

Spectroscopy and Imaging of Gas-Phase Transition Metal Clusters



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A thesis submitted for the degree of

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The field of transition metal clusters has proven to be fertile ground for study in recent years due to their interesting properties and reactivity. In this thesis, Velocity Map Imaging (VMI) has been used alongside spectroscopic techniques to study a range of diatomic metal-containing molecules which have relevance to cluster chemistry.

The photodissociation of Ag-RG complexes (RG = Ar, Kr, Xe), as well as AgO, have been studied in the 29900–31700 cm⁻¹ spectral region using VMI. The electronic states of the fragments produced have been assigned in each case and new values for the dissociation energies determined. These are presented as an update to the most recent experimental values for each molecule, about which doubts have been expressed.

VMI has also been used to study the photodissociation dynamics of isotopically-selected ⁹⁸MoO and ⁵²CrO in multiple spectral regions. Assignments have been proposed for the processes generating the observed features, and values for the dissociation energies of these species determined which are consistent with literature values from other, older experimental techniques, or indirect measurements.

Finally, a comparison has been made of different image reconstruction algorithms in order to determine which is best suited to analysing the data recorded in our group. The experimental data from the rest of this thesis have been reanalysed using various approaches, and it is demonstrated that recently-developed maximum entropy programs produce better results than the onion peeling algorithm previously used.

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List of Acronyms

(p)BASEX	(polar) BAis Set EXpansion
CID	Collision-Induced Dissociation
(TD-)DFT	(Time Dependent) Density Functional Theory
EPSRC	Engineering & Physical Sciences Research Council
FWHM	Full Width at Half Maximum
GGA	Generalised Gradient Approximation
IRMPD	InfraRed Multiple Photon Dissociation
IVR	Intramolecular Vibrational Redistribution
(f)KER	(fragment) Kinetic Energy Release
LIF	Laser-Induced Fluorescence
LSDA	Local Spin Density Approximation
LVCS	Laser Vaporisation Cluster Source
MCP	MicroChannel Plate
MEVELER	Maximum Entropy VELOCITY LEgendre Reconstructi- on
MEVIR	Maximum Entropy Velocity Image Reconstruction
MF	Magnification Factor
Nd:YAG	Neodymium: Yttrium Aluminium Garnet
OPO	Optical Parametric Oscillator
POP	Polar Onion Peeling
R2PI	Resonant Two-Photon Ionisation
REMPI	Resonance-Enhanced MultiPhoton Ionisation
SHG	Second Harmonic Generation
SNR	Signal-to-Noise Ratio
TKER	Total Kinetic Energy Release
ToF-MS	Time-of-Flight Mass Spectrometry
TPD	Temperature Programmed Desorption
VMI	Velocity Map Imaging

Chapter 1

Introduction

The field of transition metal clusters has proven to be a fruitful and interesting area of research in recent years. These clusters exhibit interesting properties distinct from atomic or bulk metals, while also serving as analogues for useful catalytic species. This thesis will focus on the study of diatomic molecules which feature bonds of particular relevance to cluster chemistry. The research by this group using spectroscopy and velocity map imaging techniques has provided many useful insights into the structure and bonding of clusters and small metal-containing molecules. This chapter provides an introduction to the field of cluster chemistry and related areas, in addition to details on the experimental, analytical, and computational techniques used throughout this thesis. Chapters 2, 3, and 4 will present the results of spectroscopic and imaging experiments on various systems, while Chapter 5 will focus on an examination of the algorithms used for the analysis. Chapter 6 will summarise the results obtained in this thesis, along with conclusions based on these and the outlook for future work.

1.1 Background of Cluster Chemistry

1.1.1 Definition of a Cluster

Roy Johnston, in his book “*Atomic and Molecular Clusters*”, broadly defined a cluster as ‘an aggregate of a countable number ($2-10^n$, where n can be as high as 6 or 7) of particles (i.e. atoms or molecules)’, which may be homo- or hetero-atomic.¹

This definition encompasses species which occupy an intermediate range of sizes between the atom and the colloidal size regime.

Here, we focus primarily on small transition metal clusters (and/or metal-containing molecules), which contain between two and a few dozen atoms, at least one of which is of a *d*-block element. These may be pure homo-atomic clusters, or they may be functionalised and contain atoms or molecules of other species. For example, previous work in this group has included studies of the structures of charged clusters of pure rhodium, as well as of the reactivity of nitrous oxide on similar species, or of carbon monoxide and oxygen on platinum clusters.²⁻⁵

This thesis focuses on diatomic molecules, which fall at the very limits of this definition. However, these species are of wider interest to cluster chemistry in terms of the properties of the bonds formed. The reasons for this applicability will become clearer over the rest of this introduction.

1.1.2 Properties of Transition Metal Clusters

Since clusters occupy a range of sizes between atomic and bulk species, it might be assumed that their properties (such as reactivity or magnetism) should resemble and vary relatively smoothly between the two regimes. In some cases this is true: there are examples of similar reactions being observed in clusters as on the corresponding bulk metal (although the properties of the reactivity may differ in the details), such as the reduction of nitrous oxide on rhodium clusters,^{4,6,7} or the oxidation of carbon monoxide on platinum clusters.⁵ These are reactions that are analogous to those observed in the three-way catalytic converter.⁸ There are also cases where there is evidence of a straightforward trend with increasing cluster size, such as the effect of cluster size on the reactivity between niobium clusters and carbon monoxide, as observed in Figure 1.1.⁹ In this case, there is a mostly monotonic rise in reaction rate as the size of the metal cluster increases. Similar results have been noted on the analogous charged clusters.¹⁰

However, this simple view of the properties of clusters does not hold true more generally. For example, clusters of the coinage metals (copper, silver, and gold)

demonstrate significant alternation effects in their properties, as shown by the rate constants for the reaction with oxygen of anionic clusters M_n^- ($M = \text{Cu}, \text{Ag}, \text{Au}$) plotted against cluster size in Figure 1.2. This is easily explained as an electronic structure effect by their ns^1 electronic configurations, which mean that as cluster size varies, the clusters alternate between having one and zero unpaired electrons, affecting reactivity and other properties. This can be further demonstrated by the fact that in the case of ionic clusters, those containing an even number of atoms, and therefore possessing an unpaired electron, are more reactive, as shown in the figure, while for neutral clusters the opposite effect is observed.¹¹⁻¹³

Similar dramatic size effects can also be observed in other metals with different atomic electron configurations. For example, in the same paper where the data in Figure 1.1 were published, it was demonstrated that the reactivity of niobium clusters with nitrogen or deuterium follows a much more complicated variation with cluster size, with no clear pattern in reaction rate with cluster size.⁹ The difference here suggests that a geometrical effect exists for certain reactions. For the reaction with CO, the molecule binds so easily and quickly to the cluster that the geometrical shape has no effect, with the rate of reaction increasing with cluster

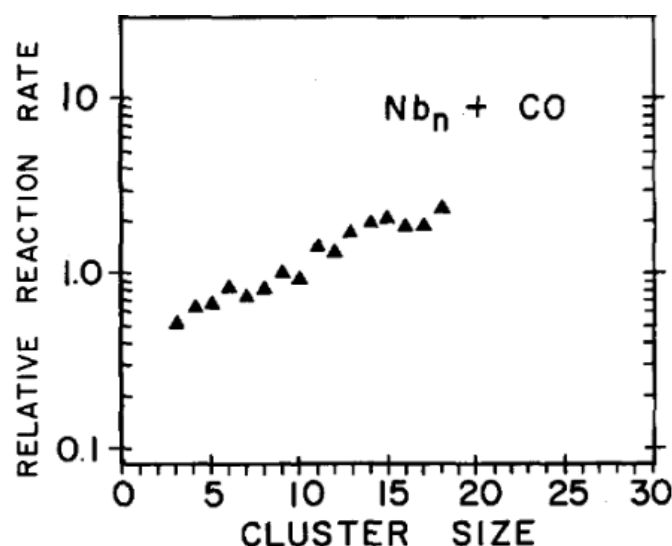


Figure 1.1: Change in relative reaction rate for chemisorption of CO on niobium clusters, Nb_n . Reproduced with permission from M. D. Morse, M. E. Geusic, J. R. Heath, and R. E. Smalley, *The Journal of Chemical Physics*, 83, 2293 (1985).⁹ Copyright 1985, American Institute of Physics.

size simply because the cluster and its collision cross-section get larger. For reaction with more weakly-bound molecules, such as N_2 or D_2 , the sticking probability is less than one, so that the geometry of the cluster affects the reaction rate because the molecule may rebound if it does not collide with a suitable binding site.

In an example from our own group, Figure 1.3 shows the change in the rate of reaction for the reduction of N_2O on rhodium cluster ions, $Rh_n^\pm$, with respect to the size of the cluster.¹⁴ The reactivity varies significantly, even with the addition of a single extra atom to the cluster; for example, there is a difference of more than two orders of magnitude in the rate constant between Rh_{19}^+ and Rh_{20}^+ .

There is further evidence of the influence of cluster geometrical structure in these data. There are some cases in Figure 1.3 where two rate constants have been derived, which are believed to correspond to different structures of the same cluster. For Rh_{12}^+ , the difference between the two values is two orders of magnitude, demonstrating how large an impact this can have. Between structural, electronic, and other effects, clusters of adjacent sizes can have markedly different properties, which leads to the doctrine in cluster chemistry that ‘every atom counts’.

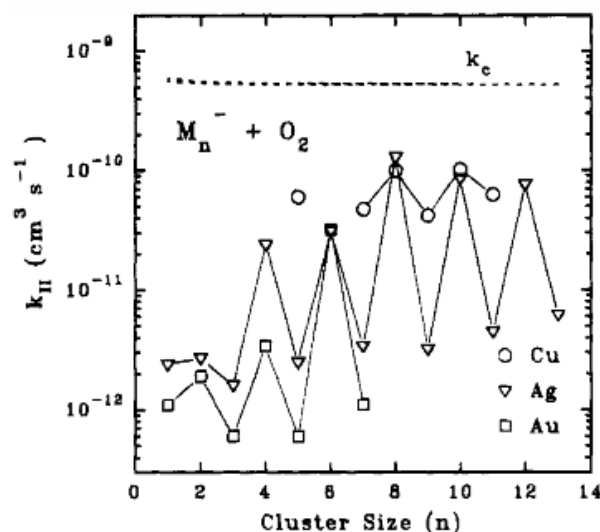


Figure 1.2: Experimental effective bimolecular reaction rate coefficients for the reaction of oxygen with coinage metal cluster anions of copper (circles), silver (triangles), and gold (squares). Reprinted with permission from T. H. Lee, and K. M. Ervin, *The Journal of Physical Chemistry* 1994, 98, 10023–10031.¹¹ Copyright 1994, American Chemical Society.

This doctrine is shown clearly by later results involving $\text{Rh}_n\text{N}_2\text{O}^+$ clusters, in which the use of infrared light to introduce energy to the system leads to dissociation of the nitrous oxide to produce Rh_nO^+ for the case where $n = 4$ or 6. However, when $n = 5$, the nitrous oxide instead desorbs in order to leave Rh_5^+ .⁴ This reactivity can then be reversed by the introduction of a single oxygen atom to the cluster, which leads to a cooperative effect such that stimulation of the $\text{Rh}_5\text{ON}_2\text{O}^+$ leads instead to dissociation of the nitrous oxide.¹⁵ This has been attributed to the finely balanced energies of the clusters, such that the cooperative binding effect of the oxygen atom raises the binding energy of the N_2O sufficiently that it leads to the dissociation pathway being favoured, as shown in Figure 1.4.

The fact that every atom counts in cluster chemistry is a major deviation from the simple initial model of smoothly varying trends in properties intermediate between the atom and the bulk. There are also significant qualitative differences, such as the fact that rhodium, which does not display ferromagnetism in the bulk material, nevertheless produces clusters Rh_n which are highly magnetic.¹⁶ Even in cases where the cluster appears to behave similarly to macroscopic properties, such as the fact that carbon monoxide can be oxidised on platinum clusters in a

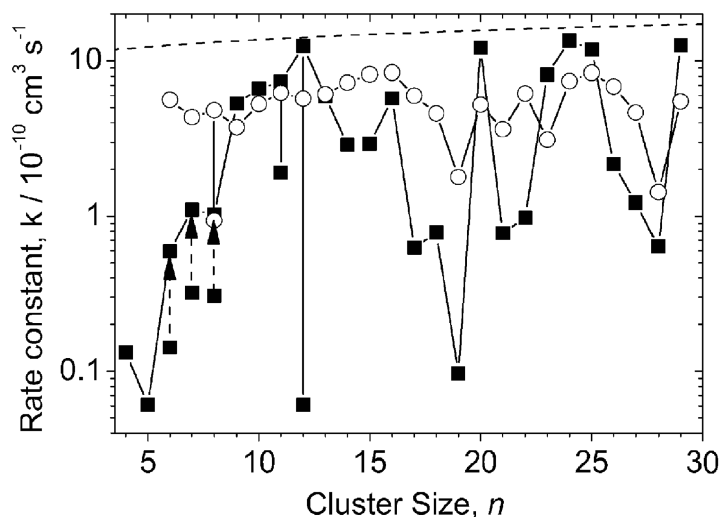


Figure 1.3: Rate constants for the reduction of nitrous oxide on rhodium cluster cations (black squares) and anions (white circles). Sizes where multiple points are present either indicate thermalisation effects (dashed arrows), or isomerisation effects (solid lines). Reproduced from D. Harding, M. S. Ford, T. R. Walsh, and S. R. Mackenzie, *Physical Chemistry Chemical Physics*, 2007, 9, 2130–2136 with permission from the PCCP Owner Societies.¹⁴

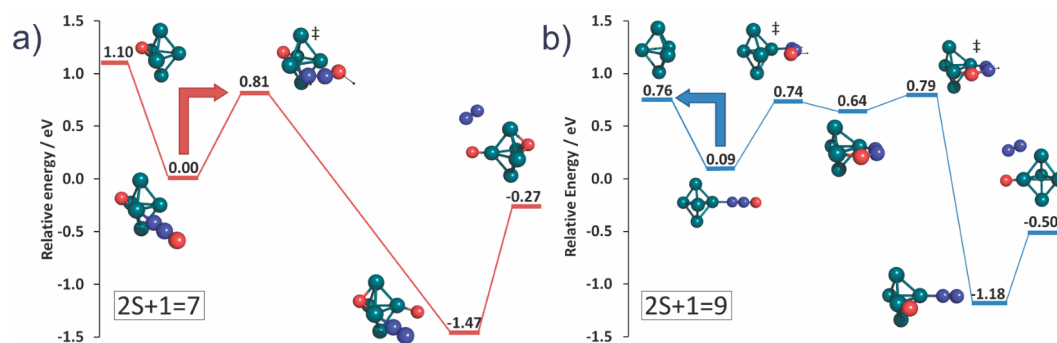


Figure 1.4: Calculated reaction pathways for the dissociation of N_2O on (a) Rh_5O^+ and (b) Rh_5^+ . Reprinted with permission from A. C. Hermes, S. M. Hamilton, W. S. Hopkins, D. J. Harding, C. Kerpel, G. Meijer, A. Fielicke, and S. R. Mackenzie, *The Journal of Physical Chemistry Letters* 2011, 2, 3053–3057.¹⁵ Copyright 2011, American Chemical Society.

similar fashion to its oxidation in catalytic converters,^{5,8} there may be significant differences. Computational work has suggested that the clusters upon which the reaction takes place may be fluxional, changing between different geometries during the reaction, as shown in Figure 1.5. In this case, the Pt_4 structure closes from a flexed diamond shape to one that is almost tetrahedral; such behaviour is not observed in the mechanism for the same reaction on a platinum surface.^{5,17} Similar fluxionality has been predicted before in gold clusters, Au_n ,¹⁸ and it has been suggested that this is key to the dissociation of H_2 on these clusters.¹⁹

In summary, while clusters occupy an intermediate size regime above the atom but below the bulk metal, their properties do not always vary smoothly with increasing numbers of atoms. They also sometimes behave in a qualitatively different fashion from that which may be expected from the potentially naïve assumption that clusters should have properties similar to the bulk. These unusual properties provide interesting and fertile ground for study.

1.1.3 Interest in the Study of Transition Metal Clusters

One reason for studying transition metal clusters may be purely academic interest in their novel and varied properties, as outlined above, but there are also close ties to useful and practical applications. They are particularly useful to investigate as small-scale, computationally tractable models for heterogeneous catalysis.

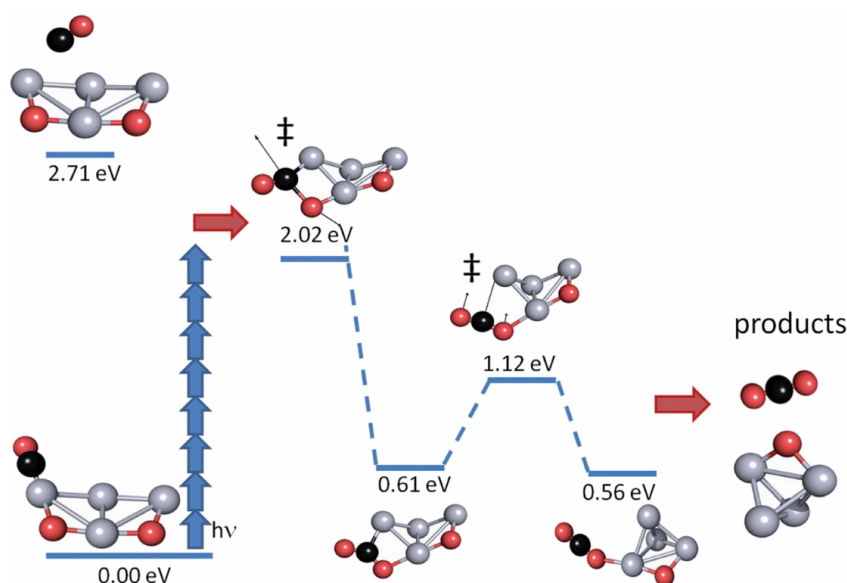


Figure 1.5: Calculated reaction pathway for the oxidation of CO on Pt_4O_2^+ . Reproduced from A. C. Hermes, S. M. Hamilton, G. A. Cooper, C. Kerpál, D. J. Harding, G. Meijer, A. Fielicke, and S. R. Mackenzie, *Faraday Discussions*, 2012, 157, 213–225 with permission from the Royal Society of Chemistry.⁵

Transition metals are common catalysts, being involved in several homogeneous catalytic processes,^{20–22} as well as important heterogeneous reactions, which are more immediately relevant to the discussion at hand. Examples of reactions on the surface of transition metals include the contact process for the production of sulfuric acid on the surface of vanadium oxide,²³ the synthesis of ammonia by the Haber process using an iron-based catalyst (which is of such industrial significance that it accounts for ca. 1% of world energy production),^{24,25} and the reactions in the catalytic converter already mentioned.⁸

The positions on the metal surface where the interesting reactivity occurs, known as the active sites, are mostly (although not universally) located at steps, edges, corners, and kinks which disrupt the flat terraces of the surface.²⁶ These active sites can be modelled using clusters, by effectively treating the cluster geometry as a high concentration of defects of the type involved in these active sites. This allows for the possibility of studying the reactivity of transition metal clusters as a way to investigate the behaviour of active sites and more generally improve our understanding of heterogeneous catalysis.

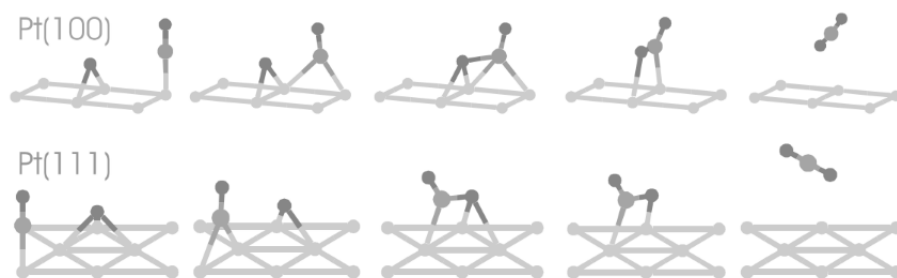


Figure 1.6: Reaction pathway for the oxidation of carbon monoxide on Pt(100) (top) and Pt(111) (bottom) surfaces. Reprinted from *Surface Science*, 498, A. Eichler, “CO oxidation on transition metal surfaces: reaction rates from first principles”, 314–320, Copyright (2012), with permission from Elsevier.¹⁷

Two examples of cases where reactivity analogous to surface chemistry has been previously observed were mentioned above. The first is the reduction of N_2O on rhodium, which is a similar reaction to the reduction of nitrogen oxides in the three-way catalytic converter;⁸ while more attention is paid to NO_x gases, which make up a larger proportion of nitrogen-based automobile emissions, nitrous oxide is also produced in car engines and is a potent greenhouse gas.²⁷ This makes the study of its removal and reduction important and relevant, and rhodium clusters provide a useful model for the catalytic process.

An important feature of this process is that while the reactivity was reported as being stimulated by infrared radiation, excitation of all three N_2O modes leads to reaction.⁴ This suggests that the reactivity is tied less to a specific vibrational mode and more to simple thermal excitation of the cluster by absorption and subsequent redistribution of energy, which is supported further by the later observation of collisional activation of the same processes.⁶ On a cluster level, there is a close analogy between these reactions and Temperature Programmed Desorption (TPD) reactions on bulk material, where heating stimulates reactivity. This supports the idea of this type of cluster reactivity as being analogous to processes on surfaces.

The second example mentioned above was the oxidation of carbon monoxide on platinum clusters, which is also an important process for car exhaust fume control.⁸ Note the resemblance between the reaction pathway calculated on the cluster as shown in Figure 1.5 and the corresponding pathway on a platinum surface in Figure 1.6.¹⁷ In spite of the fluxionality of the cluster mentioned in Section 1.1.2,

there are some significant similarities, including the migration of the CO molecule to a dissociatively bound oxygen atom before CO_2 is formed in bridging configuration prior to unbinding and desorption.^{17,28} As with the rhodium chemistry, it is also believed that the reaction is thermally stimulated.⁵

If the validity of metal clusters as models for the active sites of heterogeneous catalysis is accepted, the question remains: why would one want to investigate such models? One advantage of studying metal clusters is in their computational tractability: the small number of atoms in the species means that it is possible to study them using Density Functional methods and more expensive approaches such as coupled cluster calculations.^{29–33} These computational methods will be explored in more detail in Section 1.6, but for now suffice it to say that such calculations have proven to be very powerful in combination with experiments for purposes such as structural determination,^{2,5} and have yielded useful insights into the reaction mechanisms in determining barrier heights.^{5,15} These observations match well with observations, such as the calculated pathway in Figure 1.4 which explains the experimental difference in the reactivity of $\text{Rh}_5\text{N}_2\text{O}^+$ and $\text{Rh}_5\text{ON}_2\text{O}^+$.¹⁵

These insights from computational work on clusters thus provide useful insights into their chemistry, and in turn to the surfaces of bulk metals, which may be more computationally expensive to model. This explains much of the practical interest in transition metal clusters — they are plausible models for the active sites of heterogeneous catalysis, while being amenable to a wide and powerful array of experimental and computational methods.

1.2 Production of Transition Metal Clusters and Metal-containing Molecules

Multiple methods of metal cluster production have been developed.^{34,35} In early studies, clusters were produced by a simple oven design where bulk metal was heated to boiling point,^{36,37} while later developments include cluster production by sputtering, also known as fast atom bombardment,³⁸ in which a beam of high energy particles is directed onto a metal target to produce metal cluster ions;³⁹ and

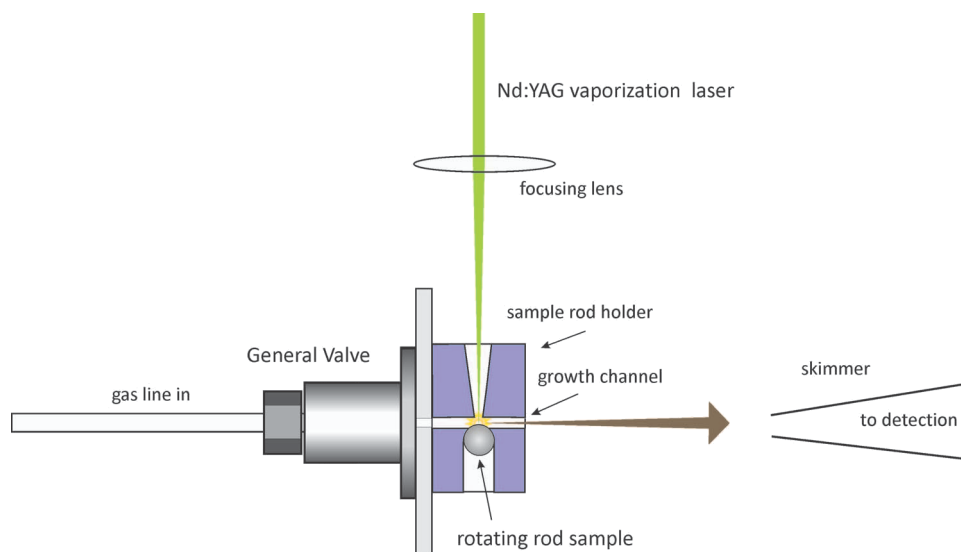


Figure 1.7: Schematic of a Laser Vaporisation Cluster Source. Adapted from M. A. Duncan, *Review of Scientific Instruments* 83, 041101 (2012),³⁵ with the permission of AIP Publishing.

the pulsed arc discharge source, where an electrical discharge is used to ablate the metal.⁴⁰ It is also possible to produce clusters from presynthesised species of the form $M(CO)_n^-$, which are vaporised using Electrospray Ionisation and subsequently have their ligands removed.⁴¹

In modern cluster studies, a common method of producing clusters is based around the use of lasers,³⁴ using the laser vaporisation cluster source (LVCS) developed independently by Smalley and Bondybey.^{35,36,42} Figure 1.7 shows a diagram of such a source; the source in our own experiments, described in Section 1.4, is fundamentally similar. This source is typically run in a pulsed fashion.

There are several key components of the LVCS: firstly, there is the metal target from which the lasers are produced. In early source designs, this was a fixed sample, but it was found that cluster production diminished over time, as a hole is produced in the target by constant ablation of the same spot.³⁵ It is therefore advantageous to use a moving target, such that a fresh surface is constantly presented to the ablation laser. The most common method of doing this, as shown, is to use a rotating rod; this can be mounted on a screw such that rotation simultaneously moves the rod translationally so that the area where ablation occurs slowly moves around and along the rod.³⁵ It is also possible to use a disc-shaped target which is rotated

while also being moved sideways in order to produce a spiral, rather than ablating constantly on the same circle.⁴³

With a suitable target in place, the surface of the metal is ablated by a focused, pulsed laser beam with high peak power.³⁵ The laser originally used for this was the second harmonic of a Nd:YAG (Neodymium: Yttrium Aluminium Garnet) laser, which has an output of 532 nm.³⁶ A variety of other lasers have been used, including excimer and copper vapour lasers; the choice of laser is usually arbitrary, but there are exceptions for particular systems. For example, one study found that use of a 532 nm beam produces large amounts of atomic silver, but few larger clusters, while other wavelengths successfully produce the latter species.³⁵

The effect of the laser beam on the target is to ablate material from the surface of the metal to create a plasma. There is a minimum amount of energy required by the laser beam to create this plasma. However, further increases in pulse power may have a detrimental effect on the number of molecules and clusters produced.³⁵ This can be attributed to excitation and heating of the plasma, preventing condensation of the species of interest, or to excitation of the carrier gas, which has a similar effect by energy transfer to the forming clusters.³⁵ Because of this, it is important to tune the power (and intensity) of the ablation laser reasonably precisely in order to optimise cluster production.

Having produced a plasma, it is necessary to condense this to form molecules and clusters. This is inefficient in the pure plasma due to the low metal atom density, which is a problem given the need for other particles to remove energy from the forming molecules and prevent them from dissociating again.³⁵

However, by introducing a carrier gas, extra collisions occur which enable cooling and condensation of clusters. This gas is introduced into the vacuum by a pulsed valve; the General Valve (Series 9, Parker) is perhaps most commonly used for this, along with the Jordan valve and other, piezoelectric designs.³⁵ The carrier gas chosen is usually a noble gas, typically helium, which provides a high degree of cooling of the clusters in multi-collision conditions, but can also be argon, neon, or sometimes nitrogen.³⁵ The backing gas can also be seeded with other species in order to change the distribution of species produced. For example, introduction of

N_2O is typically effective at increasing the quantity of oxide species produced,⁴⁴ while in other cases species such as CO may be introduced in order to decorate clusters with these moieties.⁵

The momentum of the gas pulse carries the condensing species down the growth channel (as labelled in Figure 1.7, also called the ‘clustering channel’), where further collisions can take place. A long channel can be used in an attempt to promote formation of large clusters by increasing the number of collisions between metal atoms, small clusters and the carrier gas; it can also be shortened or eliminated to produce larger quantities of the atom or complexes of the atom with other species.³⁵ After the growth channel, the beam expands into vacuum, at which point there are few, if any, collisions to form further clusters, while free expansion provides cooling of internal degrees of freedom. The beam passes through a skimmer and the central portion continues on to the next region for study of the species contained within it. Due to the fact that these species are formed from a plasma, these species include neutral molecules as well as both positively and negatively charged ions.⁴⁵

Given the number of variables which affect clustering (the main ones being: choice of target; laser pulse energy, focusing, and wavelength; choice of carrier gas and length of gas pulse; and length of clustering channel), it is possible to substantially change the make-up of the beam. The distribution of the clusters formed typically follows Poisson statistics, but the clustering process is not always predictable in terms of which clusters are produced in the highest amounts. Thus, it is often necessary to empirically optimise the production of a species of interest by altering one or more of these variables during the course of experiments.

1.3 Spectroscopic Study of Transition Metal Clusters

The spectroscopic study of the clusters produced by laser vaporisation or the other methods described in Section 1.2 is complicated by the low number density of the species produced.⁴⁶ The number of clusters produced per shot is estimated to

be less than 10^5 (i.e. 10^{-19} mol),⁴⁷ which precludes the recording of direct absorption spectra.⁴⁶ Absorption of light is related to the concentration of the absorbing species by the Beer-Lambert law, such that species with lower concentration absorb a lower fraction of the incident light.⁴⁸ This means that, in the case of the cluster beam, the absorption of the photons in the laser beam as a percentage of the total energy is immeasurably low. Therefore, other methods must be used to spectroscopically study metal clusters.⁴⁶

One way to get around the problem is to record spectra using Laser-Induced Fluorescence (LIF), which was used by Bondybey *et al.* to detect lead clusters in their first publication on the laser vaporisation source.⁴² This avoids the problem of the impossibility of measuring the almost negligible reduction in intensity of the beam energy by instead measuring the emission by fluorescence following photon absorption. By measuring the emitted photons perpendicular to the incident beam, they can be recorded against a zero background, such that the signal becomes detectable. This technique has been used to study multiple systems,^{42,49–52} although it is obviously (and severely) limited to those species which fluoresce.

Another approach which has become popular in recent years is to use methods which rely on ‘action spectroscopy’, where an observed effect is used to infer the absorption of a photon. In the case of cluster chemistry, this normally means a process which has a measurable effect on the mass distribution of the cluster beam. Given the scarcity of the clusters under observation, mass spectrometry has obvious advantages based around the fact that ion detectors, such as MicroChannel Plates (MCPs), can efficiently detect even small quantities of ions.⁵³ The rest of this section will focus on the process of obtaining cluster spectra by action spectroscopy.

1.3.1 Detection: Mass Spectrometry

Early mass spectrometry instruments, as developed in the early 20th century, relied on separating ions of differing masses by their different degrees of deflection when exposed to magnetic and electric fields.^{54,55} These led to the later development of Time-of-Flight Mass Spectrometry (ToF-MS), in an effort to overcome the primary

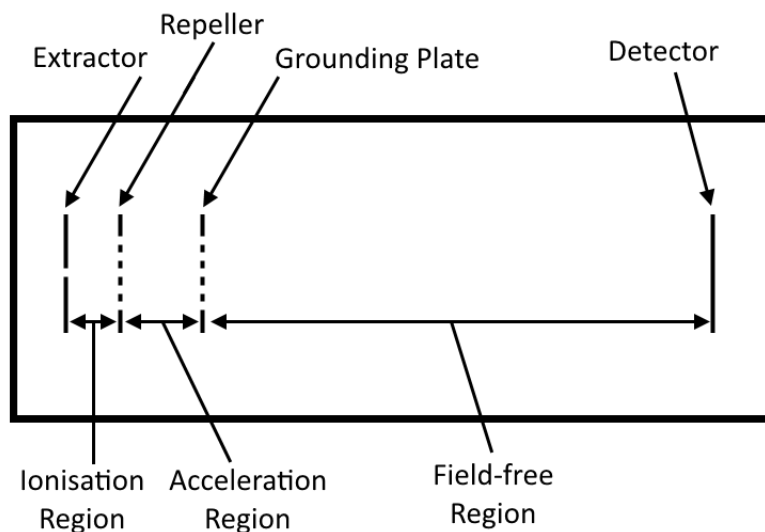


Figure 1.8: Schematic of a Wiley-McLaren Time-of-Flight Mass Spectrometer.

limitation of this technique: that it cannot record the spectrum of all species at once, but rather requires recording a spectrum as a function of the varying strength of the deflecting fields.^{56,57}

The principle behind ToF-MS is that the ions for examination are exposed to an electrical field that provides them with an increase in kinetic energy which is the same for all the ions with the same charge. Since kinetic energy is related to mass and velocity by

$$\text{KE} = \frac{1}{2}mv^2, \quad (1.1)$$

it follows that heavier (lighter) species have a lower (higher) velocity. After leaving the electric field, if the ions pass through a sufficiently long drift tube between the electrode and the detector, they will separate spatially such that the lighter, faster ions are detected first, with the heavier, slower ions having a later arrival time.

The electric field was originally created using a simple two-electrode setup, but this was improved upon by Wiley & McLaren, who introduced a third electrode, which has the effect of making the spatial resolution of the ions more forgiving of differing starting positions. Figure 1.8 shows a schematic of such a Wiley-McLaren mass spectrometer.⁵⁸ The two electrodes, the ‘extractor’ and the ‘repeller’, are held at potentials to create an electric field in order to push the ions towards the detector; the third plate, closest to the detector, is grounded, such that there is an electric

field gradient in the acceleration region before the drift tube, which is field-free. The extractor and the grounding plate usually have meshes which create a uniform field while permitting ions to pass through, although in velocity map imaging, which relies on field penetration, open electrodes are used. It may also be necessary to drill a hole in the repeller plate, as shown, depending on where the ions enter the ionisation region from.

When used with a molecular beam containing clusters created as outlined in Section 1.2, the operation of the plates depends on the charge of the species of interest. If the aim is to study ions, the plates are pulsed when the clusters are in between the electrodes, with the relative voltages determining whether cations or anions are directed into the detection region. While studying neutral clusters, the electrodes can be maintained at a constant charge in order to deflect ions before they reach the ionisation region, and a laser then used to produce ions by photoionisation which are spatially and temporally (within a mass bunch) focussed onto the detector. In this way, species of positive, negative, and no charge can all be exposed to the electric field only while they are close to the centre of the ionisation region.

In each case, it is worth noting that the ions or molecules will not occupy the same point, but will have a (hopefully) narrow spatial distribution, with some closer to the extraction electrode and others further back, closer to the repeller. This means that they have different distances to travel to the detector, but also that those produced closer the repeller will experience a larger ‘kick’ from the electric field and will thus travel faster than other ions of the same mass. If the ratio of the voltages applied to the repeller and extractor is correct, it is possible to focus all of the ions such that those with the same mass-to-charge ratio arrive at the detector simultaneously.^{57,58}

After being accelerated, the ions pass through the field free region, or drift tube, where ions with different masses are separated spatially. A longer tube will thus increase the gap between the arrival times of species travelling at different velocities, although it will not lead to an increase the resolution of the spectrum.⁵⁷ Methods have been developed to effectively increase the length of the field-free region,

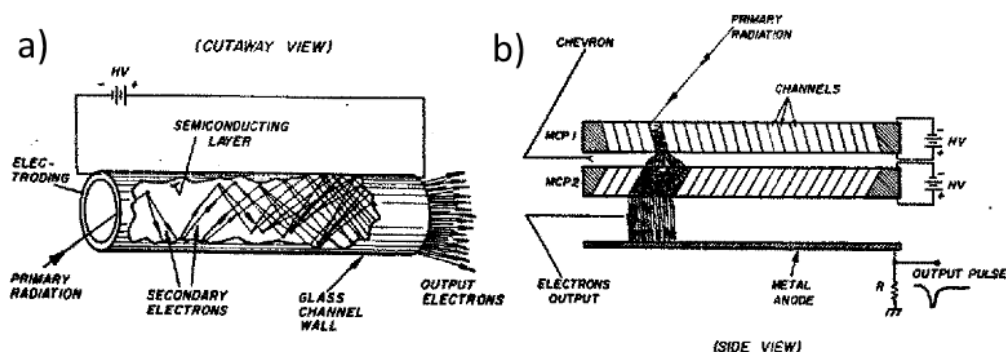


Figure 1.9: Schematic demonstration of the method of operation of a microchannel plate, showing a) the electron cascade in a single channel and b) the effect of using multiple plates in a chevron configuration. Reprinted and adapted from *Nuclear Instruments and Methods*, 162, J. L. Wiza, "Microchannel plate detectors", 587–601, Copyright (1979), with permission from Elsevier.⁵³

such as Reflectron ToF-MS, wherein a stack of electrodes at the far end of the drift tube are used to redirect the ions back along the tube in the opposite direction to a detector located near the ion source, doubling the length of the flight path. These electrodes can also increase the resolution of the mass spectrum, and, as such, reflectron mass spectrometry has been effectively used for the study of metal clusters previously.^{59,60}

Having ensured that ions of different mass-to-charge ratios reach the detector at different times, it is important to be able to detect them with high sensitivity. There are various methods of doing so, such as electron multiplier tubes,⁵⁸ but that most commonly used in modern times is the microchannel plate detector. This operates under a similar principle to the electron multiplier (and indeed, early prototypes were assembled from separate multiplier tubes),⁵³ while also offering spatial resolution which enables imaging of the locations where ions reach the detector, which is used for ion and velocity map imaging experiments.^{44,61}

Figure 1.9 shows a schematic of the key features of an MCP detector. As the figure shows, detection occurs via an electrode; however, the current generated by a single ion would be so small as to be essentially undetectable. To amplify the current, a plate with many small channels, each like the one shown in Figure 1.9a, is used.

The primary radiation, which may be a charged particle (such as an ion or an electron) or a photon,⁵³ enters one of these channels, which are angled slightly to

ensure that the radiation impacts on the side of the channel. The plate and channels have a potential difference applied across them such that when this occurs, a few electrons are emitted which are accelerated down the tube by the potential such that they impact upon the opposite wall, in turn releasing several more electrons.⁶² This process repeats itself, such that a single ion creates a cascade of many electrons.

As Figure 1.9b shows, it is common to use multiple plates with the channels arranged in a chevron configuration, such that the electrons created in the first plate subsequently impact upon the channels in the second plate, creating even more electrons, as shown. The large number of electrons created in this way are easily detectable, such that even a single ion can be detected by the electron cascade hitting the detector. The detection efficiency of an MCP detector varies, but can be as high as 85%,⁵³ such that the number of ions produced from a cluster beam are easily detectable.

It is also possible to combine MCPs with a phosphor screen in order to perform imaging, measuring not just the number of ions but their two dimensional spatial distribution; the electrons created by the plates produce a noticeable bright spot on the phosphor screen which can be recorded by a camera. This setup has been successfully used to perform imaging experiments on multiple systems in the past.^{44,63–65}

The use of this setup to perform imaging experiments is covered in Section 1.5. From here, it would be prudent to discuss different ways in which it is possible to take advantage of the detectability of cluster ions by time-of-flight mass spectrometry in order to record both electronic and vibrational spectra.

1.3.2 Electronic Spectroscopy: REMPI

Resonance-Enhanced MultiPhoton Ionisation (REMPI) is a technique which has been used for decades to study the electronic states of various species,⁶⁶ particularly since Zandee *et al.* initially used the technique in combination with a molecular beam.^{67,68} It is possible to record spectra of the electronic states of a neutral

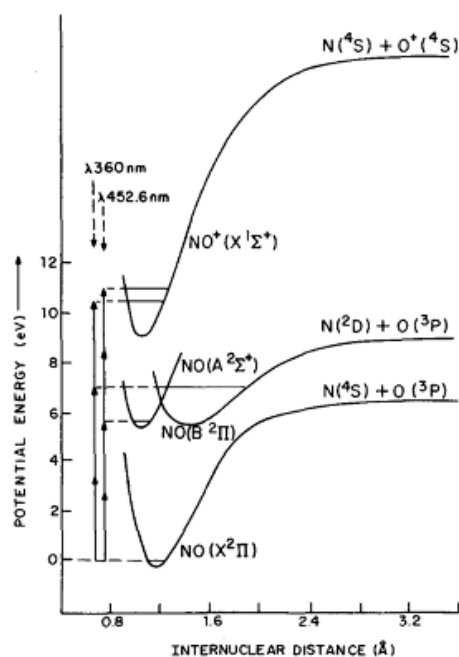


Figure 1.10: Potential energy diagram of nitric oxide, showing two REMPI schemes for ionisation, at 452.6 nm (2 + 2) and 360 nm (2 + 1). Reprinted from L. Zandee and R. B. Bernstein, *The Journal of Chemical Physics* 71, 1359–1371 (1979),⁶⁸ with the permission of AIP Publishing.

species by measuring the degree to which it is ionised by different wavelengths of light, since photon energies which are resonant with electronic states will lead to an increase in the efficiency of ionisation and hence an increase in the ion intensity.

Figure 1.10 shows a potential energy diagram to illustrate the principles of resonant multiphoton ionisation.⁶⁸ Firstly, one or more photons are used to excite the molecule from the ground state to an excited state. Further photons are then used to ionise the molecule from this excited state. While some ionisation may occur regardless of photon energy, there will be an increase in intensity at wavelengths which are resonant with the transition to the intermediate state.

There are two pathways to ionisation shown in the figure: the first, at 452.6 nm, requires two photons to excite the molecule onto the $A(^2\Sigma^+)$ state, and a further two to ionise, and is therefore denoted as a (2 + 2) transition. The second, using higher-energy photons at 360 nm, involves a two-photon $B \leftarrow X$ excitation followed by a single photon to ionise, and is designated as (2 + 1).

It is also possible to introduce a second laser of fixed wavelength, whose photon energy and fluence is chosen such that it will not efficiently ionise the ground state of a molecule, but will do so from an excited state which is reached via one or more photons from the first, tunable laser. In such a setup, it is possible to scan the first laser such that excited states are created at certain wavenumbers which enhance the number of ions created by the second beam.⁶⁹ Such ionisation schemes are denoted as $(1 + 1')$, $(2 + 1')$, and so on, where the ' indicates that the ionising photons are of a different wavelength.

By recording the intensity of the ion signal in the mass spectrum as a function of wavelength of the tunable laser, it is thus possible to record the electronic spectra of neutral cluster species. There are other means to record electronic spectra, such as laser-induced fluorescence,^{42,50} although these obviously require species which fluoresce.

1.3.3 Vibrational Spectroscopy: IRMPD

It is also possible to record vibrational spectra of metal clusters using techniques which take advantage of the sensitivity of mass spectrometry. In this case, the observed effect on the mass spectrum is from dissociation of a species using multiple infrared photons, called IRMPD (InfraRed Multiple Photon Dissociation).

In this process, infrared photons are absorbed, exciting vibrational transitions. The energy of the first photon is redistributed internally by fast Intramolecular Vibrational Redistribution (IVR),⁷⁰ and further photons are hence absorbed in the $1 \leftarrow 0$ transition of the same vibrational mode. In this way, the process proceeds via a *multiple photon* process rather than a coherent *multiphoton* transition, which involves the excitation proceeding from the $v = 1$ level on to further, higher levels.⁷¹ Due to the anharmonicity of the potential energy curves, the gap between subsequent vibrational states gets smaller as v increases, meaning that absorption of photons of the same wavelength gets progressively less efficient as the molecule continues up the ladder (known as 'anharmonic throttling'), as opposed to repeated excitation in the $1 \leftarrow 0$ transition, with IVR returning the vibrationally excited molecule to the ground state between photons being absorbed.

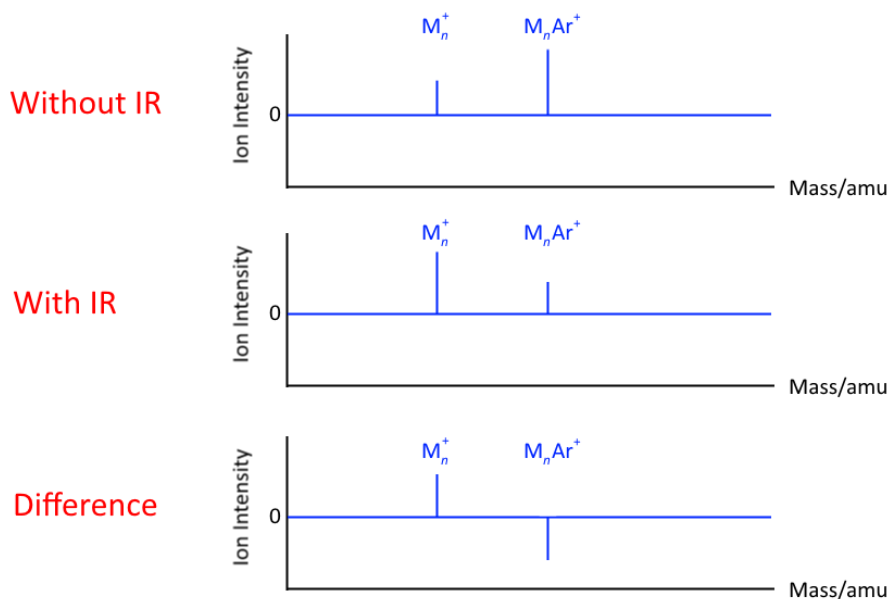


Figure 1.11: Schematic illustration of the effect of IRMPD spectroscopy. **Top:** Mass spectrum recorded before introduction of infrared beam. **Middle:** Mass spectrum recorded while cluster beam is exposed to infrared light resonant with an allowed transition in $M_n\text{Ar}^+$. **Bottom:** Difference spectrum (without IR minus with IR) illustrating the reduction in intensity of the tagged species and corresponding increase in intensity of the bare metal cluster.

