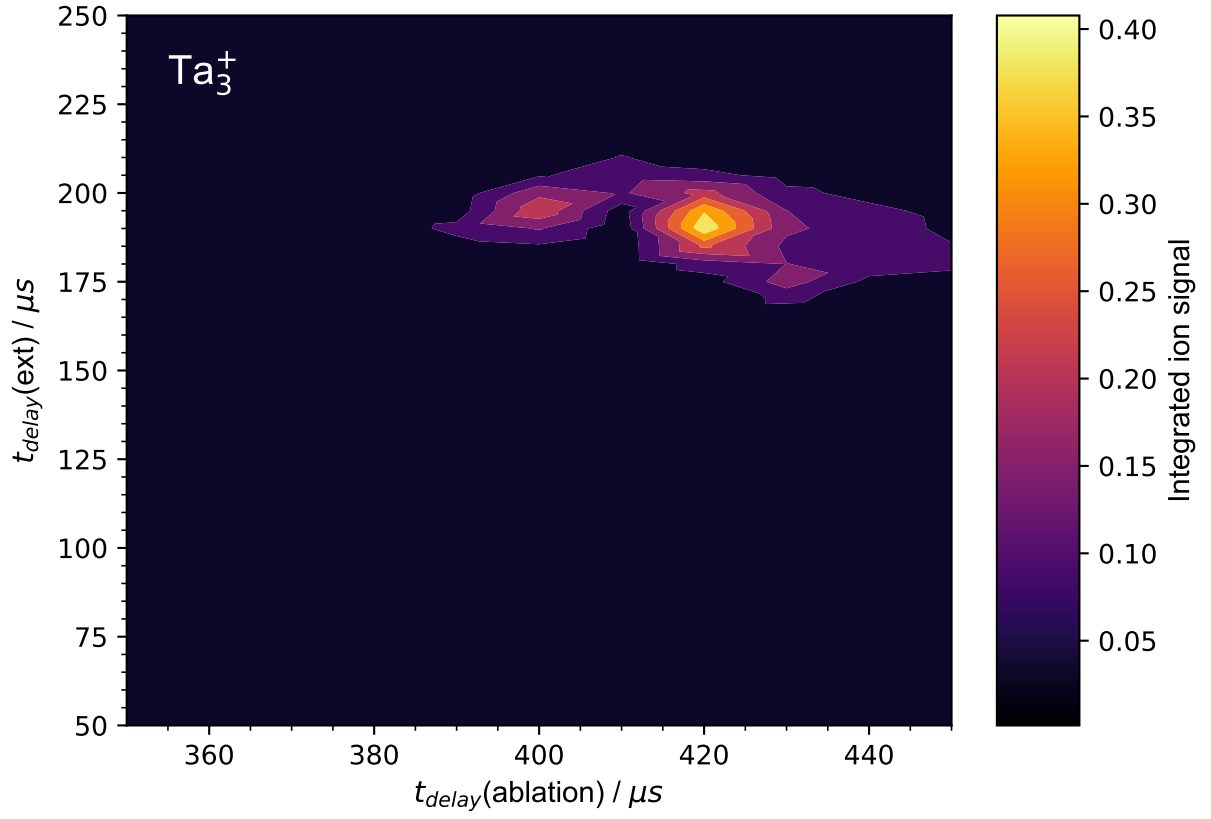


Figure D.13: A heat maps illustrating the conditions under which Ta_3^+ cations are generated and detected within the reflectron. All Ta_3^+ cations were extracted linearly with 100 eV of energy.

