Electron-cluster interactions: Excitation of neutral fragments in rare gases and simple molecules.

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ELECTRON-CLUSTER INTERACTIONS:  
EXCITATION OF NEUTRAL FRAGMENTS IN RARE GASES AND SIMPLE MOLECULES

by

Charles Patrick Malone

A Dissertation
Submitted to the Faculty of Graduate Studies and Research through the Department of Physics in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy at the University of Windsor

Windsor, Ontario, Canada

2003

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ABSTRACT

The presented work on electron-cluster interactions utilizes mass and translational spectroscopic techniques that have traditionally been applied to atomic and molecular targets. An investigation of the fluorescence and neutral metastable fragmentation of neutral clusters of various average sizes for different target compositions has been undertaken. Time-of-flight (TOF) mass spectroscopy of the ionized clusters has demonstrated an effective production source of clustered molecular (N$_2$O, H$_2$O, etc.) and rare gas (Ar, Kr, Xe, etc.) targets. The clustered targets were then studied, following electron impact, by observing the photon decay and metastable yield as a function of time (i.e., fluorescence and TOF methods). Excitation function techniques were used for specific time windows, corresponding to interesting photon and TOF features, by ramping the incident electron energy and observing the change in overall signal and appearance of energy thresholds. Furthermore, lifetime and kinetic energy analysis was utilized in order to elucidate the energy and dissociation pathways undertaken. Where available, this was compared to appropriate existing atomic, molecular, clustered, and solid results. However, it should be emphasized that, to our knowledge, these metastable yield results from clustered targets via electron impact are unique to this group.
To Heather with love. Thank you for being patient.
ACKNOWLEDGMENTS

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Thanks are in order for the loan of electronic equipment and interesting conversations with Professors Tim Reddish and Walter Kedzierski. The use of an IR workstation, by the Aroca group, is much appreciated. Thanks to Bill Baylis for kindly translating some German articles to English. Gratitude is owed to the helpful work of Erik Clausen and Louis Beaudry (Machine Shop) and Sinisa Jezdic (Electronics Shop). I am also grateful to the University of Windsor for the Tuition Scholarships. This work was funded by NSERC, OIF, and CFI of Canada. I also kindly thank NSERC for the award of the PGS-B Postgraduate Scholarships.

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Chapter 1

Introduction and Motivation

There is a theory which states that if ever anyone discovers exactly what the Universe is for and why it is here, it will instantly disappear and be replaced by something even more bizarre and inexplicable.

There is another theory which states that this has already happened.
— Douglas Adams

Physics tends to partition concepts utilizing a reductionist framework. The classic analogy of “peeling an onion” is often referred to in this light. We tend to start with what is tangible from our everyday experience and progressively reduce the physical complexity in order to gain some level of understanding. In the context of the question

---

“what is in-between an atom and a solid?”, essentially two approaches for study exist. The reductionist tactic is the typical approach for this problem from a condensed matter perspective; reduction into the basic components is attempted, leading to a study of the atomic constituents. Alternatively, an approach based upon emergent phenomena, starting from a relatively reduced situation, enables a picture to develop as the complexity of the system develops. This “from the ground up” approach is effectively the direction of study employed in this body of work. Rather than starting with a macroscopic chunk of material, a microscopic portion, beginning with an atom or molecule, is used to further our understanding of the progression from the atomic to condensed phases of matter. The “in-between” growth is referred to as clustering. Some investigators identify this research area and the “new phase of matter” as nanoscience.

*What exactly is a cluster?* Clusters are unique forms of matter, normally composed of loose aggregates of atoms or molecules, ranging from two units to more than a million. Perhaps the most famous cluster is $C_{60}$, commonly called buckyballs, for which the Nobel Prize in Chemistry was awarded in 1996. This is an example of a covalently bonded cluster. Other types also exist, such as van der Waals bound clusters. Van der Waals clusters tend to be loosely bound complexes of either atoms or molecules that have a full valence electronic level. What make clusters so interesting, compared to the microscopic and macroscopic regimes, are the discrete energy levels combined with their large surface-to-volume ratios. Thus clusters tend to have quite unique properties relative to the micro and macro areas of study. To put it briefly, the main intent of this
work is to gain insight into the dynamics of neutral cluster fragmentation, via electron impact, utilizing traditional atomic, molecular, and optical techniques.

This body of work is organized as follows. Chapter 2 introduces relevant concepts and various techniques used within the general field of cluster science. Some of these issues are required for a full discussion in later chapters. Chapter 3 addresses aspects of electron-cluster collisions (e.g., mass, fluorescence, and time-of-flight spectroscopies), which lay a foundation for interpreting our experimental results. Possible shortcomings of the utilized techniques and assumptions are also considered. Chapter 4 is the standard experimental section. Here, pertinent aspects of specific equipment, including some underlying theoretical considerations, are provided within the context of this set of investigations.

Chapters 5-8 present and discuss the electron-cluster results for various clustered targets. Chapter 5 begins with a brief synopsis of previous group work on CO₂ clusters and expounds on the results of electron collisions with several other investigated molecular targets. Chapter 6 presents a brief discussion of previous fluorescence and metastable fragment group work from electron impact on argon clusters. Further studies of argon metastable fragmentation with varying average cluster size and fragmentation of heterogeneous ArKr clusters are discussed. Chapter 7 presents results for electron collisions with clustered krypton targets. Chapter 8 explains the results of our xenon cluster investigation with a full discussion of the metastable fragmentation processes. Finally, Chapter 9 attempts to summarize the results of these electron-cluster interactions. Also, considerations and suggestions are provided for possible future work. The
appendices have been supplied to facilitate understanding by providing additional details for the main chapters. The contents of Appendix A should be noted: important unit conversions are provided.
Chapter 2

Cluster Phenomena

2.1 Introduction

Though clusters were first observed in effusive gas beams in the 1920s [1,2], cluster science has become a serious and maturing research topic since the 1980s. Advancement in experimental techniques and the requirement and availability of new technology were the underlying forces driving the cluster revolution. Superior vacuum equipment, including better pumps and improved nozzle sources and techniques, provided the experimental basis for the increase in understanding of cluster science. From the theoretical end, increases in computational ability and advancement of the understanding of causal phenomena benefited cluster science. Major discoveries, such as C₆₀, generated the necessary “buzz” to bring excitement and further interest into this area.
The various application directions include studies of carbon chemistry [3] and possible molecular electronics, novel catalysis [4], optical and impact lithography [5], condensed targets for high energy physics [6], and novel materials by cluster beam deposition [7], to name a few.

Since cluster science has seriously been investigated for over 20 years, there exist many review articles and texts on various subject areas [8-22]. Some of the more noteworthy texts for the present cluster studies are the books by Pauly [18,19] on atom, molecule, and cluster beams, Haberland [20,21] on aspects of clusters of atoms and molecules, and Johnston [22] on introductory material for atomic and molecular clusters. Many other available sources certainly provide relevant information and should be considered.

2.2 Cluster Types

A natural question to ask related to cluster science is “how are the varying types of clusters classified?” Several approaches exist; classifications via bonding, size, or number of constituents are convenient starting points. Table 2.1 provides an attempt at classifying clusters according to their type of bond. As can be seen, many types exist that are commonly found in chemistry, extending over bond strengths from the vibrational to electronic scales. Several examples are also included for each type of bond, which demonstrates the rich variety available for study. In terms of the current body of work, the majority of investigated clusters involve van der Waals bound clusters. The van der
Waals clusters are most often identified with clustered rare gases, such as argon and xenon, though other types exist. Carbon dioxide and nitrous oxide clusters are sometimes thought of as molecular clusters, though the van der Waals classification is more appropriate considering their relatively weak dipole moments [23], such that the dynamic electron correlation would be responsible for binding. (CO$_2$ does not have a permanent electric dipole moment, which is understandable considering its linear, symmetric geometry.) Other molecules, such as water, have larger dipole moments and are more correctly classified as hydrogen-bonded. It is clear that there exists an overlap, or fuzzy boundary, between classifications by this scheme.