After enough photons have been absorbed and the energy redistributed throughout the molecule, it is possible for dissociation to occur. To be able to record the vibrational spectra of species such as pure metal clusters or other molecules where the barrier to dissociation is prohibitively high, it is possible to use an ‘inert messenger’: a molecule or atom which binds weakly to the species of interest such that it does not distort the structure and can be easily removed by IRMPD. Examples of tagging entities include the H_2 molecule,⁷² and, perhaps most commonly, a rare gas atom.^{2,5,60} It has been demonstrated that use of an argon atom, in most cases, does not significantly affect the form of the vibrational spectrum,⁶⁰ and it can be used to record the spectrum of bare metal clusters.³

It is also possible to remove adsorbed molecules such as CO , N_2O , CO_2 etc. from the cluster of interest. However, in cases where reactivity such as that described in Section 1.1 is possible, the infrared light may also stimulate dissociation or reaction.^{4,5}

Figure 1.11 demonstrates the effect that this dissociation process has on the mass

spectrum of a cluster beam containing metal clusters and the argon-tagged equivalents. Introduction of infrared light at a wavelength resonant with a vibrational transition in the cluster results in loss of the argon tag, which can be measured using a difference spectrum. By recording the depletion of the $M_n\text{Ar}^+$ signal and enhancement of the M_n^+ signal as a function of infrared beam wavelength, it is possible to record a vibrational spectrum of the Ar-tagged counterpart of the cluster.

This process can be complicated when measuring loss of an adsorbed molecule, where multiple molecules are present in the same cluster. For example, if studying the spectroscopy of $M_n(\text{CO}_2)_m^+$ clusters (without the capability to mass-select an individual cluster), a measurement of the decrease in intensity of the $M_n(\text{CO}_2)_m^+$ signal and matching enhancement of the $M_n(\text{CO}_2)_{m-1}^+$ cluster signal from loss of a carbon dioxide molecule may be complicated by dissociation of $M_n(\text{CO}_2)_{m+1}^+$ (or larger clusters) to create the original species, as well as simultaneous dissociation of the smaller cluster to create $M_n(\text{CO}_2)_{m-2}^+$. This becomes even more complicated if multiple molecules can be lost simultaneously. Argon-tagging therefore has the additional advantage of making the process less ambiguous by reducing the problem to loss of an argon atom to create a bare cluster.

IRMPD can also be used on neutral clusters, if the contents of the beam are subsequently ionised by a separate laser after the action of the infrared beam.⁷³ This means that, particularly in combination with argon tagging, it is a broadly applicable method which can be used to record the vibrational spectrum of a variety of clusters.

1.3.4 Summary

Action spectroscopy methods based on measuring the contents of a molecular beam using time-of-flight mass spectrometry, and recording the effects of different wavelengths of radiation on the mass spectrum, can thus be used to record electronic and vibrational spectra of metal clusters. This thesis will contain electronic REMPI spectra, while the results will be relevant to the IRMPD spectroscopy described in Section 1.3.3.

There is one other method for the study of metal clusters which will be of particular relevance to this thesis: Velocity Map Imaging (VMI). This will be described in Section 1.5 along with the procedures used to analyse the images recorded, while Section 1.4 will outline the details of the experimental setup used for collecting the data used in this project.

1.4 Experimental Setup

Figure 1.12 shows the experimental apparatus used in this project for spectroscopy and imaging. The details of this setup are described through the rest of this section.

Experiments are conducted in a vacuum chamber (constructed of commercially made pieces) maintained at a high vacuum by three turbo-pumps. These are indicated by the large, open arrows at the bottom of the diagram: one is attached to the chamber where the clusters are produced (Edwards STP-A1603C, backed by an Edwards E2M40 rotary pump), another near the ionisation region (BOC Edwards EXT75DX, with an Edwards XDS10 dry scroll pump), and the third is attached to the drift tube (Leybold TURBOVAC361, backed by a Leybold TRIVAC rotary pump). Overall, typical pressures inside the chamber are on the order of 10^{-8} – 10^{-9} mbar.

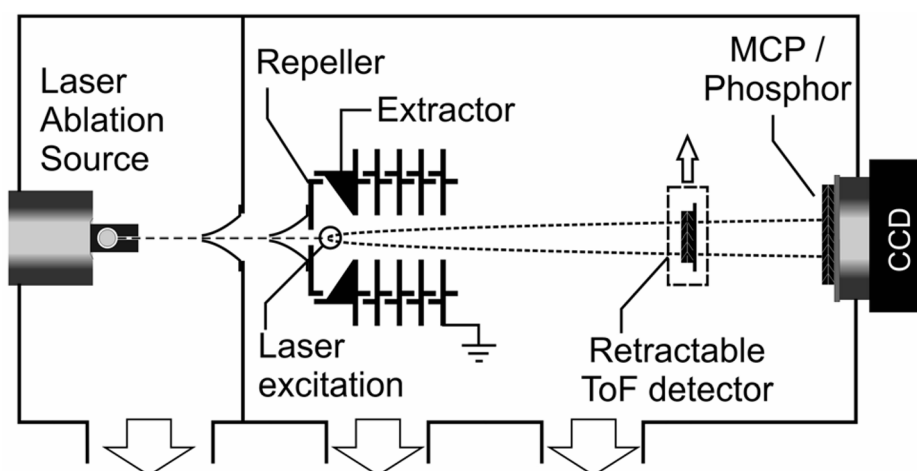


Figure 1.12: Schematic representation of the experimental setup used in this thesis, and described in detail in the text. Adapted from I. S. Parry, A. C. Hermes, A. Kartouzian, and S. R. Mackenzie, *Physical Chemistry Chemical Physics*, 2014, 16, 458-466 with permission from the PCCP Owner Societies.⁴⁴

The clusters are produced using a laser vaporisation cluster source similar to the one shown in Figure 1.7. The chief difference is that a disc of metal is used as a target, rather than a rod. This disc is rotated continuously during operation such that a circular section of metal is ablated rather than a single spot. The target is regularly translated in order to present a new track for ablation and thus prevent permanent, damaging wear to the target. The targets themselves are small discs (ca. 1 cm in diameter and ca. 1 mm in thickness) cut from foils of high purity ($> 99.9\%$) metal, which are provided by Goodfellow (silver) or Sigma-Aldrich (chromium and molybdenum).

The instrument is operated in a pulsed fashion, at a 10 Hz repetition rate; all of the steps (ablation laser, gas pulse, excitation/ionisation, detection etc.) are synchronised by a pulse generator (BNC). The target is ablated by the second harmonic of a Nd:YAG laser, at 532 nm. This was initially a Litron Nano laser, which was later replaced by a Continuum Minilite; each chapter's experimental section will detail which laser was used for each experimental run. Both lasers are capable of producing over 30 mJ per pulse, but lower powers (ca. 10–15 mJ per pulse) are typically used for ablation. The exact laser power is optimised empirically to produce the highest number of clusters in the molecular beam for the particular metal target being studied. The beam is focused by a lens ($f = 25$ cm) to a spot of less than 1 mm in diameter on the surface of the target.

Clusters are then condensed from the resulting plasma and entrained in a molecular beam using a pulse of carrier gas. This is either helium or argon, depending on the system being studied, both being of high purity ($> 99.9\%$) and supplied by BOC Gases. This can be seeded with other gases, such as N_2O , as required; these are also supplied by BOC Gases. The gas is pulsed into the chamber by a valve. In Chapter 2 and Section 3.3.3, this is a valve supplied by Jordan TOF Products, while the other chapters use a solenoid-based General Valve (Parker Series 9). The different valves have different advantages: the solenoid valve creates a gas pulse of longer duration, while the shorter pulse length of the Jordan valve allows higher backing pressures to be used (in practise, the backing pressures used here tend to be ca. 7–8 bar). When the Jordan valve was introduced to our setup, it was believed

that the higher pressures would aid clustering,⁴⁴ while there is evidence that the longer gas pulse durations also aid cluster formation.³⁵

The clusters then pass through a skimmer (Beam Dynamics, 2 mm ϕ) and into the region of the electrodes. These are maintained at a constant positive voltage by high voltage power supplies (Stanford Research Systems), meaning that only neutral molecules are studied due to the repulsion or deflection of charged species. The electrode arrangement is based on the Wiley-McLaren arrangement described in Section 1.3.1, with two notable alterations.

Firstly, a conical design is used for the extractor electrode. Based on ion modelling using the SIMION 8.0 software package,⁷⁴ it is believed that this arrangement reduces field penetration from the region between the extractor and the grounding plate into the ionisation region, creating a more homogeneous field.^{63,75} This was designed for use with unfocused laser beams, which produce ions in a larger volume. The homogeneity means that the focusing conditions are more forgiving of this, while also reducing magnification of the image (see Section 1.5.3).

Secondly, rather than the simple three-plate design, a stack of plates between the extraction electrode and the grounding plate are used. There are three extra electrodes, which are connected by resistors such that their voltages are stepped down to ground in equal increments.⁶³ This increases the time-of-flight of the ions by increasing the time and distance over which acceleration occurs, which enables processes where the fragments are created with low initial velocities to be better observed.

It is in the centre of the region between the repeller and the extractor that the clusters are excited by lasers, which intersect with the molecular beam at right angles. Since the species studied here are neutral, it is also necessary for them to be ionised in this region such that they are then projected towards the detector by the electrodes. For excitation and ionisation, three different lasers are used:

- A tunable dye laser (Sirah Cobra Stretch), which is combined with a Second Harmonic Generation (SHG) unit to create ultraviolet light. This can be used with a range of dyes to reach different wavelengths, and the dye used is detailed in each chapter as applicable. The laser is pumped by either the

second (532 nm) or third (355 nm) harmonic of a Nd:YAG laser (Continuum Surelite), depending on the requirements of the dye. Typical powers can be up to 20 mJ per pulse in the fundamental and up to 5 mJ of doubled output, although this varies with dye efficiency.

- An Optical Parametric Oscillator (OPO; Continuum Panther Ex), pumped by the third harmonic (355 nm) of a Nd:YAG laser (a separate Continuum Surelite). This outputs in the visible range (400–700 nm), with energies of around 15 mJ per pulse. The nature of the oscillator also leads to generation of a second beam called the ‘idler’ which varies in the range 700–2550 nm, but this is not used here.
- A 157 nm F₂/He excimer laser (Neweks PSX-501) which can reach pulse energies of ca. 1.3 mJ. The fill gas is supplied as a 2% fluorine mixture by CK Gases and diluted with pure helium (BOC Gases) to reach a fluorine percentage of 0.1%. Given that this is a fixed frequency laser, it is of limited use spectroscopically, but the high energy photons are very useful for their ability to ionise most neutral species. This laser is mostly used to determine the contents of the molecular beam, although it has been used for imaging experiments in the past.⁶³ This wavelength of light is readily absorbed by molecular oxygen,⁷⁶ which requires a purge tube filled with N₂ (BOC Gases) to be used.

The tunable lasers can be used with or without a focusing lens, as required by the experiment, while the purge tube required by the excimer laser precludes its use with a lens in our setup. It is also possible to use multiple beams at the same time; a combination of the OPO and the dye laser has previously been used to study copper clusters.⁴⁴ It is also worth noting that the tunable laser beams are plane polarised, with the direction of polarisation being maintained perpendicular to the velocity vector of the molecular beam (parallel to the detector). This affects the anisotropy observed in imaging experiments, as outlined in Section 1.5.5.

After the clusters (or dissociation fragments, where applicable) have been ionised, the electric field of the electrodes pushes them towards the detector. As shown in Figure 1.12, extraction is conducted parallel to the molecular beam, and there are

two possible means of detecting the ions. For the recording of mass spectra (and hence REMPI spectra), a retractable MCP detector is used, the output of which is connected to an oscilloscope (LeCroy Wavesurfer 64MXs-A). This is in turn connected to a computer running a LabView routine to record mass spectra and/or electronic spectra as described in Section 1.3.2. The voltage across the microchannel plates is maintained by two high voltage power supplies (Stanford Research Systems).

Alternatively, this detector can be translated out of the beam path such that the ions continue on to an MCP/phosphor detector at the far end of the drift tube. This is connected to a CCD camera (Photek VID240), which can record two-dimensional images of where the ions reach the detector for imaging experiments. The MCPs for this detector are pulsed, such that only ions of a certain mass are imaged, as those outside the gate will not produce an electron cascade and resultant spot on the phosphor screen. The images are recorded using a proprietary program as text images, and analysed as described in Section 1.5.

1.5 Velocity Map Imaging

1.5.1 Background and Principles

Velocity map imaging developed from earlier ion imaging techniques for imaging dissociative processes. For example, one approach to studying the shape and anisotropy of the distribution of products of fragmentation processes was to record mass spectra at different angles using a rotatable detector.⁷⁷

One of the earliest attempts to use a direct imaging process to study photodissociation was made by Chandler & Houston, who studied the dissociation of methyl iodide.⁷⁹ To do so, they dissociated the molecule, allowed time to elapse for the fragments to move apart with a particular recoil velocity, and then imaged their positions. This imaging used spatial mapping — the position on the MCP/phosphor array at which the ions were detected depended on their location in the ionisation region at the time when they were extracted.

This field of study was later enhanced by the development by Eppink & Parker of velocity map imaging.^{78,80} With this technique, rather than the spatial position of the particles being mapped to a particular location on the detector, their velocities are instead. That is, all particles with the same *velocity*, regardless of location inside the ionisation region, are mapped onto the same location on the detector (as shown in Figure 1.13).⁷⁸ This allows for a more precise measurement of their velocities.⁸⁰

VMI has been used to study a wide variety of fragmentation processes, and provided significant insight into photodissociation dynamics. Within our group alone, it has been previously used to study the dissociation of Au_2 ,⁶³ Au-RG ($\text{RG} = \text{Ar}, \text{Kr}, \text{Xe}$),^{61,81} $\text{Li}(\text{NH}_3)_4$,⁸² Xe_2 ,^{83,84} Cu_2 , and CuO .⁴⁴ This section will outline how we can convert the images recorded using VMI to Kinetic Energy Release (KER) spectra, and how these can be used to determine the dissociation energy of a molecule.

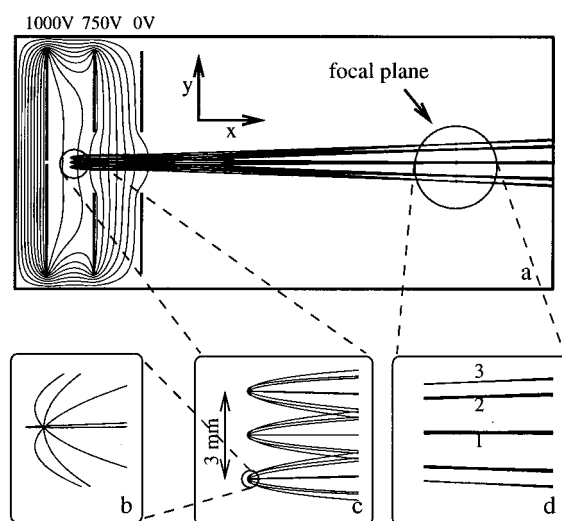


Figure 1.13: Illustration of the velocity mapping principle using simulated ion trajectories. The overall apparatus is shown in (a); ions are generated at three different points in the ionisation region, as shown in (c). These are given initial velocities along eight different vectors at 45° in the x - y plane as shown in (b). At the focal plane (d), where the detector would be located, those particles with the same initial velocity but different starting locations are focused. The three numbered trajectories are for ions generated: (1) in the x -direction ($0^\circ/180^\circ$); (2) at a $45^\circ/135^\circ$ angle; or (3) in the y -direction (90°). Reprinted from A. T. J. B. Eppink and D. H. Parker, *Review of Scientific Instruments* 68, 3477–3484 (1997),⁷⁸ with the permission of AIP Publishing.

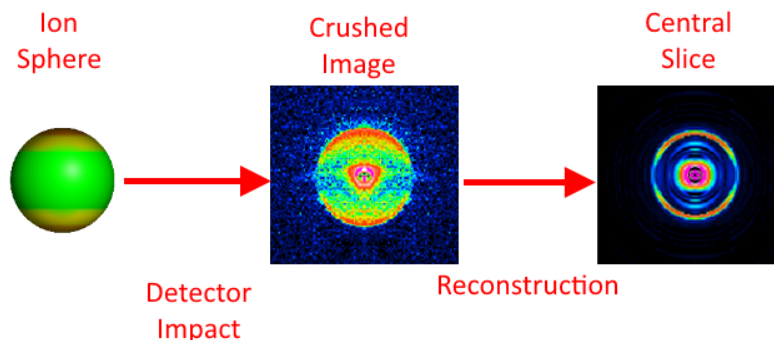


Figure 1.14: Illustration of the process of image recording and reconstruction: a three-dimensional ion sphere is flattened onto the detector to produce a two-dimensional image, from which a slice through the centre of the sphere can be reconstructed.

1.5.2 Image Reconstruction: Abel Inversion

In general, the result of a photodissociation process into a particular dissociation channel will be a sphere of expanding fragments, which are generated with initial velocities pointing in all directions (in practise, there may be some anisotropy in the sphere; this will be returned to below). As the particles are projected down the drift tube towards the detector, this will result in an expanding ‘Newton sphere’ of ions, which will collide with the detector and be flattened to a two-dimensional array. Given that there may be multiple dissociative processes, it is possible for there to be multiple concentric spheres of differing radii, which must be detected by analysing the radial intensity distribution within the overall sphere of ions.

In order to be able to determine the radial and angular structure of the sphere, it is necessary to be able to extract a slice through the centre of the sphere. There are two main ways to achieve this, one of which is to use ‘slice imaging’ to only record the central slice, by using a very narrow gate width to select only the ions in the central slice of the Newton sphere.^{65,80,85}

The other option is to record the crushed image which results from the flattening of the Newton sphere onto the detector, and reconstruct the form of the central slice from this (as illustrated in Figure 1.14). In our setup, we have focused on the latter approach, such that the whole of the relatively weak ion signal can be used.

The conversion from the central slice to the crushed image is described by an Abel transformation, which is a relatively straightforward and well-behaved function. However, the inverse Abel transformation (or Abel inversion) is a much more difficult proposition.^{80,86} A variety of techniques have been developed to calculate the Abel inverse of a crushed image in order to reconstruct the central slice. Several of these are described in Chapter 5, along with a history of their development; for now, this section will focus solely on the details of the algorithm used throughout the majority of this thesis, Polar Onion Peeling (POP).

Polar Onion Peeling in the incarnation in which it is used here is based on the implementation of the algorithm as a LabView program by Roberts *et al.*,⁸⁷ although the development can be traced back through the introduction of the use of polar coordinates by Zhao *et al.*⁸⁸ to earlier versions of the onion peeling approach.^{89,90}

The principle of the approach, from which the name derives, is that it is possible to unpick the structure of the Newton sphere by ‘peeling away’ intensity from the processes with the largest kinetic energy release and working inwards, like peeling an onion. This is performed in polar coordinates, which requires that the image (which is recorded using Cartesian pixels) be converted to polar pixels. However, these pixels do not quite match up precisely, producing some minor ‘smearing’ of intensity, where ions with a very narrow radial distribution may still end up distributed over two or more pixel radii due to the mismatch.

A sphere of ions resulting from a single process with a particular initial velocity will appear as a ring when compressed to two dimensions. The diameter of the ring observed will be equal to the diameter of the sphere, or equivalently of a slice through the centre parallel to the detector, which is what we are attempting to reconstruct. However, while in the central slice the only intensity from this process will be along the ring, the crushed image will display some intensity at smaller radii due to those ions on the sphere which are not in the central slice, but are instead closer to the axis of the molecular beam.

The approach taken by POP is to begin at the outside of the recorded image, at the largest recorded radius, and move inwards to smaller radii. When there is some intensity present in the recorded image, the algorithm calculates what the shape

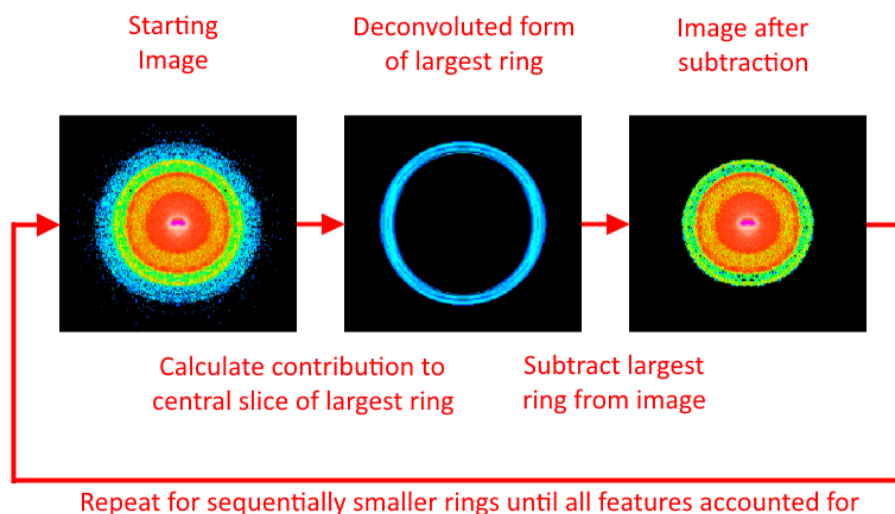


Figure 1.15: Illustration of the process followed by the Polar Onion Peeling algorithm as described in the text. Each ring is peeled away sequentially to reconstruct the overall form of the central slice.

and intensity of a sphere of that radius would have to be in order to explain the intensity in this largest radius, and records this in terms of the form of the central slice at that radius.

The algorithm then calculates what the contribution of this sphere would be to smaller radii in the crushed image, and this is subtracted from the data. The program then moves to the next largest radius, and repeats the process whenever it encounters intensity in the crushed image. This process is illustrated in Figure 1.15.

It is important to note that this approach depends upon the cylindrical symmetry of the ion sphere around the axis of polarisation of the excitation/ionisation laser. This assumption also means that the algorithm is able to symmetrise the crushed image into a single quadrant before onion peeling.

The algorithm as created by Roberts *et al.* is able to speed up the calculations required by using basis functions to calculate the relationship between a Newton sphere and its crushed form.⁸⁷ This means that the process of running an image through the POP LabView routine is computationally cheap and time efficient.

All images presented in this thesis will be shown split vertically into two halves. In each case, the left side of the image shows the raw data recorded (i.e., the crushed sphere), and the right shows the reconstructed central slice.

1.5.3 Kinetic Energy Release Spectra

After reconstructing the form of the central slice of the ion sphere from the raw, crushed image, this can then be used to extract the kinetic energy release spectrum of the photodissociation. The size of the Newton spheres, and hence the radii of the rings in the reconstructed image, depends on the velocity with which the fragments are repelled following dissociation. This section outlines how this information can be converted to the more useful knowledge of the energy released in the process.

The first step in producing a KER spectrum is to perform radial averaging; that is, to find the average intensity in all polar pixels at a particular radius, providing a spectrum of ion intensity as a function of radius. This radial distance must then be converted to initial velocity of the ions, which is possible using the fact that the distance travelled by the fragment in the centre-of-mass frame of reference, decoupled from the distance travelled by the ions from the electrodes to the detector, is known, and the time-of-flight of the ions during which they were able to move away from the centre of mass. Using a simple velocity-distance-time relationship, it is therefore possible to calculate the velocity imparted to the ions on fragmentation.

Given knowledge of the mass of the ion which is being detected, it is possible to calculate the fragment Kinetic Energy Release (fKER; the kinetic energy only of the fragment being imaged, as distinct from the total energy released) using

$$\text{KE} = \frac{1}{2}mv^2, \quad (1.2)$$

where m is the fragment mass and v is the initial velocity of the fragments as calculated above. KER can be measured in a variety of units, but is typically reported in wavenumber units throughout this thesis, to give a measurement of the dissociation energy of the parent molecule in cm^{-1} .

The nature of the VMI focusing produces a magnification effect, where the rings observed are slightly larger than they would be expected from their initial velocity and time-of-flight. This effect is described by a Magnification Factor (MF), such that the ‘true’ radius of a ring is found from the observed radius by multiplying by

a factor $\frac{1}{\text{MF}}$. Since the kinetic energy of the fragment is proportional to the square of the velocity, and hence of the radius, it is therefore true that the actual kinetic energy is related to that calculated directly from the images by a factor of $\left(\frac{1}{\text{MF}}\right)^2$.

The magnification factor varies with the particular conditions of the imaging experiment, and is calculated for each experimental run as described in Section 1.5.4, but typical values are in the range 1.05–1.10. For example, in Chapter 2, a value of 1.090 is used.

All of this examination of the kinetic energy has referred solely to the fragment being imaged. However, in a dissociation process, multiple fragments are produced. Fortunately, for a dissociation which creates two fragments, it is possible to calculate the total kinetic energy release (TKER) of all of the fragments using conservation of momentum.

For a general molecule MX, where M is the fragment being imaged and X is the co-fragment, conservation of momentum dictates that in the centre of mass frame:

$$m_M v_M + m_X v_X = 0. \quad (1.3)$$

Using Equations 1.2 and 1.3, the total kinetic energy release can be determined from the kinetic energy of the imaged fragment like so:

$$\begin{aligned} \text{TKER} &= \text{KE}_M + \text{KE}_X \\ &= \text{KE}_M + \frac{1}{2} m_X v_X^2 \\ &= \text{KE}_M + \frac{1}{2} m_X \left(\frac{m_M v_M}{m_X} \right)^2 \\ &= \text{KE}_M + \left(\frac{m_M}{m_X} \right) \left(\frac{1}{2} m_M v_M^2 \right) \\ &= \text{KE}_M + \frac{m_M}{m_X} \text{KE}_M \\ &= \frac{m_M + m_X}{m_X} \text{KE}_M \\ &= \frac{m_{\text{MX}}}{m_X} \text{KE}_M. \end{aligned} \quad (1.4)$$

When the masses of both the co-fragment and parent molecule, m_X and m_{MX} , respectively, are known, the TKER can be determined from the fragment kinetic energy. As explained in Section 1.5.4, this relationship can also be used to determine the mass, and hence identity, of the co-fragment. Figure 1.16 illustrates the overall process of how a sample TKER spectrum might be extracted from the peeled image of a fragment.

Each point in the spectrum corresponds to a ring in the peeled image, and hence to a Newton sphere resulting from a dissociation process, with peaks identifying particular exit channels. The Total Kinetic Energy Release of this process can be found by fitting these peaks to a functional form, for which, in this thesis, a Gaussian function has been used. The peak centre is then used as the TKER of the dissociation, and the full width at half maximum (FWHM) of the peak is treated as a measure of the uncertainty. In practise, the centre of the peak is somewhat better known than the FWHM, but this has been used as a slightly generous value for the error to ensure the uncertainty in the numerical values deduced from the TKER is not underestimated.

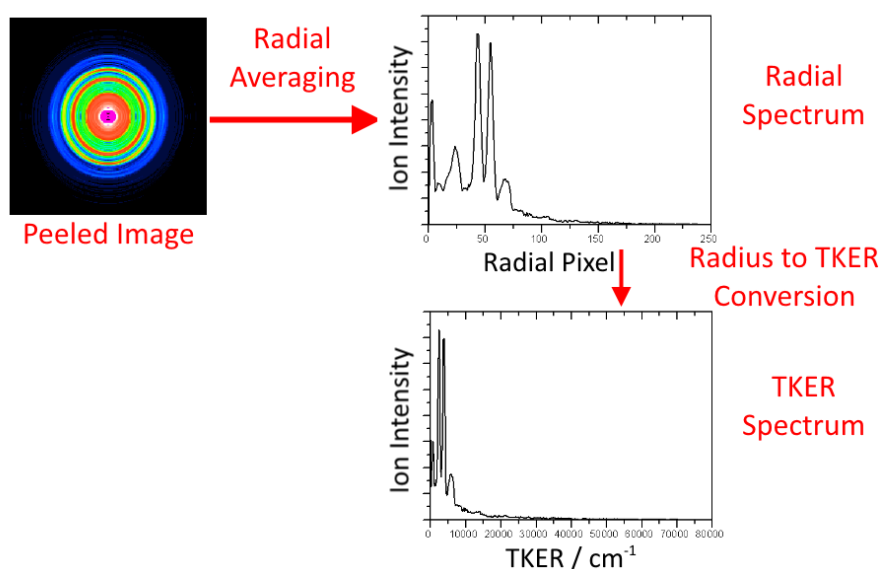


Figure 1.16: Illustration of the conversion from the peeled image produced by POP to a TKER spectrum via radial averaging and axis conversion as described in the text

1.5.4 Analysis of Kinetic Energy Data

Identity of the Parent Molecule

In order to be able to draw any conclusions from the TKER data thus acquired, it is worth considering how this energy release is related to the photodissociation process from which it originates. Figure 1.17 shows generic potential energy surfaces with a schematic of the energy changes occurring during photofragmentation.

For a process driven by n photons, it can be seen by simply equating the amount of energy added to the system to the energy required for the dissociation that:

$$nh\nu = \text{TKER} + E_{\text{M}} + E_{\text{X}} - E_{\text{MX}} + D_0(\text{MX}) \quad (1.5)$$

where $h\nu$ is the photon energy and E_{M} , E_{X} , and E_{MX} are the internal energies of the metal fragment, the co-fragment, and the parent molecule, respectively. Of all the terms in this equation, only the photon energy and the TKER are variables; the

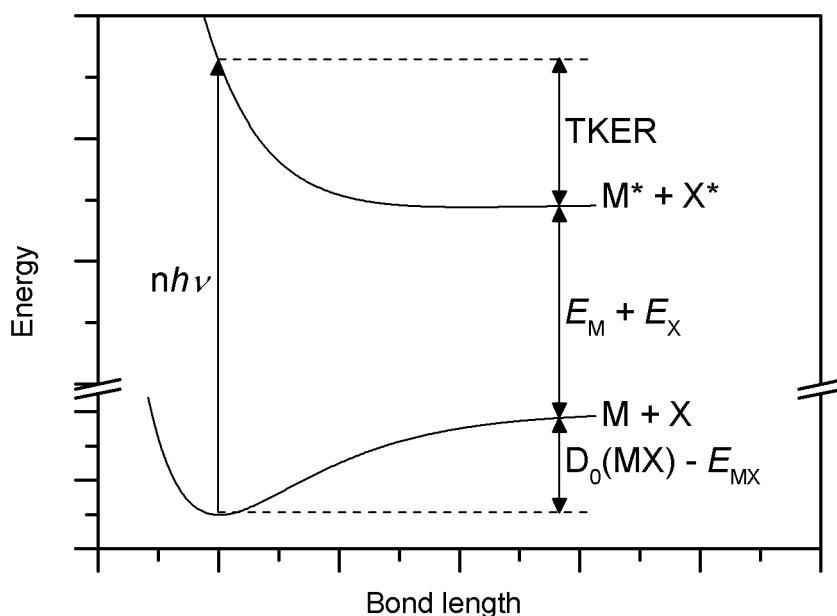


Figure 1.17: Generic potential energy surfaces of a bound ground state and dissociative excited state which correlates to excited atomic fragments. A photodissociation process is shown, which involves n photons and the resulting disposition of energy.

others are all constants depending on the identity of the parent molecule and the energy of the states involved in the dissociation process. This implies that there should be a simple linear dependence between the energy of the photons used for the dissociation and the kinetic energy release observed using VMI.

Given that the photon energy is the independent variable, it is more helpful to rewrite Equation 1.5 as:

$$\text{TKER} = nh\nu + E_{\text{MX}} - E_{\text{M}} - E_{\text{X}} - D_0(\text{MX}). \quad (1.6)$$

If multiple images are acquired at different wavelengths, and the total kinetic energy release of each observed ring is found as outlined in Section 1.5.3, these values can then be plotted as a function of photon energy. These data points, if they all correspond to the same fragmentation process, will thus form a straight line with an integer slope equal to the number of photons involved in the dissociation process.

There is, however, one complication involved in this process. Up to this point, it has been assumed that the identity of the parent molecule is known, allowing for a simple conversion from fKER to TKER. In most VMI experiments, this is a reasonable assumption, since the parent molecule can be chosen by use of either a stable precursor molecule or by dissociating mass-selected ions.⁷⁷ However, by studying the dissociation of neutral molecules, the use of mass selectivity is precluded, and the laser vaporisation cluster source tends to produce a wide range of different clusters and molecules.³⁵ This means that the parent molecule must be identified for a particular dissociation process on a case-by-case basis.

There may be various pieces of evidence for the nature of the parent molecule. For example, if changing the composition of the carrier gas for the molecular beam affects the intensity of the rings observed, this may provide evidence that formation of the parent molecule depends on the gas added or removed. It may also be that only a few species are present in the molecular beam, such that the number of candidates for the parent molecule is limited. However, there have been cases where the parent molecule for a dissociation is not observed in the mass spectrum of the molecular beam.⁴⁴

The main approach to identifying the co-fragment, and hence the parent molecule, is to chart the fragment kinetic energy against photon energy. Equation 1.6 can be simplified to give:

$$\text{TKER} = n h \nu + \alpha \quad (1.7)$$

where $\alpha = E_{\text{MX}} - E_{\text{M}} - E_{\text{X}} - D_0(\text{MX})$ is a constant, and, combining this with Equation 1.4, it can be seen that:

$$\begin{aligned} \text{KE}_{\text{M}} &= \frac{m_{\text{X}}}{m_{\text{MX}}} \text{TKER} \\ &= \frac{n m_{\text{X}}}{m_{\text{MX}}} h \nu + \beta \end{aligned} \quad (1.8)$$

where $\beta = \frac{n m_{\text{X}}}{m_{\text{MX}}} \alpha$ is another constant.

This implies that a plot of values for the fKER of a process against photon energy should be a straight line with a slope of $\frac{n m_{\text{X}}}{m_{\text{MX}}}$. In order to account for the magnification factor mentioned in Section 1.5.3, the slope, μ , of a best-fit line through the points found by plotting the observed kinetic energy of the imaged fragment as a function of photon energy will be:

$$\mu = \text{MF}^2 \frac{n m_{\text{X}}}{m_{\text{MX}}}. \quad (1.9)$$

which can be rearranged (using the fact that $m_{\text{MX}} = m_{\text{M}} + m_{\text{X}}$) to give:

$$m_{\text{X}} = \frac{\mu m_{\text{M}}}{n \text{MF}^2 - \mu}. \quad (1.10)$$

The fact that n must be an integer limits the number of solutions to Equation 1.10. Attempting to calculate both the magnification factor and the co-fragment mass simultaneously is tricky; the best approach at this stage is to assume a unity magnification factor and use the simplified version of Equation 1.10 that results to calculate the mass of the co-fragment for a particular integer value of n . These will be slightly larger than the actual mass of the co-fragment, but some knowledge of the species present in the molecular beam, common sense, and chemical intuition is sufficient to identify possible identities for the co-fragment and the values of the magnification factor which would be required in each case.

It is possible that there will be two or more potential assignments, at which point it is necessary to use other information to identify the parent molecule. Once this has been accomplished, the correct values for n , m_X , and MF will be known. In this fashion, from a simple best fit through plotted values of observed fKER as a function of photon energy, the number of photons involved in the dissociation, the identity of the co-fragment (and hence the parent molecule) and an estimate of the magnification factor can be obtained simultaneously. This process will be used throughout this thesis to justify the assignment of the parent molecule for a particular set of data.

In the case where multiple series of rings are observed in a set of experiments, this process can be repeated to assign the parent molecule and number of photons for each, and to obtain independent measurements of the magnification factor. The values for the latter can be averaged together to give a value for MF which is used for all images in that experimental run.

Dissociation Energy of the Parent Molecule

Once this has been accomplished, it is possible to convert the observed fKER to TKER values using the magnification factor and the ratio of masses (in accordance with Equation 1.4). These can be plotted against photon energy and a line of best-fit found. With the number of photons involved also identified, it is possible to fix the slope of this line (which will be equal to n) to improve the fit.

It is possible to find one more piece of information from the TKER data using Equation 1.5. By extrapolating the line of best-fit back to the threshold for the process (i.e., the photon energy at which TKER = 0), it is true that this threshold value of $h\nu$ can be related to the internal energy of the species involved and the dissociation energy of the molecule using:

$$nh\nu = E_M + E_X - E_{MX} + D_0(MX). \quad (1.11)$$

Thus, if the states involved in the fragmentation can be assigned such that the values for E_M , E_X , and E_{MX} are known, the dissociation energy can be directly measured by relating it to the threshold for a dissociative process.

There are various means to determine which states are involved, such as using the best literature values for D_0 to estimate the internal energies of the products and match these up to known energy levels. Alternatively, in cases where multiple dissociative channels from the same molecule are observed, the gap between the rings may be used to calculate the gap between the product energy levels, which can prove useful. The method used to assign each series in this thesis will be explained on a case-by-case basis.

Figure 1.18 summarises the process of using kinetic energy spectra to find an assignment of the process being observed, and hence extract a measurement of the dissociation energy.

The experimental uncertainty in the value of the dissociation energy found in this way is calculated using error propagation from several sources. Firstly, as explained in Section 1.5.3, the width of the peaks fitted to features in the kinetic energy spectra is used as the main source of uncertainty in the individual TKER values.

Secondly, prior to assigning the co-fragment mass and photon number, the gradient of the fit through the raw fKER points has some uncertainty in it, which is translated into uncertainty in the magnification factor calculated from this in the manner mentioned above. This uncertainty (or the uncertainty in the average value where multiple series are available) is propagated into the uncertainty in the TKER values, since these are calculated from the raw fragment kinetic energy using the magnification factor.

This provides an overall error for each point in a plot of TKER as a function of photon energy, which is accounted for by the process of fitting a best line through these points, resulting in an overall uncertainty in the threshold photon energy used in Equation 1.11. This thus depends on the width of the peaks in the kinetic energy spectra, how many points are available for a particular series of rings, how far from the best fit line these points lie, and the uncertainty in the magnification factor.

Finally, the uncertainty in values for the internal energies are generally negligible (the energies of atomic levels being known to high precision)⁹¹. However, there are

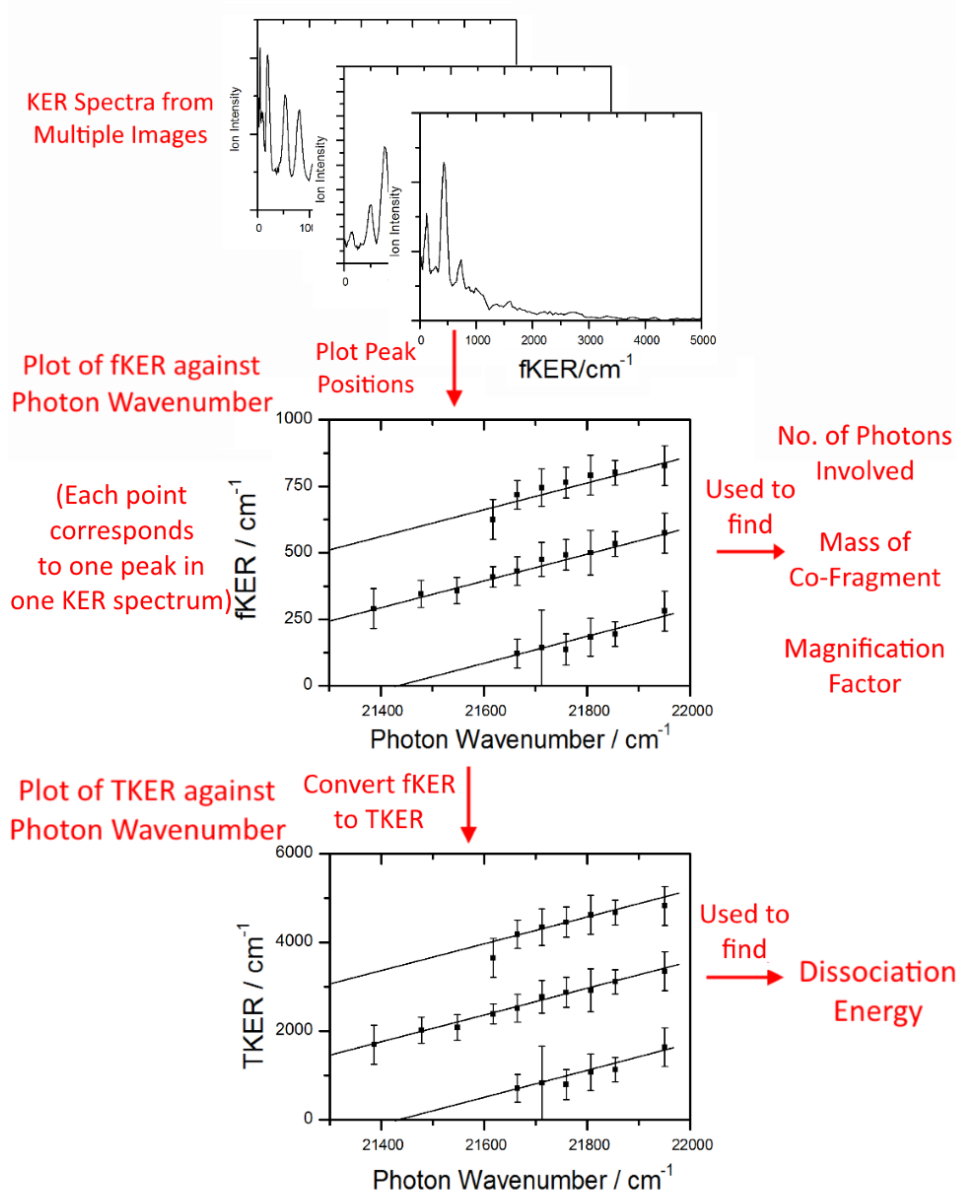


Figure 1.18: The process used to extract the number of photons used for dissociation, the mass of the co-fragment, the magnification factor, and the dissociation energy from multiple velocity map images.

sometimes cases where multiple energy levels are not resolved within the width of the peaks in the kinetic energy spectra, particularly when a level consists of multiple spin-orbit split components relatively close together. In such cases, the mean energy of the unresolved components is used for the internal energy, and the standard deviation is used as a measure of the uncertainty on this value. This is

combined with the uncertainty in the threshold photon energy to reach an overall value for the uncertainty in D_0 .

1.5.5 Anisotropy of Rings

While the radial distribution has been demonstrated to yield information about the dissociation energy of the species under examination, no mention has yet been made of the form of the angular distribution of the rings. The rings observed do not always display the same intensity at different angles, as demonstrated by the image shown in Figure 1.14, which possesses significant anisotropy.

The extent of anisotropy can be determined by plotting the intensity for a certain radius as a function of θ , defined as the angle from the direction of the polarisation vector of the laser, which is vertical for all of the images presented here. For a one-photon dissociation, this intensity function, $I(\theta)$, has been shown to have the form:

$$I(\theta) \propto 1 + \beta_2 P_2(\cos \theta) \quad (1.12)$$

where $P_2(\cos \theta)$ is the second order Legendre polynomial, $\frac{1}{2}(3 \cos^2 \theta - 1)$.^{92,93} For a parallel transition, such as $\Sigma \rightarrow \Sigma$, $\Pi \rightarrow \Pi$, and $\Delta \rightarrow \Delta$,^{92,94} it is expected that the anisotropy parameter, β_2 , will have a value of 2. This indicates high intensity in the direction of the polarisation vector and no intensity in the perpendicular direction; by contrast, a perpendicular transition will give $\beta_2 = -1$, indicating the opposite distribution.^{95,96} There are a variety of reasons why the limiting values of β_2 may not be observed, ranging from experimental causes such as noise, to mixed transitions, or depolarisation due to the lifetime of the excited state.⁹⁶

The Polar Onion Peeling algorithm automatically fits the angular distribution at each pixel radius to Equation 1.12, producing values of β_2 for every radius. However, these only have particular meaning when there is a ring present, rather than the random fluctuations of background noise. It is also possible to fit these manually over a radial range, although this tends to produce similar results.

The values of β_2 for any ring demonstrating significant anisotropy in an image can therefore be used to determine the relative symmetries of the lower and upper

states for a one-photon transition. This is useful data which can be used to support an assignment when information about the electronic states of a molecule is available.

In the case where multiple photons are involved in a transition, the picture becomes more complicated. For example, for a two-photon excitation, the θ -dependence of the intensity can be described by:

$$I(\theta) \propto 1 + \beta_2 P_2(\cos \theta) + \beta_4 P_4(\cos \theta) \quad (1.13)$$

where $P_4(\cos \theta)$ is the fourth order Legendre polynomial, $\frac{1}{8}(35 \cos^4 \theta - 30 \cos^2 \theta + 3)$,⁹⁷⁻⁹⁹ while further photons require even higher order terms.¹⁰⁰ This makes analysis more complicated, and no interpretation of β_4 or higher order anisotropy parameters is presented in this thesis. The increased number of polynomials required does play a part in the case of image extraction methods which rely on a basis set of polynomial functions in order to fit the images (such as those covered in Chapter 5), since a larger basis set is required.

1.5.6 Summary

This introduction thus illustrates the main strengths of velocity map imaging: by imaging the fragments of photodissociation processes caused by tunable light sources, and recording the kinetic energy release of the fragments as a function of photon energy, it is possible to glean significant information about the nature of the processes, and about the parent molecules. This includes the ability to assign the number of photons involved in the process, and to identify the molecule being dissociated (when this is ambiguous), as well as using angular distribution data as evidence for, or against, a potential assignment.

However, the main information that is gained by this technique is a direct measurement of the dissociation energy of a molecule. This technique has wide applicability to a variety of species, as mentioned above, and will be used throughout this project in order to determine the dissociation energy of multiple metal-containing species.