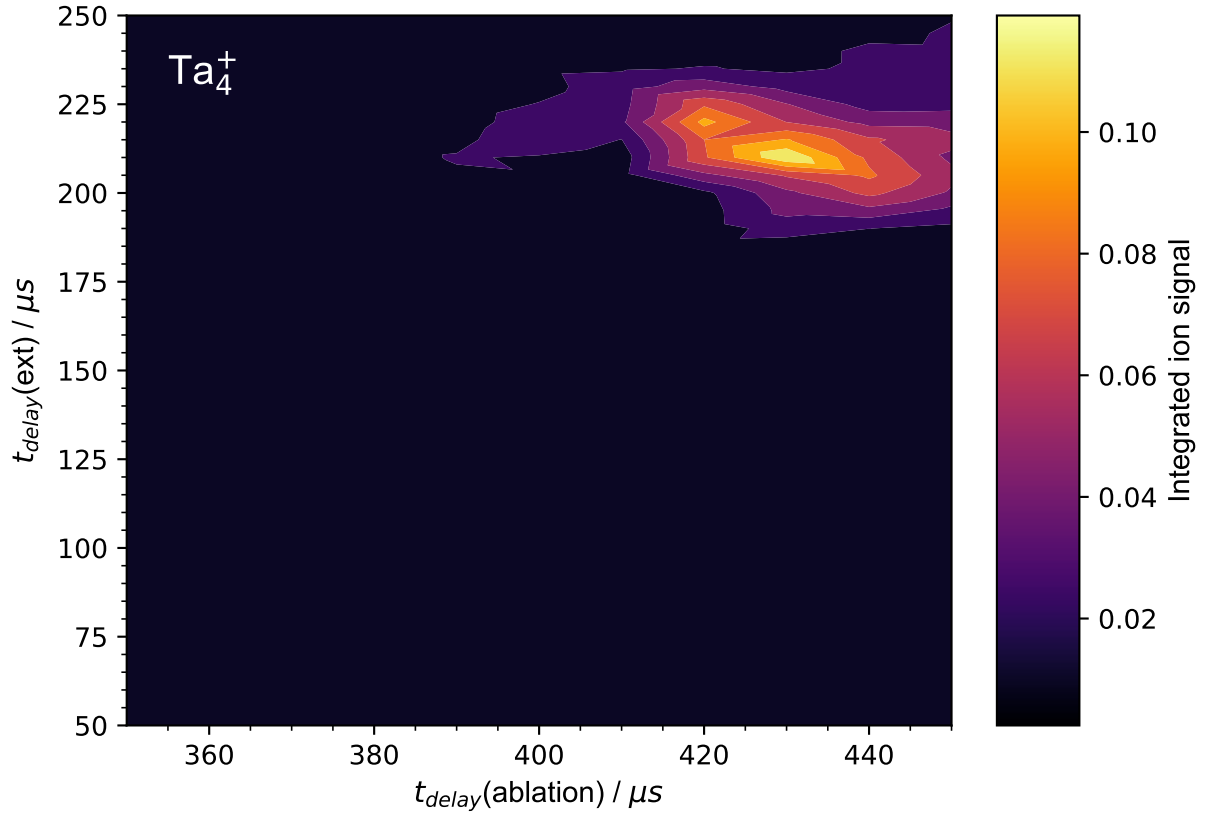


Figure D.14: A heat maps illustrating the conditions under which Ta_4^+ cations are generated and detected within the reflectron. All Ta_4^+ cations were extracted linearly with 100 eV of energy.