<table>
<thead>
<tr>
<th>Cluster Type</th>
<th>Binding Energy (eV)</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>van der Waals</td>
<td>0.3</td>
<td>(Ar)$_n$, (N$_2$)$_n$, (CO$_2$)$_n$</td>
</tr>
<tr>
<td>Molecular</td>
<td>0.3-1</td>
<td>Organic (M)$_n$, (I$_2$)$_n$</td>
</tr>
<tr>
<td>Hydrogen-bonded</td>
<td>0.3-0.5</td>
<td>(HF)$_n$, (H$_2$O)$_n$</td>
</tr>
<tr>
<td>Ionic</td>
<td>2-4</td>
<td>(NaCl)$_n$, (CaF$_2$)$_n$</td>
</tr>
<tr>
<td>Valence</td>
<td>1-4</td>
<td>C$_n$, S$_8$, As$_4$</td>
</tr>
<tr>
<td>Metal</td>
<td>0.5-3</td>
<td>Na$_n$, Al$_n$, Cu$_n$</td>
</tr>
</tbody>
</table>

Table 2.1    Classification of clusters via their type of bond.

Rather than relying on the above attempt at cluster classifications, possibly a better method relies on the size and/or number of cluster constituents (N). In this case, an associated size range, corresponding to the number of constituents, provides an alternative classification scheme. Table 2.2 presents a labelling method for several
cluster size regimes, ranging from the very small to the very large. This represents the evolution from the microscopic to macroscopic; from the atomic scale to the solid state.

<table>
<thead>
<tr>
<th>Cluster Type</th>
<th>Number of Constituents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microclusters</td>
<td>N&lt;10</td>
</tr>
<tr>
<td>Small clusters</td>
<td>10&lt;N&lt;100</td>
</tr>
<tr>
<td>Large clusters</td>
<td>100&lt;N&lt;1000</td>
</tr>
<tr>
<td>Nanoclusters</td>
<td>N&gt;1000</td>
</tr>
<tr>
<td>Nanoparticles</td>
<td>N&gt;10⁶</td>
</tr>
</tbody>
</table>

Table 2.2 Classification of clusters via their size and number of constituents.

Clusters of a particular composition generally demonstrate a wide variation of properties with evolving size. So-called microclusters can be treated with standard atomic and molecular theoretical methods. They also have essentially all constituents at the surface, a generally well-defined structure (with possible energetically degenerate isomers), and discrete vibrational and electronic energy levels. For larger clusters, traditional atomic and molecular methods generally fail or at least suffer from inaccurate results. The development of new theoretical methods to handle clusters is an active research area. Further, as the number of constituents increase, so too does the number of structural isomers, which have closely spaced energy levels. Complex vibrational modes and possible amorphous structures also are possibilities. Electronic and phonon states increase in density as the cluster size tends to the bulk. Generally, the large surface-to-volume ratio (see Table 2.3), finite size effects (e.g., finite electronic energy spacing),
and thermodynamic effects (e.g., surface tension varying with N) of clusters allow for rather unique properties compared to the solid state.

2.3 Methods of Production

For all of the many possible sizes and varieties of clusters, there needs to be some mechanism of generating them. The past several decades has seen the advancement of new production techniques, ranging from general to very specialized methods. The simplest cluster source is an effusive beam, which naturally has some dimer and cluster fraction—typically very small—resulting from the gas source. Improvements on effusive sources resulted in supersonic jets (see Chapter 4 for further discussion) with special nozzle configurations resulting in relatively controllable condensation. Supersonic expansions are used in the present body of work. Other methods include laser ablation [24], pulsed arc discharges, cluster aggregation [25], sputtering [26], etc. Practical implementation of these cluster production methods often involves combinations.

In brief, a supersonic gas expansion obtains a huge decrease (e.g., \( \approx 295 \, \text{K} \rightarrow 10 \, \text{K} \)) in local temperature relative to the stagnation (i.e., source) temperature since it is an adiabatic process (i.e., no heat exchange with the surrounding environment). The significant decrease in temperature induces condensation and cluster formation. (At this point, the isentropic approximation model fails due to the condensation and internal energy sinks, like vibrational degrees of freedom.) The primary factors that control the average cluster size are stagnation pressure and temperature, and the nozzle throat
diameter. Secondary influencing factors are the nozzle geometry and the use of a carrier gas. More discussion can be found in Chapter 4.

Gas aggregation is another method for cluster formation, though, it can be considered to be a variation on the carrier gas scheme. The gas aggregation method relies on the evaporation of a solid or liquid into a carrier gas. (Carrier gases can also be used along with other gases of interest.) The collisional cooling from the carrier gas leads to supersaturation and finally cluster formation [27]. A heavy carrier gas provides more time for clustering (but might cluster itself), while a lighter gas removes more of the condensation heat. The carrier gas is often chosen for its ability not to cluster under the specific experimental conditions. This "smoke source" typically results in a beam with much weaker cluster intensity compared to standard supersonic jet sources. The benefit, however, is colder cluster temperatures that results from the many collisions during expansion with the carrier gas. The choice of the carrier gas stagnation conditions is also an issue to contend with. If the carrier gas stagnation pressure is too low, then inadequate cooling results in evaporation of the clusters of interest. On the other hand, if it is too high, then the material that is intended for clustering may not have enough collisions with its fellow particles, resulting in inefficient and reduced clustering.

Besides the various physical techniques used to generate clusters, the basic concepts for formation, especially in the gas beam expansion techniques, deserve some consideration. In a general sense, cluster formation via condensation occurs rather close to the nozzle. A typical gas source contains a very small fraction of dimers and clusters prior to expansion, so dimer formation via three-body monomer collisions is the
dominant formation mechanism. (This occurs when the energy corresponding to the local temperature is less than the energy required for dimer formation.) These dimers then act as condensation nuclei (i.e., seeds) for further cluster growth. (In a sense, this is how cloud formation occurs in the atmosphere: water condenses on some “seed,” which can consist of a small water cluster or some other particle, like dust.)

As the cluster grows, the collision cross-section increases such that additional monomer collisions occur on the expanding surface. (Figure 2.1 presents a growth sequence for neutral rare gas clusters.) Thus, for a cluster of N constituents, bimolecular reactions with monomers result in the following processes:

\[ A_N + A_1 \rightarrow A_{N+1} \quad \text{cluster growth} \]

\[ A_N + A_1 \rightarrow A_N + A_1 \quad \text{energy exchange} \]

\[ A_N + A_1 \rightarrow A_{N-1} + 2A_1 \quad \text{sputtering.} \]

Furthermore, unimolecular reactions can also occur:

\[ A_N \rightarrow A_{N-1} + A_1 \quad \text{spontaneous decay.} \]

The spontaneous decay depends on the time required for the cluster to reach the distance of the “quitting surface.” (The quitting surface is also known as the freezing surface (see Reference [18] for more details). It is the “boundary” between the continuous condensation medium and the collisionless flow medium.)

As the cluster increases in size, without the benefit of three-body collisions relieving the excess collisional energy, the cluster temperature increases. Thus the cluster temperature is generally considerably higher than that of the surrounding gas during the formation process [20,28]. More accurately, the cluster experiences an increase in
Figure 2.1  Cluster growth sequence and structure: (a) polytetrahedral growth sequence of small neutral rare gas clusters (taken from Reference [20]) and (b) icosahedral geometric shells with 13-561 atoms.
vibrational energy. This excess energy can result in spontaneous decay (i.e., evaporation), if there is some time delay compared to the sputtering case, or other energy relief routes like infrared emission, thus resulting in cluster cooling. However, if there is sufficient monomer or carrier gas in the composite beam, then cluster cooling can occur rapidly by an energy exchange process. With increasing cluster concentration, cluster-cluster collisions become significant, which lead to heavily clustered beams.

The above discussion implied a homogeneous cluster target. Cluster science fortunately is richer and more interesting. Co-expansion of two premixed gases, using the methods above, allows for heterogeneous cluster targets to be investigated. Doping of clusters using a pick-up technique [29], after expansion, with other clustered or non-clustered gases is another possibility.