1.6 Computational Studies of Metal Clusters

1.6.1 Computational Methods

As mentioned in Section 1.1, one of the most attractive features about the study of metal clusters as analogues for catalytic systems is their computational tractability. While the Schrödinger equation, which describes the precise wavefunctions and energies of a system, cannot be solved exactly and analytically for any but the simplest systems,¹⁰¹ a wide variety of approaches have been taken to reach approximate solutions for metal clusters. These include methods such as coupled cluster,³¹ multiconfigurational self-consistent field (MCSCF),¹⁰² configuration interaction,¹⁰³ and Møller-Plesset methods.¹⁰⁴

These methods have all been reviewed by Simons,¹⁰¹ but on the whole, they represent different ways of expanding of the wavefunction with different configurations to be fitted. This makes them relatively intensive in terms of computational resource demands when applied to systems with lots of atoms and electrons. An alternative approach is taken by Density Functional Theory (DFT), which treats the energy of the system as depending on the total electron density of the system.¹⁰¹

The roots of DFT lie in Thomas-Fermi theory, via the work of Hohenberg and Kohn, by relating the potential experienced by the electrons to the electron density and showing that the latter can be used to determine the form of the Hamiltonian in the Schrödinger equation.^{105–107} This use of the electron density reduces the complexity of the problem, especially when applied to species involving a large number of heavy atoms. For these systems, DFT is less computationally demanding,¹⁰¹ leading to its use in a wide variety of cluster systems.^{46,108–111}

Although it is less computationally intensive than orbital-based methods, DFT is able to predict a wide variety of molecular properties, such as lowest-energy structures, binding energies, and vibrational spectra. It has proved accurate in many cases, and is particularly useful in combination with experimental results in studying transition metal clusters. For example, a comparison of the IRMPD spectrum of $\text{Pt}_4\text{O}_2\text{COAr}^+$ with the predicted spectrum of structures found using DFT was able to assign the structure of the cluster, while demonstrating that there was also

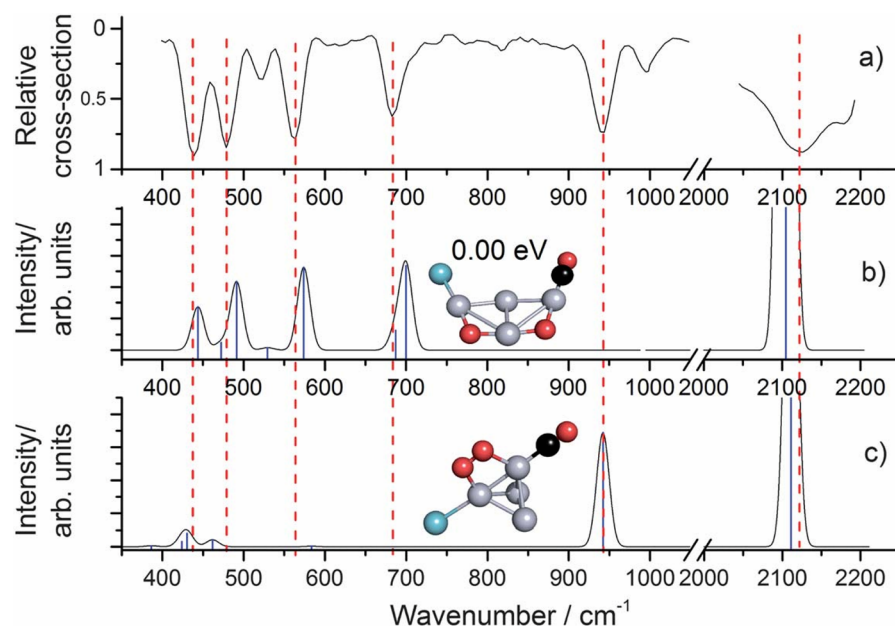


Figure 1.19: Comparison of (a) experimental IRMPD spectrum of $\text{Pt}_4\text{O}_2\text{COAr}^+$ with (b) calculated spectrum of the lowest-energy structure found using DFT (TPSSH/def2-TZVP)¹¹² and (c) calculated spectrum of an isomer containing the peroxo motif. Reproduced from A. C. Hermes, S. M. Hamilton, G. A. Cooper, C. Kerpel, D. J. Harding, G. Meijer, A. Fielicke, and S. R. Mackenzie, *Faraday Discussions*, 2012, 157, 213–225 with permission from the Royal Society of Chemistry.⁵

an isomer present in the beam which contained the peroxo (O-O) motif, as shown in Figure 1.19.⁵ It is possible to extend this work to involve electronically excited states and electronic spectroscopy using Time-Dependent Density Functional Theory (TD-DFT), while other uses include charting reaction pathways such as those shown in Figures 1.4 and 1.5.

1.6.2 Overview of Density Functional Theory

Given the demonstration that the energy of the system must be uniquely defined by the electron density function, ρ , there must exist a functional which relates this density function to the energy. Density functional methods rely on finding approximations to accurately describe this functional, which is not known exactly.¹¹³

Modern DFT is almost always based on the formulation of Kohn and Sham,^{108,114} which breaks the problem into one-electron Kohn-Sham orbitals which are either

occupied or empty, from which the overall density can be found.¹¹⁵ In this approach, all electrons in the molecule are treated as a fictitious system of non-interacting electrons which have the same electron density as a real system of interacting electrons.

The overall energy functional from DFT, $E_{\text{DFT}}[\rho]$, can then be broken down using

$$E_{\text{DFT}}[\rho] = T[\rho] + E_{\text{ne}}[\rho] + J[\rho] + E_{\text{xc}}[\rho] \quad (1.14)$$

where $T[\rho]$ describes the kinetic energy of the electrons in the occupied orbitals, $E_{\text{ne}}[\rho]$ corresponds to the electrostatic interaction between the electron density and the nuclear potential, $J[\rho]$ is the Coulomb functional describing interaction of the electron density with itself, and $E_{\text{xc}}[\rho]$ is the exchange-correlation functional.^{113,115} Due to the electrons being treated as non-interacting, all of these terms are exact, except for $E_{\text{xc}}[\rho]$, which contains corrections to account for the fact that electrons do actually interact with each other.

This exchange-correlation functional, while a relatively small part of the overall energy, is also a very important component which plays a crucial role in chemical bonding.^{113,115,116} The functional describes multiple effects: exchange includes the exchange of electrons and the correction for self-interaction (i.e., allowing for the fact that an electron will not interact with itself), and the Pauli exclusion principle. Meanwhile, the correlation functional describes the effects of electron correlation, whereby the electrons tend to avoid each other which both reduces their electrostatic repulsion, as they will be further from each other than otherwise expected, and increases their kinetic energy as they move to avoid each other.^{115,116}

Since this exchange-correlation functional is the only part which needs to be approximated in the Kohn-Sham formulation,^{113,115,116} there are many different functionals which have been created to describe it. These may include separate exchange and correlation functionals which can be combined in different ways.¹⁰⁸ Functionals can be graded into different bands depending on their complexity, the simplest being those following the Local Spin Density Approximation (LSDA), which depend only on the density.¹¹⁵

The next level is the Generalised Gradient Approximation (GGA), where the functional depends on the derivative of the density.¹¹⁵ Examples include BP86 (Becke's 1988 exchange and Perdew's 1986 correlation functionals),^{117,118} BLYP (Becke 1988 with correlation from Lee, Yang, and Parr),^{117,119} and PBE (from Perdew, Burke, and Ernzerhof).¹²⁰ This is followed by meta-GGA functionals that include the second derivative of the electron density, such as TPSS (Tao, Perdew, Staroverov, and Scuseria).¹²¹ These are joined by hybrid functionals, such as TPSSh, PBE0, and B3LYP, which include a degree of Hartree-Fock hybridisation.

Different functionals perform more or less accurately for different systems. For example, LSDA functionals behave relatively well for bulk solid systems, where the density varies sufficiently slowly that the lack of effect from the gradient is not an issue.¹⁰⁸ This is not true for clusters, where a variety of GGA and higher order functionals, such as TPSS,⁵ PBE,² and BLYP,¹²² among others, are found to give more accurate results. The functional which performs best may vary with system, and there have been various studies to compare these to experimental benchmarks.³⁰

TD-DFT is an extension of DFT based on the Runge-Gross theorem, which is the equivalent of the work of Hohenberg and Kohn expanded to include time dependence.¹²³ While electronically excited states are given by time-independent theory, the advantage of including time-dependence is that they can be treated as extensions of the ground state, and thus excitation energies can be calculated.¹²⁴ This enables charting the form of excited state potentials by calculating the change in excitation energy with molecular geometry.

1.6.3 Use of DFT in this Project

All calculations during this project were performed using the TURBOMOLE 6.0 software package,^{112,125} which includes an implementation of density functional theory as well as its time-dependent equivalent.^{124,126–130} TURBOMOLE has a variety of different capabilities in terms of available computational methods, and several different modules which allow for different calculations, including searches for minimum energy and transition state geometries, and identifying vibrational modes.

In this thesis, TURBOMOLE has been used to perform calculations to find the form of potential energy curves for both the ground state and excited states of diatomic molecules. To do so, single-point energy calculations are performed at a variety of different bond lengths throughout the range of interest.

In TURBOMOLE, the choice of functional is somewhat more limited when using the time-dependent theory rather than ‘regular’ DFT, since meta-GGA functionals such as TPSS (which has previously been found to work well for a variety of transition metal clusters)^{5,131,132} are not implemented for TD-DFT. Instead, it was decided to use B3LYP (a hybrid GGA functional) as included in TURBOMOLE.^{117,119,133–135} B3LYP is possibly the most popular and widely used functional in modern day DFT,¹⁰⁸ and while there are some doubts about its performance with transition metals compared to with main group elements,¹⁰⁸ it was decided that it would be sufficient for the calculations being performed. Other functionals such as PBE,^{120,133,134,136} and BP86,^{117,118,133,134,137} (both of which use the generalised gradient approximation) were also used for comparison and yielded similar results.

It is also necessary to choose a basis set of orbitals which will be used for the calculations. Several are implemented in TURBOMOLE with a variety of qualities from single- to quadruple-zeta valence. Of these, the triple zeta valence set, def2-TZVP,¹³⁸ was used, which has previously been used successfully in studies of transition metal clusters,^{2,5} including in combination with B3LYP.¹³⁹

1.7 Scope and Context of this Thesis

The experimental work described in this thesis primarily involves imaging experiments to investigate the dissociation dynamics of molecules containing atoms of transition metals. These compounds fall broadly into two categories: M-RG complexes (where RG is a rare gas atom), and oxides of the form M-O. Spectroscopic experiments are also performed in the spectral regions of interest, and, where possible, compared to published spectra.

The interest in complexes of transition metals with rare gases is tied primarily to the IRMPD technique outlined in Section 1.3.3. In order to record infrared spectra of metal clusters using mass spectrometry, a dissociation event must result from absorption of infrared photons. In cases where there is a species adsorbed onto the cluster (such as N_2O or similar molecules) which can be relatively easily removed by IR stimulation, it is possible to simply record loss of the molecule.⁴ However, when this is not the case (such as with pure metal clusters), it is necessary to use an inert messenger which is weakly bound to the cluster without significantly affecting its structure, and which can be removed when infrared photons are absorbed. There are a variety of possible messenger species, including rare gas atoms such as argon, which has previously been used to successfully record vibrational spectra of metal clusters.^{2,5,60}

This depends on the ability of transition metal atoms to form bonds with argon or other rare gases which are strong enough to stably bind the atom to the cluster, but weak enough to be dissociated under vibrational excitation. It is therefore of interest to study the dissociation dynamics of transition metal-rare gas complexes in order to gain further understanding of the strength of this bonding. These species are also of interest as being bound primarily by van der Waals dispersion forces,³² which means that a study of their dynamics would have applications in the fields of molecule-surface interactions and buffer gas cooling, among others.^{140,141}

The bonding between oxygen and metal atoms, on the other hand, is of particular interest in cluster chemistry because of the number of reactions on clusters which involve forming or breaking M-O bonds, some of which have been mentioned above.⁴⁻⁷ In a more particular subset of these, bimetallic clusters of the form $\text{M}_n\text{M}'_m$ have been of increasing interest over the last couple of decades due to their relationship to bulk bimetallic catalysts.⁴⁶ This has included studies of their reactivity with oxygen,¹⁴² as well as other species,¹⁴³ which can vary markedly from clusters containing only one of the metals being studied.¹⁴⁴ Rationalising their reactivity, for example, in terms of the preference for oxygen to bind to one metal rather than another, is made easier by accurate experimental values for the dissociation energies of these bonds.

More generally, the study of the spectroscopy and dissociation energies of transition metal oxides has been particularly well reported and reviewed in the field of cluster chemistry, reflecting their wider applications to fields ranging from biology to astrophysics,^{145,146} as well as their utility as simple molecules in which to study the bonding effect of *d*-electrons.¹⁴⁷ It is hoped that a direct measurement of the dissociation energies of these species using velocity map imaging will help to support or correct existing values from other methods, which may be less direct.

The thesis consists of four primary results chapters, three of which report on VMI experiments featuring different transition metals. Chapter 2 covers a study of the dissociation dynamics of silver rare gas complexes, Ag-RG (RG = Ar, Kr, Xe), as well as observations of the dissociation of silver oxide, AgO, at similar photon energies. Chapter 3 reports measurements of the dissociation energy of molybdenum oxide, MoO, in two different spectral regions, while Chapter 4 covers similar results for chromium oxide, CrO.

Chapter 5 focuses more on the methodology of the experiments and more specifically on the algorithms used to extract data from the raw images recorded using VMI. This uses data from the preceding chapters to test the relative effectiveness of four image processing programs when applied to images of different quality and containing different sets of rings.

Finally, Chapter 6 summarises the results obtained in this thesis and sets them in the context of the wider field, while also looking forward to potential further work in the area of cluster imaging.

Chapter 2

Velocity Map Imaging of Small Silver Molecules

The spectroscopy of Ag-RG molecules (RG = Ar, Kr, Xe) has been studied using ultraviolet light in the region around 315–335 nm (ca. 29900–31700 cm⁻¹), and the photodissociation of these species has also been studied using velocity map imaging (VMI) in the same region. It was observed that a single photon was capable of dissociating the molecule into the fragments Ag*(²P_{3/2}) + RG(¹S₀), and, by extrapolating the Total Kinetic Energy Release (TKER) from this dissociation back to threshold, dissociation energies, D₀, for AgAr, AgKr, and AgXe of 85.9 ± 23.4 cm⁻¹, 149.3 ± 22.4 cm⁻¹, and 256.3 ± 16.0 cm⁻¹ respectively, were determined. During the same experiments, photodissociation of AgO by a two-photon process (into two different channels which produced Ag*(²D_{3/2}) and Ag*(²S_{1/2}) plus a ground state O(³P) atom respectively) was also observed, finding a D₀(AgO) value of 15965 ± 81 cm⁻¹. Evidence for the dissociative ionisation of the silver dimer, Ag₂, was also obtained. Much of the work in this chapter has been published in *The Journal of Chemical Physics*.¹⁴⁸

2.1 Previous Work

2.1.1 Complexes of Silver with Rare Gases

Neutral diatomic molecules containing a coinage metal atom (i.e. Cu, Ag, Au) and a rare gas atom have been of significant interest, representing a species bound, at least in the ground state, predominantly by van der Waals dispersion forces.³² While this form of bonding has applications in various fields, it is of particular interest in the field of cluster science due to the use of rare gas atoms as ‘inert messengers’, i.e., as ligands which bind weakly to a cluster of interest, such that they have limited impact on the structure of the cluster and are easily removed in action spectroscopy; various metal-based clusters have been studied spectroscopically in this fashion using rare gases as the messenger tag.^{5,60,149}

Our group has previously used VMI to study Au-RG (RG = Ar, Kr, Xe) molecules,⁶¹ while the complexes of copper with rare gas atoms have been studied theoretically,¹⁵⁰ and, in the case of Cu-Kr, experimentally.¹⁵¹ Ag-RG species have not previously been studied using VMI, but have been studied computationally and spectroscopically using a range of methods.

Ag-Ar was studied in the early 90s by Jouvét *et al.*,⁵⁰ who used laser induced fluorescence excitation spectroscopy to measure the transitions between the ground state ($X(^2\Sigma_{1/2}^+)$) and the $A(^2\Pi_{1/2,3/2})$ excited states which arise from interaction between the ground state Ar atom and the low-lying $^2P_{1/2,3/2}$ excited states of the Ag atom. Transitions to the $C(^2\Sigma_{1/2}^+)$ state which also arises from the $\text{Ag}(^2P_{3/2})$ level were not observed, with this state believed to be repulsive. They also observed some transitions to the $B(^2\Pi_{3/2})$ state (there labelled as the *a*-state) arising from the $\text{Ag}(^2D_{5/2})$ atomic level. Using these spectra and Birge-Sponer extrapolations, they found a value for the dissociation energy, $D_0(\text{AgAr})$, of $90 \pm 30 \text{ cm}^{-1}$.

Brock and Duncan used resonant two-photon ionisation (R2PI) spectroscopy to study AgAr, AgKr and AgXe.¹⁵² They also used the transitions observed to the two *A*-states and the *B*-state to calculate values for the dissociation energies of the

three molecules using Birge-Sponer extrapolations. The use of LeRoy-Bernstein extrapolations was also considered,^{153,154} but the upper vibrational levels of the transition were insufficiently close to threshold to give reliable dissociation energies, such that the Birge-Sponer values were preferred.¹⁵² Since they calculated separate values for each of the three transitions, and for multiple isotopologues (Jouvet *et al.* did not have isotopic resolution due to their use of fluorescence), they provide several different values for each species (e.g. for $D_0(\text{AgAr})$ they provide values of 65, 51, 97, 72, 43 and 99 cm^{-1} — no uncertainties given) without calculating an overall value, but the average values (with standard deviations) are: $D_0(\text{AgAr})$: $71 \pm 23\text{ cm}^{-1}$; $D_0(\text{AgKr})$: $95 \pm 32\text{ cm}^{-1}$; and $D_0(\text{AgXe})$: $231 \pm 54\text{ cm}^{-1}$.

Computationally, these species have been studied several times,^{155,156} including a recent study by Loreau *et al.* who calculated potential energy curves for the ground state, as well as the two *A*-states, the *B*-state and the *C*-state explored by the aforementioned papers.³² These results were generally in agreement with the experimental results, finding values of 102.62, 163.61 and 254.25 cm^{-1} for the dissociation energies of AgAr, AgKr and AgXe respectively. The value for $D_0(\text{AgKr})$ is a bit high compared to the average value for this constant from Brock and Duncan, but their results for the dissociation energy of this molecule have a large variance and include multiple values in excess of 130 cm^{-1} , which are more in keeping with this calculated result.

This study aimed to expand upon this previous work by using VMI to directly measure the dissociation energy of these species, utilizing the strengths of the technique previously demonstrated in the study of Au-RG molecules.⁶¹

2.1.2 Other Compounds of Silver

While studying Ag-RG molecules, production of Ag_2 and AgO was also observed. Studies of the latter molecules in particular have proved particularly challenging in the past. The previously accepted value for $D_0(\text{AgO})$ comes from a measurement in the early 70s, where it was determined to be $52.7 \pm 3.5\text{ kcal mol}^{-1}$ ($18400 \pm 1200\text{ cm}^{-1}$).^{157,158} This result was not found using spectroscopy, but rather by using Knudsen Cell mass spectrometry.¹⁵⁸ In this technique, a heated cell with

a small, well-defined orifice, known as a Knudsen Cell, is used to maintain a gas phase–condensed phase equilibrium. The gas phase slowly leaks out through the orifice, and the composition of the resulting molecular beam is measured by mass spectrometry, and the resulting intensities are used to estimate the partial pressures of the species in the gas phase in the cell and, thus, the equilibrium constant. By measuring exchange equilibria between a species whose dissociation energy is known and one for which D_0 is unknown, the unknown dissociation energy can be calculated.¹⁵⁹ For example, in this case, the equilibrium between NiO and Ag was used,¹⁵⁸ $D_0(\text{NiO})$ having been previously measured by vaporisation of the solid oxide.¹⁶⁰

However, the $52.7 \pm 3.5 \text{ kcal mol}^{-1}$ value has long been under suspicion, with multiple theoretical studies using a variety of methods predicting a significantly lower value for the dissociation energy.^{30,103,122,161,162} Legge *et al.* note that multiple density functional methods which perform well for other species produce anomalously large errors compared to this value of $D_0(\text{AgO})$, and exclude it from their overall comparisons.³⁰ Bauschlicher Jr. *et al.* explicitly note that ‘there may be some systematic error in the experimental determination’.¹⁰³ It would be useful to establish whether the error lies in the value from Knudsen Cell mass spectrometric value, or whether the calculations are at fault.

Ag_2 was also studied by the Knudsen Cell method on multiple occasions in the mid-twentieth century, with Huber & Herzberg giving a value for $D_0(\text{Ag}_2)$ calculated across several papers as $38.3 \pm 2.2 \text{ kcal mol}^{-1}$ ($13400 \pm 770 \text{ cm}^{-1}$).^{157,158,163–166} A more recent measurement by Ran *et al.*, also using Knudsen Cell mass spectrometry, found a value of $158.0 \pm 3.4 \text{ kJ mol}^{-1}$ ($13200 \pm 280 \text{ cm}^{-1}$).¹⁶⁷ The dissociation energy has also been calculated on multiple occasions,^{168,169} although it does not appear to have been measured by any other method. However, other properties such as the ionisation potential and positions of excited states have been measured and/or calculated.^{170–173}

2.2 Experimental Method

The experiments in this chapter were performed on the velocity map imaging setup described in Section 1.4; this section covers details specific to this study. In each case, the ablation target was comprised of pure silver (natural isotopic abundance; 51.8% ^{107}Ag , 48.2% ^{109}Ag),¹⁷⁴ while the carrier gas varied by experiment but had a consistent backing pressure of 7 bar.

Ablation of the silver target was accomplished using the 532 nm output from the frequency-doubled Nd:YAG laser (Litron Nano), while the 157 nm F_2/He excimer laser (Neweks) was used to identify which species are present in the molecular beam, since its high photon energy is sufficient to ionise a wide variety of atoms and molecules. This overview of the contents of the beam enabled optimisation of production of the molecules of interest. For all of the spectroscopy and imaging processes observed, photoexcitation and ionisation was accomplished using the beam from the frequency doubled dye laser (Sirah). In this study, the laser was pumped with 532 nm light from a frequency-doubled Nd:YAG laser (Continuum Surelite) and the dye used was DCM dissolved in DMSO, which has a dye curve spanning the region of roughly 630–680 nm. This radiation is frequency-doubled using a BBO crystal, such that the product beam was tunable in the range 315–340 nm (ca. $29400\text{--}31750\text{ cm}^{-1}$), although the power was low towards the edges of this region, such that images were taken spanning the range $29900\text{--}31620\text{ cm}^{-1}$. The beam was also plane-polarised, with the direction indicated by arrows on the relevant images.

Some computational work was performed for the analysis outlined in Section 2.3.4; this work was performed using the TURBOMOLE 6.0 software package.¹¹² Density functional theory and its uses in cluster chemistry are discussed in greater detail in Section 1.6, but for this analysis Time-Dependent Density Functional Theory (TD-DFT) was used to calculate the form of excited states. The B3-LYP functional was used,^{119,135} with the def2-TZVP basis set.¹⁷⁵

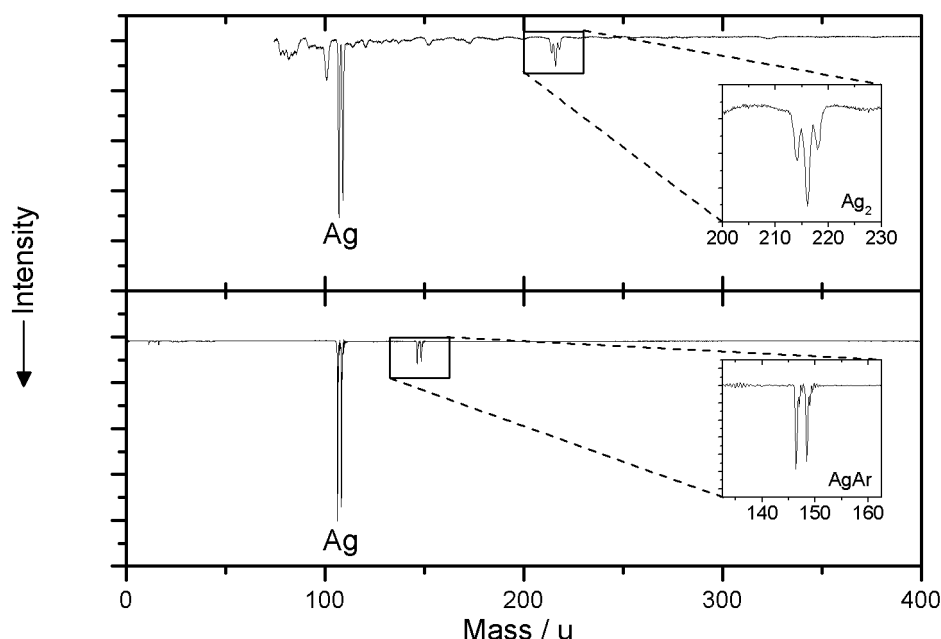


Figure 2.1: Mass spectra recorded showing the main contents of the molecular beam. **Top:** Spectrum recorded using the excimer beam at 157 nm, with pure helium backing gas. This spectrum is not background subtracted, and unassigned peaks correspond to species which are not metal-containing. The inset shows the detail of the peaks corresponding to the isotopologues of Ag_2 . Trace amounts of Ag_3 are present in the spectrum but are not visible on this scale. **Bottom:** Mass spectrum recorded using the frequency-doubled output of the dye laser around 330 nm, with pure argon backing gas. The inset shows the detail of the peaks corresponding to isotopologues of AgAr . Small amounts of AgO are present but are not visible on this scale.

2.3 Experimental Results

2.3.1 The AgAr Molecule

Spectroscopy

Using the excimer laser, it was observed that, when pure helium was used as a carrier gas, the molecular beam contained Ag and Ag_2 , with traces of Ag_3 . Switching to an argon carrier gas and instead using the dye laser to ionise the contents of the beam resulted in additional observation of AgAr with small amounts of AgO , while the amount of Ag_2 seen with this lower photon energy was significantly lower. These mass spectra are shown in Figure 2.1.

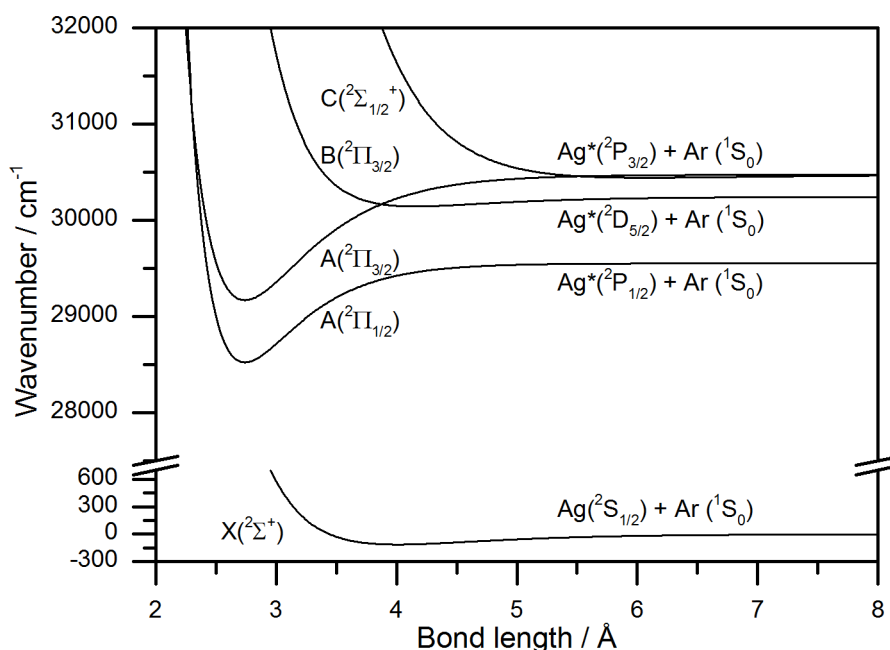


Figure 2.2: Energy level diagram of AgAr showing the ground and low-lying excited electronic states, plotted using parameters calculated by Loreau *et al.* — the curves for AgKr and AgXe are qualitatively similar.³²

As part of optimising the production of Ag-RG, an attempt was first made to reproduce the spectra previously obtained in the region of the $A(^2\Pi_{3/2}) \leftarrow X(^2\Sigma^+)$ transition by Brock and Duncan.¹⁵² The relevant electronic energy levels of AgAr, along with the others which have previously been studied experimentally and computationally (as described in Section 2.1.1) are shown in Figure 2.2.^{32,50,152} The labelling here is consistent with that used by Brock and Duncan, rather than that preferred by Jouvét *et al.* and Loreau *et al.*, who labelled the *B*-state correlating with the $\text{Ag}(^2D_{5/2})$ level as $a(^2\Pi_{3/2})$, and therefore the *C*-state as $B(^2\Sigma_{1/2}^+)$.

Brock and Duncan observed transitions in the $A \leftarrow X$ region from $v'' = 0$ in the ground state to $7 \leq v' \leq 16$ levels of the $A(^2\Pi_{3/2})$ state, along with a handful of hotbands, as well as transitions to the $B(^2\Pi_{3/2})$ state which is also in this region.¹⁵²

As shown in Figure 2.3, these spectra were successfully reproduced, observing the same transitions from the $X(v'' = 0)$ level, plus an additional transition to the $A(v' = 6)$ level. However, the spectra do not otherwise represent any significant

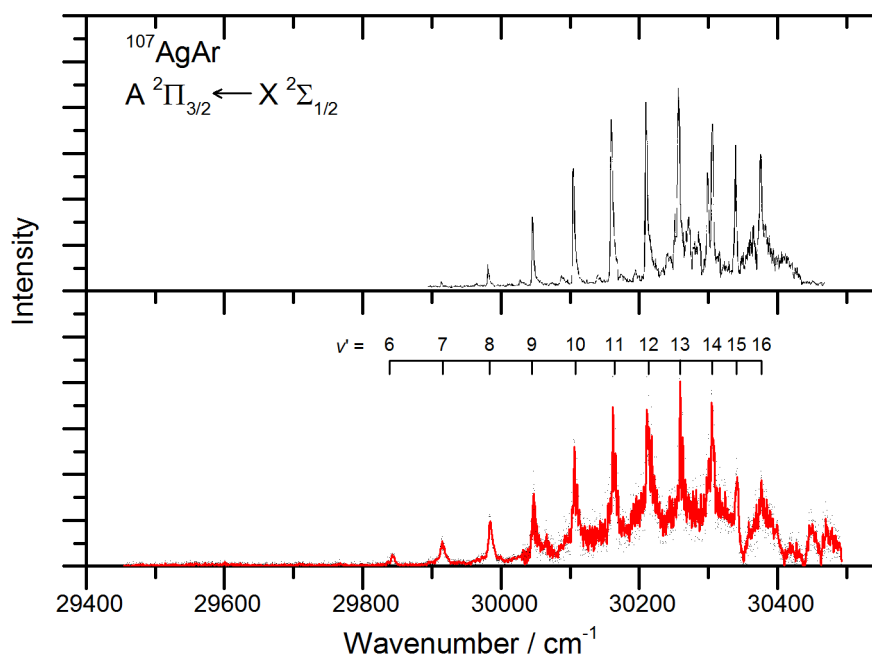


Figure 2.3: Comparison of R2PI spectra measured by action spectroscopy in the $^{107}\text{AgAr}$ channel in the region of the $A(^2\Pi_{3/2}) \leftarrow X(^2\Sigma^+)$ transition. Transitions are from $X(v'' = 0)$ to the $A(v')$ level indicated, following the assignment by Brock and Duncan.¹⁵² **Top:** Data obtained by Brock and Duncan (black trace), reproduced with permission from L. R. Brock & M. A. Duncan, *The Journal of Chemical Physics*, 103, 9200 (1995). Copyright 1995, American Institute of Physics. **Bottom:** Data obtained in the current research project (red trace).

advance over that previously observed, and the transitions to higher vibrational levels of the A -state are not as well resolved. Nonetheless, this spectrum is encouraging proof of the formation and observation of AgAr .

Imaging

With spectra of AgAr in the $A \leftarrow X$ region successfully recorded, imaging of Ag atom photofragments was performed at various wavelengths in this region. Although rings were observed in the velocity map images, indicating the dissociation of a silver-containing species, none were attributable to dissociation of AgAr , since all were observed in the absence of argon (i.e. when pure He was used as a carrier gas).

However, when images were taken at a slightly higher photon energy (i.e. in the region below 325 nm/over ca. 30700 cm^{-1}), a single ring was observed, with a noticeable wavelength dependence, which was only seen in the presence of argon. Example images obtained in this region, along with several of the fragment Kinetic Energy Release (fKER) spectra obtained by extraction using the Polar Onion Peeling (POP) algorithm described in Section 1.5.2, are shown in Figure 2.4. Note that these images and spectra (as well as all other velocity map images in this chapter) are obtained by gating the detector over both isotopes of the silver fragment, since a decision was made to sacrifice isotopic selectivity for signal intensity. The central spot in the image, which results from efficient two-photon ionisation of silver atoms in the molecular beam, has been excluded for clarity in each of the images and spectra shown.

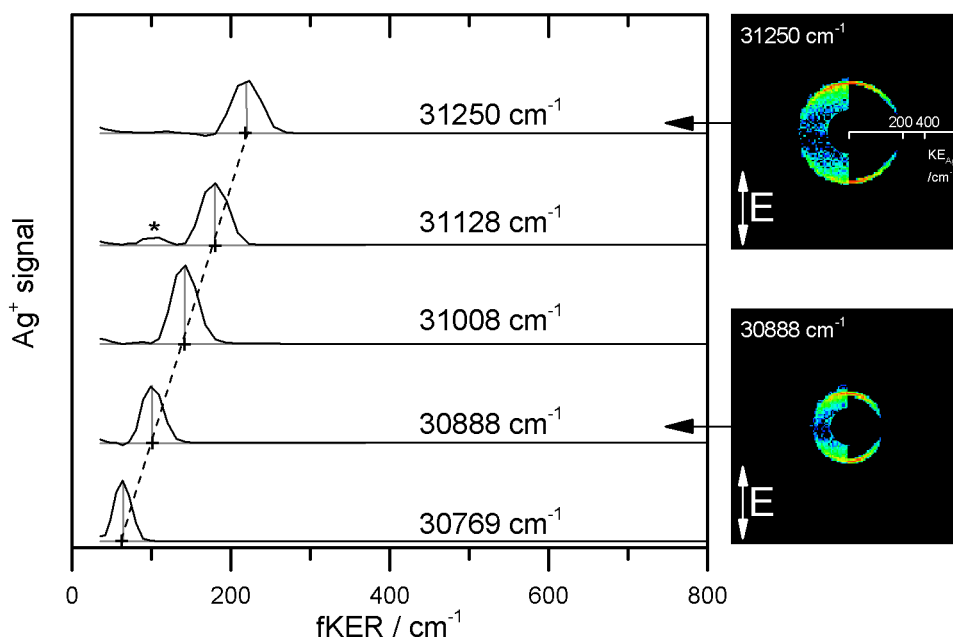


Figure 2.4: Fragment Kinetic Energy Release spectra for the silver atom fragment in the dissociation observed in the region above ca. 30700 cm^{-1} in pure argon carrier gas. Representative sample images are shown for high and low photon energy cases to demonstrate the growth of the ring as photon energy increases. The double-headed arrows labelled E show the plane of polarisation of the probe laser. The feature indicated by an asterisk in the spectrum at 31128 cm^{-1} is attributed to dissociation of Ag_2 as discussed in Section 2.3.4.

These processes are of a remarkably low kinetic energy, producing very small rings which take up only a small portion of the detector, leading to the pixelation observed in the images seen in Figure 2.4. This indicates that a near-threshold dissociation is being observed, with most of the energy from the photons being needed to dissociate the molecule or going into electronic excitation of the fragments.

A plot was drawn up of the change in the kinetic energy release with photon energy (i.e. the growth in the size of the ring). As explained in Section 1.5.4, for a photodissociation of the form



with a certain Total Kinetic Energy Release (TKER), the Kinetic Energy of the silver fragment, KE_{Ag} , is related to the TKER and thus to the photon energy by the following equation:

$$\text{KE}_{\text{Ag}} = \frac{m_{\text{X}}}{m_{\text{AgX}}} \cdot \text{TKER} \quad (2.1)$$

$$= \frac{m_{\text{X}}}{m_{\text{AgX}}} \cdot (nh\nu + E_{\text{AgX}} - E_{\text{Ag}} - E_{\text{X}} - D_0(\text{AgX})) \quad (2.2)$$

where E_{Ag} , E_{X} and E_{AgX} are the internal energies of the silver atom, the co-fragment and the parent molecule respectively. Hence, a plot of KE_{Ag} (i.e. the fKER measured by imaging) against photon energy, $h\nu$, should have a slope which depends on the ratio of masses of the co-fragment and the parent molecule, $\frac{m_{\text{X}}}{m_{\text{AgX}}}$ and on the number of photons, n .

A KE_{Ag} vs photon energy plot is shown in Figure 2.5, demonstrating the linear relationship between the wavenumber of the photon involved in the dissociation energy and the kinetic energy released. The gradient of a linear fit through the points, once the KE_{Ag} values have been adjusted by a magnification factor of 1.090 (as mentioned in Section 1.5) is 0.27675. After accounting for the mass ratio factor, $\frac{m_{\text{X}}}{m_{\text{AgX}}} = \frac{40}{147}$, this implies a photon number of 1.017, which is a very good match to a single photon dissociation of AgAr.

Having gained further evidence for the assignment of Ar as the co-fragment, with the slope providing a good fit in addition to the use of argon being necessary in order to observe the features under examination, the nature of the process that gives

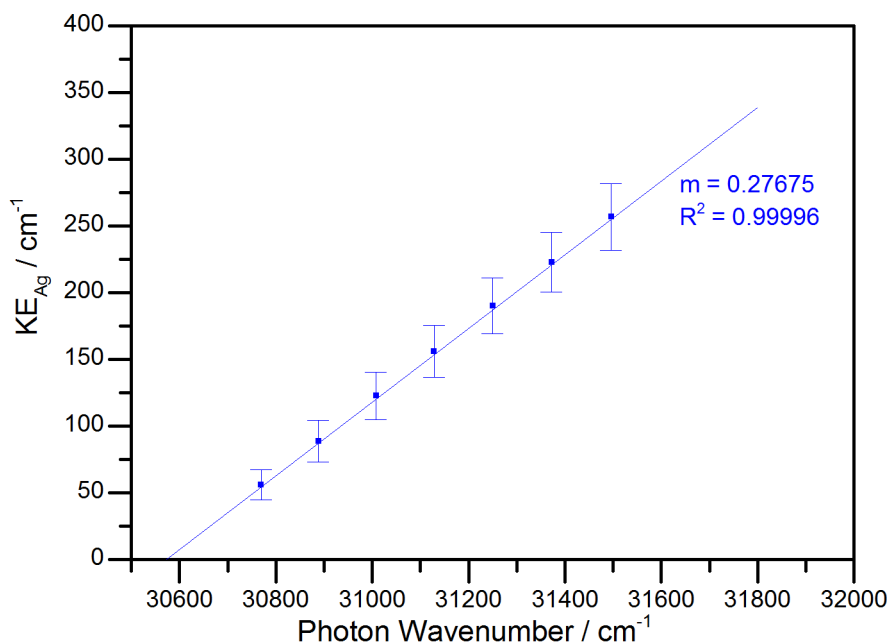


Figure 2.5: Kinetic Energy of the silver fragment, KE_{Ag} , as a function of wavenumber of the photon used. Each point represents the centre of a peak in the fKER spectra corresponding to a ring, such as the ones shown in Figure 2.4, while the uncertainties represent the Full Width at Half Maximum (FWHM) of the corresponding peaks, plus a small contribution from uncertainty in the magnification factor used. The line represents a linear fit through the points, which gives the gradient and R^2 values shown. Each image was obtained in a pure argon backing gas.

rise to the ring must be determined. This is assisted by the fact that at energies ca. 31000 cm^{-1} , the energy levels of AgAr are well known, as shown in Figure 2.2. As can be seen on this potential energy diagram, the most likely candidate around 31000 cm^{-1} above the ground state is the $C(^2\Sigma_{1/2}^+)$ level. The C -state is only very weakly bound,³² and is essentially repulsive in the Franck-Condon region, leading directly to dissociation into an excited $\text{Ag}(^2P_{3/2})$ atom and a ground state $\text{Ar}(^1S_0)$ atom. By a remarkable coincidence, the $\text{Ag}(^2P_{3/2})$ state lies 30634 cm^{-1} below the ionisation threshold.⁹¹ Therefore, in the region of interest (above ca. 30700 cm^{-1}), it is just possible to ionise the excited silver atom fragment with a single photon.

The assignment of the observed ring being due to a transition to the $\text{Ag}(^2P_{3/2})$ level is supported by three main pieces of evidence:

1. The $C \leftarrow X$ transition accesses continuum states, explaining the fact that the ring is visible continuously in the spectral region shown in Figure 2.5.
2. As seen in Figure 2.4, there is significant anisotropy in the ring, with noticeably higher intensity along the direction of the polarisation of the laser (the β_2 parameter is ca. 1.6 ± 0.1). This is explained well by the fact that the $C \leftarrow X$ transition is a $\Sigma \leftarrow \Sigma$ (i.e. parallel) transition.
3. Finally, there is good overlap between the ground state wavefunction and the continuum wavefunctions of the C -state in the region of interest. This is shown in Figure 2.6, which shows the wavefunctions in question and the Franck-Condon Factor for different photon energies. These calculations, assuming that the value for the ground state bond-length calculated by Loreau *et al.* is correct,³² show that the relative transition intensity increases sharply from roughly 30700 cm^{-1} and peaks around 31500 cm^{-1} , spanning the region covered by the images. (N.B. experimentally, scanning the excitation laser to photon energies above 31500 cm^{-1} results in a sharp decline in the intensity of the rings, perhaps suggesting that this curve should be shifted slightly to lower photon energies. This implies that the actual bond length is slightly longer than calculated. It was not possible to investigate this possibility further due to the other factors affecting ring intensity, such as the intensity curve of the dye used, making it difficult to accurately map the transition intensity to the calculated Franck-Condon Factor.)

Given the confident assignment of the observed rings to the $C \leftarrow X$ transition, and hence the produced fragments as $\text{Ag}(^2P_{3/2})$, it is now possible to use the x -intercept of the fit of kinetic energy against wavenumber, using a modified form of equation 2.2. At $\text{KE}_{\text{Ag}} = 0$,

$$nh\nu = D_0(\text{AgX}) + E_{\text{Ag}} + E_{\text{X}} - E_{\text{AgX}} \quad (2.3)$$

such that the threshold photon energy, $h\nu$, can be used to measure $D_0(\text{AgAr})$, given knowledge of the number of photons involved and the internal energies of the parent molecule and fragments.

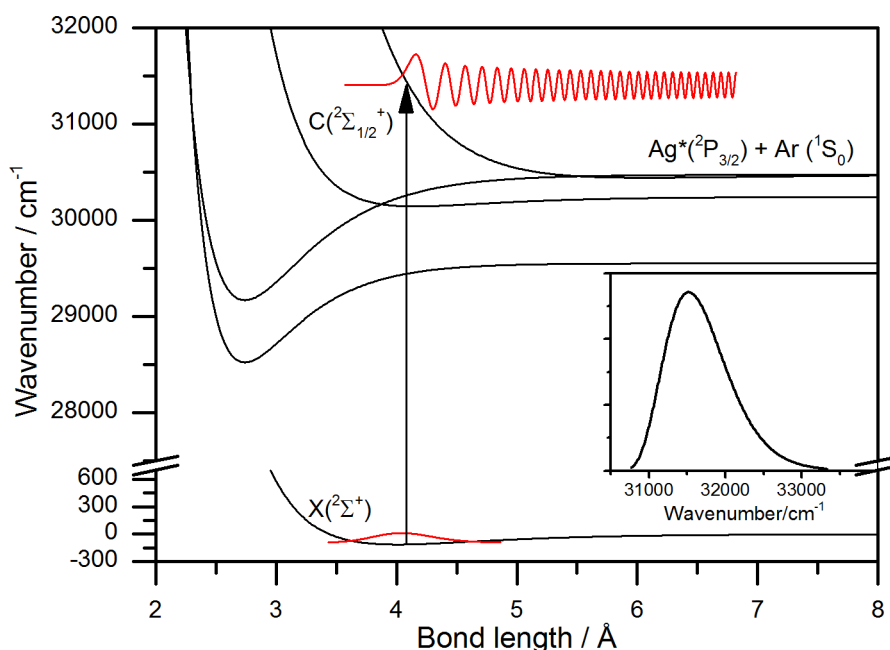


Figure 2.6: Energy level diagram of AgAr with the wavefunctions of the $X(v = 0)$ and the point on the C -state curve 31500 cm^{-1} higher in energy (i.e. accessible by a single photon at one of the wavenumbers studied), plotted using values for the potential energy curves calculated by Loreau *et al.*³² **Inset:** The calculated absorption spectrum from the ground state to the C -state continuum for a given photon energy, calculated assuming a Morse potential wavefunction for the lower state and Airy function wavefunctions for the upper state, and also using the values for the potential energy curves from Ref. 32.

By using equations 2.1 and 2.2, it can be seen that for a one-photon process, such as the one being examined here, a plot of TKER vs wavenumber should have a gradient of 1. It is therefore possible to make a linear fit through the points shown in Figure 2.5 (after converting from the kinetic energy of the silver fragment to the total kinetic energy release) with a fixed, unity gradient, and find the position of the x -intercept. Doing so gives a value for the intercept (i.e. the threshold photon energy) of $30558.6 \pm 23.4 \text{ cm}^{-1}$.

The energy of the $\text{Ag}(^2P_{3/2})$ level is $30472.66516 \text{ cm}^{-1}$,⁹¹ while the argon fragment and the parent molecule are both in their ground states, and therefore have zero internal energy. Thus, equation 2.3 simply reduces to $D_0(\text{AgAr}) = \bar{\nu} - E_{\text{Ag}} = 85.9 \pm 23.4 \text{ cm}^{-1}$.

This value compares well to the results of Jouvét *et al.*, who found a value for $D_0(\text{AgAr})$ of $90 \pm 30 \text{ cm}^{-1}$,⁵⁰ and with those of Brock and Duncan, who found a range of values from 51 to 99 cm^{-1} with an average of $71 \pm 23 \text{ cm}^{-1}$,¹⁵² as mentioned in Section 2.1. Computational values are slightly higher, with a value of 102.62 cm^{-1} from Loreau *et al.*,³² and 104.6 cm^{-1} from Gardner *et al.*,¹⁵⁶ but these are still comfortably within experimental uncertainty.

While the value obtained in this work compares well to the average of those experimentally obtained previously, and has only slightly lower uncertainty than that found by Jouvét *et al.* (N.B. Brock and Duncan do not provide uncertainties for their measurements, so the average from their paper has only a standard deviation of the results without accounting for experimental error), the main advantage is that it is a direct measurement that does not depend on extrapolation from vibrational spectra. In previous experiments, the latter method gave significantly different values for D_0 for each of the bands extrapolated to threshold ($A(^2\Pi_{1/2}) \leftarrow X$; $A(^2\Pi_{3/2}) \leftarrow X$; and $B(^2\Pi_{3/2}) \leftarrow X$). It also relies on a particular form for the potential energy curve (such as a Morse curve) which contradicts more recent evidence that the excited states of the Ag-RG complexes are not well-fitted by such simple forms — Loreau *et al.* found that the $A(^2\Pi_{1/2})$ state deviates sufficiently from Morse behaviour that the vibrational assignment is called into question.³² These current experiments do not depend on a Morse form for the potential energy curves or a correct assignment of a vibrational spectrum and provide a more direct measurement of D_0 .