E | Other Diagrams

E.1 Reflectron ToF Mass Spectrometer

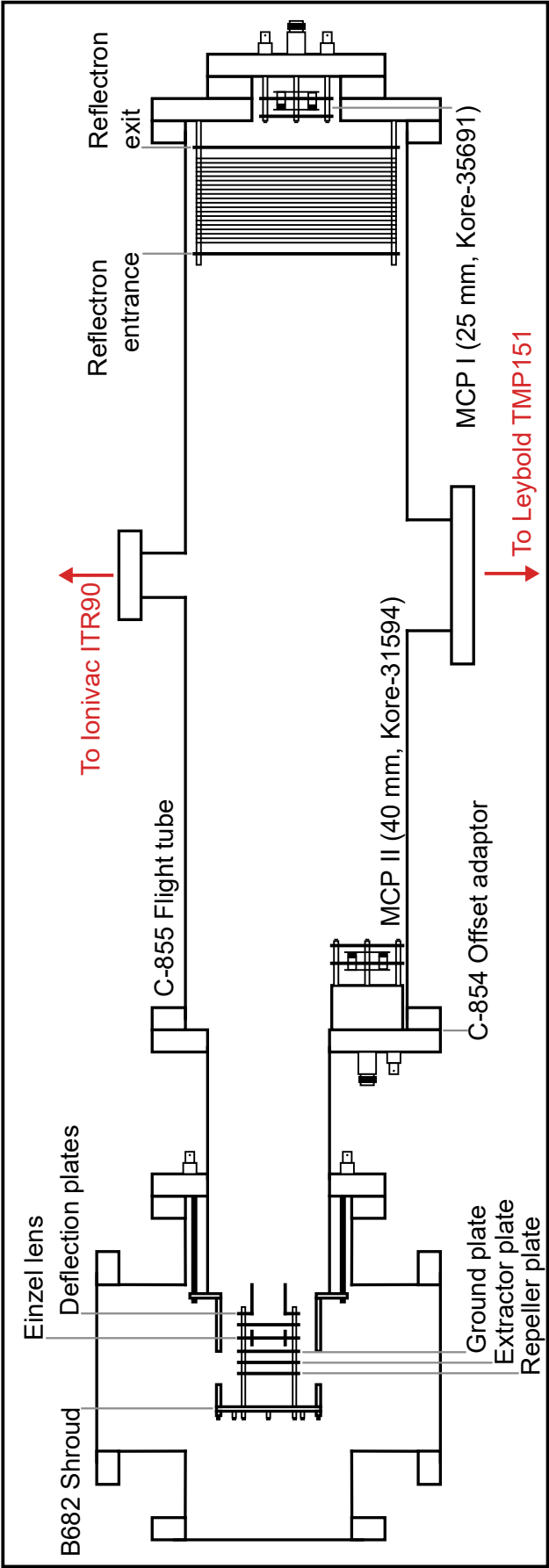


Figure E.1: Schematic of the Reflectron from R.M Jordan ToF with Kore MCPs replacing the original Jordan MCPs.

E.2 Reflectron ToF MCP Mounting

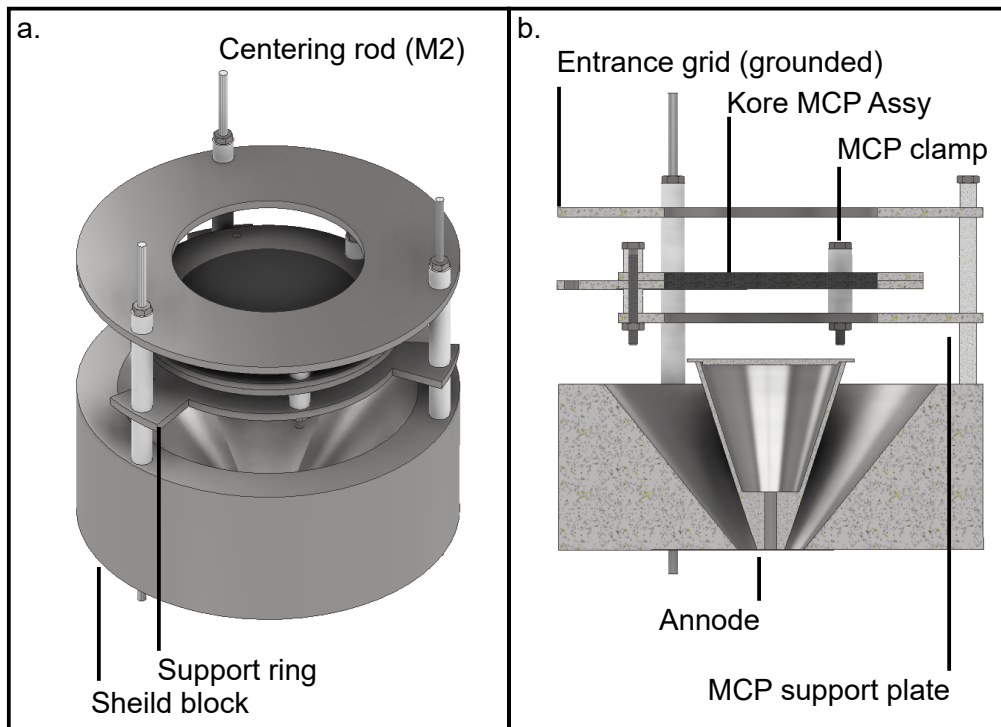


Figure E.2: (a) Full CAD render of the assembly designed to support the Kore-31594 double MCP assembly. (b) Half-section view of the CAD render of the assembly designed to support the Kore-31594 double MCP assembly

F | Software Repository Links

F.1 Collision Experiment Software

- Collision experiment controller https://github.com/Hypersor/collision_expt_controller.git
- Gas control software: https://github.com/Hypersor/Gas_controls.git

F.2 IRPD Experiment Software

- IRPD experiment controller: https://github.com/Hypersor/IRPD_expt_controller.git

F.3 Drivers

- Motor controls interfacing LabVIEW drivers: https://github.com/Hypersor/MotorControls_LabVIEW_drivers
- Oxford high voltage supply box LabVIEW drivers: https://github.com/Hypersor/Oxford_HV_supply_drivers
- MKS PDR2000 LabVIEWdrivers: https://github.com/Hypersor/PDR_2000_drivers
- VAT valve 62.2 gas dosing valve drivers : https://github.com/Hypersor/VAT_valve_drivers

G | Useful Software Links

- Ophir Starlabs v3.80: <https://www.ophiropt.com/laser--measurement/software/starlab-for-usb>
- LabVIEW Drivers for Quantum Composers 9520 pulse delay generators : http://sine.ni.com/apps/utf8/niid_web_display.download_page?p_id_guid=12C6FF12D48B4B50E0440003BA230ECF