2.4 Methods of Cluster Size Determination

Regardless of how the particular cluster composition is classified, there exists a characteristic mass distribution with some average cluster size for an ensemble of clusters. (See Chapters 3 and 4 for further discussions.) Details on the determination of the average cluster size can be found below. As for the specific geometrical structure of the various cluster sizes, and consequently relative abundances, this is an artefact of energetically stable geometries (i.e., “magic numbers”). However, multiple structural isomers are often allowed due to non-zero internal temperatures.
Various experimental techniques have been attempted in order to determine the cluster size distribution and average size. Methods ranging from electron or atom diffraction to light or gas scattering have been used. Of the many variations of the gas scattering method, work by Buck and coworkers [30] even provides a means of size selection for small neutral clusters. (It should be emphasized that neutral cluster selection of definite size, beyond the very small, is still an unsolved challenge.) However, the most popular method, due to its relative ease of use and flexibility, is various types of mass spectrometry.

Mass spectrometry is the method used for cluster verification in the present study. In general, it experiences the burden of additional fragmentation following ionization of the cluster target. The fragmentation results from momentum transfer of the ionizing event and structural relaxation following ionization. This problem can be minimized by a very narrow ionization pulse at an energy barely above threshold. Thus photoionization, rather than electron impact ionization, is a popular method for mass spectroscopic studies of clusters. Consequently, our mass spectra probably indicate smaller average cluster sizes than actually occurs, particularly in terms of the original neutral cluster beam.

For rare gas clusters, the cluster stability—magic numbers—is indicated by:

$$m(N) = 1 + \sum_{k=1}^{N} (10k^2 + 2).$$  \hspace{1cm} [2.1]

This expression represents the local intensity maxima found in the rare gas cluster distributions for clusters composed of specific numbers of constituents. Consequently, distinctly abundant mass peaks generally appear for rare gas clusters composed of 13, 55, 147, 309, 561, etc. atoms. It turns out that there are generally more magic numbers
observable (e.g., for 19, 25, etc. atoms) in rare gas cluster mass distributions. This relative abundance pattern can often be observed in experimental mass spectra (see Chapter 4), though non-equilibrium formation conditions can suppress the abundance "anomalies" [22].

Figure 2.1 shows the (calculated) growth sequence and geometrical structure for clusters composed of rare gas atoms. (Note that a full discussion and review of cluster structure is not intended, only a very brief introduction.) The magic numbers briefly discussed above are represented in this sketch (taken from Reference [20]). Energetically favoured packing geometry impacts the overall cluster structure. Theoretical and experimental works have demonstrated a growth sequence that maximizes the number of nearest neighbours. The tetrahedral geometry for N=4 can scale to larger numbers of constituents, such that a polytetrahedral growth sequence is observed for the smaller clusters. As the cluster grows in size, a five-fold icosahedral structure develops. As the shell-structure closes from the addition of monomers in the cluster growth sequence, a magic number appears as a relatively stable mass abundance. As the cluster growth sequence continues towards the bulk, eventually an fcc close-packed structure develops since the cluster icosahedral structure tends to leave packing gaps. A full discussion on the structure and related phenomena of various types of clusters can be found in References [20,22].

It is worth noting that only recently, where time-of-flight mass spectrometry was used and fragmentation was more accurately considered (via models relating the momentum transfer to sputtering), has cluster size distribution relations become reliable
Earlier measurements of the cluster size distributions by electron impact ionization (using a retarding field technique) did not properly account for fragmentation [32]. The following section addresses this more fully.

2.5 Estimating the Average Cluster Size

A rigorous theory for predicting condensation onset and cluster growth unfortunately does not presently exist [18-22]. Macroscopic approaches involve, for instance, classical nucleation theory, but are a poor choice for small, finite systems. Microscopic methods sometimes involve computational approaches, like Monte Carlo or molecular dynamic simulations, but quickly become computationally impractical.

Thus, as a first attempt at estimating the average cluster size, a hard sphere model can be employed. In this case, the number of cluster constituents \( N \) is related to the cluster radius \( R_N \), which is assumed spherical, and to the surface-to-volume ratio \( (N_{\infty}/N) \).

Here, the spherical cluster radius is assumed:

\[
R_N = R_j N^{1/3}
\]

where

\[
R_j = \left( \frac{3m_j}{4\pi\rho} \right)^{1/3}
\]

is the Wigner-Seitz radius. The Wigner-Seitz radius is obtained for a sphere that has a volume equal to the volume per constituent in the solid [22]. The particle mass is \( m_j \), the cluster density (approximated by the macroscopic solid/liquid value) is \( \rho \), and the volume
relationships for a sphere related to its radius and mass-density have been used. Furthermore, the surface area of a spherical cluster per cross-sectional area of the unit particle provides an estimate of the number of surface particles ($N_o$):

$$N_o = \frac{4\pi R^2}{\pi R^2} = 4N^{2/3}.$$  \hspace{1cm} [2.4]

Rearranging to get the ratio of surface-to-volume particles gives:

$$\frac{N_o}{N} = 4N^{-1/3}.$$ \hspace{1cm} [2.5]

Applying the above hard spherical cluster approximation to argon clusters, with a Wigner-Seitz radius of approximately 0.208 nm [19,22], generates the values in Table 2.3. Note that neglecting a proper analysis of the packing fraction is especially problematic in this case when considering that the nearest neighbour distance in solid argon is approximately 0.376 nm [33]. However, this analysis demonstrates the dramatic evolution of the surface-to-volume ratio for the indicated sizes and number of

<table>
<thead>
<tr>
<th>$R_N$ (nm)</th>
<th>$N$</th>
<th>$N_o/N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>110</td>
<td>0.8</td>
</tr>
<tr>
<td>2</td>
<td>900</td>
<td>0.4</td>
</tr>
<tr>
<td>10</td>
<td>$10^5$</td>
<td>0.09</td>
</tr>
<tr>
<td>100</td>
<td>$10^8$</td>
<td>0.009</td>
</tr>
<tr>
<td>$10^7$</td>
<td>$10^{23}$</td>
<td>$10^{-7}$</td>
</tr>
</tbody>
</table>

Table 2.3  Cluster sizes and surface-to-volume ratios for the hard sphere model. See the text for further details.
constituents. The nanoscale is reached, in this case, for clusters of several hundred atoms. Even at this relatively large size (compared to the individual atom), the number of surface atoms remains quite large.

Semi-empirical scaling laws have been developed in conjunction with experimental techniques such as mass spectrometry and atom scattering. Much of the scaling law development resulted from experimental and modelling work by Hagen and coworkers [32,34-36, etc.] on the general considerations of the condensation kinetics, with a dependence on the initial (stagnation) expansion conditions. The reassuring trend is that the different experimental methods appear to be in quite good agreement, indicating the scaling law attempt is rather accurate. (It should be mentioned that this is still an ongoing research topic, with relatively frequent revisions presented.) Though a full and proper development will not be provided here (see, for example, References [18,19]), general concepts required for the cluster size scaling law are aspects of gas dynamics, including the binary collision rate of clusters, the characteristic temperature for rare gases (depending on the sublimation enthalpy per unit atom at 0 K and the solid density), to name a few.

The cluster condensation parameter $\Gamma^*$ was first introduced by Hagen [32] and contains the characteristic parameters and stagnation conditions of the expanding gas. The nozzle geometry (i.e., conical with a particular opening angle and throat diameter) has also been taken into account. The empirical cluster condensation parameter has been refined by many experiments (see, for example, Reference [37]) and is indicated as follows:
\[ \Gamma^* = K_{ch} \cdot \frac{p_o d_{eq}^{0.85}}{T_o^{2.2875}} \]  \hspace{1cm} \text{[2.6]} \]

where \( p_o \) (mbar) and \( T_o \) (K) are the stagnation pressure and temperature, respectively, \( d_{eq} \) (\( \mu \)m) is the “equivalent” nozzle diameter, and the characteristic condensation constant \( K_{ch} \) is provided for various rare gases in Table 2.4. Equation 2.6 is valid for monatomic gases; otherwise the exponents need adjustment (see Reference [35]). Furthermore, the concept of equivalent nozzles [34] is used in Equation 2.6, where it is related to the nozzle-opening angle \( (2\alpha) \) of the divergent portion and the nozzle throat diameter \( (d) \):

\[ d_{eq} = \frac{c(\kappa)d}{\tan(\alpha)}. \]  \hspace{1cm} \text{[2.7]} \\

Here, the parameter \( c(\kappa) \) is a function of the specific heat ratio \( \kappa \), and changes for either an axisymmetric or planar expansion. For an axisymmetric expansion, as in this body of work, \( c(\kappa) \) has a value of 0.736 for a monatomic gas (with \( \kappa =5/3 \)). See Reference [18] for other expansion conditions. It should also be noted that the throat diameter \( (d) \) should be used in place of the equivalent nozzle diameter \( (d_{eq}) \) for sonic nozzles (i.e., when \( \alpha \rightarrow 0 \)).