2.3.2 Complexes of Silver with other Rare Gas Atoms

Having successfully observed, assigned and analysed the dissociation of AgAr, the same approach was extended to complexes of silver with krypton and xenon. The work of Brock and Duncan, and Loreau *et al.*, indicated that the electronic curves of AgKr and AgXe and their dissociation energies resemble those of AgAr sufficiently well that a similar process of excitation from the ground state to the dissociative C -state followed by dissociation into excited $\text{Ag}(^2P_{3/2})$ and ground state rare gas atomic fragments should be observable in the same region. The experiments were

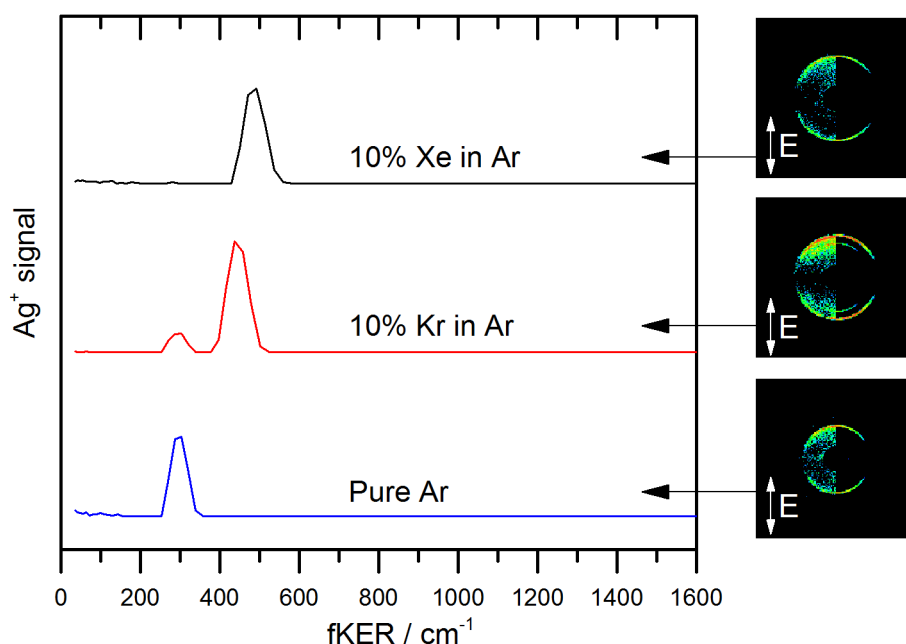


Figure 2.7: Fragment Kinetic Energy Release spectra for the silver atom fragment taken at 317.5 nm (ca. 31500 cm^{-1}) in various carrier gases, as indicated, along with the corresponding images. The double-headed arrows labelled E show the plane of polarisation of the probe laser.

therefore repeated while replacing the pure argon carrier gas with 10% krypton or xenon in argon gas mixes in order to produce the respective silver complexes.

Figure 2.7 shows a comparison of sample images produced in pure argon gas and in Kr/Ar and Xe/Ar gas mixtures, which show the addition of new features in the presence of the new rare gases. As with the images in Section 2.3.1, these images include intensity from both ^{107}Ag and ^{109}Ag fragments. There is also no resolution between isotopes of the rare gas co-fragments. Unlike argon, krypton and xenon have multiple isotopes, but it was determined that any difference in the position of the peaks resulting from different isotopologues would be within the width of the peaks (e.g. for krypton, the difference between lightest and heaviest isotopologues is $\leq 35\%$ of FWHM) and thus unresolved. In the mixture with krypton, the same ring observed in pure argon is visible, along with a new feature, while in the xenon gas mixture, the ring due to dissociation with AgAr is gone, replaced by a new, different ring. Assuming the new rings are due to dissociation of AgKr and

AgXe, this suggests that AgAr and AgKr coexist in the Kr/Ar molecular beam, while xenon is capable of displacing argon from the silver atoms such that the Xe/Ar carrier gas produces predominantly AgXe molecules. As the corresponding images show, the new features have similar anisotropies to those analysed in Section 2.3.1, supporting the idea that they result from the analogous process.

The same analytical approach as Section 2.3.1 was taken for the new data, fitting the peaks in the fKER spectra and plotting their position against photon energy. Figure 2.8 shows such a plot, showing first a plot of KE_{Ag} against $\bar{\nu}$ for all of the rings observed in the three carrier gases, which shows two important things:

1. As the points due to rings observed in the Kr/Ar gas mix (shown in red) demonstrate, in cases where two rings were visible the smaller ring corre-

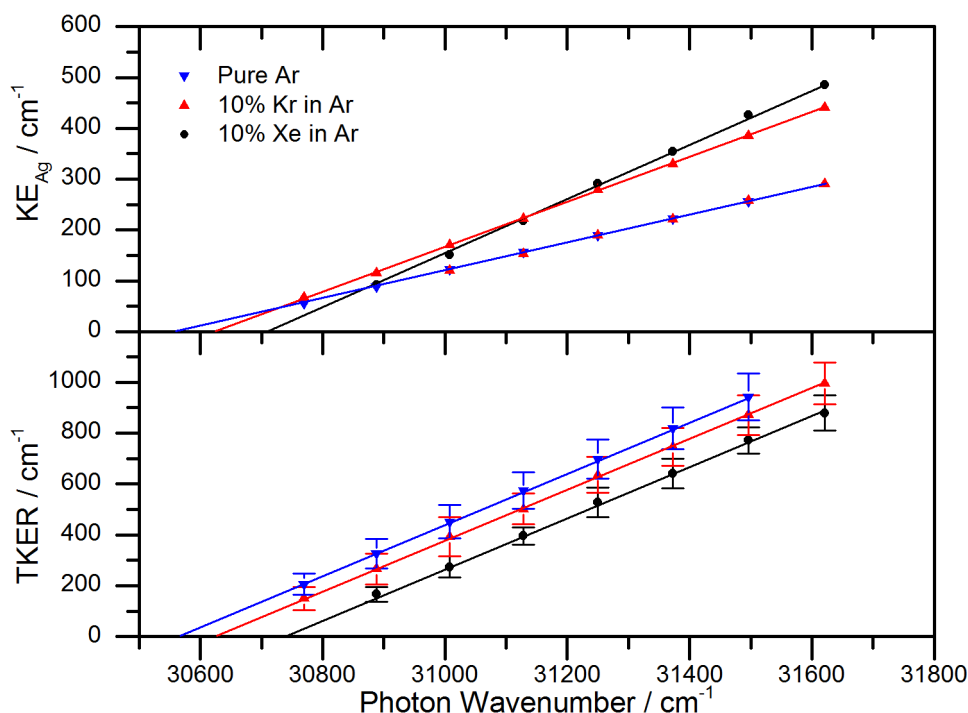


Figure 2.8: **Top:** Kinetic energy release of the silver fragment as a function of photon wavenumber. Each point corresponds to a ring observed in pure argon carrier gas (blue inverted triangles), 10% mixture of krypton in argon (red triangles) or 10% xenon in argon (black circles). Uncertainties have been omitted for clarity, while lines have been added to indicate points which form a series. **Bottom:** The same data converted to total kinetic energy release using the mass of the assigned co-fragment. Uncertainties show the FWHM of each peak, plus a minor contribution from uncertainty in the magnification factor.

sponds to the position of those seen in pure argon at each wavenumber. This demonstrates that it is indeed due to dissociation of AgAr still present in the molecular beam.

2. The new features show significantly different wavenumber dependence compared to the rings resulting from AgAr, which is to be expected due to the different mass of the co-fragment. Using equation 2.2, it is expected that the gradient of a plot of KE_{Ag} against photon energy for a one-photon process should be 0.438 for a krypton co-fragment, or 0.550 where the co-fragment is xenon. In fact, the gradients of best fit lines through these sets of points are 0.437 and 0.546, supporting the assignments.

Figure 2.8 also shows the plot of TKER against photon energy for each of the three data sets (ignoring the inner rings from the Kr/Ar gas mix as being duplicates of the pure Ar data) after converting from KE_{Ag} to TKER. As expected, this produces three parallel sets of data, since the gradient of a TKER against $\bar{\nu}$ is dependent solely on the number of photons involved in the dissociation, and the three molecules all fragment after a single-photon $C \leftarrow X$ excitation.

The x -intercepts of the three fits also increase in the order $\text{AgAr} < \text{AgKr} < \text{AgXe}$, implying that the dissociation energy of the three molecules increases in the same order, which is to be expected with the increasing polarisability of the larger rare gases. As in Section 2.3.1, D_0 for each species can be found by using the intercepts of the best fit lines, and subtracting the internal energy of the $\text{Ag}(^2P_{3/2})$ fragment (the other terms in equation 2.3 being zero). The results are shown in Table 2.1, which also includes comparisons with the experimental data sets for Jouvét *et al.* (for AgAr) and Brock and Duncan, plus computational values.

As the table shows, the values obtained in this work compare favourably with the calculated values, which lie within the experimental uncertainty of the VMI results in each case. As mentioned in Section 2.3.1, the previous experimental values by spectroscopic extrapolation vary substantially depending on which transition series is used. Table 2.1 shows the values obtained in each case by observation of the $A(^2\Pi_{1/2}, ^2\Pi_{3/2}) \leftarrow X(^2\Sigma^+)$ transitions, but Brock and Duncan proposed four

values for D_0 for AgXe (the two shown, plus two more from a second isotopologue) and six for AgKr, where the $B \leftarrow X$ transition was observed; these cover the range 68–138 cm^{-1} for AgKr and 179–278 cm^{-1} for AgXe. The VMI value for $D_0(\text{AgKr})$ is slightly higher, but is in better agreement with the computational predictions, while the new $D_0(\text{AgXe})$ falls towards the upper end of the range of values spanned by the measurements of Brock and Duncan, just as for AgAr.

It is also interesting to compare these results with those obtained previously by this group in a study on the analogous Au-RG species. The dissociation energies determined in this study were: $D_0(\text{AuAr}) = 149 \pm 13 \text{ cm}^{-1}$; $D_0(\text{AuKr}) = 240 \pm 19 \text{ cm}^{-1}$; $D_0(\text{AuXe}) = 607 \pm 5 \text{ cm}^{-1}$.⁶¹ As expected for molecules whose bonding is dominated by dispersion forces, gold bonds more strongly to rare gases than silver due to its higher polarisability, so the values for AuAr and AuKr are slightly higher than those for the respective silver molecules. However, it is noticeable that AuXe is much more strongly bound than either AgXe or AuKr. In fact, while the dissociation energies of the Ag-RG molecules increase linearly with the static dipole polarisabilities of the rare gas atoms (11.1 (Ar), 16.7 (Kr) and 27.3 (Xe) atomic units),¹⁷⁶ the gold species show a marked greater than linear dependence, as shown in Fig-

Table 2.1: Comparison of experimental and calculated values for the dissociation energies, D_0 , for silver-rare gas molecules

	D_0^a / cm^{-1}	Calc. / cm^{-1}	Expt. ^b / cm^{-1}	Expt. ^c / cm^{-1}
AgAr	85.9 ± 23.4	102.62 ^d	65	77 ± 15
		104.2 ^e	51	35 ± 45
AgKr	149.3 ± 22.4	163.61 ^d	138	
		160.3 ^e	68	
AgXe	256.3 ± 16.0	254.25 ^d	276	
		244.6 ^e	179	

^a This work

^b Brock and Duncan¹⁵² — values from Birge-Sponer extrapolations from the two $A \leftarrow X$ datasets for $^{107}\text{Ag}^{40}\text{Ar}$, $^{107}\text{Ag}^{83}\text{Kr}$ and $^{107}\text{Ag}^{129}\text{Xe}$

^c Jouvet *et al.*⁵⁰ — from Birge-Sponer fits to $A \leftarrow X$ fluorescence excitation data

^d CCSD(T), Loreau *et al.*³²

^e RCCSD(T), Gardner *et al.*¹⁵⁶

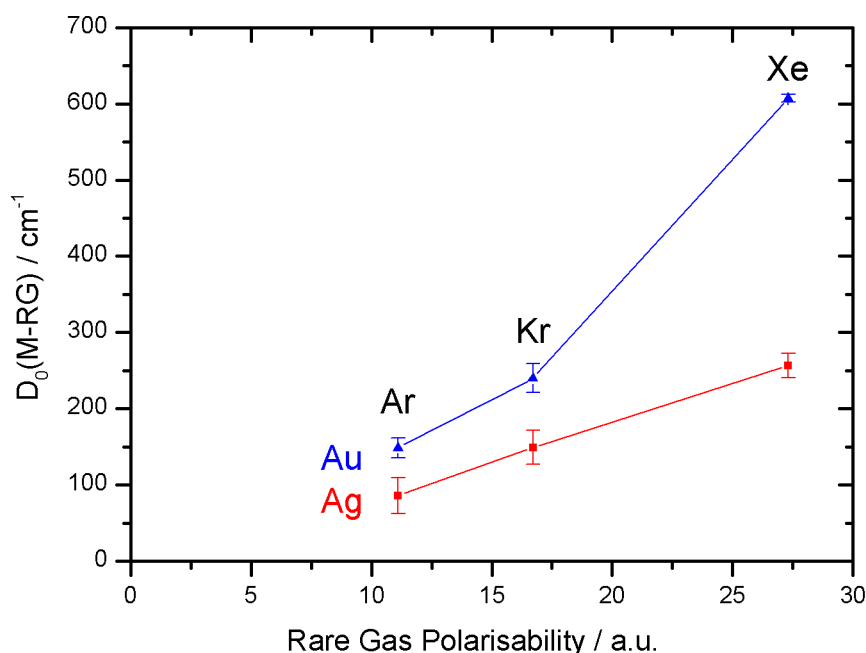


Figure 2.9: Comparison of the dependence of dissociation energy of Ag-RG (red squares) and Au-RG (blue triangles) molecules (RG = Ar, Kr, Xe) on the polarisability of the rare gas atom.

ure 2.9. This suggests that the silver-rare gas complexes are bound almost entirely by dispersion forces, while non-dispersion forces play a greater role in the binding of their gold analogues.

2.3.3 Dissociation of Silver Oxide, AgO

During the course of observing the spectroscopy and imaging of AgAr, several rings were observed in the region of the $\text{AgAr}(A \leftarrow X)$ transition which were not attributable to dissociation of this species, since they were observed in the absence of argon, as mentioned in Section 2.3.1.

As shown in Figure 2.10, in addition to the three overlapping series at higher wave-number which correspond to dissociation of AgAr, AgKr and AgXe, there are three different series which are observed. These are seen in both pure argon and pure helium carrier gases at slightly lower photon energy, meaning that they must originate from some other species. One of these series also continues as weak features in

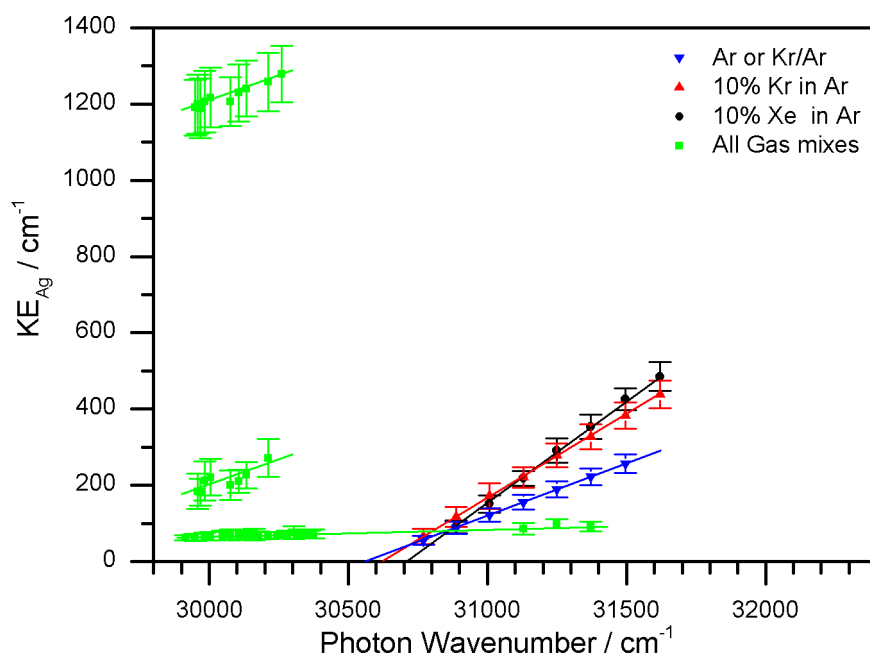


Figure 2.10: Plot of kinetic energy release of the silver fragment against wavenumber. **Blue inverted triangles:** rings due to dissociation of AgAr observed in pure argon carrier gas and a krypton/argon mix; **Red triangles:** rings observed in 10% krypton in argon gas due to AgKr dissociation; **Black circles:** dissociation of AgXe observed in xenon/argon gas; **Green squares:** features observed regardless of carrier gas. Lines have been added to indicate points which form a series.

the region where dissociation of Ag-RG was observed, after being obscured when these rings are small. For example, this feature appears in the fKER spectrum from the image at 31128 cm^{-1} , as shown in Figure 2.4.

The series of rings with the lowest KE_{Ag} values shows a very weak photon energy dependence gradient compared to the other sets, while the other two sets form parallel series which appear to have a gradient very similar to that of the series due to dissociation of AgAr. However, argon cannot be the co-fragment in this case since these rings are observed when there is no argon in the molecular beam. In fact, this apparent similarity in slope is due to a simple coincidence; the gradient of a line of KE_{Ag} against photon energy for the single-photon dissociation of AgAr is $0.27 (= n \cdot \frac{m_X}{m_{AgX}})$; see equation 2.2), while that for the two-photon dissociation of AgO is 0.26 . Of the species remaining in the molecular beam when helium is used as the carrier gas (i.e. AgO and pure silver clusters Ag_n), oxygen is the only

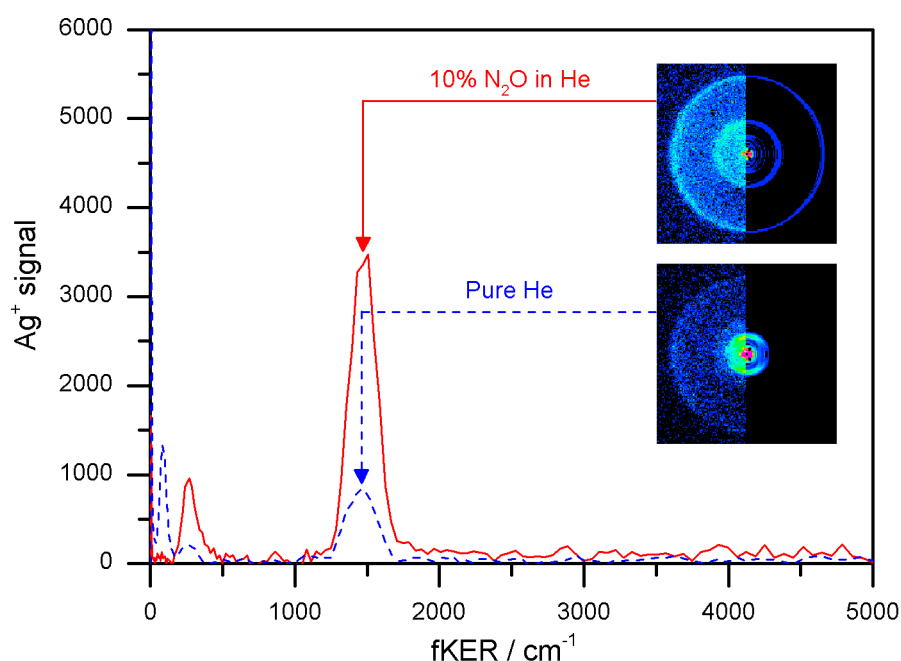


Figure 2.11: Fragment Kinetic Energy Release spectra and corresponding images measured at 332.8 nm (ca. 30050 cm^{-1}) in pure helium carrier gas (blue dotted trace and lower image) and a mixture of 10% N_2O in He (red solid trace and upper image). Both images are taken with the same overall intensity.

plausible co-fragment which can produce this gradient with an integer number of photons.

To test the possibility that silver oxide was responsible for these rings, N_2O was added to the beam as an oxidising agent in the hopes that it would lead to an increase in the amount of AgO in the beam, and hence an enhancement in the intensity of these rings. Nitrous oxide has previously been observed to oxidise the surface of bulk and powdered silver,^{177,178} which suggests that it might generate extra AgO molecules either by oxidation of the metal target surface prior to ablation, or by oxidising silver atoms in the beam.

Figure 2.11 shows a comparison between two velocity map images and their fKER spectra; one obtained using a pure helium carrier gas, and the other with N_2O seeded in the beam. As the spectra show, the peaks corresponding to the outer two rings — i.e. those which were suspected to be due to an oxygen co-fragment — are substantially enhanced (roughly four to five times the intensity), while the inner

peak is significantly depleted to the point of disappearing almost entirely. This can be seen visually in the accompanying images, which show the two rings (which are faintly visible in the raw data side of the image taken in pure helium) becoming very intense when N_2O is added, while the inner ring essentially vanishes. This is strong evidence for the fact that the outer two rings in this region are due to dissociation of AgO , while the inner ring (as discussed in Section 2.3.4) is due to a different species which is depleted when an oxidising agent is introduced.

Having determined the identity of the co-fragment, a value for the dissociation energy of AgO was found in the same fashion as for the Ag-RG molecules. Converting to TKER and using best-fit lines with a fixed gradient of two (i.e. the number of photons involved), values are obtained for the thresholds of the two processes of $25360.6 \pm 69.5 \text{ cm}^{-1}$ for the outer series and $29249.1 \pm 50.2 \text{ cm}^{-1}$ for the inner series.

Using these photon energies, equation 2.3 and the current best experimental value for the dissociation energy of $52.7 \pm 3.5 \text{ kcal mol}^{-1}$ ($= 18400 \pm 1200 \text{ cm}^{-1}$) from Smoes *et al.*¹⁵⁸ (despite the reservations about its accuracy)^{30,103,122,161,162} allows us to get an estimate for the internal energy of the Ag^* fragment in each case. The best estimate for these electronic energies is ca. 32300 cm^{-1} and ca. 40100 cm^{-1} for the outer and middle rings respectively. However, since the value used for the dissociation energy is believed to be too high,^{30,103,122,161,162} the actual fragments are likely to have a somewhat higher internal energy.

With this in mind, the best assignments for the two fragmentation pathways would appear to be $\text{AgO} \rightarrow \text{Ag}^*(^2D_{3/2}) + \text{O}(^3P)$ for the outer series and into $\text{Ag}^*(^2S_{1/2}) + \text{O}(^3P)$ fragments for the lower TKER series. These silver states have electronic energies of $34714.22643 \text{ cm}^{-1}$ and $42556.147 \text{ cm}^{-1}$ respectively.⁹¹ As expected, these values are slightly higher than predicted, but are the most likely states in this region. These states are also within one photon of the ionisation threshold of the silver atom, allowing for efficient ionisation and detection.

Since there are two series which result from the same species, the gap between them can be used to confirm the assignment. There are eight independent measurements of this gap (i.e. eight images in which both rings were seen), giving an

overall value of $7721 \pm 191.4 \text{ cm}^{-1}$ for the separation. This is within experimental uncertainty of the actual gap of 7841.9 cm^{-1} , thus supporting the assignment.

With appropriate values for the internal energies of the fragments, it is possible to combine this with the values for the threshold photon energy and use equation 2.3 to find two values for the dissociation energy, one from each series. It is also possible to fit a line simultaneously through both series by fixing the gap between them, which is now known. Table 2.2 shows these values in comparison to previous experimental and calculated values.

The final value for the dissociation energy of the silver oxide molecule, $15965 \pm 81 \text{ cm}^{-1}$ (1.98 eV), is ca. 2400 cm^{-1} lower than the previous experimental value; however, it is much more in line with computational predictions of $D_0(\text{AgO})$, which have created a long-standing suspicion that this previous value was too high.

This value can be compared with those for the other coinage metals to establish periodic trends. $D_0(\text{CuO})$ has been previously found to be $3.041 \pm 0.030 \text{ eV}$ ($24530 \pm 240 \text{ cm}^{-1}$) using velocity map imaging.⁴⁴ As for the gold analogue, Smoes *et al.* found that the dissociation energy was $53.8 \pm 3.5 \text{ kcal mol}^{-1}$ ($18800 \pm 1200 \text{ cm}^{-1}$) in the same study with the silver oxide.¹⁵⁸ A more recent spectroscopic investigation corroborated this, finding a value for D_e of 233 kJ mol^{-1} (19500 cm^{-1}), assuming a

Table 2.2: Comparison of experimental and calculated values for the dissociation energy, D_0 , for silver oxide

	D_0^a / cm^{-1}	Expt. ^b / kcal mol^{-1}	Calc. / eV
AgO	15965 ± 81	52.7 ± 3.5	$1.91^{179} (15400 \text{ cm}^{-1})$
	16007 ± 139^c	$(18400 \pm 1200 \text{ cm}^{-1})$	$1.82^{103} (14700 \text{ cm}^{-1})$
	15942 ± 100^d		$1.71 - 2.2^{122}$
			$(13800 - 18000 \text{ cm}^{-1})$
			$1.74^{162} (14000 \text{ cm}^{-1})$

^a This work

^b Smoes *et al.*¹⁵⁸

^c Calculated using only the data for the $\text{Ag}(^2D_{3/2}) + \text{O}(^3P)$ channel

^d Calculated using only the data for the $\text{Ag}(^2S_{1/2}) + \text{O}(^3P)$ channel

Morse oscillator.¹⁸⁰ Other computational values are in broad agreement, with the 2006 study of O'Brien *et al.* finding $D_0 = 2.17\text{eV}$ (17500 cm^{-1}).¹⁸¹

The overall trend observed is that the dissociation energy of AgO is substantially lower than that of CuO, but there is a slight increase on continuing down the group to AuO. This is consistent with the common trend in binding energy for coinage metal-containing species, where an overall decrease down the group is reversed for gold due to strong relativistic effects,^{182,183} and has previously been observed in other molecules such as M-H and M-CH₃ species.^{184,185} In cases like these which involve metal-ligand bonds of almost entirely σ -bonding character, bond energies usually follow the trend $D_0(\text{AuX}) > D_0(\text{CuX}) > D_0(\text{AgX})$, while in cases where the bonding is more synergic, involving π -character, then the order $D_0(\text{CuX}) > D_0(\text{AuX}) > D_0(\text{AgX})$, as seen here with the oxides, is more prevalent.¹⁸⁶

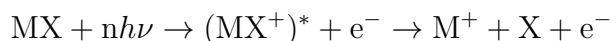
2.3.4 Dissociative Ionisation of the Silver Dimer

There remains one series of rings unaccounted for among those shown in Figure 2.10; the series seen at lower photon energy alongside the dissociation of AgO. As shown in Figure 2.11, this ring is depleted when nitrous oxide is added to the molecular beam as an oxidising agent, suggesting that the parent species is not silver oxide. It is also seen in both pure argon and pure helium carrier gas, suggesting that it does not originate from dissociation of a silver-rare gas species.

The other interesting feature of these rings is that the kinetic energy release of the silver fragment depends very weakly on photon energy, such that a fit through the corresponding points has a very shallow gradient. As shown by the feature indicated by an asterisk in Figure 2.4 and by the points shown in Figure 2.10, they are even visible at a similar energy in the region of the $C \leftarrow X$ dissociative transition in Ag-RG molecules, with an overall increase of only $30\text{-}40\text{ cm}^{-1}$ in the kinetic energy of the silver fragment for an increase of almost 1500 cm^{-1} in photon energy. In fact, the gradient is so shallow that using equation 2.2 to determine the mass of the co-fragment would suggest one that is impossibly light, with a mass of ca. $2u$. The lightest possible co-fragment is helium, which can be ruled out since these features are observed in an argon carrier gas. Atomic and molecular hydrogen can also be

discounted as they do not provide a good fit to the data, and due to the lack of any evidence for the presence of these species in the molecular beam.

A series of this sort has previously been observed by this group during a study of AuXe and was assigned to a dissociative ionisation process, where the molecule is ionised into a dissociative cationic state and subsequently fragments:⁸¹



In a dissociative process, where the fragment(s) are subsequently ionised, it is possible to linearly relate the kinetic energy release of the two fragments to the photon energy, since all other energies involved in the process are quantised. However, the fact that the electron is released prior to dissociation breaks this relationship, and the equation linking the total kinetic energy release to the photon energy becomes:

$$\text{TKER} = nh\nu + E_{\text{AgX}} - E_{\text{Ag}^+} - E_{\text{X}} - D_0(\text{AgX}) - E_{e^-} - \text{IE}_{\text{Ag}} \quad (2.4)$$

where E_{e^-} is the energy of the ionised electron and IE_{Ag} is the ionisation energy of the silver atom.

The energy of the electron is not fixed, unlike the internal electronic energies of the other fragments, so when the photon energy increases, the amount of energy taken away by the electron also increases such that the actual increase in TKER is much lower than expected. This can give rise to very shallow gradients in KER against wavenumber plots, as is the case with the set of rings under examination now.

The problem with this is that the gradient of a KE_{Ag} against photon energy plot can no longer be used to determine the mass of the co-fragment as in Sections 2.3.1–2.3.3. The most that can be found for this dataset is the most likely identity for the co-fragment by using other evidence.

As mentioned in Section 2.3.1, the species identified in the beam when argon is used as a carrier gas are Ag, AgO, AgAr, Ag₂ and traces of Ag₃. The same species (with the obvious exception of AgAr) are observed when the carrier gas is replaced with helium. Given that the dissociative ionisation process is observed in both cases, AgAr or similar Ag-RG species are not responsible, and AgO has already

been ruled out since addition of nitrous oxide reduces, rather than increases, the intensity of the rings. This leaves the only plausible candidate for the parent species as a pure silver cluster, Ag_n . Given that the rings are of considerable intensity and that significant amounts of the dimer are observed with only traces of the trimer, Ag_2 is the mostly likely parent molecule.

The ionisation energy to the ground state of the Ag_2^+ ion has been previously determined using Zero Kinetic Energy (ZEKE) photoelectron spectroscopy to be $61746 \pm 3 \text{ cm}^{-1}$.¹⁷¹ Since the process occurs down to at least a photon energy of 29915 cm^{-1} , at least three photons must be involved in the ionisation. However, three photon ionisation provides an excess energy of ca. 28000 cm^{-1} , suggesting significant excitation of the produced ion. Note that this is near the low-energy end of the dye curve so it is uncertain whether the process is possible with an even lower wavenumber.

Bonačić-Koutecký *et al.* have previously used CCSD-level calculations to predict the existence of a $^2\Sigma_u^+$ state at 3.15 eV (25400 cm^{-1}) above the $^2\Sigma_g^+$ ground state,¹⁷³ which is easily accessible with three photons from the ground state of the neutral molecule. Time-dependent density functional theory in the TURBOMOLE software package has been used to plot the potential energy curve of this excited state.¹¹² The result is shown in Figure 2.12 alongside Morse curves corresponding to the ground states of Ag_2 and Ag_2^+ plotted using experimental values for the atomic ionisation energy, bond dissociation energies, vibrational constants and bond lengths (except for the cationic bond length which is a computational value).^{91,104,167,170,187–189}

While this is quite a low level of theory for the plot of the excited state curve, it provides a good idea of the general shape, showing that it is a mostly dissociative curve, with a very shallow minimum in the Franck-Condon region. The unusual form of the curve originates from an avoided crossing with another $^2\Sigma_u^+$ state. Hence, there is sufficient knowledge of the energies involved from previous papers using experimental evidence or higher levels of theory to demonstrate that

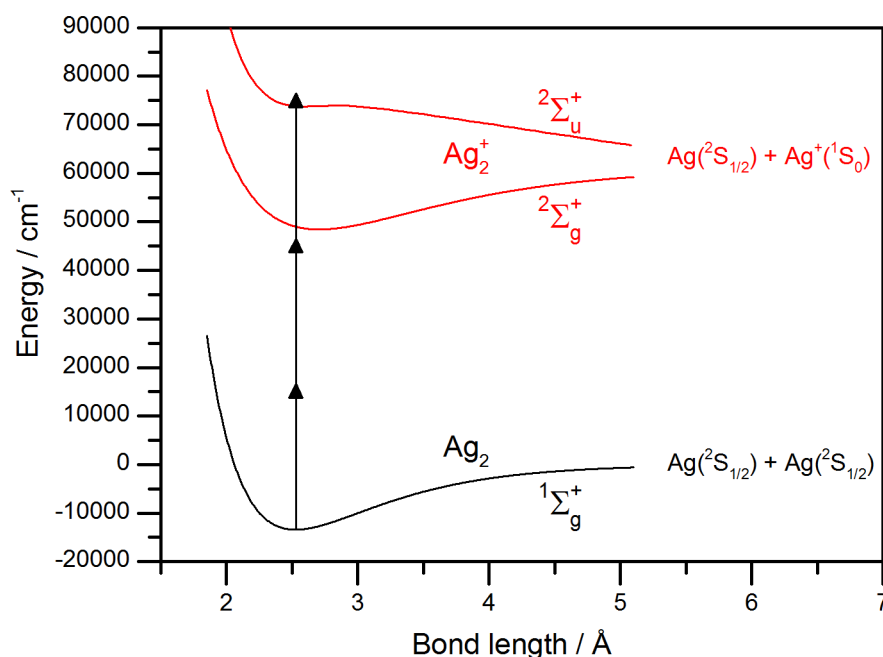


Figure 2.12: Energy level diagram of Ag₂ (black) and Ag₂⁺ (red). Ground state curves are plotted as Morse curves using previously published parameters.^{91,104,167,170,187–189} The excited state curve for the cation is calculated at the TD-DFT level with the TURBOMOLE software package using the B3-LYP functional and a def2-TZVP basis set, offset vertically to match up to the transition energy previously calculated by Bonačić-Koutecký *et al.* at a higher level of theory.¹⁷³ The length of the arrow indicates one photon of 29915 cm⁻¹, the lowest photon energy at which the rings were observed.

three photons are enough to get onto this curve, as explained above. It is also important to note that, as seen in Figure 2.11, the rings of interest have significant parallel anisotropy, which would fit well with a $\Sigma \leftarrow \Sigma$ transition.

It is therefore plausible that the rings originate from a three-photon excitation from the ground state of the neutral dimer to a dissociative excited state of the cation, which falls apart to generate Ag⁺(¹S₀) and Ag(2S_{1/2}) fragments (there is insufficient energy to reach a higher threshold and generate electronically excited fragments). Unfortunately, this assignment cannot be confirmed with as much certainty as those for the other ring series due to the nature of the dissociative ionisation. The extra variable term, E_{e-} , in equation 2.4 means that the gradient of the fit through the points on a KE_{Ag} against photon energy plot no longer corresponds to the photon number and co-fragment mass. It also means that the intercept cannot

be used to identify the electronic states of the fragments and find the dissociation energy, since the energy of the electron is unknown unless it can also be detected. This is impossible with the current experimental setup.

2.4 Conclusions

In the course of velocity map imaging of the silver fragment in the region between 29900 and 31620 cm^{-1} , multiple rings were observed corresponding to dissociation of three different silver-rare gas molecules: AgAr, AgKr and AgXe. Alongside these molecules, two different dissociation pathways of the gaseous silver oxide, AgO, and a dissociative ionisation event most likely resulting from dissociation of the silver dimer, Ag₂, were also observed. Figure 2.13 shows the position of all of these rings against the wavenumber at which they were observed, along with the assigned dissociation pathways.

As a result of the VMI observations of Ag-RG molecules, it was possible to di-

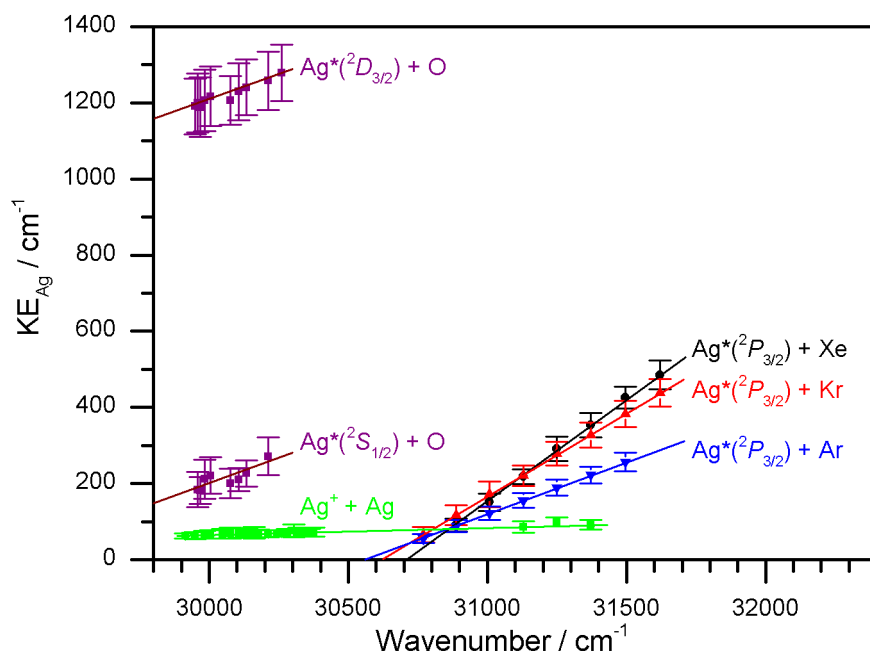


Figure 2.13: Assignment of all features observed using velocity map imaging in this study.

rectly measure the dissociation energy of these species. While the values obtained were in broad agreement with previous observations, they represent an important advance as they do not depend on Birge-Sponer extrapolations from vibrational spectra. This is particularly relevant in these species, as Loreau *et al.* have pointed out that the form of potential energy surfaces is sufficiently different to a Morse curve so as to call the vibrational assignments into question. This places values for the dissociation energy which depend on those assignments under suspicion.³²

As for the silver oxide, a new value for the dissociation energy has been obtained which departs substantially from the previously accepted value. However, this value has been repeatedly contradicted by calculations, which have suggested a lower value regardless of computational method. The new value gives much better agreement with these calculations and will hopefully resolve some questions about the effectiveness of theoretical methods for studying this molecule.

While the dissociative ionisation of Ag_2 proved somewhat more frustrating in that it was impossible to determine the dissociation energy of this species, sufficient evidence has been obtained through the current experiments and from knowledge of the electronic structures of the silver dimer molecule and cation that the assignment of these rings seems relatively sound. Any future work on this molecule would have to focus on searching for a separate dissociation of this species in another wavelength region, which may allow more information to be gained.

In summary, the photodissociation processes in this region have been thoroughly examined and a greater understanding of the Ag-RG (RG = Ar, Kr, Xe) and AgO molecules has been obtained. Future work could focus on either a different area of the spectrum where different processes corresponding to other silver species may be observed, or on different, related species such as other transition metal oxides or rare gas complexes where the same techniques could be applied.

Chapter 3

Velocity Map Imaging of Molybdenum Oxide

Light in the region 455–465 nm ($21500\text{--}22000\text{ cm}^{-1}$) has been used to study the spectroscopy and photodissociation dynamics of isotopically-selected molybdenum oxide, ^{98}MoO . In this spectral region, it was found that this molecule can dissociate into multiple fragmentation pathways via a multi-photon process. This has been used to obtain independent measurements of the dissociation energy, $D_0(^{98}\text{MoO})$, which yielded an average value of $44027 \pm 151\text{ cm}^{-1}$. Separate studies in the 307–320 nm ($31250\text{--}32500\text{ cm}^{-1}$) region have also observed two-photon dissociation of MoO, supporting this dissociation energy. The work in this chapter is currently in preparation for publication.¹⁹⁰

3.1 Previous Work

As mention in Section 1.7, transition metal oxides are of interest due to their applications in fields such as astrophysics,^{145,146} since they are highly stable and thus are important in high-temperature chemistry.⁶⁹ As diatomic molecules containing a single *d*-metal atom, they are also interesting as a study in the effect of *d*-electron bonding.¹⁴⁷

Molybdenum oxide has previously been studied both to understand its dissociation dynamics, and its spectroscopy. Hamrick, Taylor & Morse used $1 + 1'$ resonant two-photon ionisation (R2PI) spectroscopy to record the spectra of multiple bands

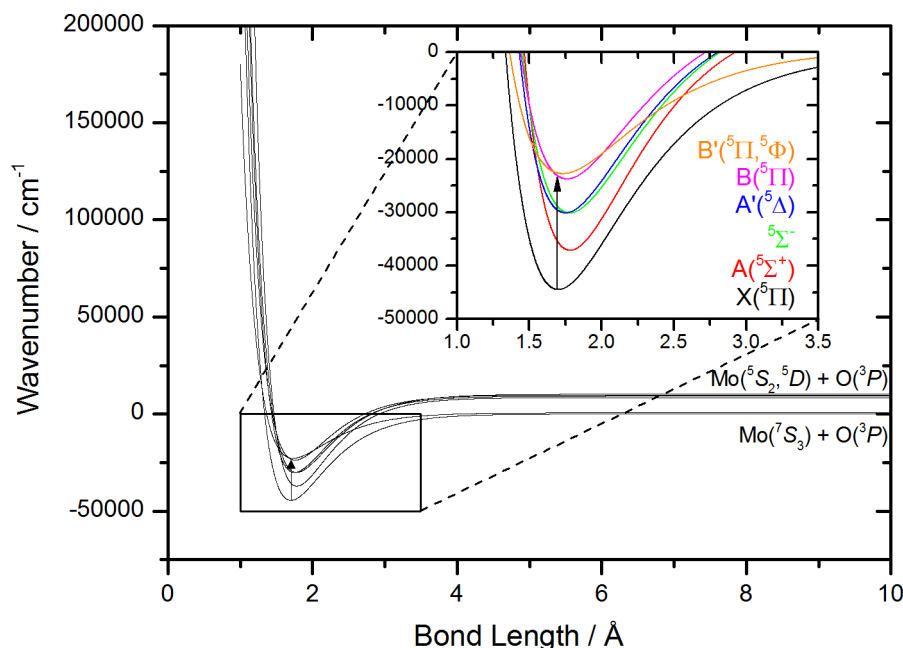


Figure 3.1: Energy level diagram of MoO showing low-lying electronic excited states, plotted as Morse curves. Experimental data was used where available,⁶⁹ and density functional calculations from the literature were used otherwise.^{191,192} The arrow corresponds to the one-photon $B \leftarrow X$ transition observed by Hamrick *et al.* in the region of interest.⁶⁹ **Inset:** Detail of the states inside the well of the X-curve, colour-coded to indicate the quintet states present in this region.

between 10000 and 23100 cm^{-1} .⁶⁹ For the current purposes, the most interesting of these are the $B(^5\Pi) \leftarrow X(^5\Pi)$ and $B'(^5\Pi) \leftarrow X(^5\Pi)$ bands around 21700 cm^{-1} , in the middle of the region studied. Figure 3.1 shows a potential energy level diagram with the low-lying electronic states of MoO, with the $B \leftarrow X$ transition indicated.

In terms of dissociation of MoO, Huber & Herzberg cite a study by De Maria *et al.*, who used Knudsen Cell Mass Spectrometry to determine a value of $116 \pm 15 \text{ kcal mol}^{-1}$ ($40600 \pm 5200 \text{ cm}^{-1}$).^{157,193} A later review by Pedley and Marshall casts doubt on this experiment, and instead cites a value from 1977 by Emelyanov *et al.*, who also used the Knudsen Cell technique (in this case relative to YO) to find a value of $132.9 \pm 5.0 \text{ kcal mol}^{-1}$ ($46550 \pm 1800 \text{ cm}^{-1}$).^{146,194}

More recently, molybdenum oxide has been studied by Looock *et al.*, who suggest that the value for $D_0(\text{YO})$ used by Emelyanov *et al.* was inaccurate based on their

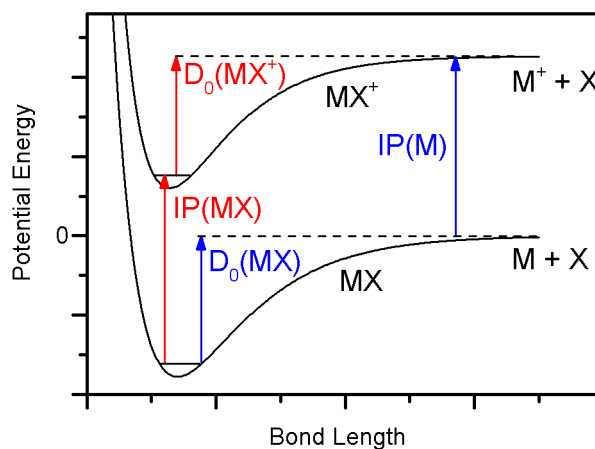


Figure 3.2: Schematic Energy Level Diagram demonstrating Equation 3.1 for a generic molecule MX. Dissociation followed by ionisation (blue arrows) is equivalent in energy terms to ionisation followed by dissociation (red arrows).

own, more recent research.¹⁹⁵ Instead, they measured $D_0(\text{MoO})$ indirectly by using a thermodynamic cycle, which utilises the fact that, since ionisation of a molecule followed by dissociation of the ion results in the same products as dissociation of the molecule followed by ionisation of the metal ion:

$$D_0(\text{MoO}) + \text{IP}(\text{Mo}) = \text{IP}(\text{MoO}) + D_0(\text{MoO}^+) \quad (3.1)$$

where $\text{IP}(\text{Mo})$ is known to be $7.02943 \pm 0.00004 \text{ eV}$,^{91,196} as illustrated by Figure 3.2.

For the dissociation energy of the oxide cation, MoO^+ , Looock *et al.* used two studies. The first, by the group of Peter Armentrout, used guided ion beam reactivity to find a value of $D_0(\text{MoO}^+) = 5.06 \pm 0.02 \text{ eV}$.¹⁹⁷ The second, from Helmut Schwarz's group, used ion/molecule bracketing experiments in a Fourier-transform ion cyclotron resonance (FTICR) mass spectrometer combined with computational results to reach a result of $118 \pm 2 \text{ kcal mol}^{-1}$ ($= 5.12 \pm 0.09 \text{ eV}$).¹⁹⁸ The value used in the thermochemical cycle was a straightforward average of $5.09 \pm 0.04 \text{ eV}$.¹⁹⁵

Looock *et al.* then used two-color photo-ionisation efficiency (PIE) spectroscopy and mass-analysed threshold ionisation (MATI) to measure the ionisation potential of the molybdenum oxide molecule as $7.4504 \pm 0.0005 \text{ eV}$, and used the three different values in equation 3.1 to give a dissociation energy for MoO of $5.44 \pm 0.04 \text{ eV}$

(ca. $43900 \pm 300 \text{ cm}^{-1}$).¹⁹⁵ This compared well to the two earlier thermochemical measurements (despite the question marks over the parameters used in those studies) whilst having a substantially lower uncertainty.

Recently, Luo *et al.* used the same thermochemical cycle and their own measurement of IP(MoO) as $7.4508 \pm 0.0001 \text{ eV}$, determined by photo-electron spectroscopy, to measure the difference in D_0 between MoO and MoO^+ .¹⁹⁹ Although they did not state a preference between using Armentrout's value of $D_0(\text{MoO}^+)$ or the older Knudsen-cell measurement of $D_0(\text{MoO})$ as the reference value to determine the other, it would seem prudent to prefer the more recent guided ion beam measurement to find the dissociation energy of the neutral molecule. In this case, they found a dissociation energy of $5.42 \pm 0.02 \text{ eV}$ (ca. $43700 \pm 200 \text{ cm}^{-1}$). This is slightly lower than the value from Looock *et al.*, with the difference coming from whether the dissociation energy of the cation is taken from just Armentrout's measurement (by Luo *et al.*), or from a combination of that value and Schwarz's experiments (by Looock *et al.*). The main failing of these values is that they were all measured indirectly; a more direct measurement using velocity map imaging which corroborated or corrected the value of $D_0(^{98}\text{MoO})$ would be valuable.

MoO has also been studied computationally, including a density functional theory study of various molybdenum oxide clusters by Oliveira *et al.* in 2003, who found a value for D_e of 5.58 eV (ca. 45000 cm^{-1}).²⁰⁰ This is somewhat high relative to the experimental dissociation energy but compares well, especially considering that some of the difference will come from zero-point energy, which is known spectroscopically to be ca. 450 cm^{-1} .⁶⁹

3.2 Experimental Method

The experiments in this chapter were performed on the velocity map imaging setup described in Section 1.4; this section covers details specific to this study. Clusters were produced by ablation of a molybdenum foil into a molecular beam

where the carrier gas was pure argon. The target used was a disc of pure molybdenum, of natural isotopic abundance. Unfortunately for mass spectrometric studies, molybdenum has seven isotopes with significant abundance: ^{92}Mo : 14.84%; ^{94}Mo : 9.25%; ^{95}Mo : 15.92%; ^{96}Mo : 16.68%; ^{97}Mo : 9.55%; ^{98}Mo : 24.13%; and ^{100}Mo : 9.63%.¹⁷⁴ Given the variety of isotopes, signal was sacrificed for selectivity in the spectroscopy and imaging on molybdenum oxide by gating only on the ^{98}Mo isotope and its relative compounds.

In the studies of ^{98}MoO reported in Section 3.3.2, two lasers were used; the first is a frequency-doubled (532 nm) Nd:YAG laser (Continuum Minilite) used for ablation of the metal target, while the second is a OPO (optical parametric oscillator) (Continuum Panther) pumped by the 355 nm frequency-tripled radiation from a Nd:YAG laser (Continuum Surelite). The signal beam of the latter setup can cover a spectral range of 400–700 nm; the spectroscopy and imaging of MoO was observed towards the low-wavelength end of this region. The frequency-doubled output from a tunable dye laser (Sirah) (pumped by the third harmonic (355 nm) from a different Nd:YAG laser (Surelite), with a dye of Coumarin 460 in ethanol), which outputs in a wavelength range of ca. 220–240 nm (after doubling), was used to efficiently ionise the species present in the molecular beam for optimisation purposes but was not used for the main VMI or spectroscopy experiments.

In Section 3.3.3, the ablation laser used was a frequency-doubled Nd:YAG laser (Litron Nano) — again at 532 nm, while the probe laser was the aforementioned frequency-doubled Sirah dye laser, this time pumped with the second harmonic (532 nm) output of the same Nd:YAG pump laser (Surelite) mentioned previously, and using a dye solution of DCM in ethanol. This dye lases in the 595–665 nm range which is then doubled to reach the 297.5–332.5 nm range.

3.3 Experimental Results

3.3.1 Spectroscopy of Molybdenum Oxide

Initial experiments identified and optimised the species present in the molecular beam. Figure 3.3 shows a mass spectrum recorded at a photon energy of

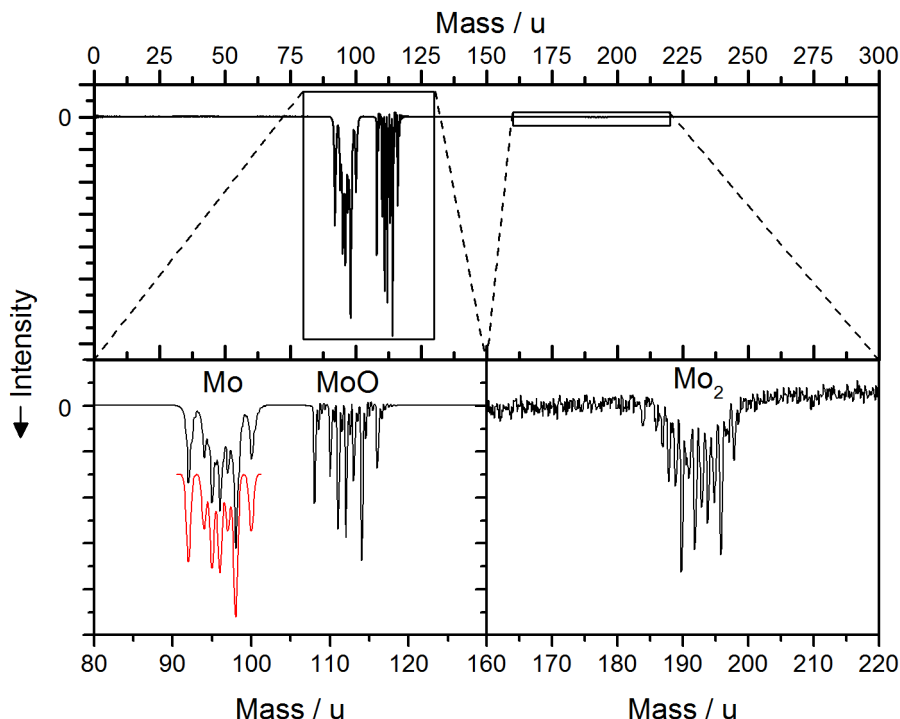


Figure 3.3: Time-of-flight mass spectrum recorded with a probe laser wavelength of 460 nm (21740 cm^{-1}). **Top:** Broad view of entire mass spectrum. **Bottom Left:** Detail showing peaks resulting from molybdenum atom and molybdenum oxide, including comparison to the trace in red indicating the expected intensity ratio of the isotopes of Mo. **Bottom right:** Detail showing the peaks around 200 u which result from isotopologues of Mo₂.

21740 cm^{-1} , which demonstrates that the major species present in the beam are the various isotopes of Mo (92–100 u) and MoO (108–116 u). There are also several much smaller peaks around 200 u which result from the 15 isotopologues of Mo₂ which have significant natural abundance. When the mass spectrum was recorded using UV light, it was revealed that there was a small quantity of MoO₂ in the beam, but no larger clusters were observed.

Having optimised production of Mo and MoO, their spectra were subsequently recorded by scanning the OPO wavelength between 450 and 470 nm (ca. $21300\text{--}22200\text{ cm}^{-1}$). While multiple peaks with significant intensity were observed for the molybdenum atom, these have proven highly difficult to assign. However, the spectra observed in the ^{98}MoO channel have proven far more informative. Figure 3.4 shows a comparison between one of these spectra and the results presented by Hamrick *et al.*⁶⁹ Unlike the earlier study, which used a second photon of higher

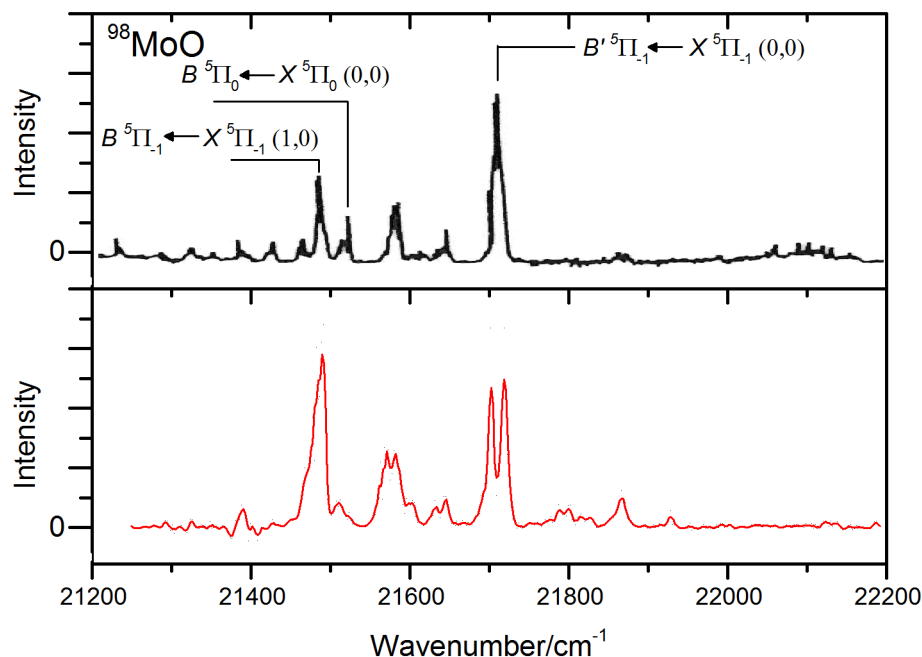


Figure 3.4: Comparison of resonant multi-photon ionisation (REMPI) spectra in the ^{98}MoO channel obtained in the region of the $B \leftarrow X$ and $B' \leftarrow X$ bands. **Top:** Excerpt from $1 + 1'$ R2PI data obtained by the group of Michael Morse (black trace) with their assignments indicated. Reprinted from *Journal of Molecular Spectroscopy*, 146, Y. M. Hamrick, S. Taylor and M. D. Morse, “Optical spectroscopy of jet-cooled MoO”, 273-313, Copyright (1991), with permission from Elsevier. **Bottom:** $1 + 2$ REMPI data obtained in this study in the same region (red trace).

energy to produce a $1 + 1'$ R2PI scheme, the current data were recorded in single-colour spectroscopy, requiring three photons to reach the ionisation threshold in this region in a $1 + 2$ REMPI scheme.

This comparison demonstrates that the spectrum of the peak assigned as ^{98}MoO in this region strongly resembles that previously recorded. The two largest peaks, assigned by Hamrick *et al.* as the (1,0) transition of the $B(^5\Pi_{-1}) \leftarrow X(^5\Pi_{-1})$ band (at 21487 cm^{-1}) and the (0,0) transition of the $B'(^5\Pi_{-1}) \leftarrow X(^5\Pi_{-1})$ band (at 21712 cm^{-1}), are well-reproduced, along with a number of smaller features. The latter of these two major features demonstrates a double peak structure in the new data which is not evident in the reference spectrum. It is possible that this is an additional feature not seen in the $1 + 1'$ spectra obtained by Morse’s group, or that the low-resolution spectrum presented in the published data did not resolve this

structure.

The precise details of the assignment are not crucial to further analysis; however, it is important that this confirms the assignment of the masses in the time-of-flight spectrum and that it is possible to reproduce previously observed spectra of the MoO species. It also allows confirmation of the calibration of the OPO laser by comparison with the known positions of these lines, which is important for the velocity map imaging studies laid out over the rest of the chapter, as the photon energy is an important variable in determining the threshold for the dissociation processes and hence finding D_0 .

These spectra were recorded without using a focussing lens, which is usually employed in order to obtain velocity map images of dissociation processes. The spectra were repeated with the focussing lens in place, which demonstrated that the same features as those in Figure 3.4 were observed, but with additional off-resonance intensity, which reduced the quality of the spectra obtained. This indicates that the spectra discussed here are relevant to the imaging discussed below, despite the differing conditions.

3.3.2 Velocity Map Imaging of Molybdenum Oxide in the Visible Region

With the spectroscopy of the MoO molecule in this region having been recorded and found to be consistent with previous observations, imaging experiments on the molybdenum ion (formed from photodissociation processes and subsequently ionised) in this region were carried out. To eliminate complications from the seven different isotopes of molybdenum, all of the images recorded are gated solely over the most abundant isotope, ^{98}Mo . As shown by the sample images and fragment kinetic energy release (fKER) spectra shown in Figure 3.5, significant intensity was observed away from the central spot caused by the molecular beam, indicative of photodissociation processes.

To investigate the possibility that these rings were related to the features observed in the spectrum shown in Figure 3.4, images were recorded at wavelengths reso-

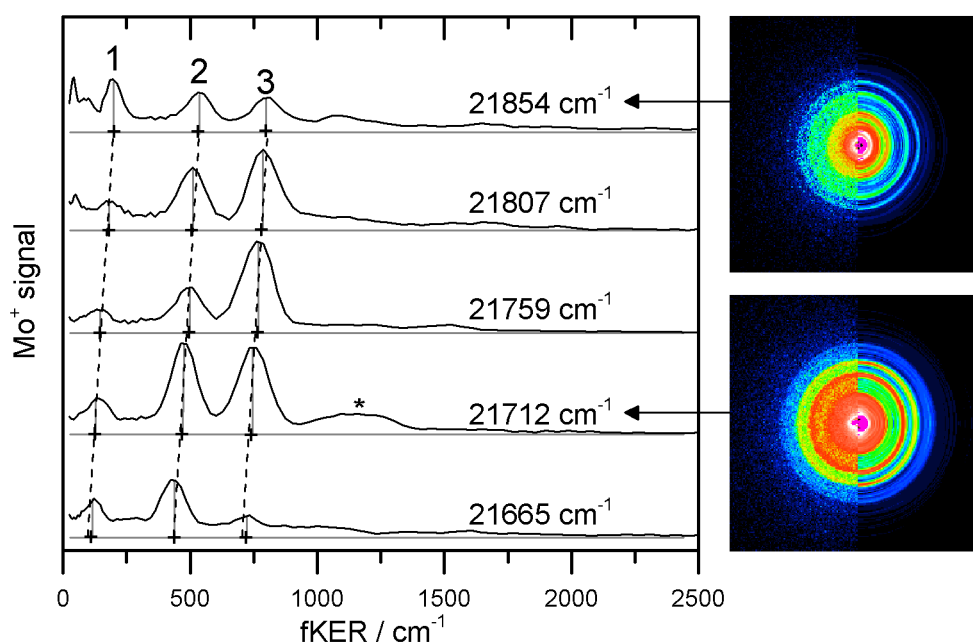


Figure 3.5: Fragment Kinetic Energy Release spectra for the ^{98}Mo fragment in the dissociation observed in the region around 460 nm in pure argon carrier gas, with the main series labelled to match Figure 3.6. Representative sample images are shown for two of the spectra, with the left half of each image showing the raw image and the right the central slice reconstructed by Polar Onion Peeling. The feature marked by * corresponds to the weak extra ring seen in the lower image.

nant with the transitions, and compared to those recorded off-resonance. However, none of the features observed in the images were dependent on the photon energy being resonant with the transitions in the REMPI spectrum, suggesting that the dissociation processes were not directly related.

Having established this, images were recorded in regular wavelength intervals to ensure good coverage in this spectral region. This can be seen in Figure 3.5, which shows fKER spectra extracted from images taken at 1 nm intervals (ca. 50 cm^{-1} in this region). These show three main features visible in each spectrum, which are indicated by crosses and joined by dotted lines in order to indicate the slight but noticeable increase in kinetic energy released as the photon energy increases.

This increase in fKER is expected, as explained in Section 1.5.3, which showed that from the dissociation of a general molybdenum-containing molecule Mo-X, the

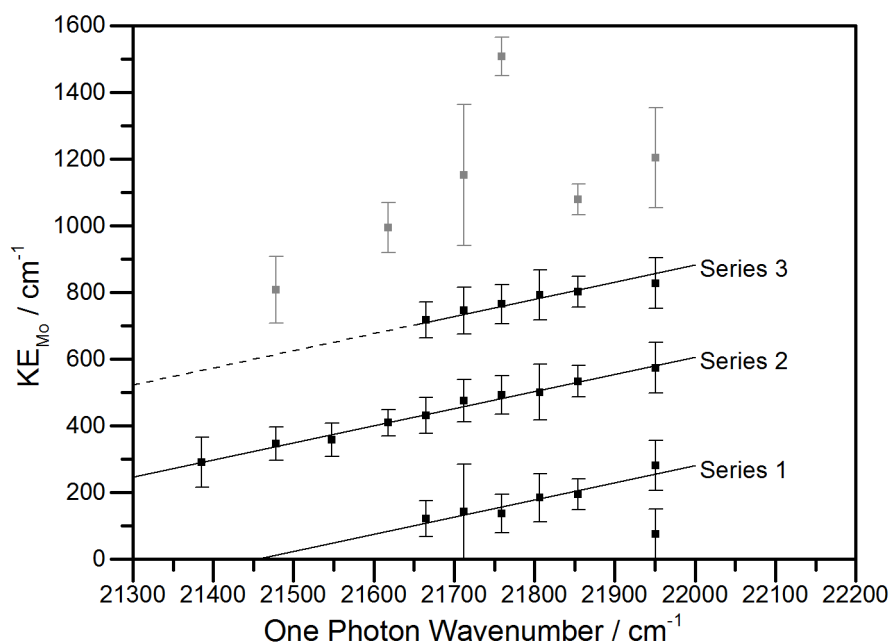


Figure 3.6: Plot of the Kinetic Energy of the ^{98}Mo fragment, KE_{Mo} , against wavenumber of the photon used. Each point represents the centre of a peak in the fKER spectra corresponding to a ring, such as the ones shown in Figure 3.5, while the error bars represent the Full Width at Half Maximum (FWHM) of the corresponding peaks. Each image was obtained in a pure argon backing gas. Points shown in grey correspond to much weaker features also observed. Lines have been added to indicate points that form a series.

kinetic energy of the molybdenum fragment released, KE_{Mo} , could be related to the TKER (Total Kinetic Energy Release), and hence to the photon energy $h\nu$ by:

$$\text{KE}_{\text{Mo}} = \frac{m_{\text{X}}}{m_{\text{MoX}}} \cdot \text{TKER} \quad (3.2)$$

$$= \frac{m_{\text{X}}}{m_{\text{MoX}}} \cdot (n h \nu + E_{\text{MoX}} - E_{\text{Mo}} - E_{\text{X}} - D_0(\text{MoX})) \quad (3.3)$$

where E_{Mo} , E_{X} and E_{MoX} are the internal energies of the molybdenum atom, the co-fragment and the parent molecule respectively, and n is the number of photons involved in the dissociation.

Equation 3.3 demonstrates that if the position of the peaks in the spectra shown in Figure 3.5 were plotted against photon energy, they should form a straight line with a gradient which depends on the mass of the co-fragment via the ratio $\frac{m_{\text{X}}}{m_{\text{MoX}}}$,

and on the number of photons. Figure 3.6 shows such a plot, which can be used to determine the identity of the co-fragment and the number of photons involved.

Identification of the Parent Molecule

As Figures 3.5 and 3.6 show, there are several distinct rings in this region. However, three sets of rings stand out, forming three series which have been labelled as Series 1, 2 and 3 as shown. The other points correspond to weaker features in the fKER spectra, which makes them difficult to assign. The three series all appear to be fitted by lines of the same gradient, indicating that they likely come from three different dissociation processes of the same molecule. To identify the molecule, Series 2 is initially used, since it contains the most points, which all fit very well to a straight line.

The gradient of the best-fit line through these points is 0.51903. As explained above, this is equal to $n \cdot \frac{m_X}{m_{\text{MoX}}}$ and can therefore be used to find what the mass of the co-fragment would have to be for a given integer number of photons, since the mass of the molybdenum atom is known to be 98 *u*. However, there is also a need to account for the magnification factor of the imaging system. This is described in Section 1.5, but, in brief, the ion optics introduce a magnification effect into the images, such that the observed radii of the rings are larger than that which you would expect from the recoil velocity of the fragments by a magnification factor MF. Since the kinetic energy is related to the square of these radii, the value calculated directly from the image is larger than the actual kinetic energy release, such that:

$$\text{KE}_{\text{true}} = \frac{\text{KE}_{\text{calculated}}}{\text{MF}^2}. \quad (3.4)$$

As explained in Section 1.5, the magnification factor is usually found to be around 1.05–1.10. However the exact value is determined by finding the gradient of a fit through the raw data, since this gradient depends on *n*, MF, and *m_X*.

It is possible to try different values of the magnification factor to find what values would give sensible assignments for the dissociation processes, given the species

present in the molecular beam (see Figure 3.3). There are two values which give plausible values for the mass of the co-fragment for an integer value of n :

No. of photons	m_X/u (MF = 1.024)	m_X/u (MF = 1.110)
1	95.95	71.27
2	32.21	26.13
3	19.35	16.00
4	13.83	11.53

All other values for the magnification factor do not give any plausible values of m_X for an integer number of photons. The two possible assignments from this are thus:

1. A single-photon dissociation of Mo_2 ; this would give a value for the mass of the co-fragment of $95.95 u$ (since it cannot be determined which isotopologue is the parent dimer), and would require a magnification factor of 1.024.
2. A dissociation of ^{98}MoO using three photons, such that m_X is 16.0, and the magnification factor would have to be 1.110.

The former assignment is unlikely due to the fact that, since the photon energy is in the region of ca. $21400\text{--}22000\text{ cm}^{-1}$, Mo_2 would have to be unusually weakly bound in order to be dissociated by a single photon. The dissociation energy of the dimer has been studied previously, with a value of $95 \pm 15\text{ kcal mol}^{-1}$ ($= 33000 \pm 5200\text{ cm}^{-1}$) determined by a ‘tentative’ assignment of the rovibrational lines from Mo_2 produced by flash photolysis of $\text{Mo}(\text{CO})_6$.²⁰¹ More recently, Simard (who also worked on MoO)¹⁹⁵ and coworkers studied the dimer by photoionisation spectroscopy and narrowed down the dissociation energy to $36100 \pm 80\text{ cm}^{-1}$.²⁰² Unless there are significant problems with both spectroscopic measurements, this one-photon dissociation of the molybdenum dimer in this region is an unlikely assignment.

The more plausible explanation is thus dissociation of ^{98}MoO using three photons. This would complement the observation made in Section 3.3.1 that a focussing lens is not necessary to observe the spectra of ^{98}MoO shown in Figure 3.4, which proceeded via a one-photon excitation, but is necessary for the production of rings

in the velocity map images. This would fit with a higher number of photons being involved in the initial transition.

An attempt was made to use the same process used in Section 2.3.3 to confirm that the oxide was the parent molecule by adding N_2O to the carrier gas. However, this did not result in an increase in the amount of MoO present in the beam, and was thus inconclusive.

Repeating the process with the other two series indicated in Figure 3.6 shows that this assignment is consistent with all three, and provides a value for the magnification factor of 1.109, which is used for the duration of this section.

Assignment of the Exit Channels

The next step of the analysis requires a conversion from KE_{Mo} to the total kinetic energy release and production of fits through a plot of those values against photon number (with the gradient now fixed at three, since the number of photons is now known). This gives values for the x -intercepts of the three series:

- Series 1: $21457 \pm 54 \text{ cm}^{-1}$
- Series 2: $20826 \pm 52 \text{ cm}^{-1}$
- Series 3: $20293 \pm 103 \text{ cm}^{-1}$

This threshold value for $h\nu$ is related to the dissociation energy of the molecule and the internal energies of the fragments by:

$$nh\nu = D_0(\text{MoO}) + E_{\text{Mo}} + E_{\text{O}} - E_{\text{MoO}} \quad (3.5)$$

This means that it is necessary to next assign the electronic states of the fragments produced in order to determine D_0 . The most straightforward way to do this is to use an average of the best existing values for the dissociation energy ($43800 \pm 300 \text{ cm}^{-1}$ from Looock *et al.* and Luo *et al.*)^{195,199} in order to get an estimate of the fragment energies. Once these are used to assign the identity of the electronic states of the fragments, the assignments can then be used with equation 3.5 to get an updated value for D_0 .

For each series, the values of $3h\nu - 43800 \text{ cm}^{-1}$ are (in ascending order):

- Series 3: ca. 17050 cm^{-1}
- Series 2: ca. 18460 cm^{-1}
- Series 1: ca. 20370 cm^{-1}

which compare remarkably well with the following known energy levels of the molybdenum atom:⁹¹

- Mo(^5G_J): 16641, 16693, 16748, 16784 and 16785 cm^{-1}
- Mo(^5P_J): 18229, 18356 and 18480 cm^{-1}
- Mo(^5D_J): 19970, 20130, 20158, 20281 and 20351 cm^{-1}

The mean energies of these states (and standard deviations of the spin-orbit components) are $16730 \pm 62 \text{ cm}^{-1}$, $18355 \pm 125 \text{ cm}^{-1}$ and $20178 \pm 147 \text{ cm}^{-1}$ respectively. Unfortunately, unlike the dissociation processes studied in Chapter 2, the spin-orbit split levels in the transition metal considered here are too close together to be resolved given the width of the peaks of the kinetic energy spectrum; similarly, the O(^3P) levels of the co-fragment are also unresolved. The internal energy of the atomic fragments for each channel is thus treated as the mean energy of the spin-orbit components.

In each case, the actual energy of the molybdenum electronic state is slightly lower than predicted, with some of the difference accounted for by the energy going into the oxygen atom (the average value of the energy of the spin-orbit components of the oxygen ground state is 128 cm^{-1}).⁹¹ The following assignments are therefore proposed:

- Series 1: $^{98}\text{MoO} \rightarrow ^{98}\text{Mo}(^5D) + \text{O}(^3P)$
- Series 2: $^{98}\text{MoO} \rightarrow ^{98}\text{Mo}(^5P) + \text{O}(^3P)$
- Series 3: $^{98}\text{MoO} \rightarrow ^{98}\text{Mo}(^5G) + \text{O}(^3P)$

Figure 3.7 shows Morse curves corresponding to the ground states of the MoO and MoO⁺ dimers, to demonstrate the nature of the proposed assignments. Although three photons with energies in the region considered are enough to ionise

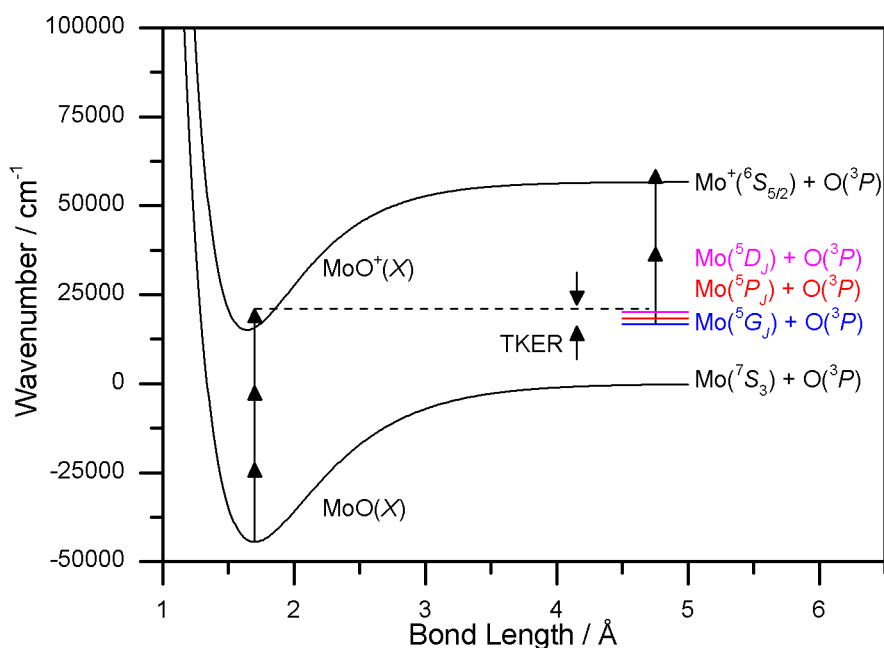


Figure 3.7: Energy level diagram of MoO and MoO⁺ showing the ground states of the cation and the neutral molecule, plotted from literature values,^{69,192,195,197–199} along with the positions of the Mo ⁵G, ⁵P and ⁵D energy levels.⁹¹ Each arrow represents a photon with an energy of 21700 cm⁻¹.

the molybdenum oxide (and, as seen in Figure 3.3, plenty of MoO⁺ is produced), the molecule is also excited onto the dissociative wall of a neutral MoO state. From here, the molecule then dissociates to produce molybdenum in a ⁵G, ⁵P or ⁵D state, which is then ionised by a further two photons.

This assignment can be checked by comparing the differences between the TKER peaks with the difference between the assigned energy levels. In this instance, there are six cases where all three peaks are observed and thus independent measurements of each energy gap, with the average gaps being $1584 \pm 389 \text{ cm}^{-1}$ between peaks in Series 3 and 2, and $1879 \pm 309 \text{ cm}^{-1}$ between peaks in Series 2 and 1. These compare well to the gaps between the pertinent molybdenum energy levels of $1625 \pm 140 \text{ cm}^{-1}$ and $1823 \pm 193 \text{ cm}^{-1}$, thus providing supporting evidence for the assignment. Figure 3.8 shows points corresponding to each peak in the KER spectra, converted to TKER and plotted against wavenumber, along with the relevant assignments.

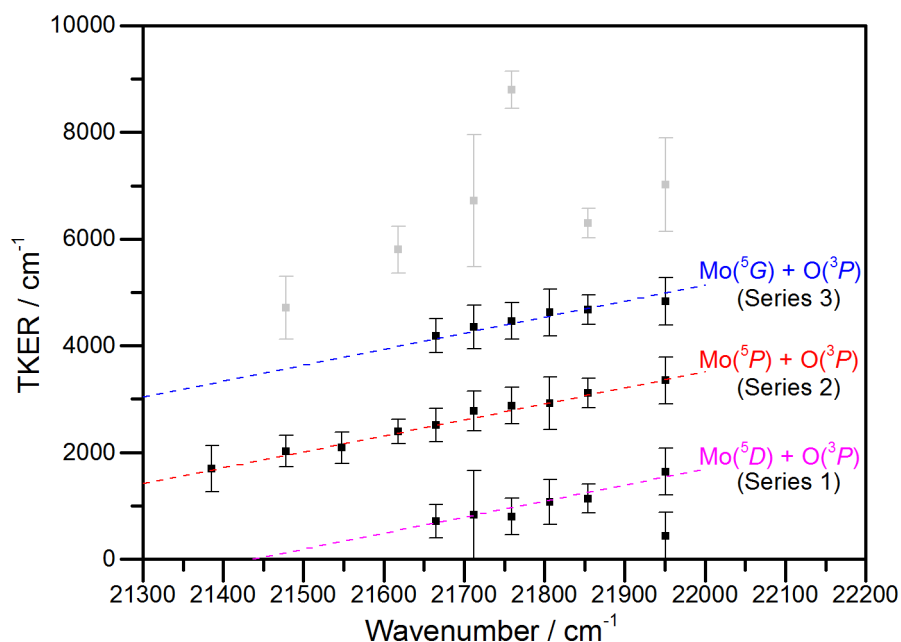


Figure 3.8: Plot of the total kinetic energy release, against wavenumber of the photon used for each ring observed in the region. Lines corresponding to the expected positions of rings resulting from dissociation into the assigned levels have been added, representing the average of the spin-orbit components; the individual components each lie within the error bars of the respective series.

Determination of the Dissociation Energy

It is now possible to calculate the dissociation energy of ^{98}MoO from each of the three series, since the threshold of the dissociation, the number of photons, and the internal energies of the co-fragments are now known.

Since, as mentioned above, the spin-orbit components are unresolved, there is thus some uncertainty in the internal energy of the fragments which must be accounted for in the overall uncertainty in D_0 . This is accomplished by using the standard deviation of the spin-orbit components for both the molybdenum and oxygen product energy levels as an uncertainty and including this in the uncertainties for the values for D_0 found from each of the three channels.

Using equation 3.5 to calculate D_0 from each series, and accounting for the width of the peaks in the TKER spectrum and the uncertainties in both the molybde-

num and oxygen fragment energy levels, three different values for the dissociation energy can be found. Unlike in Section 2.3.3, where it was possible to use the fixed gap between two series to fit both datasets together, the spin-orbit splitting complicates this here and as such, the best approach is to simply average the three separate values. Table 3.1 shows the three separate calculated D_0 and the weighted average.

The new proposed value for $D_0(^{98}\text{MoO})$ of $44027 \pm 151 \text{ cm}^{-1}$ is in good agreement with the values found by Luo *et al.* and Looock *et al.*,^{195,199} while being directly measured rather than calculated by a thermodynamic cycle.

3.3.3 Two-photon Dissociation of MoO in the Ultraviolet Region

Determining the dissociation energy of ^{98}MoO prompted the re-examination of some older data which had been previously recorded in the ultraviolet region around ca. 32000 cm^{-1} , using an expansion of ablated molybdenum in pure argon, that had previously proven difficult to assign. These images were of somewhat lower quality, as the peaks in the fKER spectra were harder to fit and less well-resolved, with a poorer signal-to-noise ratio. The images were also not isotopically-resolved, with the image being taken on all seven molybdenum isotopes

Table 3.1: Experimental and calculated values for the dissociation energy, D_0 , of molybdenum oxide

	D_0^a / cm^{-1}	Expt./eV	Calc. ^b /eV
^{98}MoO	44027 ± 151	5.44 ± 0.04^f	5.58
	44022 ± 335^c	$(43900 \pm 300 \text{ cm}^{-1})$	(45000 cm^{-1})
	43995 ± 232^d	5.42 ± 0.02^g	
	44065 ± 248^e	$(43700 \pm 200 \text{ cm}^{-1})$	

^a This work

^b D_e from Oliveira *et al.*²⁰⁰

^c Calculated using only the data for the $\text{Mo}(^5G) + \text{O}(^3P)$ channel

^d Calculated using only the data for the $\text{Mo}(^5P) + \text{O}(^3P)$ channel

^e Calculated using only the data for the $\text{Mo}(^5D) + \text{O}(^3P)$ channel

^f Looock *et al.*¹⁹⁵

^g Luo *et al.*¹⁹⁹

simultaneously. However, as Figure 3.9 shows, two sets of peaks were observed after polar onion peeling of the corresponding images. The inner marked peak has been fitted in each case and is included in the analysis that follows, while the outer set have only been successfully fitted in lower photon energy images, as indicated, as it becomes too diffuse and ill-defined at higher photon energies.

The position of these fKER peaks has been plotted against photon energy as shown in Figure 3.10, which groups them into two new series: I and II. As explained in Section 3.3.2 and with equation 3.3, the gradient of the best-fit lines through these points depends on the mass of the co-fragment, and the number of photons involved in the dissociation. The same process as used previously can thus be used to determine the mass of the co-fragment and the magnification factor, as outlined in Section 3.3.2.

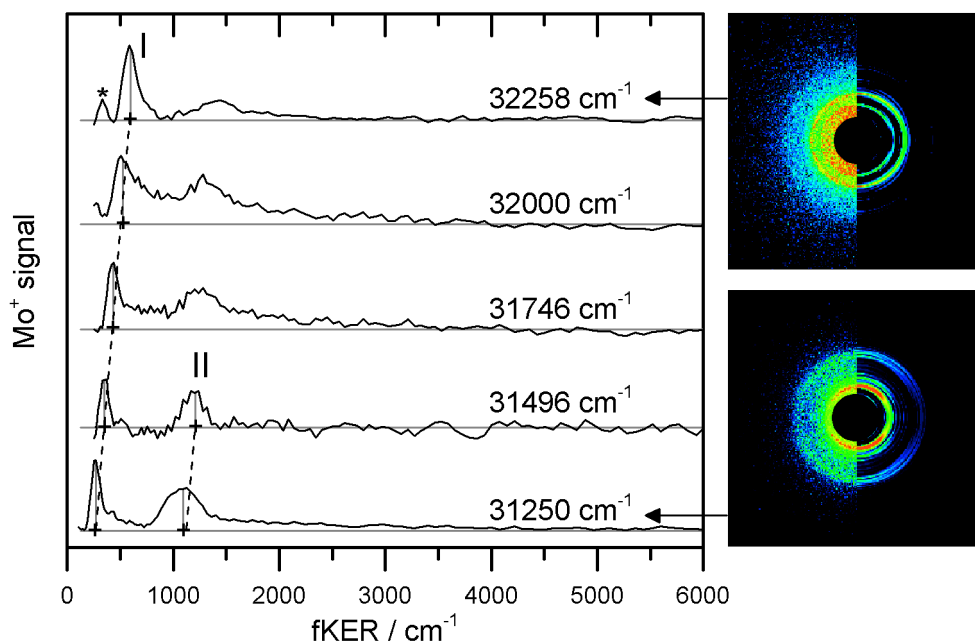


Figure 3.9: Fragment Kinetic Energy Release spectra for the molybdenum atom fragment from photodissociation observed in the region around 315 nm in pure argon carrier gas, with the two main series labelled to match Figure 3.10. Representative sample images are shown for two of the spectra, with the left half of each image showing the raw image and the right the central slice reconstructed by Polar Onion Peeling. The feature marked by * corresponds to the inner ring seen in the upper image which is not part of the indicated series. The central spot has been removed in both the images and the spectra for clarity.

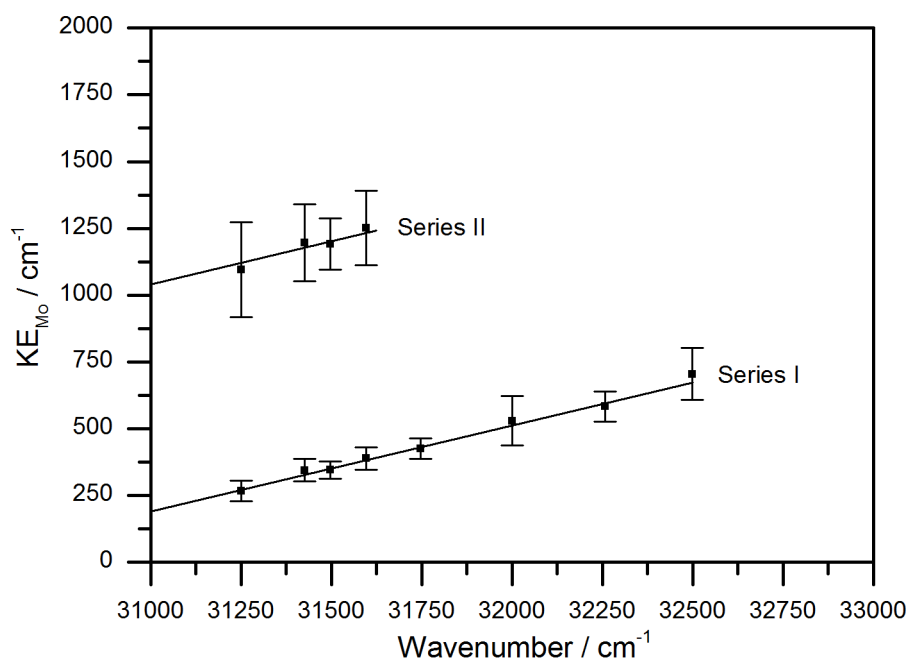


Figure 3.10: Plot of the Kinetic Energy of the Mo fragment, KE_{Mo} , against wavenumber of the photon used. Each point represents the centre of a peak in the fKER spectra corresponding to a ring, such as the ones shown in Figure 3.9, while the error bars represent the Full Width at Half Maximum (FWHM) of the corresponding peaks, plus a contribution from the isotopic distribution of molybdenum. Each image was obtained in a pure argon backing gas. Lines have been added to indicate points that form a series. The point shown in grey corresponds to the starred feature in Figure 3.9.

Using the better-defined Series I, which has a gradient of 0.32137, there are once again two possible magnification factors which give a sensible value of m_X for an integer number of photons, n :

No. of photons	m_X/u (MF = 1.045)	m_X/u (MF = 1.060)
1	40.01	38.44
2	16.55	16.01
3	10.44	10.11
4	7.62	7.39

The two potential assignments are:

- A single-photon dissociation of MoAr, with a co-fragment mass of 40 u, requiring a magnification factor of 1.045.

- A two-photon dissociation of MoO, with a co-fragment mass of 16 u, requiring a magnification factor of 1.060.

Both assignments are plausible; this is to be expected, given that the gradient as given by $n \cdot \frac{m_X}{m_{\text{MoX}}}$ is 0.294 for when the parent molecule is MoAr with $n = 1$, and 0.286 for a two-photon dissociation of MoO. However, with the understanding of MoO gained in Section 3.3.2, and the fact that there are no electronic states of molybdenum with the correct energies to assign these processes to a dissociation of MoAr, the features are well-explained using the previous measurement of D_0 from Section 3.3.2 and the energy levels accessible after a dissociation of MoO using two photons.

The x -intercepts of the best fit lines are $27761 \pm 206 \text{ cm}^{-1}$ and $30405 \pm 46 \text{ cm}^{-1}$ for Series II and I respectively. Using equation 3.5 with $n = 2$ and the new value of 44027 cm^{-1} for D_0 , this would allow for ca. 11500 cm^{-1} and ca. 16800 cm^{-1} to be distributed into internal energy of the fragments respectively. These correspond very well to the following states of the molybdenum atom:⁹¹

- Mo(^5D_J): 10966, 11143, 11454, 11858 and 12346 cm^{-1}
- Mo(^5G_J): 16641, 16693, 16748, 16784 and 16785 cm^{-1}

which have average energies of $11554 \pm 558 \text{ cm}^{-1}$ and $16730 \pm 62 \text{ cm}^{-1}$ respectively. Note that the higher of these energy levels is in fact the same state as produced in the three-photon dissociation Series 3 in Section 3.3.2. The splitting in the Mo(^5D) level is very large compared to the other states studied thus far in this chapter. However, as can be seen in Figure 3.9, the peaks in Series II are very broad and the spin-orbit components are thus still not resolved. This explains the noticeably broader error bars for Series II and the larger uncertainty in the threshold photon energy.

As in Section 3.3.2, it is possible to support the assignment by comparing the gap between the TKER peaks and the gap between the proposed product energy levels. In this case, the gap in the energy levels is $5176 \pm 561 \text{ cm}^{-1}$, while the average observed gap over the four images where both peaks have been fitted is $5271 \pm$

524 cm^{-1} . This all compares very favourably and provides supporting evidence for the assignment.

Using equation 3.5 to calculate D_0 from each series, two different values are obtained, with a weighted average of $43946 \pm 157\text{ cm}^{-1}$. These values are shown in Table 3.2, which compares them to the values from Section 3.3.2. Although the values are not directly equatable due to the lack of isotopic selectivity in the dissociation in the UV region, this dissociation energy compares very favourably to the value found in the experiments in the visible region, agreeing to well within the uncertainties.

3.4 Conclusions

In summary, the dissociation of ^{98}MoO has been investigated using VMI. With isotopic selectivity in the region ca. $21300\text{--}22200\text{ cm}^{-1}$, rings observed in the velocity map images are assigned as photodissociation into three different exit channels,

Table 3.2: Experimental dissociation energy, D_0 , for molybdenum oxide

	D_0^a / cm^{-1}	D_0^b / cm^{-1}	Previous Expt./eV
MoO	43946 ± 157	44027 ± 151	5.44 ± 0.04^g
	43841 ± 704^c	44022 ± 335^d	$(43900 \pm 300\text{ cm}^{-1})$
	43951 ± 161^d	43995 ± 232^e	5.42 ± 0.02^h
		44065 ± 248^f	$(43700 \pm 200\text{ cm}^{-1})$

^a From dissociation in the ultraviolet region

^b From dissociation of ^{98}MoO in the visible region - see Section 3.3.2

^c Calculated using only the data for the $\text{Mo}(^5D) (4d^4 5s^2) + \text{O}(^3P)$ channel (Series II)

^d Calculated using only the data for the $\text{Mo}(^5G) (4d^5 5s) + \text{O}(^3P)$ channel (Series I & 3)

^e Calculated using only the data for the $\text{Mo}(^5P) (4d^5 5s) + \text{O}(^3P)$ channel (Series 2)

^f Calculated using only the data for the $\text{Mo}(^5D) (4d^5 5s) + \text{O}(^3P)$ channel (Series 1)

^g Looock *et al.*¹⁹⁵

^h Luo *et al.*¹⁹⁹

which have been identified with a high degree of certainty. Other experiments in the region around ca. 31500 cm^{-1} were found to have observed the dissociation of non-isotopically selected MoO into two exit channels, and as such, support the more recent work.

From these two different experiments, a new value for the experimental dissociation energy of ^{98}MoO was determined to be $44027 \pm 151\text{ cm}^{-1}$. This is in good agreement with the best existing direct measurements of $40600 \pm 5200\text{ cm}^{-1}$ and $46550 \pm 1800\text{ cm}^{-1}$, which come from Knudsen Cell measurements.^{193,194} The new value gives a higher degree of precision and less reliability on values for other metal oxides since Knudsen Cell mass spectrometry is only capable of measuring the dissociation energy relative to that of another species, creating problems if the reference value is incorrect. The most recent values are indirect measurements via a thermodynamic cycle of $43700 \pm 200\text{ cm}^{-1}$ and $43900 \pm 300\text{ cm}^{-1}$,^{195,199} with the VMI measurement being in excellent agreement with these values while also being more direct, and independent of measurements of the dissociation energy of the cation.

The two-photon dissociation experiments give a value for $D_0(\text{MoO})$ of $43946 \pm 157\text{ cm}^{-1}$, supporting the assignment and analysis of the three-photon data. This value has somewhat lower significance attached to it since these experiments were not isotopically selective and one of the two series observed had extremely broad features, arising from the wide spread of the spin-orbit components of the electronic state in which the molybdenum fragment is produced. Nonetheless, it is in good agreement, within experimental error, with the value from the three-photon experiments, providing additional supporting evidence.

Further experiments on this system may include repeating the imaging in the ultraviolet region while gating solely on the ^{98}Mo fragment in order to gain isotopic resolution. However, given the success of imaging the dissociation using lower energy photons, there is likely to be little advantage in doing so.

Chapter 4

Velocity Map Imaging of Chromium Oxide

Spectroscopy and imaging experiments in the 445–475 nm (ca. 21000–22500 cm⁻¹) region were performed to study isotopically-selected chromium oxide, ⁵²CrO. A three-photon dissociation of the molecule into multiple exit channels was observed. These channels have been assigned in order to obtain independent measurements of the dissociation energy, D₀(⁵²CrO), with an average value of 37130 ± 117 cm⁻¹ obtained. In the ultraviolet region between 230 and 245 nm (ca. 40700–43572 cm⁻¹), a multitude of features were observed which have been assigned to dissociation of the same species, and which also support this measurement of the dissociation energy.