<table>
<thead>
<tr>
<th></th>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_{ch} )</td>
<td>3.85</td>
<td>185</td>
<td>1646</td>
<td>2980</td>
<td>5554</td>
</tr>
</tbody>
</table>

Table 2.4 Gas specific condensation constants for the rare gases (obtained from Reference [31]).
The following indicates typical trends for the cluster condensation parameter and the amount of cluster production:

\[ \Gamma^* < 200 \quad \text{essentially no clustering observed} \]
\[ 200 < \Gamma^* < 1000 \quad \text{intermediate cluster range} \]
\[ \Gamma^* > 1000 \quad \text{typically heavy clustering.} \]

These outcomes are mirrored in the data presented in Figures 2.2 and 2.3. Based upon a wealth of research, the cluster condensation parameter is shown to correlate to the mean cluster size. Figure 2.2 shows data points for several targets (small clusters) composed of

\[ N \]
\[ 100 \]
\[ 10 \]
\[ 1 \]
\[ 150 \ 200 \ 300 \ 500 \ 1000 \ \Gamma^* \]

**Figure 2.2** Measured average cluster sizes as a function of the cluster condensation parameter \( \Gamma^* \) for various rare gases using different methods (taken from Reference [19]). The scale shows the scaling law correlation for relatively small cluster sizes. See Figure 2.3 for an extended region.
Figure 2.3  Comparison of the results for the mean cluster size as a function of the parameter $\Gamma^*$ obtained from different measurements with various methods (taken from Reference [37]). See the text for further details.

rare gases obtained with various techniques (taken from Reference [19]). The straight line through the data points represents the scaling law relationship between the cluster condensation parameter and the mean cluster size (see below).
The data displayed in Figure 2.3 represents experimental attempts, using a variety of methods, at correlating the cluster condensation parameter with the average cluster size. The displayed data points are representative of that which is obtained from a neutral cluster distribution. The dotted line (over all displayed $\Gamma^*$) resulted from the use of a sonic nozzle; the dash-dotted line (for $\Gamma^* \geq 1800$) indicates data from conical nozzles; the solid line ($\Gamma^* \geq 1000$) represents mass spectroscopic data from Reference [36]. It can be seen that the average cluster size extends over a much larger range compared to Figure 2.2. See Reference [37] for further details.

A recent analysis of the relationships between the cluster condensation parameter and the average cluster size was provided by Buck and Krohne [37]. Their recommendations for the rare gas (e.g., argon) cluster size equation based on bounds of the cluster condensation parameter follows:

(a) For $\Gamma^* < 350$ use

$$\bar{N} = 2.23 + 7.00 \times 10^{-3} \cdot \Gamma^* + 8.30 \times 10^{-5} \cdot (\Gamma^*)^2 + 2.55 \times 10^{-7} \cdot (\Gamma^*)^3; \quad [2.8]$$

(b) For $350 \leq \Gamma^* \leq 1800$ use

$$\bar{N} = 38.4 \left( \frac{\Gamma^*}{1000} \right)^{164}; \quad [2.9]$$

(c) For $\Gamma^* > 1800$ use

$$\bar{N} = 33 \left( \frac{\Gamma^*}{1000} \right)^{235}. \quad [2.10]$$

Case (c), as presented, is the normal evaluation used in the literature—even for divergent geometries. However, it should be noted that there is a recognized discrepancy for
conical nozzles (see Reference [37]). An alternate possibility for case (c), as discussed in Reference [37] and references contained therein, is the following:

$$\overline{N} = \exp \left[ -12.83 + 3.51 \cdot (\ln(\Gamma^*))^{0.8} \right].$$  \[2.11\]

For clusters with more than 50 constituents, it is expected that deviations, using this scaling law, from the actual neutral cluster size distribution will be of minor importance [38].
2.6 References:


9. T. Kondow, K. Kaya, and A. Terasaki (Eds.), *Structures and Dynamics of Clusters*, (Universal Academy Press, Tokyo, 1996).


Chapter 3

Electron-Cluster Collisions

3.1 Introduction

A scattering experiment involves a target and a projectile, with the resultant outcome of the projectile-target collision probed by specific experimental techniques. In our case the projectiles are composed of electrons, though general choices range from photons to heavy ions. In this body of work, the target is a beam of gas, which is either clustered or non-clustered. The benefit of using electrons over other choices of projectiles (e.g., photons) is the lack of constraint on accessible quantum states. However, paradoxically, this is also a shortcoming of using electrons for collision studies. Unfortunately, an unambiguous identification and control of excited states is often not possible using electrons with our experimental energy resolution. The
experimental detection techniques all essentially involve some form of separating the observed counts in time. The following sections discuss relevant aspects of our detection methods.

3.2 Time-of-Flight and Fluorescence Spectroscopy

Time-of-flight (TOF) spectroscopy has been utilized for many years in various venues and schemes, such as within the Atomic, Molecular, and Optical Physics community. TOF (i.e., neutral particle detection) and fluorescence (i.e., photon detection) spectrosopies tend to be passive while TOF mass spectrometry is active. A discussion of the experimental layout and detection schemes will be further discussed in later chapters. Traditional TOF and fluorescence spectrosopies have been utilized within these cluster studies. The active use of the flight time of ions is in terms of the accelerating and drift stages of the TOF mass spectrometer. More on this will be presented in a following section.

3.2.1 The Dissociation Process

The general concept for our experiment incorporates pulsed, perpendicular, crossed beams of gas and electrons. The clustered target beam is actually a composite of various sized clusters—with some characteristic average size—and monomers that are
either atoms or covalent molecules. The electron collision process allows for many possibilities, such as:

\[ \text{AB} + e \rightarrow \text{AB}^+ + e' \quad \text{Ionization} \]
\[ \text{AB} + e \rightarrow \text{AB}^* + e' \quad \text{Excitation} \]
\[ \text{AB} + e \rightarrow \text{A} + \text{B} + e' \quad \text{Dissociation} \]
\[ \text{AB} + e \rightarrow \text{A}^+ + \text{B} + e' \quad \text{Dissociative Ionization} \]
\[ \text{AB} + e \rightarrow \text{A}^* + \text{B} + e' \quad \text{Dissociative Excitation} \]

Etc.

Only some of the above allowed processes, or combinations thereof, for the hypothetical molecule composed of A and B, are actually investigated using our detection techniques.

The composite nature of the gas beam is an unfortunate by-product of neutral cluster formation. In principle, detection of many different radiative and non-radiative emissions is possible due to the complex allowed energy pathways. The atomic (or molecular) excitation case is relatively straightforward compared to the cluster case. In the case of an excited (and/or ionized) atom or intact molecule, the excited state will eventually radiate a photon. The associated lifetime is an indicator of whether the excited state is metastable or not. Metastable states are known to have long lifetimes, and for the purpose of this body of work, an operational definition of a metastable state is one that reaches the detector prior to photon emission. Alternatively, the vast majority of the observed fluorescence will be due to optically allowed transitions.

Obviously the situation is greatly complicated when a molecular target undergoes dissociation, in addition to excitation and/or ionization. For large enough electron impact
energy, the dissociation of the molecule results in fragments being ejected with some released kinetic energy, often in an isotropic distribution. A two-body break-up is the simplest case to handle. In the case of a polyatomic molecule (i.e., more than two atoms), the situation is potentially more complex. If the dissociation results in two fragments, with at least one fragment being composed of multiple atoms, then the energetics are more complicated: excitation of vibrational and rotational energies is a possibility, besides the translational pathway. Unless other information is available that suggests a significant alternative energy channel, normally within a first approximation, only translational kinetic energy is considered. When a polyatomic molecule dissociates into at least three fragments, the mathematics quickly become intractable. Solutions of the conservation of energy and momentum, to obtain expressions for the released kinetic energy, are not analytical and certain educated guesses are then required to interpret the experimental results (see, for example, Reference [1]).