4.1 Previous Work

Chromium was chosen as a system of interest due to the potential observation of dissociation of the neutral chromium dimer, Cr₂ and/or the chromium oxide, CrO. Of these, the dimer is perhaps the more intriguing, due to the potential sextuple bond order.²⁰³ A number of older theoretical studies were published in support of this possibility,²⁰⁴ as well as some suggesting a much lower bond order.²⁰⁵ An early measurement of the bond length at 1.68 Å (using spectroscopy on products generated from the flash photolysis of Cr(CO)₆) by Efremov *et al.* in the mid-70s was initially viewed with some suspicion, including by the group reporting the

result, who stated that it could result from CrO_2 or CrC_2 products.²⁰⁶ However, this result was later supported independently by the groups of Richard Smalley and Vladimir Bondybey, who produced the dimer by laser ablation and reported the same value for the bond length using rotationally-resolved spectroscopy.^{49,203} This extremely short bond length supported the sextuple-bond hypothesis, and the chromium dimer has since been treated as having a formal sextuple bond.²⁰⁷

Despite the high bond order and very short bond length, the dissociation energy of the dimer, $D_0(\text{Cr}_2)$, is not believed to be particularly high. While its second-row cousin, Mo_2 , has a bond energy of 36100 cm^{-1} , Cr_2 has a significantly weaker bond due to smaller orbitals and poorer overlap.²⁰² Huber and Herzberg give a value of $1.56 \pm 0.3 \text{ eV}$ ($12600 \pm 2000 \text{ cm}^{-1}$) from a Knudsen Cell measurement by Kant & Strauss,^{157,208} while a later study using the same method by Hilpert & Ruthardt reported a bond energy of $142 \pm 5 \text{ kJ mol}^{-1}$ ($11900 \pm 2000 \text{ cm}^{-1}$).²⁰⁹

In the late 1990s, Simard *et al.* studied the dissociation energy of Cr_2 using a thermodynamic cycle similar to that used on MoO and other molecules as discussed in Chapter 3.^{195,202} In this case, photoionisation spectroscopy was used to measure the ionisation energy of the chromium dimer as being $56449 \pm 8 \text{ cm}^{-1}$. This was then combined with the known ionisation energy of the atom ($54575.6 \pm 0.3 \text{ cm}^{-1}$)^{210,211} and a previous collision-induced dissociation (CID) measurement of the dissociation energy of Cr_2^+ ($10500 \pm 500 \text{ cm}^{-1}$)²¹² to give a new value for $D_0(\text{Cr}_2)$ of $12400 \pm 500 \text{ cm}^{-1}$.²⁰² This is the most recent value, and continues to be used in computational investigations.²⁰⁷

The chromium oxide molecule, meanwhile, has been the subject of a large number of studies which aimed to investigate its photodissociation over the years. In this case, both Huber & Herzberg and the later review of transition metal oxides by Pedley & Marshall cite a Knudsen Cell measurement using Cr_2O_3 by Grimley *et al.*, which found $D_0(\text{CrO})$ to be $101.1 \pm 7 \text{ kcal mol}^{-1}$ ($35410 \pm 2000 \text{ cm}^{-1}$).^{146,157,213} This replaced earlier values of 3.78 eV (30500 cm^{-1}) from a 1932 spectroscopic study,²¹⁴ and of $35550 \pm 3900 \text{ cm}^{-1}$ from a flame spectroscopic measurement.²¹⁵ Another thermochemical measurement using a tungsten oxide reference state provided a slightly higher value of $436.2 \pm 8.9 \text{ kJ mol}^{-1}$ ($36510 \pm 750 \text{ cm}^{-1}$).²¹⁶

Subsequently, two ion beam studies further increased the estimated value for the dissociation energy of CrO. Firstly, Kang & Beauchamp measured the dissociation energy of CrO^+ and used their value along with the known ionisation energies of the chromium atom ($54575.6 \pm 0.3 \text{ cm}^{-1}$)^{210,211} and the oxide ($7.85 \pm \text{eV} \simeq 63300 \pm 200 \text{ cm}^{-1}$ from Dyke *et al.*²¹⁷), to find a $D_0(\text{CrO})$ value of $110 \pm 2 \text{ kcal mol}^{-1}$ ($39000 \pm 700 \text{ cm}^{-1}$) using a similar thermodynamic cycle to that described for MoO in Section 3.1.²¹⁸ Separately, Georgiadis & Armentrout used the reactions of Cr^+ with organic molecules to find what they described as a ‘lower limit’ of $4.58 \pm 0.07 \text{ eV}$ ($36900 \pm 600 \text{ cm}^{-1}$).²¹⁹ In a review of the available data, Ebbinghaus combined data from Kang & Beauchamp with that from Grimley *et al.* to find a dissociation energy of 464 kJ mol^{-1} (38800 cm^{-1}).²²⁰

A crossed molecular beam (CMB) study of Cr with O_2 by Hedgecock *et al.* found a value for $D_0(\text{CrO})$ of $4.74 \pm 0.09 \text{ eV}$ ($38200 \pm 700 \text{ cm}^{-1}$), which is between the previous ion beam-derived values.²²¹ Finally, a more recent study on the kinetics of oxidation of chromium atoms found a value of $460.1 \text{ kJ mol}^{-1}$ (38510 cm^{-1}).²²² Table 4.1 shows a summary of all of these past experimental values for $D_0(\text{CrO})$.

There have also been a number of computational works performed with the aim of determining the CrO dissociation energy, which have produced values in the region around $37100\text{--}41100 \text{ cm}^{-1}$.^{223–225} These works include relatively recent (2010) coupled cluster calculations which found a value of $104 \text{ kcal mol}^{-1}$ (36400 cm^{-1}).³³

Table 4.1: Literature Values of the Experimental Dissociation Energy, D_0 , of CrO

Year	Author	D_0 / cm^{-1}	Experimental Method
1932	Ghosh ²¹⁴	30500	Electronic Spectroscopy
1952	Huldt & Lagerqvist ²¹⁵	35550 ± 3900	Flame Spectroscopy
1961	Grimley <i>et al.</i> ²¹³	35410 ± 2000	Knudsen Cell
1981	Balducci <i>et al.</i> ²¹⁶	36510 ± 750	Knudsen Cell
1986	Kang & Beauchamp ²¹⁸	39000 ± 700	Guided Ion Beam
1989	Georgiadis & Armentrout ²¹⁹	36900 ± 600	Guided Ion Beam
1993	Ebbinghaus ²²⁰	38800	Review
1996	Hedgecock <i>et al.</i> ²²¹	38200 ± 700	Crossed Molecular Beam
2010	Smirnov & Akhmadov ²²²	38510	Reaction Kinetics

This paper also included a review of most of the previous experimental work on CrO and expressed a preference for Georgiadis & Armentrout's value, believing the later CMB experiment had overestimated the dissociation energy, although this was based mostly on their own calculations. As can be seen in Table 4.1, an experimental study from the same year appears to support the value of Hedgcock *et al.* instead.

In summary, the chromium dimer, despite its 'formal sextuple bond',²⁰⁷ has a relatively weak bond dissociation energy around 12000 cm^{-1} , with the most recent value in use being $12400 \pm 500\text{ cm}^{-1}$.²⁰² Meanwhile, chromium oxide has been studied by a wide range of techniques which have proposed values ranging mostly between 35000 and 40000 cm^{-1} ; recent studies have narrowed this down to being closer to $38000\text{--}38500\text{ cm}^{-1}$.^{221,222} However, neither species has been previously studied using velocity map imaging, thus allowing their photodissociation dynamics to be investigated via this method, which has proved useful in similar systems in the past.^{44,61,148}

4.2 Experimental Method

The experiments in this chapter were performed on the velocity map imaging setup described in Section 1.4; this section covers details specific to this study. A molecular beam of pure helium carrier gas was created, with clusters seeded into the beam by ablation of a target of pure chromium with natural isotopic abundance. Chromium has four isotopes of significant abundance, but is dominated by the ^{52}Cr isotope, with 83.789% abundance (the other isotopes are ^{50}Cr : 4.345%; ^{53}Cr : 9.501%; and ^{54}Cr : 2.365%).¹⁷⁴ In the interests of resolution, the images were recorded by gating the detection MCPs only over the ^{52}Cr isotope.

The ablation of the metal target was accomplished using the focussed 532 nm frequency-doubled output of a Nd:YAG laser (Litron Nano initially, later Continuum Minilite due to technical difficulties, although this had no material effect on the species produced). To dissociate and ionise the species in the molecular beam, radiation in two different spectral regions was used. Firstly, in the visible region,

an OPO (Continuum Panther) with a range of 400–700 nm was used. Secondly, in the ultraviolet region, the frequency-doubled output of a dye laser (Sirah) using a dye solution of Coumarin 480 in ethanol was used, with an output range of ca. 226–250 nm. Both lasers were pumped by the frequency-tripled 355 nm output from separate Nd:YAG lasers (Continuum Surelite).

4.3 Experimental Results

4.3.1 Spectroscopy in the Visible Region

Several species were observed from ablation of the chromium target; the most intense was the chromium atom, with all four isotopes mentioned above, along with a smaller amount of diatomic chromium oxide, CrO, and traces of the chromium

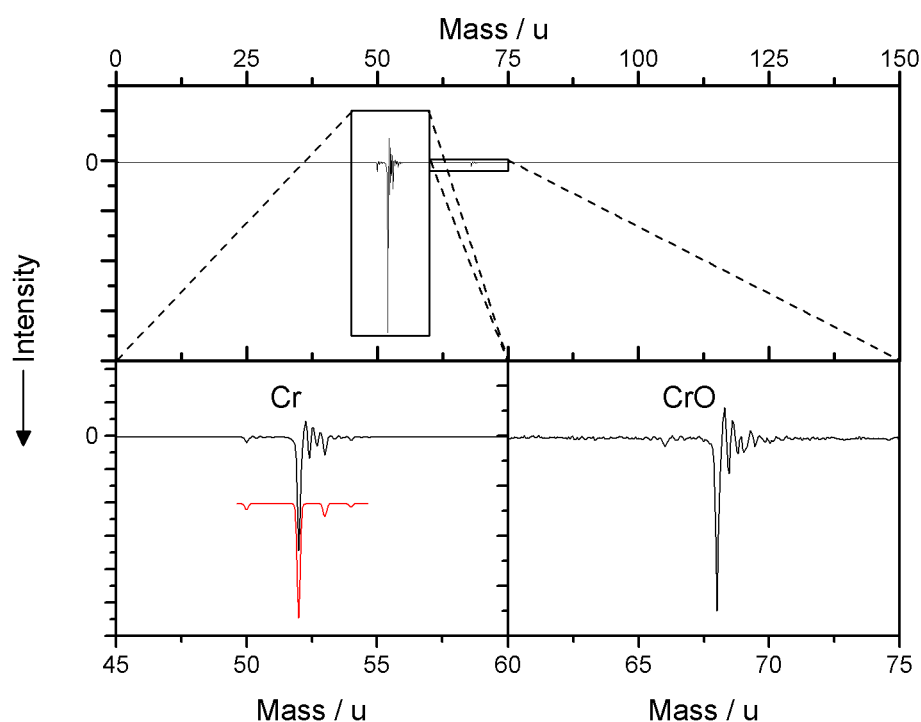


Figure 4.1: Time-of-Flight Mass Spectrum recorded around 455 nm with a chromium target and a helium carrier gas. **Top:** Overview of the mass spectrum in the appropriate region. **Bottom Left:** Detail showing the isotopes of the chromium atom, with a comparison to the predicted intensity ratio in red. **Bottom Right:** Detail showing peaks resulting from chromium oxide, CrO.

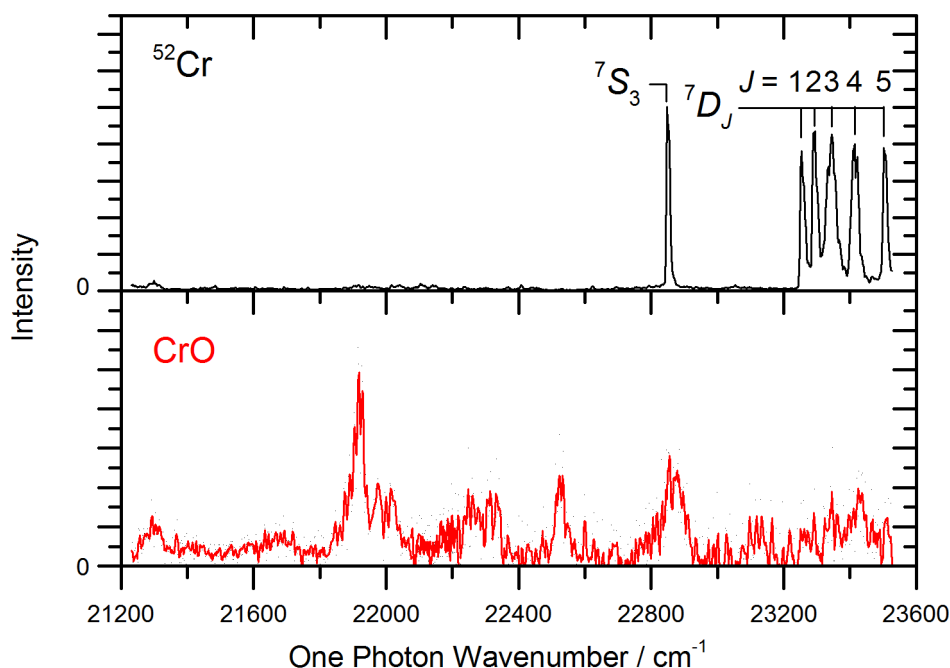


Figure 4.2: Resonant multi-photon ionisation (REMPI) spectra of isotopically-selected ^{52}Cr (top, black) and isotopically-unresolved CrO (bottom, red). Atomic transitions are from the $^7S_3$ ground state to the excited levels indicated.

dimer, Cr_2 , as shown in the time-of-flight mass spectrum in Figure 4.1 (Cr_2 is not visible on this scale, but can be seen if the range of the oscilloscope is changed to view weak features at the expense of the strong atomic signal).

Scans were performed in the visible region to obtain electronic spectra, between 425 and 470 nm (ca. $21300\text{--}23500\text{ cm}^{-1}$), and, while it was not possible to extract any spectra in the Cr_2 channel, spectra were recorded in both the atomic channel and the oxide channel. These are shown in Figure 4.2.

There were six main features observed in the spectroscopy of ^{52}Cr ; these have been assigned to resonant two-photon transitions in the atom. This is supported by the strong dependence on photon intensity; the spectra were recorded using a focussing lens, under the conditions used in the imaging in Section 4.3.2, and the intensity of these features is significantly reduced in the absence of this lens. This is expected from the greater-than-linear dependence on photon intensity of a multi-photon transition.

These six transitions have therefore been assigned to transitions to known atomic energy levels.⁹¹ The first of these is a $4s \rightarrow 6s$ transition between the ${}^7S_3$ ($3d^5 4s$) and ${}^7S_3$ ($3d^5 6s$) levels. The other five are assigned to transitions from the ${}^7S_3$ ($3d^5 4s$) state to the spin-orbit components of the ${}^7D_J$ ($3d^4 4s 5s$) state, which represents a $3d \rightarrow 5s$ transition. While not of particular use to the imaging experiments, these peaks are helpful in confirming the assignment of the mass spectrum to chromium as well as checking the calibration of the OPO laser.

The observed spectrum of the chromium oxide proved somewhat more difficult to assign. There are some features of the CrO spectrum which have been previously observed and assigned as transitions from the ground state to what was labelled the *C*-state by Devore and Gole, although the spectra were not particularly well resolved.^{33,145,226} The observed features in this region could be related to this; however, given how weak these peaks are and the poor signal-to-noise ratio of the spectrum, there is not sufficient evidence to convincingly assign the transitions, particularly given that the molecular energy levels above ca. 20000 cm^{-1} are not particularly well-known, even computationally.³³

In summary, while the spectrum of CrO has not been assigned, the oxide has been observed alongside the atom, for which the $2 + 1$ REMPI spectrum has been recorded and assigned. These are reported here to support the assignment of the mass spectrum and calibration of the photon energy in the setup used for subsequent imaging experiments.

4.3.2 Velocity Map Imaging of Chromium Oxide in the Visible Region

Velocity map images of the ${}^{52}\text{Cr}$ isotope were recorded throughout the region covered by the spectrum in Figure 4.2. The wavelengths at which these were taken were chosen both to obtain an evenly-distributed coverage of the spectral region, and to investigate the possibility of a difference in the images when the photon energy was resonant with peaks in the spectrum, although no effects from these resonances were observed.

Figure 4.3 shows representative images and fragment kinetic energy release (fKER) spectra from this region. It can be seen that there are two main features which are present in all of the images observed in this region, and the increasing kinetic energy of these rings is indicated. None of the features are enhanced when the wavelength of the exciting light is resonant with observed peaks in the REMPI spectra.

There are also multiple features which appear in some, but not all of the spectra. To summarise all of the features observed, Figure 4.4 shows the kinetic energy release corresponding to all rings observed throughout this region. The main features indicated in Figure 4.3 correspond to Series IV and V as labelled in this figure. The other features observed appear to correspond to six other channels, labelled I to III and VI to VIII on the plot.

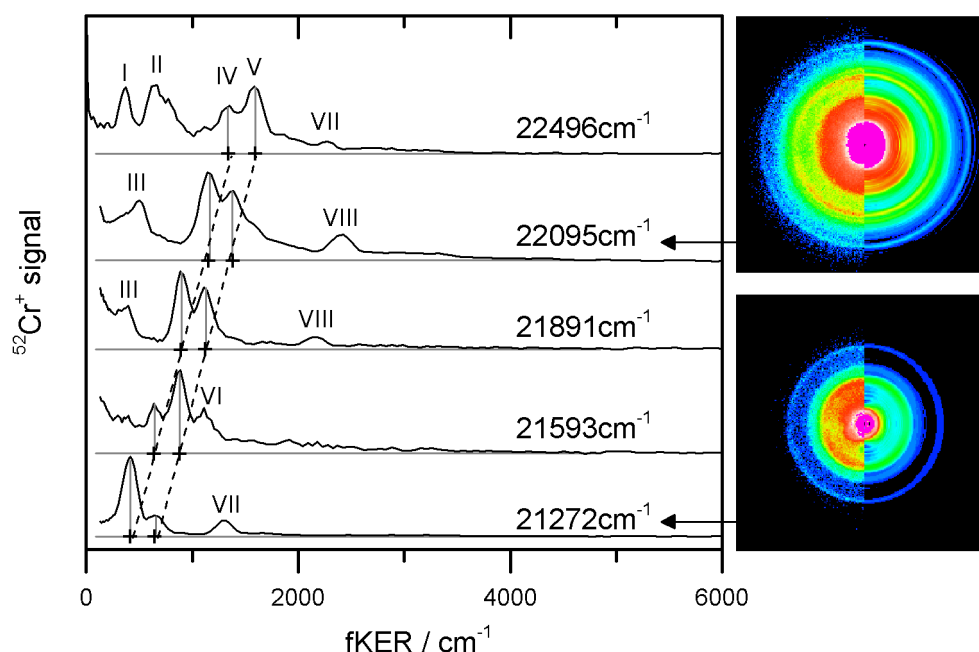


Figure 4.3: Fragment Kinetic Energy Release spectra for the ^{52}Cr fragment in the dissociation observed in the $21000\text{--}22500\text{ cm}^{-1}$ region in pure helium carrier gas. Representative sample images are shown for two of the spectra, with the left half of each image showing the raw image, and the right half displaying the central slice reconstructed by Polar Onion Peeling. Crosses and lines have been added to indicate the photon energy dependence of the main two features which are present in all images (Series IV and V in Figure 4.4). Other peaks which have been fitted are labelled as in Figure 4.4.

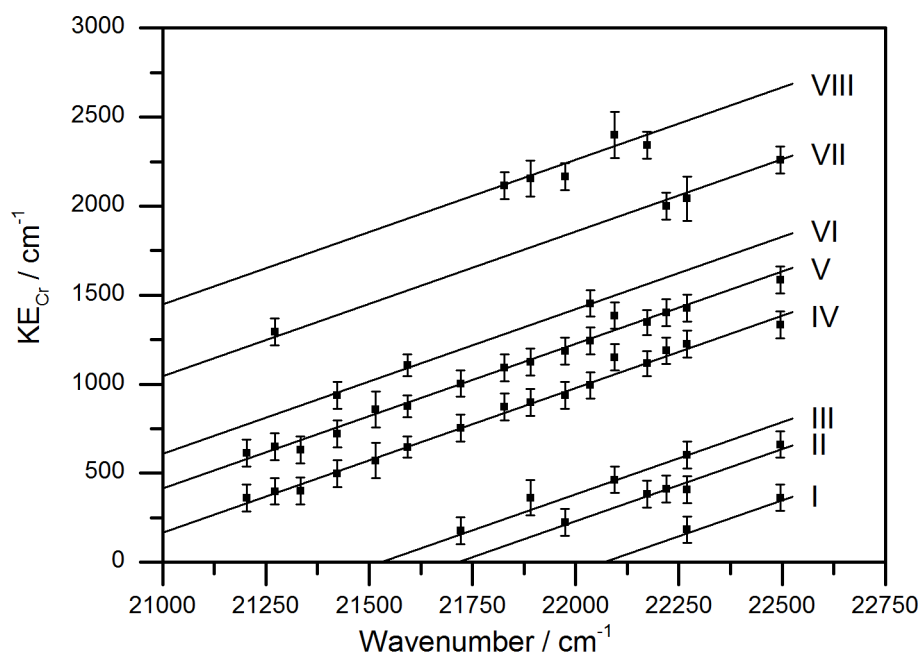


Figure 4.4: Kinetic Energy of the ^{52}Cr fragment, KE_{Cr} , as a function of wavenumber of the photon used. Each point represents the centre of a peak in the fKER spectra corresponding to a ring (such as the ones shown in Figure 4.3), while the uncertainties represent the Full Width at Half Maximum (FWHM) of the corresponding peaks. Each image was obtained in a pure helium backing gas. Lines and labels have been added to group these points into series for analysis.

The procedure for analysing these images is the same as used for silver and molybdenum fragments in the preceding chapters. As mentioned previously, the first step is to determine the nature of the co-fragment by finding the gradient of lines relating KE_{Cr} to photon energy; this gradient is equivalent (after accounting for the magnification factor) to $n \cdot \frac{m_{\text{X}}}{m_{\text{CrX}}}$, where X is the co-fragment (as explained in Section 1.5.3). In this case, only the data from Series IV and V are used to determine the mass of the co-fragment, as these contain the most points to fit.

The gradients of lines of best fit through these two sets of data are 0.81857 and 0.80520 respectively. Experimenting with the magnification factor, there is only one value for the MF which produces plausible values for m_{X} in each case, considering the species identified in the molecular beam (Cr, CrO and trace amounts of Cr_2): 1.0769 for Series IV and 1.0680 for Series V.

Using these magnification factors and setting the ‘corrected’ gradient equal to $n \cdot \frac{m_X}{m_{CrX}}$ produces the following values for the mass of the co-fragment, should a particular (integer) number of photons be involved in the dissociation:

No. of photons	m_X/u (Series IV; MF = 1.0769)	m_X/u (Series V; MF = 1.0680)
1	124.77	124.83
2	28.36	28.37
3	16.00	16.00
4	11.14	11.14

As shown, the most plausible assignment is for a three photon process, which corresponds to an oxygen co-fragment ($m_X = 16$) with a magnification factor of 1.0769 (from Series IV) or 1.0680 (from Series V). On this basis, the parent molecule is identified as chromium oxide with a magnification factor of 1.0725 (from the average of these two values), which will be used throughout this section, for all eight series.

At this point, knowledge of the atomic energy levels of the fragments in each channel is required. In the previous chapters, this was relatively straightforward since there were relatively few possible states of the silver or molybdenum fragment in the region of interest. However, with these images, the task is more difficult due to the abundance of chromium states available. Additionally, the variety of literature values for the dissociation energy of the parent molecule, which range between ca. 35000 and 39000 cm^{-1} as outlined in Section 4.1, exacerbate the difficulty of the assignment. This means that the usual method of assigning KER spectra, where the fragment energy levels can be determined simply from the position of the peaks and the difference between peaks from different series, was confounded by the sheer number of potential assignments. Furthermore, the difference in kinetic energy release between different series is hard to determine in this case, given the paucity of data points for Series I–III and VI–VIII.

In order to overcome this difficulty, a new method for determining the assignment was devised. The TKER (Total Kinetic Energy Release) for dissociation of CrO at a photon energy $h\nu$ is:

$$\text{TKER} = n h \nu + E_{\text{CrO}} - E_{\text{Cr}} - E_{\text{O}} - D_0(\text{CrO}) \quad (4.1)$$

where n is the number of photons involved in the dissociation, $D_0(\text{CrO})$ is the dissociation energy of chromium oxide and E_{Cr} , E_{O} , and E_{CrO} are the internal energies of the chromium atom, the oxygen atom, and the parent molecule respectively. Therefore, by using an estimate for D_0 , we can predict where we would expect to observe features in the TKER spectrum corresponding to exit channels into certain atomic energy levels.

To use this prediction to assign the observed series, the TKER spectrum was plotted. Gaussian features corresponding to possible exit channels were then superimposed on the experimental data. To simplify matters, it was assumed that the parent CrO molecule was in its ground state before dissociation occurs; this is consistent with previous cases which have found that molecules in the cluster beam tend to be in their electronic ground state.

It was further assumed that the oxygen fragment was in its ^3P ground state, while the chromium fragment was created in excited states. As well as simplifying the fitting procedure, this also accounts for the fact that the chromium fragment also has to be ionised after dissociation, requiring additional photons. In the region of interest, ionisation from the atomic ground state is a three-photon process, with the first ionisation energy of chromium being 54575.6 cm^{-1} .⁹¹ The chromium states involved in this assignment lie at 20500 cm^{-1} or higher than the ground state, meaning that they lie within two photons of the ionisation threshold. This means that processes which create ground state oxygen and excited state chromium atoms will be favoured in imaging over those where the oxygen fragment is created in the excited state, since the metal fragment will be more easily ionised.

These assumptions simplify Equation 4.1 to:

$$\text{TKER} = nh\nu - E_{\text{Cr}} - D_0(\text{CrO}) \quad (4.2)$$

which was used to place the Gaussian peaks used to fit the spectrum. Each peak was positioned by taking E_{Cr} as the average of the spin-orbit components of a state and using the standard deviation of the components to predict the width. A value of 38500 cm^{-1} was initially used for the dissociation energy, based on the most recent literature value from Smirnov & Akhmadov.²²² This was then adjusted in

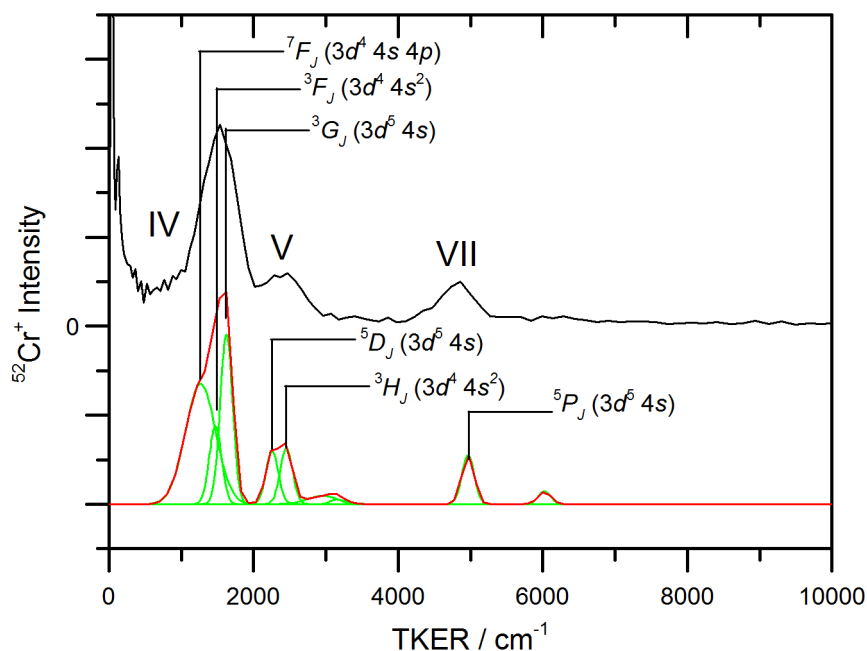


Figure 4.5: Experimental Total Kinetic Energy Release spectrum recorded at 21272 cm^{-1} compared to predicted peak positions, assuming a dissociation energy of 37000 cm^{-1} . **Black:** Experimental Data, with peaks labelled according to their matching series. **Green:** Gaussian peaks corresponding to exit channels into separate chromium energy levels. The positions of the peak centres were calculated using the average of the energies of the spin-orbit components, while the FWHM was based on the spread of these components, with a minimum of 200 cm^{-1} . Amplitudes were fitted to the experimental data. Labels have been added for states discussed in the text. **Red:** Cumulative fit from sum of Gaussian peaks.

order to improve the fit to the experimental data, until the predicted peak positions best corresponded with features in the TKER spectrum in order to assign the exit channels for each series. The amplitudes of each Gaussian curve were fitted to the spectrum, with peak position and width fixed.

Figure 4.5 shows the TKER spectrum at a photon energy of 21272 cm^{-1} (corresponding to the bottom spectrum in Figure 4.3 after conversion from fKER to TKER), which features peaks corresponding to Series IV, V and VII. It was found that if the dissociation energy was slightly reduced, to ca. 37000 cm^{-1} , the TKER spectrum was relatively well fitted by the chromium energy levels. Unfortunately, the two main peaks, which correspond to Series IV and V, both contain multiple possible assignments within their widths.

For Series IV, the peak corresponds relatively well to the position predicted for the ${}^7F_J (3d^4 4s 4p)$ level, which has an average energy of 25280 cm^{-1} . However, the seven spin-orbit components of this level cover a wide range of values between 24972 and 25771 cm^{-1} , and there are two other states which lie mostly within this range: ${}^3G_J (3d^5 4s)$ and ${}^3F_J (3d^4 4s^2)$, which themselves have average energies of 24923 and 25075 cm^{-1} respectively. As shown in Figure 4.5, the possibility that all of these states contribute to the peak cannot be ruled out.

As for Series V, there are two possibilities: the ${}^3H_J (3d^4 4s^2)$ level at 24063 cm^{-1} and the ${}^5D_J (3d^5 4s)$ level at 24290 cm^{-1} . Both states fall within the width of the peak and there appears to be little to discern between them. Overall, the most that can be said about the series is that it is down to one or both of these two levels, and it will henceforth be assumed that both states contribute.

For the other peak, from Series VII, there is one state which falls in the correct energy range: the ${}^5P_J (3d^5 4s)$ level around 21849 cm^{-1} . This state corresponds well to the position of the peak, although the experimental peak is noticeably wider. Nevertheless, the fact that the three main features correspond well with known chromium energy levels is encouraging.

The process was repeated for all of the other spectra recorded, and similarly good fits were found when considering a dissociation energy around 37000 cm^{-1} . This leads to the following assignments for the eight series indicated in Figure 4.4:

- Series I matches well to the ${}^3P_J (3d^5 4s)$ state at 28666 cm^{-1} .
- Series II and III lie very close to each other in a region with multiple possible assignments and it is difficult to distinguish which exit channels may correspond to which series. The possible levels for the assignment of one or both series are ${}^3P_J (3d^5 4s)$ (27187 cm^{-1}), ${}^7D_J (3d^4 4s 4p)$ (27532 cm^{-1}), ${}^3G_J (3d^4 4s^2)$ (27706 cm^{-1}) and ${}^7P_J (3d^4 4s 4p)$ (27828 cm^{-1}).
- Series IV is assigned to a combination of the ${}^3G_J (3d^5 4s)$, ${}^3F_J (3d^4 4s^2)$, and ${}^7F_J (3d^4 4s 4p)$ with energies of 24972 , 25075 and 25280 cm^{-1} respectively, as explained above.

- Series V has also been assigned above, to one or both of the $^3H_J (3d^4 4s^2)$ or $^5D_J (3d^5 4s)$ levels at 24063 cm^{-1} and 24290 cm^{-1} respectively.
- Series VI is assigned to the $^3P_J (3d^4 4s^2)$ level around 23589 cm^{-1} . This feature is very close to Series V but is distinguished enough to be fitted in some images.
- Series VII corresponds to the $^5P_J (3d^5 4s)$ state at 21849 cm^{-1} , as explained above.
- Series VIII has been assigned to the $^5G_J (3d^5 4s)$ state at 20521 cm^{-1} , which is the lowest energy chromium state in this region before a 12500 cm^{-1} decrease to the next energy level. This is consistent with the fact that Series VIII contains the largest TKER rings observed in this region.

With all this in mind, it was decided to focus on Series IV–VIII. While Series I has a convincing assignment, there are only two data points, due to the threshold for this series lying towards the upper edge of the region studied. No high quality images could be recorded at higher photon energies since this is approaching the limits of the OPO laser's range. Series II and III, meanwhile, are ignored because it was not possible to select a convincing assignment. While Series IV and V both also have the issue of multiple possible energy levels, these series are also the most consistently observed and the data were therefore not disregarded. Instead, the values for E_{Cr} were treated as being the average of the possible energy levels, and the uncertainty in D_0 accounts for the uncertainty in the fragment internal energy. Series VI–VIII contain fewer fragments but have been convincingly assigned and are thus also included in the analysis.

With the identity of the parent molecule and the electronic states of the fragments known, it is possible to draw best-fit lines through Series IV–VIII, determine their respective thresholds, and use these in the zero-TKER version of Equation 4.1, which rearranges to:

$$D_0(\text{CrO}) = nh\nu - E_{\text{Cr}} - E_{\text{O}} \quad (4.3)$$

if the parent molecule is in its ground state (i.e. $E_{\text{CrO}} = 0$), and $h\nu$ corresponds to the photon energy at the threshold. E_{O} is taken as 128 cm^{-1} from the average of the

spin-orbit components of the ground state, while E_{Cr} is taken as the average of the spin-orbit components of the states assigned to the particular series. The standard deviations of these spin-orbit components are used, along with the uncertainty in the threshold of the best-fit line, to determine the overall uncertainty in D_0 in each case. The values calculated from each series, along with a weighted average of these, are shown in Table 4.2. Various experimental literature values (excluding those using Knudsen Cell or older techniques) and some calculated values are also included for comparison.

Overall, the value of $D_0(\text{CrO})$ found here by velocity map imaging (37130 cm^{-1}) is slightly lower than the most recent literature values, which tend towards ca. 38500 cm^{-1} . However, our value is within the range previously reported, and also within the range of values predicted by computational studies, suggesting that it is plausible. The values for the separate series agree well with each other, being within experimental error. They also all lie within ca. 100 cm^{-1} of each other, with the exception of Series V; this, along with the large error bars for this value, can be explained by the uncertainty in choosing which of the two energy levels should be used for the assignment. The agreement of multiple different series si-

Table 4.2: Experimental and calculated values for the dissociation energy, D_0 , for chromium oxide

	D_0^a / cm^{-1}	Expt. / cm^{-1}	Calc. / cm^{-1}
^{52}CrO	37130 ± 117	38510^{222}	36400^{33}
	37085 ± 301^b	38200 ± 700^{221}	41100^{225}
	36783 ± 1115^c	38800^{220}	38000^{224}
	37017 ± 538^d	36900 ± 600^{219}	37800 ± 810^{223}
	37184 ± 191^e	39000 ± 700^{218}	
	37120 ± 182^f		

^a This work

^b Calculated using only the data for Series IV

^c Calculated using only the data for Series V

^d Calculated using only the data for Series VI

^e Calculated using only the data for Series VII

^f Calculated using only the data for Series VIII

multaneously supports the assignment of the spectrum and the resultant D_0 value extracted.

It is also possible to compare this value with that determined experimentally for the corresponding molybdenum oxide dimer, ^{98}MoO , by VMI in Section 3.3.2, which is the corresponding d^5s^1 element from the period below. This was discovered to be 44027 cm^{-1} , demonstrating an increase down the group from the first to the second row, which is consistent with the general trend for increasing bond energy down a group in the transition metals,²²⁷ as well as with trends in the dissociation energy of bonds of the Cr–Mo–W triad with hydrogen and carbon.²²⁸

4.3.3 Velocity Map Imaging of Chromium Oxide in the Ultraviolet Region

Velocity map imaging was performed, at regular intervals, throughout the 229.5 to 245.5 nm region (ca. $40700\text{--}43600\text{ cm}^{-1}$). These were gated over the ^{52}Cr isotope, as in Section 4.3.2, to reduce complications from the involvement of multiple isotopes. Multiple rings were observed in the images; some samples are shown in Figure 4.6, along with KER spectra.

It can be seen from the images that there is substantial off-axis intensity, resulting from a very large number of rings in close proximity, which is more easily seen in the lower of the two images, taken at 40733 cm^{-1} . This is reflected in the KER spectra, which show multiple peaks over a wide range of values. The position of the peaks can be shown to be dependent on photon energy, as demonstrated by the lines joining reappearances of the same peak in multiple spectra. To represent the effect of wavenumber on kinetic energy release, the positions of these peaks have been plotted as a function of photon energy in Figure 4.7.

As Figure 4.7 shows, there are a large number of rings observed at all photon energies in this region, which are grouped into 17 series (labelled A–Q). Some of these features are present at almost all wavelengths (Series D–F, H, and J–M), some are observed intermittently (Series A–C, G, and I), and some are below threshold for a substantial part of the region (Series N–Q). This complicates the analysis, but also provides opportunities due to the large amount of data measured simultaneously.

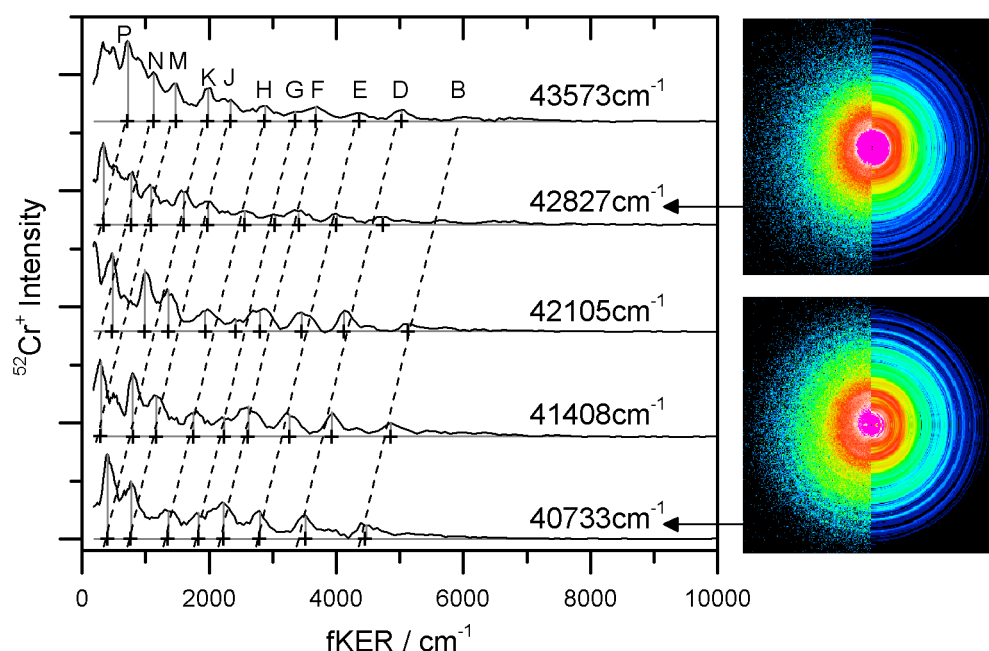


Figure 4.6: Fragment Kinetic Energy Release spectra for the ^{52}Cr fragment generated via the dissociation observed in the $40700\text{--}43600\text{ cm}^{-1}$ region in pure helium carrier gas. Representative sample images are shown for two of the spectra, with the left half of each image showing the raw image and the right the central slice reconstructed by Polar Onion Peeling. Crosses and lines have been added to indicate the photon energy dependence of the main features, which are labelled to match Figure 4.7.

To determine the identity of the parent molecule from the slope of best-fit lines through the data, it was decided to initially focus on the eight series which occurred most frequently in the region (i.e. D–F, H, and J–M). The gradients of lines of best-fit through these series are:

Series	Gradient
D	0.53769
E	0.54565
F	0.50804
H	0.52765
J	0.53873
K	0.53693
L	0.53126
M	0.55482
Average	0.53510

Rather than calculating the mass of the co-fragment from eight different series separately (as in Section 4.3.2), in this case the average gradient is used, which is 0.53510. As in the previous section, this can be equated to $n \cdot \frac{m_X}{m_{CrX}}$, and solve for m_X at different values of n . There are two possible values for the magnification factor which produce plausible values for the mass of the co-fragment:

No. of photons	m_X/u (MF = 1.0345)	m_X/u (MF = 1.0663)
1	52.00	46.23
2	17.33	16.00
3	10.40	9.68
4	7.43	6.93

The two potential assignments for the parent molecule are:

- The chromium dimer, Cr_2 , such that $m_X = 51.9961$,¹⁷⁴ with one-photon dis-

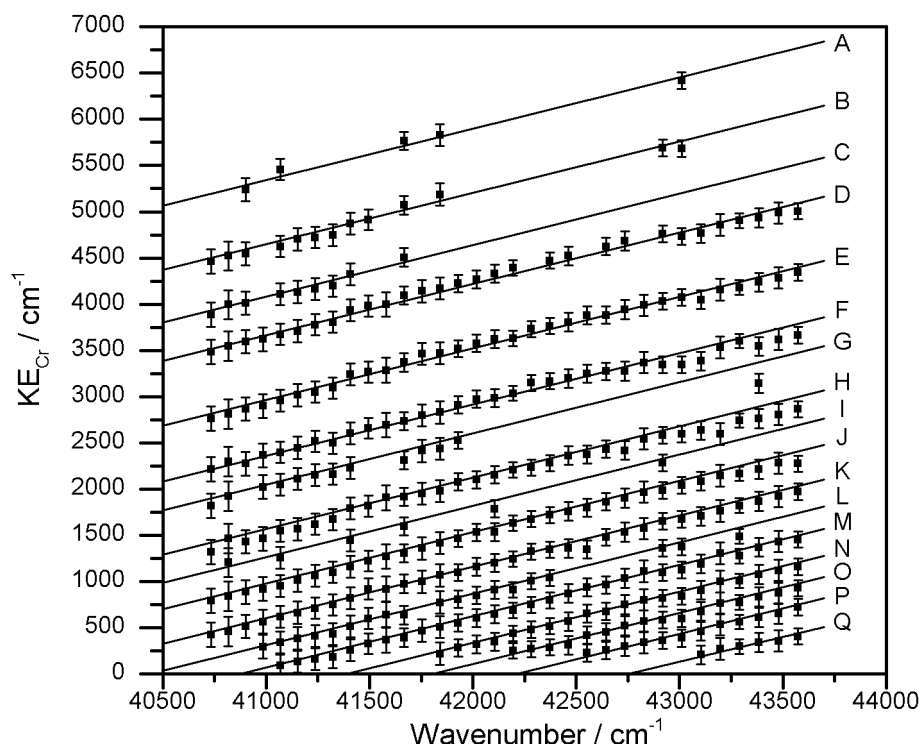


Figure 4.7: Kinetic Energy of the ^{52}Cr fragment, KE_{Cr} , as a function of the wavenumber of the photon used. Each point represents the centre of a peak in the fKER spectra corresponding to a ring, such as the ones shown in Figure 4.6, while the error bars represent the Full Width at Half Maximum (FWHM) of the corresponding peaks. Each image was obtained in a pure helium backing gas. Lines and labels have been added to group these points into series for analysis.

sociation. This would require a magnification factor of 1.0345, on average.

- The chromium oxide dimer, ^{52}CrO , with $m_x = 16$, undergoing two-photon dissociation, with an average magnification factor of 1.0663.

Upon inspection, both of these assignments are plausible. In Section 3.3.2, one possibility was eliminated on the basis that one photon was insufficient to dissociate the Mo_2 dimer. In this case, the dissociation energy of the Cr_2 dimer, at ca. $12400 \pm 500 \text{ cm}^{-1}$,²⁰² is much lower, while the photon energy is much higher, allowing for single-photon dissociation to potentially occur. Similarly, the dissociation energy of ^{52}CrO was determined to be $37130 \pm 117 \text{ cm}^{-1}$ in Section 4.3.2, which makes a two-photon dissociation of the oxide also plausible.

Complications arise once more due to the large number of atomic energy levels of the chromium fragment. In order to be able to assign the source of each series, the procedure from Section 4.3.2 was used again on these data. Using the best existing values for the dissociation energy of each species (12400 cm^{-1} for Cr_2 , 37130 cm^{-1} for ^{52}CrO), the TKER of a ring corresponding to each plausible exit channel was calculated and an attempt was made to fit the resulting peaks to the experimental data.

It is also worth considering the selection rules for the processes under examination, the most relevant of which is the spin-selection rule, $\Delta S = 0$. This is particularly relevant to the chromium dimer, whose molecular ground state has a $^1\Sigma_g^+$ term symbol.²⁰² Given this, the dissociative state to which the molecule is excited must also be a singlet state, as spin-orbit effects are not sufficiently strong for Cr to break this selection rule. This requires that the two atomic fragments must be of the same spin state, since only these combinations will be able to form singlet molecular states. For example, an assignment pairing $\text{Cr}(^7S_3)$ and $\text{Cr}(^3H_J)$ fragments is not plausible, since the transition to any molecular state correlated with these fragments is spin-forbidden.

For the chromium oxide, there are fewer restrictions on potential assignments. The ground state of the CrO molecule has $^5\Pi$ symmetry,²²¹ and thus any combination of atomic fragments capable of producing a quintet upper state is possible. Assuming that the oxygen fragment is in its ^3P_J ground state, this means that the chromium

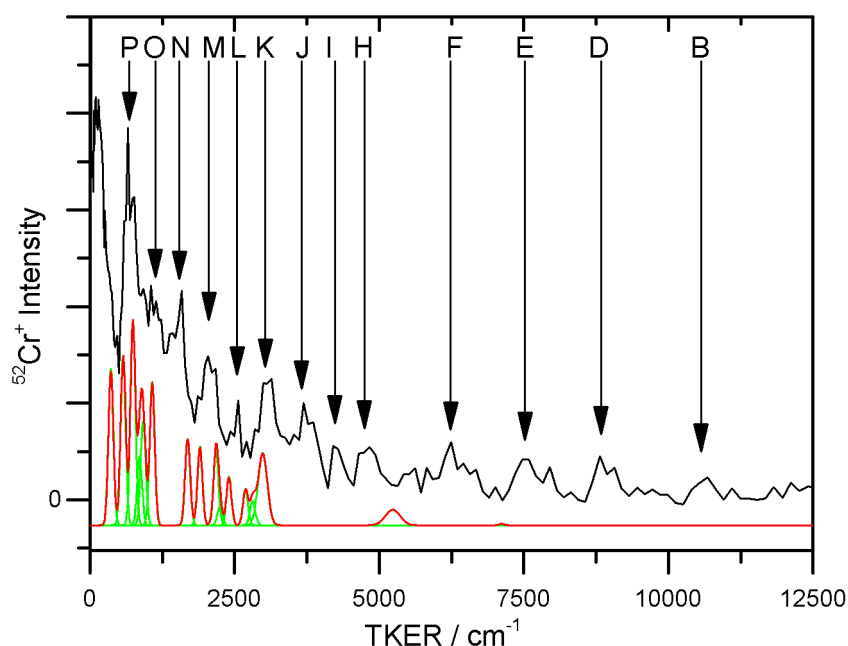


Figure 4.8: Experimental Total Kinetic Energy Release spectrum recorded at 42918 cm^{-1} compared to predicted peak positions for dissociation of Cr_2 , assuming $D_0 = 12400\text{ cm}^{-1}$. **Black:** Experimental Data. Peaks corresponding to the series indicated in Figure 4.7 are labelled. **Green:** Gaussian peaks corresponding to exit channels into separate chromium energy levels. The positions of the peak centres were calculated using the average of the energies of the spin-orbit components, while the FWHM was based on the spread of these components, with a minimum of 200 cm^{-1} . Amplitudes were fitted to the experimental data. **Red:** Cumulative fit from sum of Gaussian peaks.

fragment must be of triplet, quintet, or septet spin state, which eliminates only the singlet atomic states as plausible assignments.