For a heavily clustered target that is excited by the electron collisions, many processes result. For an ionized cluster, the model proposed by Haberland [2] is widely accepted for rare gas clusters. In this model, a positive ionized molecular core develops, which results from the localization (on a ps time scale) of a positive hole created by the electron collision event. An ionized atom can also produce the same effect via attraction of a surrounding neutral ground state atom, thus forming at least an ionized dimer. More recent research [3-9] has demonstrated that the localization possibly occurs on a larger molecular unit than a dimer. However, in any core size case, it has been determined that subsequent relaxation of the ionized molecular core releases about 1 eV of energy into
the cluster causing vibrational modes to be excited [10-12]. Several monomers with very small kinetic energies are then evaporated from the cluster (on a sub-ns time scale) prior to a stable geometry developing [13,14]. In terms of mass spectra (see Section 3.3), this results in ion abundance anomalies (i.e., magic numbers), though the initial cluster size distribution is also a factor.

On the other hand, a neutral cluster obviously involves some other mechanism. For a rare gas cluster, this neutral excited case is actually quite similar to the ionized case. The obvious difference is that of charge, though the polarization interaction is still quite strong. The similarity rests in that the excited potential energy curves lie lower in energy than and closely resemble the ionized ground state potential energy curve. After localization of the exciton (i.e., a bound electron-hole pair; see Reference [15]) onto an atomic or molecular center (i.e., a-STE and m-STE, which represent atomic and molecular self-trapped excitons, respectively), ensuing cluster deformation and relaxation results in neutral ground state monomer ejection. (It should be noted that larger clusters, with a larger number of vibrational modes, tend to sputter relatively fewer monomers. Instead, they keep more of the vibrational energy with the result of a hotter cluster.) The a-STE can attract a surrounding neutral ground state atom, thus forming an excited dimer (similar to the m-STE case). In fact, a Rydberg description of the excited state, such that the excited electron is almost in the ionization continuum, is quite similar to the ionized case. Here, the interpretation can be modelled as an ion core with a surrounding loosely bound electron. This is analogous to a Frenkel exciton in the language of condensed matter physics. (It should be noted that the exciton description approaches an
intermediate description between that of Frenkel and Wannier-Mott excitons, as the energy approaches the ionization limit (i.e., conduction band) and the electron "orbit" increases, for rare gas clusters. This is based on a solid-like descriptive approach to the accessible energetics.) It is possible that a neutral excited trimer or larger center could develop, parallel to the ionized case, though this is open to debate [16].

Molecular clusters are somewhat easier to understand: the general picture is one in which the excited molecule is essentially decoupled from the cluster. From a bond strength perspective, the covalent bond of the molecule is much larger than the van der Waals bonds holding the cluster together, so the localization of the exciton onto the covalently bonded molecule in the cluster causes processes to occur in and from the molecular site. (The work of our group has verified this.) When the strength of the bond for a molecule and the bond strengths of the cluster constituents are comparable, or at least closer, the excitation picture is even more interesting and involved. Hydrogen bonded molecules and clusters (e.g., water) fall within this exciting scenario.

An atomic cluster composed of two atoms (i.e., a dimer) is the easiest and most basic cluster to consider. The dimer really is just a simple molecule, but in the case of the neutral, ground state rare gases, the strength of the attraction (van der Waals) is quite weak compared to a covalently bound dimer (e.g., N$_2$). After localization and relaxation, as described above, the excited dimer then undergoes radiative and non-radiative decay. Radiative decay involves photon emission while the dissociation of the excimer results in a fragmentation distribution. These processes are then investigated by fluorescence and TOF techniques.
The metastable fragmentation is only observed if the localized exciton decays to a repulsive potential energy curve with sufficient internal energy of the metastable fragment to be detected and sufficient kinetic energy to reach the detector. The localized exciton (i.e., resultant m-STE) is normally interpreted in terms of the dimer potential energy curves. If a trimer (or larger) center actually was produced, it is unlikely that there would be ample released kinetic energy available from the dissociative process for a larger fragment (e.g., excited dimer) to be detected.

We interpret our fluorescence and especially the TOF results in terms of an excited dimer picture. Figure 3.1 provides an understanding of the potential energy curves involved for this situation. Considering a hypothetical dimer AB, composed of parts A and B, the huge mass difference between the electron and nuclei provide justification for illustrating the electronic potential energy curve as a function of the internuclear distance. In other words, the Born-Oppenheimer approximation makes this separation of the molecular wavefunction into that of electronic and nuclear wavefunctions possible. As a consequence, the Franck-Condon principle states that the relative positions and momentum of the nuclei are essentially unchanged during the electronic transition. This is indicated in Figure 3.1 for the classical turning points at internuclear distances \( r'' \) and \( r' \), such that the Franck-Condon region is located between these points. Figure 3.1 is an example of the many possible combinations of available bound and repulsive potential energy curves. It is not meant to be comprehensive, but to provide some understanding and context for the methods of interpretation used in the data analysis sections.
Figure 3.1 shows potential energy curves for a bound (notice the minima) ground state, \( X \), and an excited electronic state, \( Y \), of the dimer AB. The dimer AB separates into constituents A and \( B^* \) for large internuclear distances, where \( B^* \) can be metastable. In Figure 3.1(a), the excited state, \( Y \), is repulsive. The bell-shape curve in state \( X \) is the ground state vibrational (\( v=0 \)) wavefunction, the modulus squared of which represents the relative probability distribution of the nuclei. For electron collisions of sufficient energy, the Franck-Condon principle allows for the \( X \rightarrow Y \) transition between the dashed vertical lines. \( AB^* \) then is formed and dissociates into A and \( B^* \) with a released kinetic energy (RKE) between \( E' \) and \( E'' \).

Figure 3.2(a) shows the characteristic distribution of the RKE corresponding to the fragmentation via the repulsive curve of Figure 3.1(a). This characteristic shape comes from the Reflection Principle [1]: reflection of the nuclear wavefunction of \( X(v=0) \) in the Franck-Condon region by the potential energy curve of \( Y \). Figure 3.2(a) is described as the RKE distribution resulting from dissociation from a purely repulsive state.

Figures 3.1(b) and 3.2(b) are similar to the purely repulsive case, but this is described as dissociation from the repulsive wall of a bound state. The repulsive wall of potential energy curve \( Y \) results in the RKE distribution of Figure 3.2(b). A distinctly different shape is observed, compared to Figure 3.2(a), such that the truncated distribution at lower RKE is due to the bound state of \( Y \). The Franck-Condon region partially overlaps with both the repulsive wall and bound well of state \( Y \). Thus the RKE
Figure 3.1 Potential energy curves for hypothetical diatomic molecule AB to illustrate (a) dissociation from a purely repulsive state, and (b) dissociation from the repulsive wall of a bound upper state.

Figure 3.2 Released kinetic energy spectra for dissociation processes (a) and (b) in Figure 3.1.
occurs from a transition to the left of the dotted vertical line (in the Franck-Condon region). Otherwise, transitions to the right will populate bound vibrational levels of \( Y \) (with typically subsequent radiative emission). The dotted line corresponds to dissociation with essentially zero RKE, with larger RKE at smaller internuclear distances.

If the Franck-Condon region completely overlaps the bound well of a hypothetical potential energy curve \( Y \), similar to what is presented in Figure 3.1, then dissociation from \( Y \) does not occur. Eventually optical emission to some allowed lower state occurs from this unperturbed situation. However, if another repulsive curve crosses the bound potential energy curve \( Y \), then pre-dissociation can occur.

We note that in our heavily clustered case, excitation of the repulsive state of the localized dimer does not occur by excitation from a lower bound state. This is discussed in detail in later chapters.

### 3.2.2 Fluorescence Analysis

The passive nature of the detection of photons and neutral particles allows for counting in time with respect to the initial excitation event, thus falling within the realm of fluorescence and TOF spectroscopy. Since particles resulting from the electron-target collision are counted in time as they arrive at the detector, an initial time of zero must be associated with some physical event. In our experiment, the zero on the time scale is synchronized with the arrival of photons coincident with the electron beam pulse. From this particle detection in time, a temporal picture of the excitation events can be
determined. Apparent lifetimes can be ascertained from the trailing edge of the fluorescence decay by fitting scaled \((C)\) exponential expressions that depend on the number of counts, \(N\), detected in a very short time period \(dt\) at time \(t\):

\[
N(t) = \sum_i C_i \exp\left(-\frac{t}{\tau_i}\right). \tag{3.1}
\]

Here, the subscript \(i\) represents an index over possibly multiple lifetimes \((\tau)\) being fitted.