By using spin considerations to select the potential exit channels and calculating the predicted TKER for each of these using Equation 4.2 (or the equivalent for Cr_2 , $\text{TKER} = nh\nu - E_{\text{CrI}} - E_{\text{CrII}} - D_0(\text{Cr}_2)$, where E_{CrI} and E_{CrII} are the energies of the two chromium atom fragments), Figures 4.8 and 4.9 were produced showing a comparison between these expected peak positions and the actual experimental data (using the TKER spectrum at 42918 cm^{-1} , which shows the highest proportion of the peaks seen throughout the region).

Firstly, Figure 4.8 shows a comparison to positions where peaks might be expected if the parent molecule were the chromium dimer. Given the restriction on possible

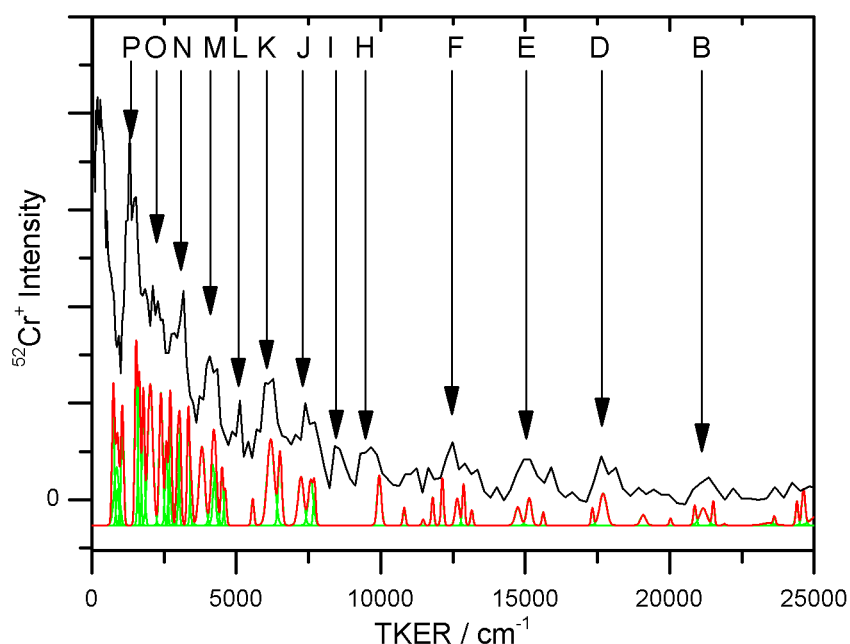


Figure 4.9: Experimental Total Kinetic Energy Release spectrum recorded at 42918 cm^{-1} compared to predicted peak positions for dissociation of ^{52}CrO , assuming a D_0 value of 37130 cm^{-1} . **Black:** Experimental Data. Peaks corresponding to the series indicated in Figure 4.7 are labelled. **Green:** Gaussian peaks corresponding to exit channels into separate chromium energy levels. The positions of the peak centres were calculated using the average of the energies of the spin-orbit components, while the FWHM was based on the spread of these components, with a minimum of 200 cm^{-1} . Amplitudes were fitted to the experimental data. **Red:** Cumulative fit from sum of Gaussian peaks.

exit channels from the spin-state selection rules, there are relatively few allowed exit channels for the dissociation of Cr_2 . As the figure shows, a significant number of the peaks observed in this spectral region (including several of the major, consistent peaks which occur throughout the range, such as Series D, E, F) are unexplained by this model. It is possible that the literature value for the dissociation energy of this species is incorrect. However, there is no value of $D_0(\text{Cr}_2)$ which accounts for all of the observed peaks in the TKER spectrum, as there are significant gaps between allowed transitions. This suggests that the parent molecule is unlikely to be the chromium dimer, since this would require spin-forbidden molecular transitions to occur.

Figure 4.9 instead shows a comparison of the TKER spectrum to positions where

peaks could plausibly be expected for dissociation of chromium monoxide, assuming that the oxygen fragment is in its atomic ground state. In comparison to the case involving Cr_2 , this provides a better fit to the experimental spectrum, with more potential assignments for far more of the peaks.

It is also worth noting that it is possible that exit channels are observed in which the oxygen fragment is excited. These were eliminated as a possibility in Section 4.3.2 on the basis that it would require extra photons to ionise the chromium fragment, favouring the observation of exit channels where the oxygen atom was generated in the ground state. However, in this case there are two factors which make it more plausible. Firstly, more energy is absorbed by the CrO molecule (two photons in this region correspond to ca. 80000 cm^{-1} ; three photons in the visible region add up to ca. 60000 cm^{-1}), such that the chromium states which can be produced when the oxygen atom is excited have a higher energy. Secondly, because the photon energy is higher, more chromium energy levels lie within range of single-photon ionisation.

Given the combination of these effects, it is more likely that cases where the oxygen fragment is in an excited state would be observed. These were not included in Figure 4.9 for clarity, given the large number of potential exit channels already present from consideration solely of cases where the oxygen atom is in the ground state. However, consideration of excited state oxygen formation could account for any unexplained peaks (e.g. Series I and L).

It is possible that dissociation of both species is being observed, but this is unlikely for two reasons. Firstly, as the calculated magnification factors for the two scenarios above indicate, slightly different gradients would be expected for different series, which is not the case; secondly, CrO is far more abundant in the beam than Cr_2 , so if dissociation of both were to be observed, the dimer dissociation peaks would be expected to be small relative to those from dissociation of the oxide. Thus, the parent molecule for these features is therefore assigned as ^{52}CrO .

Despite the above caveats about the possibility of other exit channels being present where the oxygen fragment is excited, it is notable that the predicted peak positions in Figure 4.9 compare well to the experimental features in several cases. To

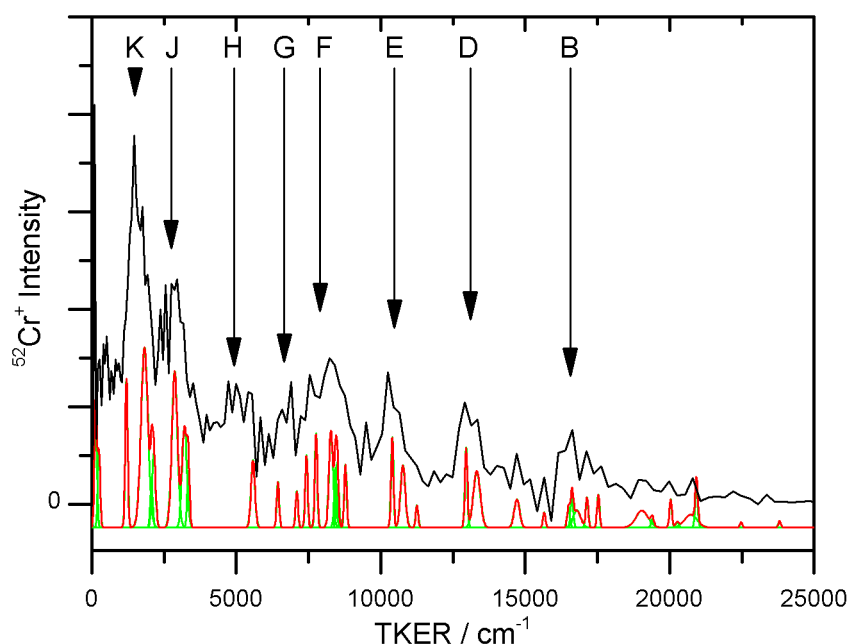


Figure 4.10: Experimental Total Kinetic Energy Release spectrum recorded at 40733 cm^{-1} compared to predicted peak positions for dissociation of ^{52}CrO , assuming a D_0 value of 37130 cm^{-1} . **Black:** Experimental Data. Peaks corresponding to the series indicated in Figure 4.7 are labelled. **Green:** Gaussian peaks corresponding to exit channels into separate chromium energy levels. The positions of the peak centres were calculated using the average of the energies of the spin-orbit components, while the FWHM was based on the spread of these components, with a minimum of 200 cm^{-1} . Amplitudes were fitted to the experimental data. **Red:** Cumulative fit from sum of Gaussian peaks.

investigate this further, the procedure was repeated at other wavelengths; one of these, from the other end of the region at a photon energy of 40733 cm^{-1} is shown in Figure 4.10.

This spectrum shows a similarly good match to the predicted exit channels, as do others throughout the region. Given this, and checking that it is not possible to improve the fit by adjusting the value of D_0 used (as done previously in Section 4.3.2), a tentative assignment can be made for some of the features. The low-TKER region (Series M–Q), has an overwhelming number of possible assignments, to the point where it is difficult to make a definitive assignment. For the other features, especially those which feature in a high proportion of the recorded images, there are six series which can be potentially assigned: D, E, F, H, J, and K. For these, the best

possible assignments based on fits such as those shown in Figures 4.9 and 4.10 are:

- Series D: A combination of $^5F_J (3d^4 4s 4p)$ at ca. 31000 cm^{-1} and $^5F_J (3d^5 4s)$ at ca. 31369 cm^{-1} .
- Series E: A combination of $^3F_J (3d^5 4s)$ at ca. 33071 cm^{-1} , $^5D_J (3d^4 4s 4p)$ at ca. 33558 cm^{-1} , $^3P_J (3d^4 4s 4p)$ at ca. 33960 cm^{-1} , and $^3D_J (3d^4 4s^2)$ around 33926 cm^{-1} .
- Series F: A combination of $^5D_J (3d^6)$ at ca. 35536 cm^{-1} , $^3F_J (3d^5 4s)$ around 35828 cm^{-1} , $^3H_J (3d^5 4s)$ at ca. 35896 cm^{-1} , $^3F_J (3d^4 4s 4p)$ at ca. 36048 cm^{-1} , $^3F_J (3d^5 4s)$ at ca. 36563 cm^{-1} , and $^7S_3 (3d^5 5s)$ at 36896 cm^{-1} .
- Series H: The $^3D_J (3d^4 4s 4p)$ level at ca. 38746 cm^{-1} .
- Series J: A combination of $^5F_J (3d^4 4s 4p)$ at ca. 41116 cm^{-1} , $^5P_J (3d^4 4s 4p)$ at ca. 40985 cm^{-1} , and $^5D_J (3d^4 4s 4p)$ at ca. 41456 cm^{-1} .
- Series K: A combination of $^5H_J (3d^4 4s 4p)$ at ca. 42180 cm^{-1} and $^5D_J (3d^4 4s 4p)$ at ca. 42501 cm^{-1} .

Table 4.3: Experimental and calculated values for the dissociation energy, D_0 , for chromium oxide

	D_0^a / cm^{-1}	Expt./ cm^{-1}	Calc./ cm^{-1}
^{52}CrO	37192 ± 119	37130 ± 117^h	36400^{33}
	36889 ± 283^b	38510^{222}	41100^{225}
	37098 ± 398^c	38200 ± 700^{221}	38000^{224}
	37033 ± 444^d	38800^{220}	37800 ± 810^{223}
	37407 ± 203^e	36900 ± 600^{219}	
	37080 ± 300^f	39000 ± 700^{218}	
	37302 ± 301^g		

^a This section

^b Calculated using only the data for Series D

^c Calculated using only the data for Series E

^d Calculated using only the data for Series F

^e Calculated using only the data for Series H

^f Calculated using only the data for Series J

^g Calculated using only the data for Series K

^h From the visible region experiments in Section 4.3.2

If multiple possible assignments lie within the range of a particular peak in the TKER spectrum, it is presumed that all are potential contributors rather than making assumptions about the assignment. Using these tentative assignments, the value of the dissociation energy was calculated for each series, and a weighted average was taken, which gives an overall value for $D_0(\text{CrO})$ of $37192 \pm 119 \text{ cm}^{-1}$. This and the separate values are shown in Table 4.3, together with the average value found in Section 4.3.2 and other literature values for comparison.

Overall, given that the assignments here are less secure than in Section 4.3.2 (with the potential for other exit channels producing electronically excited oxygen fragments which are not included in the assignment), it is encouraging to see that these TKER spectra can be rationalised as occurring from dissociation of ^{52}CrO into known atomic energy levels, with a corresponding value of D_0 which agrees well with that measured previously.

4.4 Conclusions

Velocity map images were recorded in the isotopically-selected ^{52}Cr channel in two spectral regions: in the visible region of the spectrum between 21000 and 22500 cm^{-1} , and in the ultraviolet region of $40700\text{--}43600 \text{ cm}^{-1}$. In both cases, the features observed have been determined to result from dissociation of ^{52}CrO , using three and two photons respectively.

The results in the visible region allow for the measurement of the dissociation energy of the oxide based on a reasonably secure assignment. This value of D_0 , at $37130 \pm 117 \text{ cm}^{-1}$, lies within the region expected on the basis of experimental and computational results from the literature. There has been significant disagreement between past measurements, which in the last thirty years have ranged between $36900 \pm 600 \text{ cm}^{-1}$ and $39000 \pm 700 \text{ cm}^{-1}$ (see Table 4.1). VMI here establishes that the dissociation energy lies towards the lower end of this range.

The images in the UV region were more difficult to analyse. However, it has been shown that a two-photon dissociation of chromium oxide, with a dissociation energy of ca. 37000 cm^{-1} , provides the best explanation for the observed features. A

tentative assignment of the TKER spectra observed in the ultraviolet region yields a value of $37192 \pm 119 \text{ cm}^{-1}$ for $D_0(^{52}\text{CrO})$. This is in good agreement with the earlier value and provides support for it, even if the analysis which produced it is less secure. It is therefore proposed that the value of $D_0(^{52}\text{CrO})$ is $37130 \pm 117 \text{ cm}^{-1}$ on the basis of the experiments in the visible region, while the images in the ultraviolet region are used to support this assertion.

Further imaging experiments on the CrO molecule may provide more insights into the species. One relatively straightforward extension would be to use another laser which can reach wavenumbers just above 22500 cm^{-1} , where the power of the OPO reduces significantly. This would allow for more points to be added to Series I from Section 4.3.2, which appeared to be promising but lacked data points. More generally, imaging in other regions of the electromagnetic spectrum may be able to probe dissociation in circumstances where there are fewer potential energy levels for the chromium fragment, vastly simplifying the analysis by reducing the number of peaks and potential assignments.

Chapter 5

Methods of Image Reconstruction

Based on evidence from other studies that the current Polar Onion Peeling algorithm used by the group for image analysis may be outperformed by other approaches, a review is undertaken of the data presented throughout this thesis. The results obtained previously are compared with those obtained when the same data are analysed using three alternative methods: Maximum Entropy Velocity Legendre Reconstruction, Maximum Entropy Velocity Image Reconstruction, and polar-coordinate Basis Set Expansion. Using data from each of the preceding chapters, it is demonstrated that, while the results of these studies are not invalidated, Polar Onion Peeling indeed produces demonstratively poorer results than the other algorithms, and consideration is given as to which approach should be used in future.

5.1 Background

As mentioned in Section 1.5 and shown in Figure 5.1, the Newton sphere of ions produced during photodissociation is ‘crushed’ onto the 2D plane of the detector in the process of velocity map imaging. Unless it is possible to use ‘slice’ imaging, where the gate width on the detector can be reduced sufficiently in order to image only the central slice (where $\phi = 0$), it is necessary to reconstruct this central slice from the raw data. A variety of methods have been developed for this in recent years.

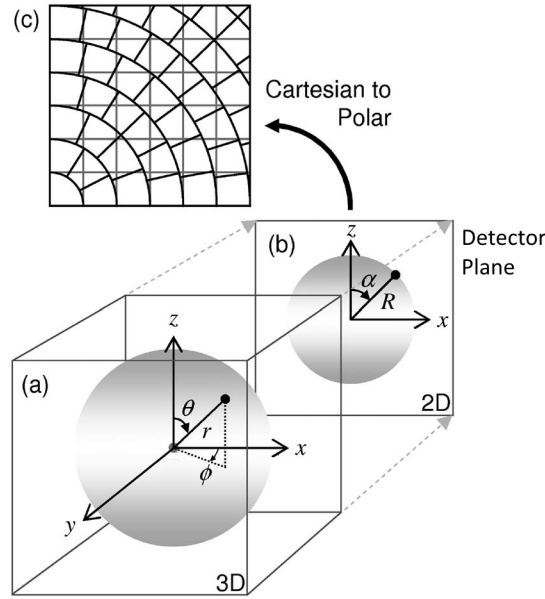


Figure 5.1: Illustration of the process of ‘crushing’ the sphere of ions created during dissociation onto a detector and subsequent extraction. The Newton sphere produced is shown in (a) with r , θ , and ϕ coordinates; this is mapped onto a 2D plane in (b) with R and α coordinates. The process of converting from the Cartesian pixels of the detector to polar pixels is shown in (c). Figure adapted and reproduced with permission from G. M. Roberts, J. L. Nixon, J. Lecointre, E. Wrede & J. R. R. Verlet, *Review of Scientific Instruments*, 80, 053104 (2009).⁸⁷ Copyright 2009, American Institute of Physics.

The mathematical transformation which relates the Newton sphere to the crushed image is the Abel transformation, while the inverse Abel is used for image reconstruction. The problem with this is that the inverse Abel integral is not well-behaved; as Dribinski *et al.* say, it is ‘numerically impractical as it has singularities and requires derivative estimation for a generally noisy function defined on a grid’.²²⁹

This has led to a number of approaches being used for image reconstruction. For example, one early approach, the Fourier-Hankel technique, represented the inverse Abel transform by successive Fourier and Hankel transforms.^{229,230} Since then, a variety of other algorithms have been developed using different techniques, as described in Section 5.2.

Polar Onion Peeling (POP) is the image reconstruction method which has been consistently used throughout recent experimental imaging work in the Mackenzie group.^{44,61,63,148} However, over the course of this research project there have been

some indications that this may not be the best method of image analysis.

Recently, a 2014 review from the group of Lai-Sheng Wang included a comparison of different image reconstruction methods.²³¹ This study compared five inversion methods: the Basis Set Expansion (BASEX) Abel transform method and its polar equivalent, pBASEX;^{229,232} Onion Peeling and POP;^{87,233} and a recursive method.²³⁴ The conclusions drawn from this comparison were that none of the methods were significantly better than the others, and that they all had their advantages. However, POP seems to have one of the poorest resolutions in the comparisons, as well as relatively high levels of baseline noise, and thus it was thought that a study of which methods would be best applied to metal cluster dissociation images would be worthwhile. Images from our research group tend to have comparatively low signal intensities, and, as such, an improvement in resolution would be particularly important in detecting and fitting weak features.

5.2 Analytical Details

5.2.1 Polar Onion Peeling

The details of the POP method have been covered in detail in Section 1.5.2, and is thus described only briefly here. The basic principle is that one can reconstruct the central slice through the three dimensional Newton sphere by ‘peeling away’ the contributions of successively smaller rings, hence the name. This depends on the idea that for a particular sphere of ions, there will be those for which ϕ (as defined in Figure 5.1) is zero and which will hence be at the maximum radial extent in the two-dimensional image. Ions from the same process for which $\phi > 0$ lead to an intensity contribution at lower R in the crushed image. The algorithm begins at maximum value of R and works inwards. When signal intensity is encountered, the program simulates the 3D form of a sphere which would create a ring of that radius and hence the contribution of ions of that same kinetic energy release (KER) at lower R . This is subtracted from the total intensity, peeling away the contribution of the largest KER process before the algorithm continues on to the next largest feature. This process is continued until it reaches the centre of the image.⁸⁷

In the Mackenzie Group, the onion peeling algorithm is used as a LabView routine, which has multiple advantages, such as integration with other experimental routines. It also allows for a quick representation of the output without further data processing software. This is particularly important for determining an accurate centre of the image, since the algorithm does not automatically detect it. In its current form, as published by Roberts *et al.* in 2009, it is also computationally cheap and therefore quick to run, due to the use of basis functions in the simulation of the 3D sphere from a given R , an idea borrowed from the BASEX and pBASEX methods described in the following section.⁸⁷

5.2.2 Basis Set Expansion

The Basis Set Expansion method for the Abel inversion was initially developed to overcome the deficiencies of older approaches, such as the Fourier-Hankel method that dominated at the time, which performed well for high-quality images but suffered from cumulative noise issues and introduction of artificial features.^{229,230}

The BASEX method developed a solution to the problem of the badly-behaved inverse Abel integral by using an expansion of a basis set of functions to fit the image data. As the forward Abel transform is a well-behaved operation, this is a much easier approach, turning the problem into a simpler case of fitting coefficients of an expansion of a suitable basis set.²²⁹ The later pBASEX technique further developed this approach by using polar, rather than Cartesian, basis functions, claiming that this leads to a significant enhancement in computational speed.²³² Lai-Sheng Wang's review also noted that pBASEX has good performance when dealing with noisy images, which may prove useful when reconstructing some of the low-intensity images obtained during this project.²³¹ One important feature of pBASEX is that, unlike the POP method, it deals with the images as a whole when fitting rather than focussing on one radius at a time.

The basis sets which are used for the fitting procedure can be selected in terms of the number of Legendre polynomials used, up to the tenth order. The first time a particular basis set is used, a significant amount of time is required for it to be

built and saved for future use. However, after this process is completed, image reconstruction is computationally cheap, requiring only fractions of seconds to complete. The algorithm is implemented in a Linux program, which generates live displays of input and output images, as with the POP LabView routine, although with a somewhat lower degree of detail.

5.2.3 Maximum Entropy Methods

The recently published (and still under-development) maximum entropy programs from Bernhard Dick *et al.* are a reaction against existing techniques for finding the inverse Abel transform of a dataset.⁸⁶ Dick proposes a method of avoiding the problematic Abel inversion entirely, which relies on treating an experimental data set, labelled D , by finding a velocity map, F . This F is equivalent to the results of the inverse Abel transform in other techniques. The programs perform the Abel transform on F (as stated, this is a well-behaved process) to find a simulated ‘ideal’ image, A , and then optimise F such that it yields a representation A which most resembles the dataset being fitted, D .⁸⁶

The process for finding the best velocity map F , illustrated in Figure 5.2, relies on Bayesian statistics,⁸⁶ but fundamentally has two main steps. First, the likelihood of the velocity map giving the observed data D (indicated by the likelihood estimator L) is optimised, finding those maps which are most compatible with observation. From here, the *a priori* probability of a given map occurring is maximised; that is, of the possible maps, the one which is most like a default map before any data are obtained is selected. This selects the map which contains the least information while still fitting with the experimental data. This latter step is the ‘maximum entropy’ process referred to in the name of the algorithms, as indicated by S in Figure 5.2. By following this process, the program fits all of the available data while avoiding the introduction of any artificial features.⁸⁶

This approach does not assume any correlation between neighbouring pixels. It is possible to include this assumption as a factor to aid fitting by using ‘Hidden Maps’. These maps are the same as the velocity maps generated when this feature is unused: they are optimised in the same way and have few basic assumptions

about the structure of a sensible map. The output velocity map is related to the hidden maps by a transformation, $\mathcal{J}$, which forces a correlation in neighbouring pixels by replacing the value of a pixel in the hidden map with a weighted average of this pixel and its nearest neighbours. The number of hidden maps is optional - the more which are used, the higher the correlation included. This feature was found in the original paper to be very useful for fitting images with very low ion counts,⁸⁶ and is tested in this chapter.

In the course of this algorithm, the Abel transformation, $\mathcal{R}$, is used to map F onto A , but Abel inversion, $\mathcal{R}^{-1}$, is not used at any point. This is indicated by the dotted arrow in Figure 5.2, to demonstrate that this approach avoids the inverse Abel transformation entirely.

There are two implementations of this techniques: Maximum Entropy Velocity Image Reconstruction (MEVIR) and Maximum Entropy Velocity Legendre Reconstruction (MEVELER). The main difference is that MEVELER assumes that the an-

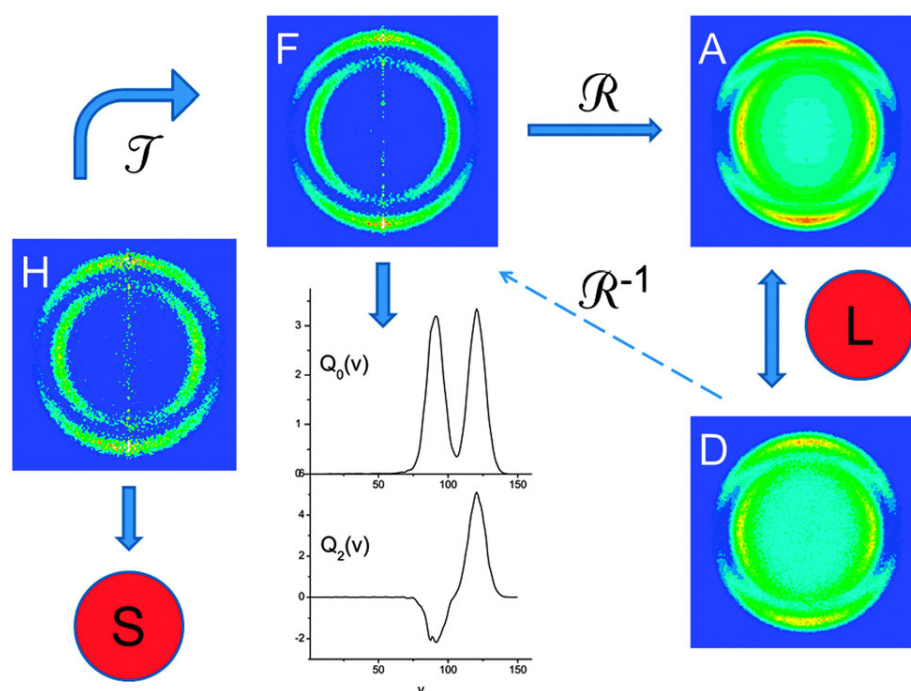


Figure 5.2: Illustration of the process image reconstruction using MEVIR, as explained in the text. The process used by MEVELER is fundamentally similar but relies on optimising Legendre polynomials, Q_n , rather than optimising the map F and extracting the polynomials from this. Reproduced from B. Dick, *Physical Chemistry Chemical Physics*, 2014, 16, 570–580 with permission from the PCCP Owner Societies.⁸⁶

gular distribution of F can be expanded in terms of Legendre polynomials, while MEVIR makes no assumptions beyond that the distribution is cylindrically symmetrical about the axis of polarisation.⁸⁶ The original publication claims results as good as or better than pBASEX in cases of high intensity images, and significant improvement in low intensity cases.⁸⁶

The version of MEVELER used is a beta version from February 2015, which is only capable of calculating the first two Legendre polynomials (giving β_2 but not β_4). This is fine for a single-photon process, but the program will thus fail to accurately fit the anisotropy of dissociation processes involving multiple photons. For MEVIR, version 1.1 (January 2014) is used, which is capable of calculating two further Legendre polynomials, giving β_4 and β_6 anisotropy parameters, which are used for multiple photon processes.

The data is first run through another program (F2Q.exe) which sums up the four quadrants of the image into a single quadrant which is then operated on. Quadrants can be excluded as required (due to damage to the detector or similar). While the program possesses the code to automatically detect the centre of an image, this was found to perform unreliably on our datasets and was thus unused, requiring manual determination of the centre as previously used during analysis using the POP algorithm. This leads to one of the main drawbacks of these programs: they do not provide an instant representation of the output, requiring the radial spectra to be analysed with other data processing software. This makes accurate determination of the image centre far more laborious, such that in this study the image centres were found using the POP software and then used for maximum entropy analysis, which obviously leads to an advantage for POP in usability terms. There is also the need to convert the image saved by the camera software into a format usable by the reconstruction algorithm. This conversion is integrated into the POP LabView VI and thus the POP software is needed for this step as well.

F2Q also possesses one minor but important difference to POP and pBASEX: the latter two algorithms treat the centre of the image as being in the centre of a pixel, while F2Q places the centre at the lower-left corner of the named pixel. This leads

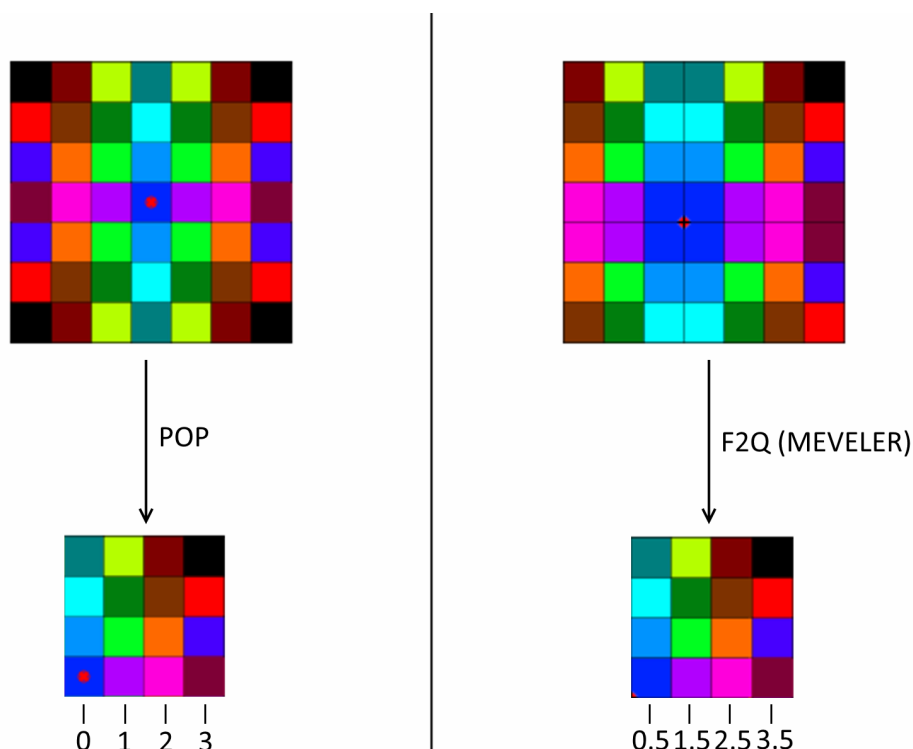


Figure 5.3: Illustration of the different approaches taken by the methods under examination to the process of ‘folding’ the full image to produce a single quadrant, where the same coordinates of the centre are input in both cases. Pixels in the folded quadrant contain contributions from pixels of the same colour in the complete image. **Left:** The Polar Onion Peeling algorithm locates the centre in the middle of a pixel and numbers the pixels with integers. This method is also used by the polar Basis Set Expansion approach. **Right:** The F2Q algorithm used in the Maximum Entropy methods locate the centre in the corner between four pixels and numbers pixels with half-integers.

to slight differences in the summing/averaging of pixels when folding the quadrants, and also means that each pixel in the POP algorithm is an integer distance from the centre, while those in the maximum entropy output are half-integer distances away. This difference is shown in Figure 5.3.

Having outlined the different methods under examination, the capabilities of the three approaches will be compared by using pBASEX, MEVIR and MEVELER to re-analyse the data previously studied using POP in previous chapters. The output results from the different algorithms are contrasted in terms of ability to fit weak features, resolution/width of peaks produced, and noise/artefacts.

5.3 Dissociation of Silver-Argon Dimer

These images were previously studied in Section 2.3.1, where they were determined to be due to dissociation of the AgAr molecule into excited state $\text{Ag}(^2P_{3/2})$ and ground state $\text{Ar}(^1S_0)$ with a dissociation energy of $85.9 \pm 23.4 \text{ cm}^{-1}$. These images are some of the simplest observed during this project, almost all containing a single, relatively intense feature with strong anisotropy (some images show a weak feature due to dissociative ionisation of Ag_2). These should provide a relatively simple case for comparison of the reconstruction methods.

In the full analysis used previously, thresholding was used to minimise the effects of noise, by ignoring the first two or three counts in a pixel as being due to a pervasive background noise. To keep things simple, and to investigate how well the techniques handle noise in images, they will be straightforwardly analysed with no thresholding and using the same coordinates for the centre for each algorithm (N.B. as mentioned above, this does not directly mean that the folded quadrant will be exactly the same in each case).

Figure 5.4 shows KER spectra produced from the same raw data by each of the reconstruction algorithms (POP, MEVELER, MEVIR, and pBASEX). The main difference between the algorithms is the level of baseline noise in the spectrum produced relative to using the POP method. The Signal-to-Noise Ratios (SNRs, measured as peak height divided by standard deviation of the base line) for each of the spectra shown in Figure 5.4 are:

Algorithm	SNR
POP	34
MEVELER	180
MEVIR	277
pBASEX	99

This can be seen visually in the figure, where the maximum entropy methods produce noticeably less noisy spectra than POP and have a better ability to resolve less intense features, as demonstrated by the weak signal at lower kinetic energy which is due to dissociative ionisation of Ag_2 (see Section 2.3.4). This is resolved as

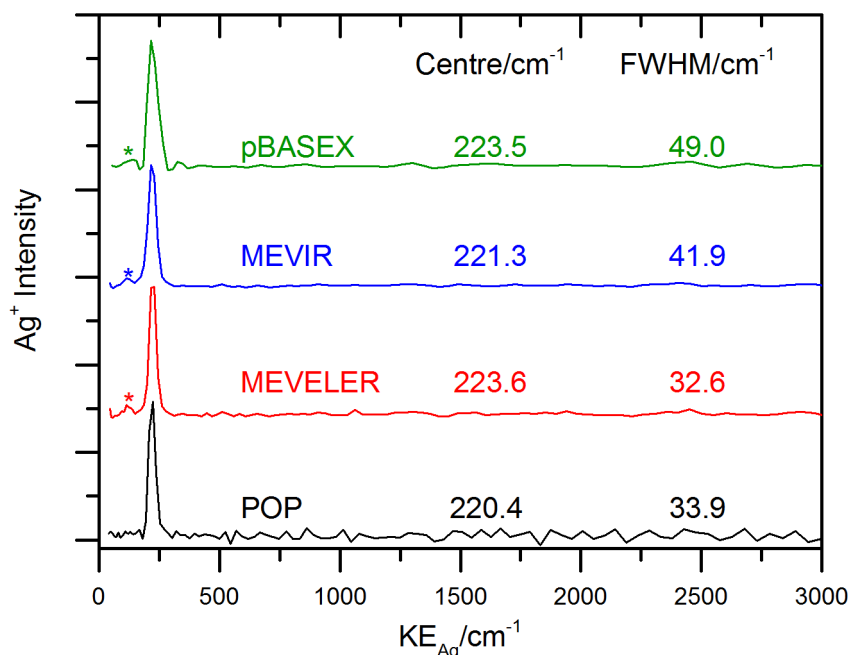


Figure 5.4: Kinetic Energy Release spectrum of Ag^+ produced from photodissociation of AgAr at 31250 cm^{-1} and extracted using the four different reconstruction algorithms under examination: Polar Onion Peeling (black), MEVELER (red), MEVIR (blue) and pBASEX (green). The quoted values for peak centre and full widths at half maxima are the parameters from a Gaussian fit through the main peaks. The asterisk indicates a minor feature due to the dissociative ionisation of Ag_2 discussed in Section 2.3.4.

a very weak feature in both the MEVIR and MEVELER spectra, but is completely absent in the POP spectrum.

The baseline in the pBASEX spectrum is also smoother than that produced by POP due to the fact that it treats the image as a whole rather than radius-by-radius. However, it is somewhat noisier than the maximum entropy spectra and also copes poorly with areas of low intensity, which is not apparent from Figure 5.4, where the x -axis is limited in range in order to effectively display the main feature. The pBASEX algorithm produces increasing amounts of noise at larger radius as intensity decreases, and fits a number of spurious features in an attempt to explain the noise.

In terms of the additional peak at lower KER than the main feature, this is apparently visible in the pBASEX spectrum, although it appears much broader. How-

ever, there is lower confidence that this is a real feature since pBASEX also indicates a peak just outside the main feature which does not appear in the spectra produced by MEVIR and MEVELER. The existence of this high energy feature is not attested to by the raw data in the way that the lower energy feature is - the smaller ring is visible but weak in the image, as indicated below. Between this, and the issues with fitting areas of low-intensity mentioned above, it is still questionable as to whether pBASEX has the same ability to resolve weak features as the maximum entropy methods.

It is also noticeable that the peaks produced in the KER spectrum by pBASEX appear broader, as indicated in Figure 5.4. MEVIR has a similar problem, but to a lesser extent, while there is no significant difference between POP and the MEVELER algorithm. The ‘hidden maps’ feature discussed in Section 5.2.3 was also tried for both maximum entropy methods. In both cases, it made little impact to the form of the spectra but did result in broader peaks, presumably due to the adjacent-averaging ‘smearing’ the intensity to a certain extent. For a more general comparison, Table 5.1 shows the FWHM obtained at each photon energy throughout this region by the different algorithms, presented in pixels as a direct comparison of the immediate output of the data.

There is a general trend that the peaks, in terms of radial pixels, are wider at lower

Table 5.1: FWHM (in pixels) of the main peak in the radial intensity spectra obtained from the AgAr data by various extraction methods

$\bar{\nu}/\text{cm}^{-1}$	POP	MEVELER	MEVELER (H1) ^a	MEVIR	MEVIR (H1) ^a	pBASEX
30769	2.68	2.61	2.90	3.42	3.40	3.70
30888	2.64	2.40	2.88	3.23	3.38	3.47
31008	2.43	2.57	2.84	3.26	3.29	3.65
31128	2.37	2.16	2.69	2.91	3.04	2.96
31250	2.30	2.19	2.68	2.83	3.01	3.30
31373	2.15	2.08	2.68	2.86	3.06	3.49
31496	2.29	2.04	2.64	2.62	2.81	3.59

^a Using one hidden map

photon energy. This may be tied to the fact that the rings at these low wavenumbers are very small and heavily pixelated, with each pixel representing a narrower range of fragment kinetic energies. However, with the slightly larger rings, it is noticeable that in both POP and MEVELER the width of the peaks is just over two pixels, which is easily explained by the nature of binning the continuous distribution into discrete pixels. Even if the camera recorded the image with radial and angular pixels to start with, it is likely that the radius corresponding to peak kinetic energy would fall between two pixel radii, resulting in a split of intensity between them. However, there is the further issue that the images are actually converted from Cartesian to radial pixels, and the nature of this process will almost always separate the intensity over at least two sets of radial pixels due to the imperfect overlap. This result, where the peak width varies in the range 2–2.6 pixels, is consistent with the comparison reported by León *et al.*²³¹

Overall, there is still a difference in performance among the values reported. The values reported using POP and MEVELER (without using hidden maps) are very similar, with perhaps a slight reduction when using the maximum entropy algorithm. MEVIR, and especially pBASEX, perform noticeably worse by this measure. Using hidden maps in MEVELER or MEVIR further worsens the situation, as might be expected when adjacent-averaging between pixels is introduced. Overall, this suggests that MEVIR and pBASEX introduce some artificial width to the peaks, thus reducing resolution, while POP and MEVELER have comparable performance, at least on these terms.

Figure 5.5 shows the reconstructed images produced by each algorithm corresponding to the KER spectra in Figure 5.4. MEVIR stands out amongst these in that it does not have any form of radial fitting. Contrary to this, Onion Peeling processes the image by radius, while the use of Legendre polynomials in MEVELER and pBASEX also produces clear radial/angular behaviour. However, MEVIR imposes no constraints on the angular form at each radius, leading to much more obvious pixelated noise in the reconstructed image. It also features substantial ‘centre-line noise’, a known feature of several reconstruction methods, which Dick suggested was not a significant issue due to its limited impact on the velocity distributions (KER spectra).⁸⁶ As might be expected from Figure 5.4, the MEVELER

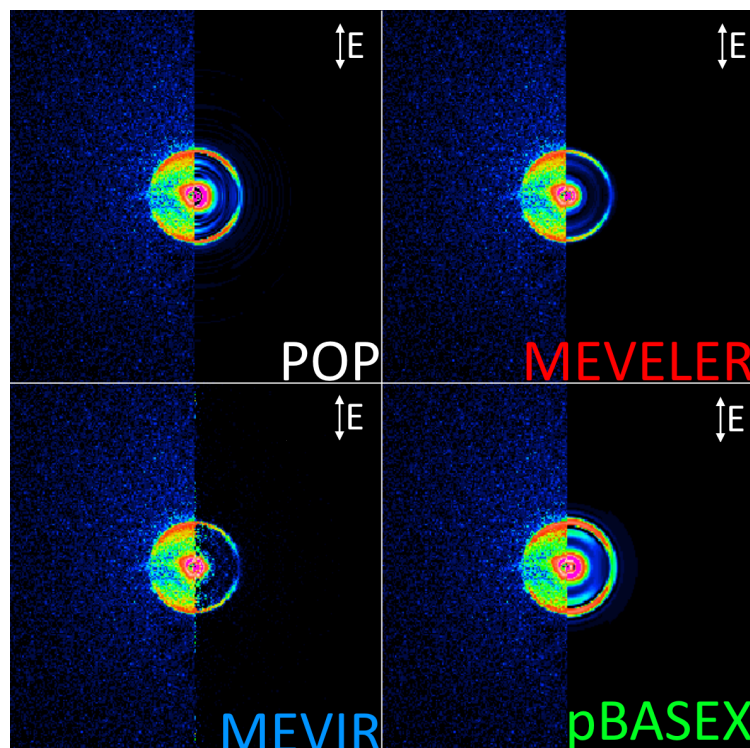


Figure 5.5: Images obtained in the Ag^+ channel at 31250 cm^{-1} ; in each case the left hand side of the image is the raw data, while the right hand side is the reconstructed image. The double-headed arrows indicate the plane of laser polarisation. **Top Left:** Polar Onion Peeling; **Top Right:** Maximum Entropy Velocity Legendre Reconstruction; **Bottom Left:** Maximum Entropy Velocity Image Reconstruction; **Bottom Right:** Polar Basis Set Expansion.

image is noticeably smoother than that produced by POP, with little intensity between the main features. pBASEX is an interesting case, in that it produces a relatively smooth image, and it helps the smaller, weaker ring stand out more. However, the rings are also noticeably wider, which is most likely related to the effect noted above in the width of the peaks in the spectra.

The anisotropy parameters calculated by the various methods were also studied. In this case, the process was assigned to a single-photon dissociation, and hence, only the β_2 parameter is relevant. This is particularly important for MEVELER, which cannot calculate β_4 in its current iteration.

Before focussing on the experimental data, a simulated dataset produced using SIMION was used to examine the effect of reconstruction method on the anisotropy parameters.⁷⁴ A series of images was created with known β_2 parameters of 2,

1.5, 1, and -1 , and with no contribution from higher order terms. The results are shown in Table 5.2.

At the extreme positive value, it can be seen that POP and MEVELER produce very similar results, while MEVIR gives a more accurate value and pBASEX significantly underestimates β_2 . At more moderately positive values, the same trends repeat, with larger values from MEVIR and lower values from pBASEX, although the magnitude of the differences are less significant. For $\beta_2 = 1$, the larger value given by MEVIR is actually further away from the true value than that from POP and MEVELER, a shortcoming which is again witnessed for the extreme limiting value of -1 , when the absolute value from MEVIR is markedly too high.

Overall, this suggests that MEVIR tends to produce values for β_2 which are further from zero than POP or MEVELER, while pBASEX noticeably underestimates the anisotropy parameter, at least for positive values. This should be borne in mind while analysing the experimental data.

Table 5.3 shows the β_2 anisotropy parameters produced by each algorithm for the main feature due to dissociation of AgAr at the various wavelengths studied. As Figure 5.5 demonstrates, the ring being studied is heavily anisotropic. The experimental images feature a much higher level of noise than the simulated data, and this is expected to bring the β_2 parameters closer to zero. Even if the ‘true’ value of β_2 for this dissociation were 2, the noise would distort it from the idealised case of zero intensity perpendicular to the axis of polarisation of the exciting laser beam.

Table 5.2: Values for the β_2 anisotropy parameter obtained for the AgAr data by various extraction methods

β_2	POP	MEVELER	MEVIR	pBASEX
2	1.88	1.89	1.97	1.69
1.5	1.46	1.46	1.48	1.37
1	0.97	0.97	1.06	0.89
-1	-1.02	-1.00	-1.17	-1.04

However, there is still a clear difference in the values of the anisotropy parameters produced by the different methods. MEVIR produces similar results to POP, while MEVELER gives noticeably lower values in several cases. This is exacerbated by the use of hidden maps, an effect which is oddly not replicated in MEVIR. pBASEX is similar to MEVELER for these data; it produces more isotropic rings with lower β_2 parameters than POP or MEVIR, although not as badly as the case where hidden maps are used with MEVELER.

These results are mostly consistent with those from reconstruction of the simulated data with positive β_2 values, suggesting that pBASEX and MEVELER have potentially underestimated the actual value of β_2 , while MEVIR is probably closer to the mark. POP noticeably gives larger values than MEVELER for the experimental data, perhaps suggesting a better capacity to deal with the additional noise in the angular distribution. Overall, in combination with the simulated data, these results potentially suggest a weakness of MEVELER and pBASEX when it comes to anisotropy parameters relative to MEVIR, while the status of POP is more uncertain.

In summary, after studying the various algorithms in the case of a simple spectrum with one major feature and one very weak feature, maximum entropy methods have demonstrated a noticeably better ability to handle noisy images and to

Table 5.3: Values for the β_2 anisotropy parameter obtained for the AgAr data by various extraction methods

$\bar{\nu}/\text{cm}^{-1}$	POP	MEVELER	MEVELER (H1) ^a	MEVIR	MEVIR (H1) ^a	pBASEX
30769	1.24	1.16	0.99	1.35	1.36	1.14
30888	1.46	1.49	1.18	1.63	1.57	1.28
31008	1.57	1.35	1.24	1.42	1.44	1.24
31128	1.66	1.36	1.09	1.46	1.41	1.23
31250	1.58	1.33	1.33	1.42	1.46	1.38
31373	1.83	1.43	1.28	1.47	1.49	1.31
31496	1.59	1.40	1.21	1.53	1.52	1.19

^a Using one hidden map

resolve weak rings which are impossible to see or fit in the KER spectra produced by POP. pBASEX has provided some evidence that it can also resolve these weak features, but there are some doubts over its ability to cope with areas of the image with low ion intensity which may affect this. There is not a substantial difference in peak width between the spectra generated by POP and MEVELER, but MEVIR and pBASEX produce slightly broader peaks. This suggests that in terms of resolving features and fitting peaks, MEVELER has an advantage over the POP method currently used, but mostly when dealing with weak rings in noisy spectra. However, MEVELER does not perform quite as well in terms of β_2 parameters, which is expected to be exacerbated when more photons are involved and the lack of higher-order Legendre polynomials becomes an issue. Use of hidden maps does not appear to have many advantages for this dataset — in the original publication it was stated to have benefits mostly when extracting very low intensity images,⁸⁶ and it would seem that these images do not fall into this category, despite the low count-rate. Instead, using hidden maps does not bring out any new features but does reduce resolution.