In the case of very small electron pulse widths, the following expression can be used for extracting lifetimes:

\[
N(t) = C \left[1 + \text{erf}\left(\frac{ht - \frac{1}{2ht}}{2\sqrt{2}}\right)\exp\left(\frac{1}{4h^2\tau^2} - \frac{t}{\tau}\right)\right]. \tag{3.2}
\]

A convolution of an exponential decay expression with a Gaussian results in Equation 3.2, known as Gale’s equation [17]. Equation 3.2 provides information on the tail of the fluorescence signal and also the detector response. A summation over multiple lifetimes may be considered for complex fluorescence signals. Here, \(h = \left(\sigma\sqrt{2}\right)^{-1}\), where \(\sigma\) is the standard deviation of the Gaussian apparatus function, and “erf” is the well-known error function. However, the relatively complicated Equation 3.2 is not necessary in view of our relatively large (microsecond) pulse width, such that Equation 3.1 is sufficient for photon decay analysis.
3.2.3 TOF and Kinetic Energy Analysis

Studies of neutral metastable fragments were originally employed in the electron and photon impact dissociation of molecules. Reviews of this subject area have been provided by Zipf [18], Freund [19], and Compton and Bardsley [20]. TOF techniques are also valuable for monitoring the metastable (long lifetime) fragments ejected from the electron-cluster interactions. Knowing the fixed distance, \( D \), between the interaction region (electron and gas beam overlap) and the detector provides information on the speed distribution \( g(v) \) of the neutral fragments in terms of the distribution in time \( f(t) \).

\[
g(v) = \frac{t^2}{D} f(t). \tag{3.3}
\]

Equation 3.3 has been derived using the same methods as the fragment kinetic energy (FKE) distribution expression (Equation 3.6) below. If the mass of the detected neutral fragment is known (at least within an “educated guess”), then the FKE distribution can be determined. In terms of the flight time \( t \), fragment mass \( m \), and flight distance \( D \), the fragment kinetic energy \( T_{EF} \) is given by

\[
T_{EF} = \frac{1}{2} m (D/t)^2. \tag{3.4}
\]

In order to convert the time distribution from the time domain to the FKE domain, Equation 3.5 must be considered, such that the transformation takes into account the (infinitesimal) increments that make-up the respective domains.

\[
\int f(t) dt = \int F(T_{EF}) dT_{EF}. \tag{3.5}
\]
The physical interpretation is the number of excited fragments arriving at the
detector between time \( t \) and \( t + dt \). Consequently, the derivative of Equation 3.4 must be
taken with respect to time and inserted into Equation 3.5 (noting that the minus sign has
been neglected on a physical basis).

\[
F(T_{EF}) = \frac{t^3}{mD^2} f(t) \tag{3.6}
\]

Equation 3.6 represents the conversion of the experimental TOF data to the FKE domain.
Thus, the distribution of kinetic energies can be determined that are associated with the
detected fragments that occur via the electron-impact process with the clustered (atomic
or molecular) and non-clustered molecular targets. The feature of Equation 3.6 to note is
the \( t^3 \) factor. This generally leads to relatively extreme data scatter at small fragment
kinetic energies, which correspond to large flight times.

In general terms, determining the released kinetic energy (RKE) of a
fragmentation process can be quite difficult since the excited parent (molecule or cluster)
can be composed of multiple particles (three or more). (Regarding the clustered case, we
have determined that the observed fragmentation patterns, via the TOF data and further
analysis, result from two-body break-up. Evidence for this will be presented in following
chapters.) In the case of two body fragmentation from the excited parent, whether it be
two atoms, or more generally two bodies with small vibrational population(s), the
released kinetic energy \( (T_{ER}) \) of the fragmentation process is related to the fragment
kinetic energy, in this case of fragment 1 \( (T_{EF1}) \), by the following:

\[
T_{ER} = \frac{M}{m_2} T_{EF1} \tag{3.7}
\]
where $m_2$ is the mass of fragment 2 and the parent mass is $M=m_1+m_2$. The indices can easily be switched to put Equation 3.7 in terms of the FKE of fragment 2. Using similar arguments and analysis carried out with Equation 3.6, the distribution of RKE is related to the FKE distribution as follows:

\[
\int F(T_{ER})dT_{ER} = \int F(T_{EF})dT_{EF} \quad [3.8]
\]

\[
F(T_{ER}) = \frac{m_2}{M} F(T_{EF}) = \frac{m_2 t^3}{M m_1 D^2} f(t) \quad [3.9]
\]

Here, the indices can be switched to vary the fragment dependence of Equation 3.9.

For fragmentation of an excited parent body that consists of two atoms, such as with an excited rare gas dimer (RG\(_2^*)\), the RKE equations above simplify to the following:

\[
T_{BR} = 2T_{EF} \quad [3.10]
\]

\[
F(T_{ER}) = \frac{1}{2} F(T_{EF}) = \frac{t^3}{2 m D^2} f(t) \quad [3.11]
\]

where the masses and fragment kinetic energies are the same.

In the case where the distribution is known in a particular domain (time, speed, kinetic energy, etc.), then the equations above can be evaluated for that particular distribution. Furthermore, useful experimental and comparative quantities, such as the average and most probable values within the various domains, can be derived based on an analytical form of the distribution. The key example is the Maxwell-Boltzmann (MB) distribution (see Appendix B) that describes the population of ground state particles of a certain speed in a random, three-dimensional gas. In the context of our set of
experiments, the MB distribution represents the fraction of random background gas (e.g., RG monomer) that happens to become excited and subsequently detected.

3.2.4 Systematic Errors

The discussion and analysis above is rather ideal from multiple perspectives. Many considerations like the size of the interaction volume of the electron and gas beams, the detector geometry, etc., have been bypassed in order to ease the mathematical discussion and analysis. Furthermore, a specific discussion of experimental uncertainties involved with TOF spectroscopy should be considered. The main artefact of uncertain TOF measurements is poor translational energy resolution, which directly influences the ability to obtain accurate information on, for instance, different dissociation channels. The following parts discuss aspects of possible errors involved with TOF spectroscopy.

(a) Finite Electron Beam Pulse Width

For a given TOF distribution, where the arrival time at the detector is given by time \( t \), the electron beam pulse width (\( \Delta t \)) should be considered. This has the effect of broadening the TOF distribution and influences the accuracy of the kinetic energy analysis. The resultant uncertainty in the RKE scale is given by

\[
\Delta T_{ER} = T_{ER} \cdot 2\Delta t / t .
\]  

[3.12]

It is clear that the most significant broadening of the RKE (and FKE) distribution occurs at smallest flight times, especially close to the photon decay tail. This corresponds to the largest values of kinetic energy. For example, given an electron pulse width of 1 \( \mu \)s and a
peak in a TOF distribution at approximately 65 µs, the ensuing uncertainty in the RKE value (4.79 eV) is approximately 0.15 eV. On the other hand, a flight time of 303 µs (RKE of approximately 0.22 eV) results in a relatively small uncertainty of 0.001 eV. This example corresponds to xenon cluster data from Figures 8.1, 8.5, 8.6, and 8.9 in Chapter 8.

(b) Thermal Energy Spread of the Parent Targets

The thermal motion of the parent target beam results in an additional velocity component, either away or towards the detector, of the metastable fragment. The spread in the fragment velocity translates to an uncertainty in the kinetic energy of the fragment. The resultant spread in the RKE distribution is given by Equation 3.13 [18], where \( E_{th} \) is the thermal energy of the parent target. This uncertainty is more significant at larger kinetic energies, corresponding to smaller flight times. Effusive gas sources and (diffuse) vapour cells, in particular, can be burdened by this uncertainty.

\[
\Delta T_{ER} = 2\sqrt{2E_{th}T_{ER}} \tag{3.13}
\]

In our case, this systematic error is not very significant (assuming a "cold" cluster distribution) due to our crossed-beam arrangement (see Chapter 4). Briefly, the experiment consists of a perpendicular geometry of the electron beam with that of the skimmed gas beam, using a detector in the scattering plane, but not in-line with the gas beam. A skimmed gas beam (with few internal collisions) results in a very cold radial "temperature," or more precisely, a small velocity component in-line with the electron beam.
(c) Frames of Reference

The highly directed nature of our gas beam induces an additional velocity component onto the fragmentation distribution. In the beam frame, the metastable fragments have a velocity component \((u)\) due to the fragmentation process, such that the speed is then directly related to the RKE. However, in the lab frame (i.e., the frame that measurements are performed in), the fragmentation has the additional beam velocity \((V; \approx 600 \text{ m/s for Ar}, \text{ see Chapter 4})\) component superimposed onto the velocity from the beam frame. A simple application of the cosine law for the velocity vectors, over the fixed flight distance \((D)\), along with some algebraic manipulation, generates a transformation between flight times in the beam \((t_B = D/u)\) and lab \((t = D/v)\) frames:

\[
t_B = \frac{t}{\sqrt{1 - 2 \cos(\theta) \frac{V_f}{D} + \left(\frac{V_f}{D}\right)^2}} \tag{3.14}
\]

where \(\theta\) is the angle between the direction of the detector and cluster beam. In the present body of work, an angle of 45 degrees has been used, though previous argon cluster studies also used a 90 degree detection angle (see Chapter 6). Equation 3.14 can then be used to relate the measured flight time \((t)\) to the kinetic energy \((\frac{1}{2} mu^2)\) of the fragmentation processes.

In our case, this transformation has been neglected on the basis of an insignificant contribution to the RKE at our fixed detector position. Only at very long flight times will the beam-to-lab frame transformation have any significance. (Or if measurements at multiple detector positions are compared.) However, large flight times correspond to small RKEs. Thus any slight shift in the RKE, based upon our flight time measurements,
is negligible in terms of the measured onset energy, which is limited by the electron impact energy resolution. Furthermore, at a detector position of 45 degrees, Equation 3.14 has a maximum at approximately 292 μs for the case of argon. This has the additional affect of providing a kinetic energy lower cut-off of approximately 0.037 eV (for the argon cluster case). Any fragments with FKEs less than this cut-off are not observed in our set-up.

(d) In-Flight Decay

A correction for radiative emission from a metastable fragment while in-flight has been developed [21], using a Maxwellian distribution in the time domain (see Appendix B), given by

\[ f(t) = \frac{C}{t^2} \exp\left(-\frac{\alpha}{t^2}\right) \exp\left(- \frac{t}{\tau}\right), \]  

[3.15]

for a known temperature \((T)\), mass \((m)\), flight distance \((D)\), and a scaling factor \((C)\), where

\[ \alpha = \frac{mD^3}{2k_B T}. \]

[3.16]

A general TOF distribution (i.e., not necessarily Maxwellian) would be corrected by just the photon decay term of Equation 3.15. This in-flight decay correction can be used when the lifetime (and state) of the metastable fragment is known. Otherwise, it has the largest effect on the accuracy of the RKE distribution at longest flight times (corresponding to the lowest kinetic energies). In our case, no direct evidence was observed for this process to be considered significant.
(e) Large Dwell Time

A correction for large dwell times is required in some cases. This is relevant for slow targets that spend more time in the electron beam. If the ratio of the electron beam diameter \(d\) to the electron beam pulse width \(w\) is smaller than the speed \(v\) of the target (see Equation 3.17), then a correction to the speed distribution has been observed to be necessary [22]. TOF experiments that use an effusive source or a (diffuse) vapour cell type of arrangement sometimes need to consider this uncertainty. Generally, situations involving large pulse widths and/or small beam diameters are a concern.

\[ v > d/w \]  \hspace{1cm} [3.17]

In terms of a Maxwell-Boltzmann (MB) distribution (see Appendix B), this correction amounts to dividing the speed distribution (Equation B.1) by the speed \(v\), such that associated MB distributions in other domains require correction.

For an electron pulse width of 1 \(\mu\)s and an estimated electron beam diameter of 4 mm (in the probable worst case of divergence, related to the lowest impact energies), the ratio is approximately 4,000 m/s. A measurement of the gas beam speed (see Chapter 4) resulted in a most probable value of approximately 600 m/s. Even in the case of a 1 mm beam diameter (at higher impact energies), the ratio of Equation 3.17 is 1,000 m/s. Fortunately, this correction is not required for our investigations.

(f) Uncertainty in the TOF Distance

Similar to part (a), the uncertainty in the TOF distance can enhance error in the RKE for smaller flight times. The overlap of the electron beam and gas beam pulses, each of certain diameters, and the angle-of-acceptance and impact surface of the
metastable detector contribute to the error in the TOF distance. For a flight distance of $D$ with an uncertainty of $\Delta D$, the uncertainty in the RKE is given as

$$\Delta T_{ER} = T_{ER} \cdot 2\Delta D / D.$$  \[3.18\]

In our case, a flight distance of approximately 122 mm was used for the xenon cluster investigations (using a “new” detector), while 124 mm was used for previous studies. The electron beam diameter (approximately 2 mm) and the gas beam diameter (skimmed with a 1 mm diameter, approximately 53 mm upstream) had negligible impact on the RKE uncertainty. However, the detector had a cone shape with the inner wall as the detection surface. For an entrance diameter of 10 mm, a maximum increase in path length ($\sim 122.1$ mm) from the center of the interaction volume was negligible. The cone depth was approximately 10 mm, so realizing that the majority of the surface area of the detection surface was closer to the entrance, half the cone depth (5 mm) is a reasonable estimate of the flight distance uncertainty. Consequently, the RKE error is approximately 8% of a particular RKE value.

(g) Timing and Sampling Errors

Much like the uncertainty caused by the width of the electron pulse, the data acquisition can limit the accuracy of results in terms of the channel width of the electronics. A multichannel scalar (MCS) with a minimum time resolution of 200 ns was used for most of our measurements (see Chapter 4). In some cases a time-to-amplitude converter (TAC) was used with a multichannel analyser (MCA) operating in the pulse-height analyser (PHA) mode, such that the channel width for time was much smaller.
Generally, this uncertainty was significant at the shortest flight times. However, the stability of the timing electronics amounted to this error being negligible.

(h) Recoil Effects

For relatively heavy targets, the momentum transfer from the electrons in the collision process is negligible. This was observed to be the case for molecules such as \( \text{N}_2 \) and heavier [18]. For less massive targets, like helium atoms, recoil effects have been studied [23], and under certain conditions, can be significant. For the majority of the present investigations, uncertainty resulting from recoil effects is not significant.

(i) Detector Response Time

Most channel electron multipliers (CEMs) have a pulse width of about 20 ns and can distinguish between input pulse events as long as the count rate is not in excess of about 10 MHz [24]. Even with relatively high background pressures (~ 1×10^{-5} Torr) in the detector chamber, count-rates of 10 kHz can be tolerated before any degradation of performance occurs. This results in a negligible detector response time for our work.

(j) Detection Efficiency versus Metastable Fragment Speed

The detectors used in the present body of work are (channel) electron multipliers. For the detection of neutral metastable fragments, there appears to be little if any change in detection efficiency with the speed of the fragment. (On the other hand, the detection efficiency for both photons and metastable fragments varied significantly, with the amount of internal excitation and the quality of the CsI coating (see Chapter 4) on the detector surface being influencing factors.) However, with the use of the TOF mass spectrometer (see Section 3.3), the detection of positively ionized clusters of relatively
large mass was dramatically improved by using larger accelerating potentials (~5 kV on the CEM dynode).

(k) Angular Distribution of the Fragments

The random alignment, the complex nature of the targets—atoms, molecules, and/or clusters—in the beam, and the large number of possible fragmentation channels combined to give an assumed isotropic distribution (in the beam frame). It should, however, be noted that there will be a preference particularly for the slower fragments to remain roughly in the gas beam direction (in the lab frame). Though anisotropic distributions have been observed [25] with relatively simple molecules, such as H₂, and low impact energies near threshold, this will probably not be the case for our targets and impact energies.