5.4 Dissociation of Molybdenum Oxide Dimer

Having studied the simple data from dissociation of AgAr, it is worth comparing how the reconstruction algorithms perform in a more complicated case. The data re-examined in this section were previously studied using POP in Section 3.3.2, and contained three peaks from dissociation of the ^{98}MoO molecules into $\text{Mo} + \text{O}(^3P)$ fragments, where the molybdenum atoms were produced in ^5G , ^5P , or ^5D states. In this case, the opportunity is presented to test the capabilities of the different methods with multiple features.

These images and kinetic energy release spectra present a much different challenge. Firstly, the peaks are much broader, since they consist of contribution from multiple spin-orbit components. Secondly, a combination of noise and multiple peaks in the spectrum makes fitting the peaks much harder than in the AgAr dissociation cases. Thirdly, there is a significant variation in ring intensity between different images, unlike in the data recorded from dissociation of the silver-argon

dimer, where the observed ring had a consistently high intensity. This provides an opportunity to study how the different methods cope with images of differing ring intensities. Figure 5.6 shows the extraction results using the different methods for an image measured at a photon wavenumber of 21739 cm^{-1} , which contained strong rings.

As can be seen from the figure, the results are similar at this photon energy. The results from pBASEX and the maximum entropy methods are slightly smoother than those from the standard POP algorithm, but the same features are present in each case, and the widths of the peaks are also comparable in each case. Unlike in Section 5.3, each peak results from a combination of multiple spin-orbit components, such that the primary width does not result from pixelation but from the range of energies of the different components. Hence, in this case the peaks have widths of

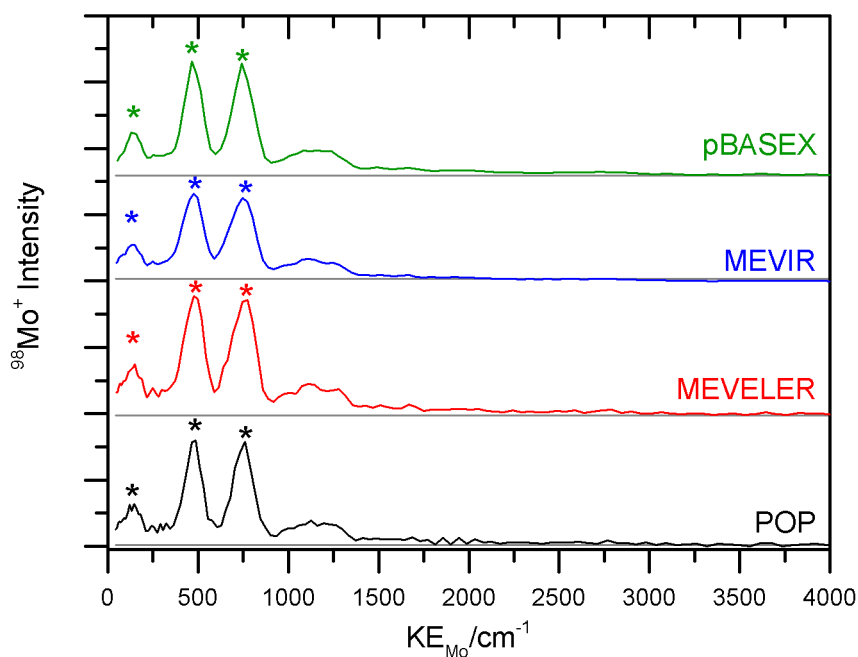


Figure 5.6: Kinetic Energy Release spectrum of $^{98}\text{Mo}^+$ produced from three-photon dissociation of ^{98}MoO at 21739 cm^{-1} and extracted using the four different reconstruction algorithms under examination: Polar Onion Peeling (black), MEVELER (red), MEVIR (blue) and pBASEX (green). As in the assignments in Section 3.3.2, the three starred peaks (from left to right) result from formation of $\text{Mo}(^5G)$ (Series 1), $\text{Mo}(^5P)$ (Series 2), and $\text{Mo}(^5D)$ (Series 3) states respectively, while other features are unassigned.

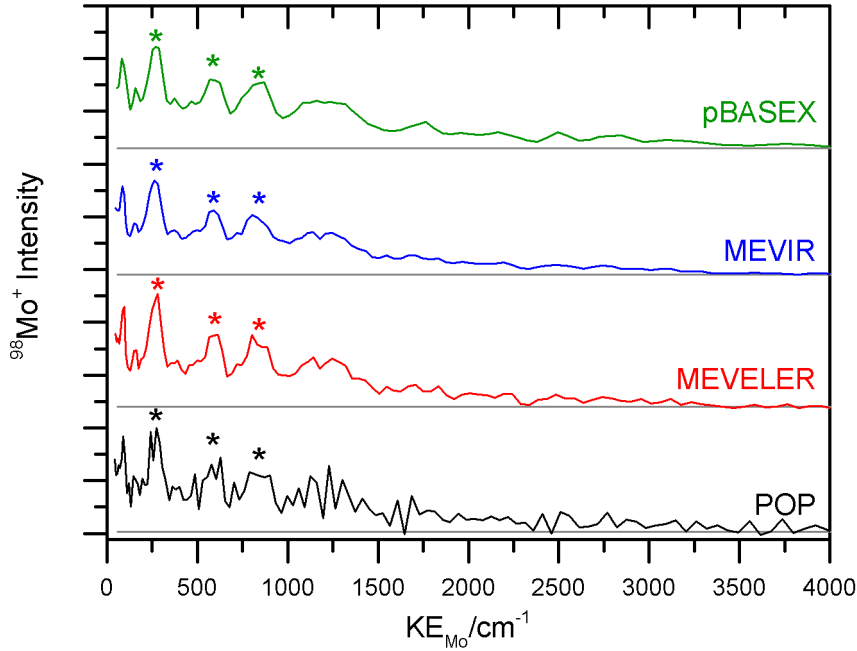


Figure 5.7: Kinetic Energy Release spectrum of $^{98}\text{Mo}^+$ produced from three-photon dissociation of ^{98}MoO at 21978 cm^{-1} and extracted using the four different reconstruction algorithms under examination: Polar Onion Peeling (black), MEVELER (red), MEVIR (blue) and pBASEX (green). As in the assignments in Section 3.3.2, the three starred peaks (from left to right) result from formation of $\text{Mo}(^5G)$ (Series 1), $\text{Mo}(^5P)$ (Series 2), and $\text{Mo}(^5D)$ (Series 3) states respectively, while other features are unassigned.

ca. 8, 7, and 5 pixels for Series 1, 2, and 3 respectively. Given this, minimising the width of the peaks is a less crucial test than in the previous section.

To test the capabilities of the different methods when given a more challenging image, the test was re-run using data from a photon energy which produced weaker features - this time at 21978 cm^{-1} , the results of which are shown in Figure 5.7. In this case the peaks are somewhat visible but very poorly resolved when extracted using Polar Onion Peeling. However, the maximum entropy methods produce substantially better results with well-defined peaks. This is consistent with our observation in Section 5.3 that MEVIR and MEVELER are much better at resolving low-intensity features. Notably, pBASEX performs just as well for this spectrum, resolving the same features to a similar degree, and thus indicating that the observation in Section 5.3 that pBASEX was able to resolve the weaker inner ring from

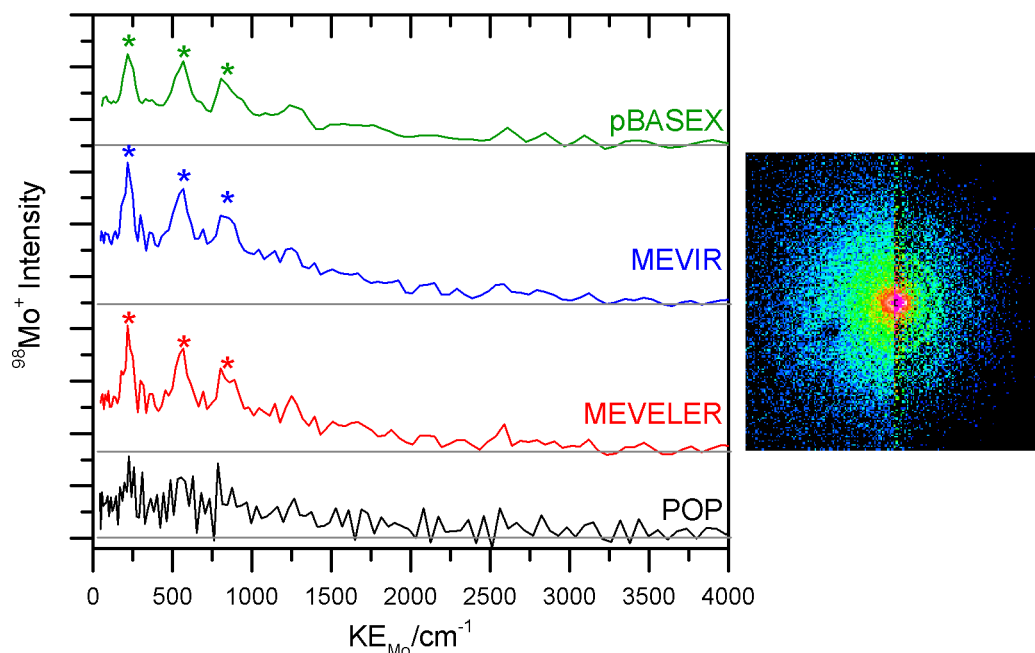


Figure 5.8: Kinetic Energy Release spectrum of $^{98}\text{Mo}^+$ produced from three-photon dissociation of ^{98}MoO at 21930 cm^{-1} and extracted using the four different reconstruction algorithms under examination: Polar Onion Peeling (black), MEVELER (red), MEVIR (blue) and pBASEX (green). As in the assignments in Section 3.3.2, the three starred peaks (from left to right) result from formation of $\text{Mo}(^5G)$ (Series 1), $\text{Mo}(^5P)$ (Series 2), and $\text{Mo}(^5D)$ (Series 3) states respectively, while other features are unassigned. **Inset:** The corresponding image, with the raw data on the left and the MEVIR-reconstructed central slice on the right.

dissociative ionisation of Ag_2 was not spurious, but a real effect of the resolving power of the algorithm.

Finally, to further investigate the limits of this ability, another image was used; this was measured later in the experimental run at a photon energy of 21930 cm^{-1} , and contained less than half the number of ion events measured in the images shown in Figure 5.7, such that POP had failed to resolve any extractable peaks from these data. Figure 5.8 shows the results of re-extraction with the other methods, compared to the results from Polar Onion Peeling. The figure also includes the image in order to demonstrate that the rings are weak enough that they are difficult to see amongst the noise.

As the figure shows, the signal-to-noise ratio of the POP-extracted data is very

poor, but features corresponding to all three of the usual series are evident in the data obtained using the other three methods. In combination with the extra peak revealed in Section 5.3, this supports the idea that pBASEX, MEVIR and MEVELER are significantly better at resolving features in cases involving weaker rings.

5.5 Dissociation of Chromium Oxide Dimer

In order to examine the limits of the ability of pBASEX, MEVIR or MEVELER to resolve peaks in KER spectra from poor quality or low intensity images, it is worth re-examining the data from dissociation of ^{52}CrO previously analysed in Chapter 4. There were two datasets based around this process: one in the visible region of the spectrum, and one in the ultraviolet region, each presenting different challenges. The former contains images with a similar number of peaks to those in Section 5.4, but contains further images with weak features which POP struggled to resolve sufficiently well to fit for inclusion in the analysis procedure; this is a further examination of the resolving power for weak features. The latter has fewer issues with low off-axis intensity, but instead has a large number of peaks, with seventeen different series observed; the aim of analysing this data is to examine how POP, pBASEX, and the maximum entropy methods cope with so many peaks.

Figure 5.9 shows an example of spectra from a high-quality, well-resolved image taken in the visible region. As before, with a high-quality image there is little qualitative difference in the results from the different extraction methods, which all produce similar spectra. In each case, multiple features are resolved, with two of the most prominent features appearing almost as a double peak. These are the most reliably occurring features in this region, appearing in every image taken throughout the range explored by the data in Section 4.3.2.

However, the fact that these twin features lie so close together can be problematic with lower quality images; in some cases, POP was unable to resolve the two features sufficiently to enable them to be fitted separately. This meant that the image could not be included in the overall summary used to measure the dissociation

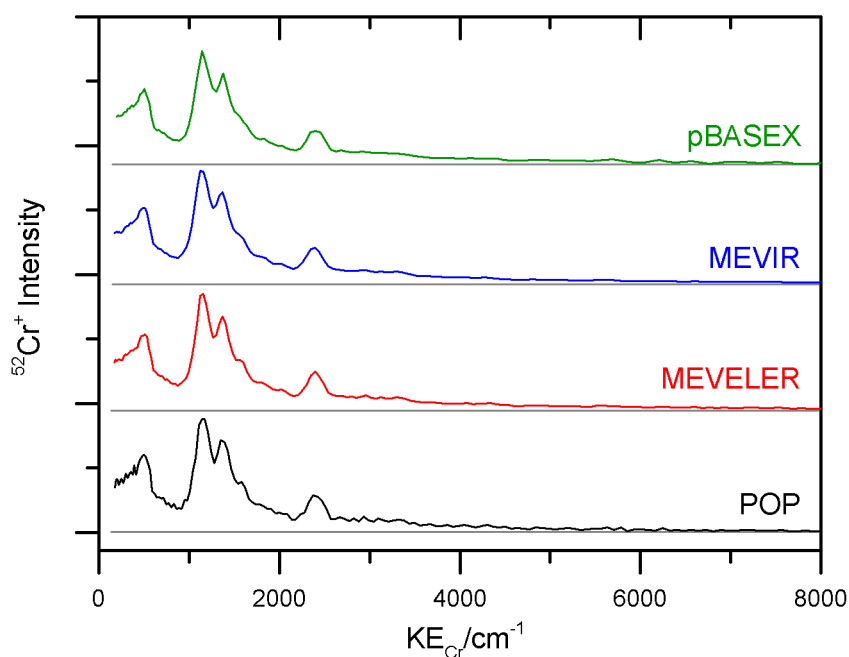


Figure 5.9: Kinetic Energy Release spectrum of $^{52}\text{Cr}^+$ produced from three-photon dissociation of ^{52}CrO at 22095 cm^{-1} and extracted using the four different reconstruction algorithms under examination: Polar Onion Peeling (black), MEVELER (red), MEVIR (blue) and pBASEX (green). The main peaks (from left to right) are those corresponding to Series III, IV, V and VIII as defined in the assignments in Section 4.3.2.

energy. One such case, recorded at a photon energy of 22075 cm^{-1} , is shown in Figure 5.10a.

As shown in the figure, the original extraction using Polar Onion Peeling revealed a feature indicating intensity at the appropriate kinetic energy, but the two peaks were not resolved, with the overall appearance being one broad, noisy peak. Re-extracting with the other algorithms improves the results, with pBASEX producing a much less noisy spectrum and indicating that there are two peaks, with one being a shoulder of the other. However, it is the maximum entropy methods that have the advantage here, as both of them clearly resolve the tops of the two peaks enough so that they can be fitted separately. The inability of pBASEX to resolve two distinct features may be related to the observation made in Section 5.3 that this algorithm produces broader peaks, which would lead to a tendency for two rings close to each other to overlap.

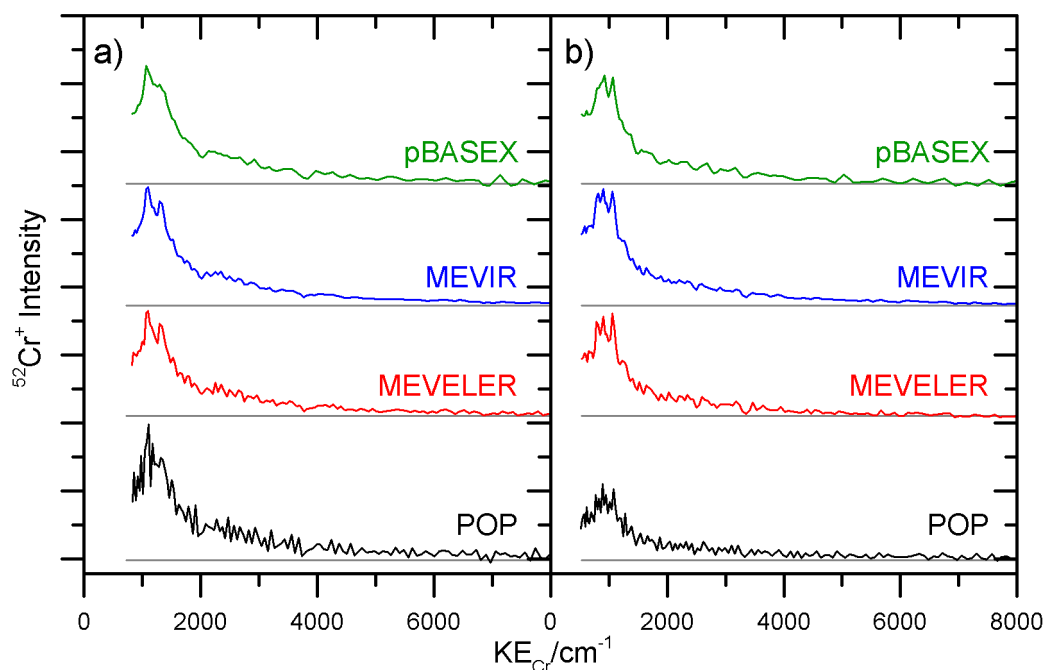


Figure 5.10: Kinetic Energy Release spectrum of $^{52}\text{Cr}^+$ produced from three-photon dissociation of ^{52}CrO at a) 22075 cm^{-1} and b) 21790 cm^{-1} , extracted using the four different reconstruction algorithms under examination: Polar Onion Peeling (black), MEVELER (red), MEVIR (blue) and pBASEX (green). In accordance with the assignments in Section 4.3.2, the main peaks (where resolved) correspond to Series IV and V.

Spectra extracted from another image, this time recorded at a photon wavenumber of 21790 cm^{-1} , are shown in Figure 5.10b. This is from an image of particularly low quality, with a very poor signal-to-noise ratio. In this case, the ‘peak’ produced by onion peeling was so weak that it is barely visible as a bump in the spectrum, and could not be fitted at all. Once again, the other methods demonstrate their greater ability to deal with such images and produce a clear spike in intensity, thus indicating the presence of the ring. However, the spectra are much noisier than those normally produced by pBASEX or the maximum entropy algorithms, and it is debatable as to whether the double peak is resolved. There is some indication that all three methods show a double peak. However, it is difficult to distinguish this from the noise in the spectrum. This may indicate that such images present an almost limiting case in terms of the ability of these approaches to handle noise and resolve peaks.

In the paper accompanying the release of MEVELER and MEVIR, it was suggested that low-intensity images were the sort of data that the ‘Hidden Maps’ feature explained in Section 5.2.3 was best at handling.⁸⁶ In Section 5.3, it was established that the ‘smearing’ introduced by the adjacent-averaging used in the hidden maps increased the width of peaks and made rings more isotropic. However, now that we are presented with an image with such a poor signal-to-noise ratio that the maximum entropy methods are struggling to cope with the noise and resolve the peaks, it is worth inspecting whether the feature is of use in such a case.

Figure 5.11 shows kinetic energy spectra from the same image as Figure 5.10b, recorded at 27190 cm^{-1} . However, rather than comparing the effect of using different extraction algorithms, all of the spectra in Figure 5.11 were extracted with MEVELER in order to show the effect of enabling one or two hidden maps during analysis. The most obvious effect is an apparent smoothing of the noise, as might be expected directly from the adjacent-averaging. Notably, it also cleans up the

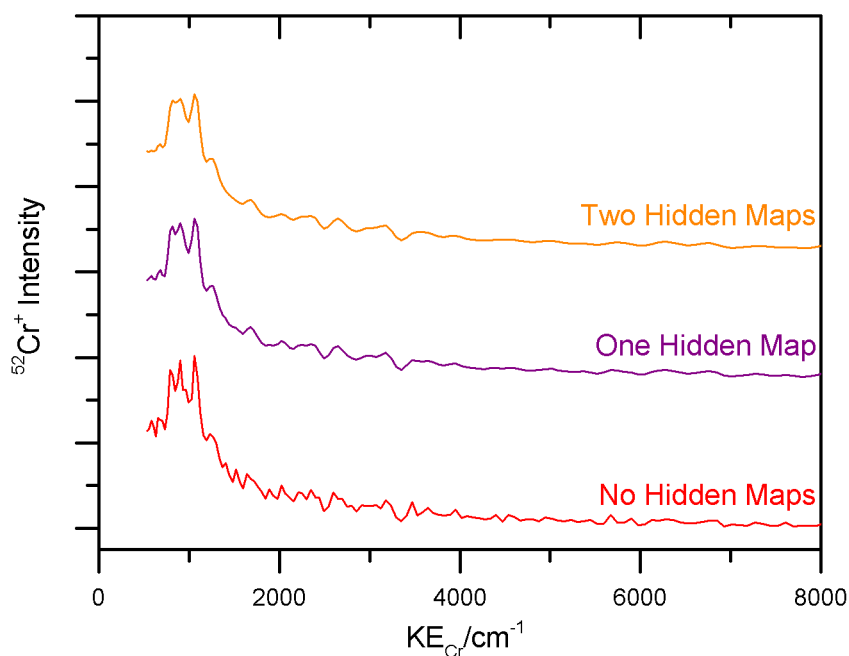


Figure 5.11: Kinetic Energy Release spectrum of $^{52}\text{Cr}^+$ produced from three-photon dissociation of ^{52}CrO at 27190 cm^{-1} extracted using MEVELER, with zero (red), one (purple) or two (orange) hidden maps.

top of the peak, more clearly demonstrating that there is a double peak as a real feature, not just as an artefact from the noise.

Using a second hidden map increases the noise-reduction effect and enhances the clarity of the spectrum. However, this added clarity is not of particular utility, given that the spectrum acquired using a single map is sufficiently resolved to be fitted. Furthermore, increased numbers of hidden maps become more computationally costly and require extra time for analysis. Furthermore, in this case using an excessive number of hidden maps will ultimately have the effect of ‘smearing’ the two peaks together.

It is therefore apparent that the maximum entropy algorithms and pBASEX are able to extract higher-quality data from images which had proven unusable using POP. MEVELER and MEVIR have a slight edge over pBASEX when resolving peaks which are particularly close together. The hidden maps feature of these algorithms may also prove useful when handling particularly low-quality images.

Regarding the imaging in the ultraviolet region, these images were of a more consistent quality and instead present a different challenge, based around the large number of features and peaks observed. In order to examine the possibility that MEVELER, MEVIR, and/or pBASEX may be able to extract these more easily, the images were re-extracted using these methods. Figure 5.12 shows a comparison of the various resulting spectra from a sample imaged obtained at a wavelength of 43384 cm^{-1} .

This comparison shows that the spectrum as extracted using POP is noticeably the noisiest. However, unlike in some previous cases, no new features are revealed by the other extraction algorithms. This is a consistent result throughout the dataset: in each case, pBASEX and the maximum entropy methods produce cleaner spectra but no new peaks. However, this reduction in noise is helpful, making the shapes of the peaks clearer and increasing confidence that increases in intensity are due to genuine features rather than random fluctuations from noise.

There are some notable characteristics of the spectra. For example, there is the possible revelation of a double peak structure in the peak corresponding to Series Q. Unfortunately, as explained in Section 4.3.3, the number of possible assignments

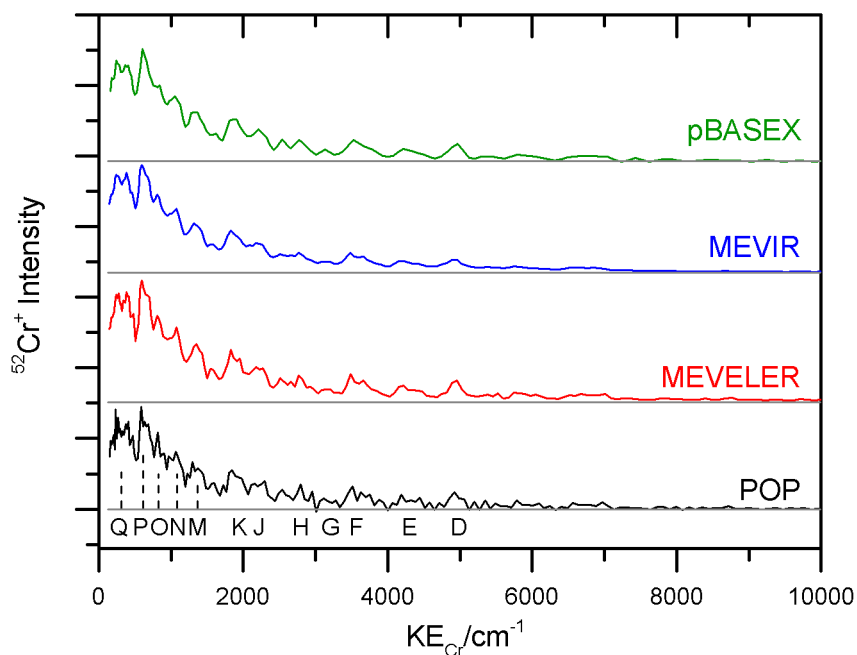


Figure 5.12: Kinetic Energy Release spectrum of $^{52}\text{Cr}^+$ produced from three-photon dissociation of ^{52}CrO at 43384 cm^{-1} and extracted using the four different reconstruction algorithms under examination: Polar Onion Peeling (black), MEVELER (red), MEVIR (blue) and pBASEX (green). The features are labelled in accordance with the assignments in Section 4.3.3.

in this region is so high that it is difficult to assign states which may correlate with each of these two peaks. However, it does further imply the possibility that better extraction methods may reveal two peaks where POP produces only one. One other noticeable feature is that pBASEX renders the peak corresponding to Series O into a shoulder of the peak from Series P, where both peaks are better resolved by MEVIR and MEVELER. This is consistent with the observations above from Figure 5.10a.

Overall, the gains in this region are less than those from the visible region, but there is still the strong suggestion that MEVELER, MEVIR, and pBASEX are able to produce less noisy spectra which are more easily interpreted, in keeping with the conclusions from the other datasets.

5.6 Conclusions

A comparison of the Polar Onion Peeling method against the commonly used pBASEX algorithm and the newer Maximum Entropy approach has now been performed for various datasets studied in Chapters 2, 3, and 4. The results of this have highlighted certain deficiencies in the POP technique.

As illustrated in this chapter, there is little difference in the performance of the algorithms for high-quality images with high ion intensities and clearly defined rings. As indicated in Section 5.3, there are some minor differences in peak width and anisotropy parameters. In terms of peak width, POP and MEVELER produce narrower peaks than MEVIR and pBASEX, while POP and MEVIR produce values for the β_2 parameter which match the expected value better than those from MEVELER or pBASEX.

More importantly, in Sections 5.4 and 5.5, it is demonstrated that, in cases where the image quality is lower, POP is demonstrably poorer at handling noise and resolving features than the other three algorithms. In most cases, there is little difference in the ability of MEVIR, MEVELER, and pBASEX to identify rings. However, the data from dissociation of ^{52}CrO in the visible region of the spectrum, which contains two peaks in close proximity, suggests that the maximum entropy programs may be better able to handle such cases than pBASEX.

Given the evidence from this section, it is clear that the onion peeling approach has significant issues when applied to noisy or low-intensity images, and one of the other methods should be applied in such cases. However, it is also possible that low-intensity features in images with otherwise strong rings may also be better resolved using MEVELER, MEVIR, or pBASEX, as in the case of the small peak due to dissociative ionisation of Ag_2 in Section 5.3. Thus, even if an image appears to have a sufficiently high signal-to-noise ratio such that POP would perform sufficiently well, it is still safer to use one of the other approaches to minimise the risk that dissociative channels will go undetected.

It is therefore recommended that, in the future, one of the other methods is used for image analysis. With regards to which algorithm is preferred, there are fewer

differences distinguishing the non-POP programs. The evidence from Section 5.5 that pBASEX is inferior when extracting double peaks, or two peaks close enough to appear so, suggests that it may be preferable to select one of the maximum entropy methods. Of these, MEVELER produces narrower features, while MEVIR produces anisotropy parameters which are perhaps more accurate, at least when β_2 is positive, as well as the capability to handle higher order Legendre polynomials, which is relevant in the case of dissociations involving multiple photons. Given this, MEVIR appears to be the current best choice of algorithm by a narrow margin. However, MEVELER and MEVIR are still in development and this may change as more Legendre polynomials are added to the former program and both gain extra improvements.

Some consideration of the impact of these inferiorities of POP on the results of this thesis must be made. Since the main effect of the other extraction methods is to reveal extra peaks which can be included in the analysis, there is an effect from this. However, in each case, there were sufficient peaks fitted using the POP-extracted data that the results are not fundamentally altered, and similar values for the dissociation energies are obtained. This is demonstrated by Table 5.4, which shows a comparison between the final results of Section 3.3.2, where the old Polar Onion Peeling algorithm was used, and the results obtained by re-analysing the data from scratch using MEVIR.

Table 5.4: Experimental dissociation energy of ^{98}MoO obtained by different image reconstruction methods

	$D_0(\text{POP})/\text{cm}^{-1}$	$D_0(\text{MEVIR})/\text{cm}^{-1}$
^{98}MoO	44027 ± 151	44064 ± 133
	44022 ± 335^a	44069 ± 265^a
	43995 ± 232^b	44027 ± 217^b
	44065 ± 248^c	44100 ± 222^c

^a Calculated using only the data for the $\text{Mo}(^5G)(4d^5 5s)$ + $\text{O}(^3P)$ channel (Series 3)

^b Calculated using only the data for the $\text{Mo}(^5P)(4d^5 5s)$ + $\text{O}(^3P)$ channel (Series 2)

^c Calculated using only the data for the $\text{Mo}(^5D)(4d^5 5s)$ + $\text{O}(^3P)$ channel (Series 1)

There is a relatively minor change in the final value for D_0 calculated, particularly in comparison to the experimental uncertainty. Some of this change may result from the fact that in this case there is one additional datapoint for each series (those obtained by fitting the spectrum shown in Figure 5.8). This may affect the final results, and also aid in reducing the uncertainty in the measurement from each series.

There is also a slight increase in each value found by MEVIR when compared to the values from POP. The values are systematically higher for MEVIR, but only by about 0.09%, or ca. 14% of the uncertainty. Possible reasons for this may include the different methods of folding the image outlined in Section 5.2.3 and illustrated in Figure 5.3. A quick examination reveals that a shift of half a pixel in the kinetic energy axis can result in a shift of up to 35 cm^{-1} in the value of D_0 found, which is similar in magnitude to the shift observed in Table 5.4. However, given that the difference in folding is not just a change in labelling from integer to half-integer pixel numbers, but also in which pixels in the original image are mapped to which pixels in the folded quadrant, it is difficult to entirely disentangle this effect.

Both methods of folding and labelling the pixels seem reasonable, such that no judgement is made here as to which approach is 'correct'. Rather, it is believed that the minor differences in D_0 found using POP and MEVIR represent different methods of handling the data, but do not compromise the overall results, especially considering that the difference is well within the uncertainty from other factors.

Similar results are found for the data presented in the other chapters, suggesting that the historic use of Polar Onion Peeling does not fundamentally undermine these and previous results from this group. However, it is recommended that MEVIR or another similar method be used for any future data collected by VMI, given the advantages it possesses.

In terms of future work, it will be worth carrying out a periodic review of analysis techniques within the group in case the situation changes. This will become more pertinent when MEVIR and MEVELER are better developed, with newer capabilities, as well as if a new algorithm is released which may perform even better.

Chapter 6

Conclusions

This thesis has covered the study of a variety of small, diatomic transition metal-containing clusters. This includes a study of their spectroscopy, where appropriate, but has mainly focused on imaging of their photodissociation dynamics. This novel use of velocity map imaging has enabled the direct determination of the dissociation energies, D_0 , of several molecules as the primary results of this project. These values are presented in Table 6.1, in comparison to the previous experimental values in each case.

A study of the effect of image reconstruction algorithms was also conducted to examine the effectiveness of the Polar Onion Peeling (POP) approach currently used relative to other methods of extracting kinetic energy data. This chapter summarises the main findings of the previous chapters, along with the outlook for further experiments in each system. This is concluded with an overall view of the future of VMI experiments in our group in general.

Silver Clusters

In Chapter 2, silver argon dimer, AgAr, was formed by ablation of a silver target into an expansion of pure argon carrier gas. The $1 + 1$ REMPI spectrum of this species for the $A(^2\Pi_{3/2}) \leftarrow X(^2\Sigma^+)$ transition in the ultraviolet region was successfully obtained and compared with that previously observed by Brock & Duncan.¹⁵²

At a slightly higher photon energy, a one-photon photodissociation process resulting in formation of excited state $\text{Ag}(^2P_{3/2})$ and ground state $\text{Ar}(^1S_0)$ was observed using velocity map imaging. It was shown that addition of krypton to the molecular beam results in observation of the analogous photodissociation of AgKr alongside the existing features, while addition of xenon results in observation only of dissociating AgXe , suggesting that formation of AgXe is predominant in this case.

From these imaging experiments, the D_0 values for AgAr , AgKr , and AgXe were determined to be $85.9 \pm 23.4 \text{ cm}^{-1}$, $149.3 \pm 22.4 \text{ cm}^{-1}$, and $256.3 \pm 16.0 \text{ cm}^{-1}$ respectively. These compare well with the existing experiment values, which were obtained by Birge-Sponer extrapolation from REMPI or fluorescence excitation spectroscopic data.^{50,152} These values, however, have been called into question by computational evidence which suggests that the shape of the excited state potential

Table 6.1: Values for experimental dissociation energy, D_0 , of species studied in this project

Species	D_0 / cm^{-1}	D_0 / cm^{-1}
	This work	Previous studies (Year)
AgAr	85.9 ± 23.4	71 ± 23^a (1995) ¹⁵²
		90 ± 30 (1991) ⁵⁰
AgKr	149.3 ± 22.4	95 ± 32^a (1995) ¹⁵²
AgXe	256.3 ± 16.0	231 ± 54^a (1995) ¹⁵²
AgO	15695 ± 81	18400 ± 1200 (1972) ¹⁵⁸
⁹⁸ MoO	44027 ± 151	43900 ± 300 (1998) ¹⁹⁵
	43946 ± 157^b	43700 ± 200 (2015) ¹⁹⁹
⁵² CrO	37130 ± 117 37192 ± 119^c	38510 (2010) ²²²
		38200 ± 700 (1996) ²²¹
		38800 (1993) ²²⁰
		36900 ± 600 (1989) ²¹⁹
		39000 ± 700 (1986) ²¹⁸

^a Average and standard deviation of independent values

^b Isotopically unresolved

^c From a tentative assignment

energy curve diverges significantly from the Morse model, such that accuracy of the assignment is questionable.³² The current study makes no assumptions about the form of the potential energy surfaces involved, so this issue does not affect the results.

In the same experimental run, dissociation of silver monoxide, AgO, was also observed, giving rise to two features which are visible in the velocity map images. The exit channels corresponding to these features have been assigned to silver fragments in the $^2D_{3/2}$ and $^2S_{1/2}$ excited states, with a value of $15695 \pm 81 \text{ cm}^{-1}$ determined for $D_0(\text{AgO})$. This value is noticeably lower than the existing experimental value of $18400 \pm 1200 \text{ cm}^{-1}$. However, this old Knudsen Cell measurement has been called into question by multiple computational papers.^{30,103,122,161,162} The new value from VMI is in much better agreement with these computational values, which are, for the most part, significantly lower than the value from Smoes *et al.*.

A further feature was also observed during imaging, which is believed to originate from dissociative ionisation of the silver dimer, Ag₂. TD-DFT calculations were performed to confirm the plausibility of this assignment. However, it was not possible to corroborate this to the same degree of certainty as the other assignments, and no value for $D_0(\text{Ag}_2)$ was obtainable from this channel. The work in this chapter has been published in *The Journal of Chemical Physics*.¹⁴⁸

There are a few possible avenues for further experiments related to this work. One would be to study the analogous charged clusters to compare the effect this has on the bond dissociation energies. Argon tagging, as described in Section 1.3.3, is not restricted to neutral clusters, being used to obtain vibrational spectra of charged clusters.⁵ The experimental setup being used here is currently being modified to enable imaging of the photodissociation dynamics of charged species with mass-selectivity, as mentioned below.

Given that the complexes of gold atoms with rare gases have previously been studied with velocity map imaging,⁶¹ it may also be interesting to attempt to study the analogous copper species in order to complete a survey of the coinage metal triad. The dissociation energy of CuKr has previously been determined spectroscopically,¹⁵¹ although there is some computational evidence to suggest that this

measurement was significantly larger than would be theoretically expected.²³⁵ If the Cu-RG dimers could be produced in our apparatus, it would therefore be useful to corroborate or correct this value using VMI.

One other, smaller, project may be to repeat the experiments under similar conditions but at a different excitation wavelength in order to find another dissociative channel for Ag_2 , which would enable a measurement of its dissociation energy. Knudsen cell mass spectrometry has previously been used to determine $D_0(\text{Ag}_2)$, but this cluster does not appear to have been studied using velocity map imaging. Given the error in Knudsen cell measurements of other dissociation energies (such as AgO , as mentioned above), VMI may provide a more reliable value, assuming another exit channel which does not correspond to dissociative ionisation could be found.

Molybdenum Oxide

Chapter 3 reported on spectroscopy and photodissociation of the molybdenum oxide molecule, MoO , in the visible and ultraviolet regions of the electromagnetic spectrum. In the former case, the $1 + 1$ REMPI spectrum of MoO was recorded in the $B \leftarrow X$ and $B' \leftarrow X$ transitions. Separately, isotopically-selected ^{98}MoO was dissociated in a three-photon process into three exit channels, corresponding to production of ground state $\text{O}(^3P)$ atoms along with excited state $^{98}\text{Mo}(^5G\ 4d^5\ 5s)$, $^{98}\text{Mo}(^5P\ 4d^5\ 5s)$, and $^{98}\text{Mo}(^5D\ 4d^5\ 5s)$ fragments. These enabled three independent measurements of $D_0(^{98}\text{MoO})$, which gave a weighted average of $44027 \pm 151\text{ cm}^{-1}$.

In the ultraviolet experiments, where imaging was conducted without isotopic selectivity, two dissociative channels were observed, which led to production of molybdenum atoms in $^5D(4d^4\ 5s^2)$ and $^5G(4d^5\ 5s)$ excited states. The two resulting measurements of the dissociation give an average value for $D_0(\text{MoO})$ of $43946 \pm 157\text{ cm}^{-1}$, agreeing well with the experiments in the visible region.

As shown in Table 6.1, these values agree well with the existing experimental measurements, which were calculated using a thermodynamic cycle and values for the ionisation energies of Mo and MoO , and guided ion beam measurements of

$D_0(\text{MoO}^+)$. The current VMI experiments represent an advance on these measurements by directly observing $D_0(\text{MoO})$ and removing the dependence on the value obtained for the dissociation energy of the cation.

In terms of related further experiments, the photodissociation dynamics of MoO appear to be well characterised, but there may be interest in studying related species (e.g., see below for studies of the analogous species containing chromium, which is the $3d$ metal from the same triad).

Alternatively, it may be possible to study other molybdenum-containing clusters. The original intended target of the experiments in the ultraviolet region was MoAr, to follow on from the previous work on AgAr, since molybdenum and silver are related as analogous $d^5 s^1$ and $d^{10} s^1$ metals respectively. Although it transpired that the observed molybdenum fragments resulted from dissociation of MoO, it may prove worthwhile to perform experiments in other spectral regions in an attempt to examine the binding of argon to molybdenum. It is also possible that introduction of krypton or xenon would be useful, since their larger polarisabilities would be likely to lead to more strongly bound dimers which may be easier to produce.

Chromium Oxide

Experiments in two different spectral regions featuring the velocity map imaging of chromium fragments were reported in Chapter 4. In the visible region of the spectrum, eight features were observed in the isotopically-selective $^{52}\text{Cr}^+$ channel, which have been assigned to three-photon dissociation of the chromium monoxide monomer into different electronic states of the chromium atom. Five of these channels were used to find a value for $D_0(^{52}\text{CrO})$ of $37130 \pm 117 \text{ cm}^{-1}$.

In the ultraviolet spectral region, a large number of exit channels were observed, which proved more difficult to analyse. It was determined that the parent molecule was CrO, and a tentative assignment of the electronic states was made for six of the peaks. From these, a value of $37192 \pm 119 \text{ cm}^{-1}$ was found, which was taken to support the findings of the more conclusively-assigned data from the visible region.

These values for $D_0(^{52}\text{CrO})$ compare favourably to existing experimental values from the literature. There have been a large number of studies in recent decades which have used different methods and produced a variety of different results, as shown in Table 6.1. The value found by velocity map imaging falls within the range of these, and it is hoped that this direct observation of the dissociation energy will lend some additional certainty to the dissociation energy of this molecule.

In terms of further work, the main objective of further experiments would be to alter the conditions in order to change the composition of the molecular beam. During the course of this project, large quantities of CrO were observed, along with traces of Cr_2 . However, if it were possible to generate more of the chromium dimer, it may be possible to observe dissociation of this species. As outlined in Section 4.1, there is a large degree of interest in Cr_2 because of the possible existence of a sextuple bond.

Further experiments on CrO may be useful if it were possible to observe dissociation using different photon energies which generate simpler images. The analysis in this chapter was made significantly more complex by the abundance of possible assignments for the chromium atomic energy levels. In contrast, despite the fact that both metals have a d^5 configuration, the experiments on molybdenum in Chapter 3 were simpler because there were few energy levels in the particular region probed by the excitation wavelength chosen. Experiments which could generate chromium atoms with energies in a region with fewer levels may prove easier to assign - for example, if the internal energy of the chromium fragments were ca. 7500 cm^{-1} , where only two levels are present with large gaps separating them from higher or lower energy configurations.

It may also be interesting to use VMI and other, spectroscopic techniques to investigate larger chromium clusters of the form Cr_nO , or, even better, bimetallic clusters featuring a choice of possible binding sites for the oxygen atom, such as $\text{Cr}_n\text{Mo}_m\text{O}$. The latter in particular would provide an opportunity to apply the knowledge of the relative strength of various metal-oxygen bonds to the problem of rationalising the structure of such species. As mentioned in Section 1.7, mixed metal clusters are of particular interest due to their similarity to bimetallic catalysts.⁴⁶

Image Reconstruction Methods

In response to concerns about the possible limitations of Polar Onion Peeling as used in image reconstruction, a comparison was made between the results obtained and those found when re-analysing the data using the pBASEX algorithm or the maximum entropy methods, MEVIR and MEVELER. The findings of this comparison were that there is little difference between the results found when reconstructing high-quality images, but that significant differences were present for those with lower ion intensities.

POP produces kinetic energy spectra which have a poorer signal-to-noise ratio, and struggles to resolve less intense features, while the other three methods had similar levels of success at producing well-defined spectral peaks from weak rings. In deciding between the methods examined, a recommendation was made that MEVIR be used for future experimental analysis, on the basis that it is currently further along in its development than MEVELER, and that pBASEX produces broader peaks which can lead to loss of resolution for rings in close proximity.

Further work in this area is likely to be important, given that development of new techniques and refinement to the existing algorithms (particularly the maximum entropy programs, which are still under development) will lead to a shifting relative performance of reconstruction approaches. In addition, as new datasets are recorded, it may be worth producing similar comparisons between the results of different algorithms on these, to ensure there are not further circumstances under which certain methods perform noticeably poorer than others. For this reason, a periodic review of reconstruction methods may be helpful to ensure maximum performance going forward.

General Conclusions and Outlook

Over the course of this project, the utility of velocity map imaging for determining the dissociation energy of transition metal clusters has once more been demonstrated, building on previous successes on other systems using the same instrument.^{44,61,63,81–84} These experiments have allowed the direct determination of dis-

sociation energies in cases where the existing literature values were from indirect methods (such as MoO), or where more recent evidence had called previous experiments into question (such as AgO, or the Ag-RG dimers).

The experiment in its current configuration has demonstrated its continued usefulness and applicability, and it would almost certainly be possible to continue to find further systems to study where velocity map imaging would provide useful insights into photodissociation dynamics. However, there are multiple ways in which the capabilities of the instrument could be enhanced to enable new and varied projects.

One possibility is to alter the ion optics such that charged clusters can be studied alongside the neutral molecules currently observed. This would enable a direct comparison of the effect of charge on the dissociation energy of molecules, as well as opening the door to other possibilities. Notably, when studying charged species it is possible to introduce mass gating such that the parent molecule can be selected, significantly simplifying the analytical process by removing the requirement to identify the co-fragment.

Another modification which would simplify the analysis would be to enhance the camera used for imaging to introduce a time-slicing ability, which would overcome the limitations of image reconstruction, although at the potential expense of signal intensity. One approach to this problem is the Pixel Imaging Mass Spectrometry (PImMS) camera currently under development, which is able to record time-stamped imaging data.²³⁶ This enables the form of the ion sphere to be recorded, avoiding the need for reconstruction from a crushed image.

PimMS also makes it possible to record images in multiple ion channels simultaneously, which has two major benefits. Most obviously, it speeds up data acquisition where images in more than one channel are desired, since these have to be recorded consecutively in the current setup. On top of this, it enables a measure of the correlation between the recoil of the two fragments, which has already proven useful when determining the structure of larger, organic molecules.²³⁷

Finally, one further modification which enable a large variety of new experiments would be the introduction of a second molecular beam to enable Crossed Molecular Beam (CMB) experiments, which allow the collision-induced reactivity to be studied.⁶⁵ It is hoped that velocity map imaging will enable significant information to be gleaned about the product states of these reactions, providing further insight into the reaction dynamics.

Some of these changes are already in progress, with the experimental apparatus having recently begun a major overhaul. It is expected that the instrument will soon have the ability to perform VMI on charged clusters, and further modifications to introduce a crossed molecular beam array are also being prepared. With regards to the PImMS camera, the development of this in Oxford by the Brouard and Vallance groups (among others) continues to be followed with interest, and the potential utility of this instrument for studies of the photodissociation dynamics of transition metal clusters considered.

In summary, the field of velocity map imaging continues to demonstrate its ability to provide insights in metal cluster systems. Current developments promise to further widen its applicability and utility, and it is hoped that VMI will prove useful when studying transition metal-containing clusters in the future.

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