3.2.5 Excitation Functions

In the proceeding sections, TOF and fluorescence analysis techniques were discussed. From TOF measurements, it is clear that the RKE can be determined for many situations. However, to help provide identification of the actual potential energy curve Y (see Figure 3.1), compared to other possibilities, the energy of the transition must be known. Figure 3.3 shows sample potential energy curves X and Y for a dimer AB, with relevant quantities as follows. By measuring the onset energy (i.e., the energy required for particular metastable features to appear), the transition energy can be determined, and often the identity of the curve Y.
In practice, a measurement of metastable yield as a function of electron impact energy, for a selected TOF window, generates a curve (i.e., excitation function) with some slope. The intercept of this slope of the excitation function with the energy axis provides the appearance energy of the metastable fragment. Changes in slope near threshold indicate new appearance energies and thus new production channels for the fragment. It should also be pointed out that the excitation function techniques could also be applied to the fluorescence for particular photon decay windows. Thus, the radiative

![Diagram of internuclear potential energy curves](image)

**Figure 3.3** Illustration of internuclear potential energy curves for diatomic molecule AB and relevant quantities (see text).
emissions can be probed.

Figure 3.3 indicates the previously discussed RKE ($T_{ER}$) for fragmentation along the potential energy curve $Y$. Other quantities indicated are the appearance energy, $E_t$, also known as the threshold energy, corresponding to the energy of the incident electron beam; $E_A$ and $E_B$ are the excitation energies of the metastable atoms $A^*$ and $B^*$, respectively, which result from curve $Y$; and $E_d$ is the dissociation energy of molecule $AB$ that is in its ground vibrational state $X(v=0)$ with respect to the separated atoms $A$ and $B$ in their ground states.

Conservation of energy applied to Figure 3.3 indicates that

$$E_t = E_A + E_B + E_d + T_{ER}. \quad [3.19]$$

Here, the dissociation limit is given by

$$E_{dl} = E_A + E_B + E_d. \quad [3.20]$$


$$T_{EF1} = \frac{m_z}{M} (E_t - E_{dl}) \quad [3.21]$$

This relates the FKE ($T_{EF}$) from the TOF spectra to the onset energy and dissociation limit in terms of the fragment and parent masses. Equation 3.21 is very useful when multiple fragments with different masses are possible. It is especially relevant for molecular cluster work, such as with N$_2$O clusters.

If the fragment mass is not otherwise known (based upon comparable measurements, etc.), then a plot of $T_{EF}$ versus $E_t$, for specific TOF windows, generates a
straight line with slope \( m_2/M \) and an intercept of \( E_{dl} \). This procedure was extensively discussed by Allcock and McConkey [26].

In addition to obtaining the excitation function near threshold, the general shape of the excitation function curve, for a particular TOF window, can aid in the identification of the detected fragments. General trends for the shapes of the excitation functions, based upon the first Born approximation, have been thoroughly discussed by LeClair [25]. Optically allowed states in the parent molecule typically have a maximum at about five times the threshold energy and fall off with a \( \ln(E)/E \) dependence. Optically forbidden states normally rise sharply near threshold (typically peaking several electron-volts above onset) and fall off with an \( E^{-1} \) dependence. Optically forbidden states are often associated with excitation of metastable states. In the event that electron exchange occurs (e.g., between a singlet ground state and a triplet excited state, as is typical with the rare gases), the excitation function of the optically forbidden state falls off with an \( E^{-3} \) dependence [27] after an initial maximum close to threshold.

3.3 Mass Spectrometry

Mass spectrometry is the technique that allows us to verify that we actually have a clustered gas beam, such that the methods discussed above can then be employed to extract information from the collision events. A linear time-of-flight (TOF) mass spectrometer (MS) employing two stages (in-line with the gas beam) was used in this work. This design is commonly known as a Wiley-McLaren TOF-MS. Stephens put the
original concept for a linear TOF-MS forth in 1946 (see References [28,29]), though the (two-stage) implementation came later by Wiley and McLaren in 1955 [30]. The general layout is shown in Figure 3.4, with the relevant distances and potentials indicated. (See reference [31] for further discussion.)

![Figure 3.4](image)

**Figure 3.4** A simplified layout of the Wiley-McLaren TOF-MS (see text).

The TOF-MS achieves mass separation by first accelerating the ionized masses from the ionization volume via an applied potential \( U_d \) on an "accelerating grid" towards the detector. Another accelerating potential \( U_L \), applied to the "drift tube," causes further acceleration towards the detector. The electrode materials (indicated as solid black lines) are metal. Optically transparent metal meshes (indicated in Figure 3.4 as dotted lines across the ion flight path; see Chapter 4 for further details) help to reduce
fringing fields etc. In practice, the drift tube voltage is normally much larger than the accelerating grid voltage, such that the accelerating voltage acts as a means of fine-tuning the performance of the mass spectrometer. In a nutshell, this is the main benefit of a two-stage TOF-MS versus one-stage (see Appendix C for further details).

After accelerating for distances \( s \) and \( d \), the ions enter the field-free drift tube of uniform potential. The separation of ionized mass bunches occurs over the flight distance, normally dominated by distance \( L \). Equation 3.22 describes (in a simplified manner) the relationship between the applied voltage \( (U) \), charge \( (q) \), mass \( (m) \), and speed \( (v) \), in terms of the kinetic energy \( (T_E) \):

\[
qU = T_E = \frac{1}{2}mv^2. \tag{3.22}
\]

The least massive ions, for a given charge (e.g., singly ionized), arrive at the detector first. The most massive ions are detected last. (In the case of the same mass, a larger charge results in a smaller flight time.) Equation 3.23 illustrates these concepts for a given mass-to-charge ratio. It is clear that a larger accelerating potential results in a shorter flight time, while a larger drift tube distance increases the flight time.

\[
t = \left( \frac{L}{\sqrt{2U}} \right) \sqrt{\frac{m}{q}} \tag{3.23}
\]

The separation into mass bunches (for a particular charge) produces the characteristic pattern of counts occurring in time at the detector that indicate the masses and intensities of a mass spectrum. See Appendix C for further discussion of the TOF-MS, including details on spatial focusing. (Spatial focusing, as the expression implies,
generates narrower mass bunches, resulting in better resolved mass spectra.) Furthermore, Equation 3.23 is easily re-arranged to provide

$$m = \left(\frac{2qU}{L^2}\right) \cdot t^2, \quad [3.24]$$

which indicates that the mass bunches tend to pile-up for larger flight times (corresponding to larger masses) due to the $t^2$ dependence. This is illustrated conceptually in Figure 3.5 for multiples of an arbitrary unit mass (e.g., homogeneous clusters).

In terms of the actual experiment, mass "lines" (i.e., mass bunches) are detected as a function of flight time. In order to generate a mass scale for the flight time intensities, a calibration procedure is required. Since the mass is proportional to $t^2$ for

<table>
<thead>
<tr>
<th>Mass Number</th>
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<td>1</td>
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**Figure 3.5** A representation of Equation 3.24 for 15 mass lines within the time domain. Note the characteristic bumping as the mass increases. See text for further discussion.
given conditions (see Equation 3.24), a polynomial fit to the observed peaks in time yields the calibrated mass scale. The simplest polynomial satisfying the form of Equation 3.24 is quadratic in time:

\[ m = at^2 + bt + c \]  \[3.25\]

where \( a, b, \) and \( c \) are real scalars. For an educated guess of the mass lines (especially in the homogeneous cluster case), or using well-known standards (such as non-clustered nitrogen, argon, etc.), a plot of flight time versus mass along with Equation 3.25 generates a calibrated mass scale.
3.4 References:


Chapter 4

Experimental Details

4.1 Vacuum System Overview

The following text describes various aspects of the experimental apparatus used to obtain the presented electron-cluster interaction results. Since this is the first thesis provided using this experiment, it is appropriate to present a reasonably detailed description of the equipment used. With this in mind, the following attempts to convey particulars that are essential for performing the enclosed set of cluster experiments.

The experiment consists of two differentially pumped chambers: the expansion and collision regions. A skimmer separates the two chambers. The vacuum system is mounted on an aluminum frame with accompanying vacuum pumps mounted under the suspended stainless steel (SS 304) chambers. The chambers utilize ASA flange
connections with Viton O-rings. Both chambers are pumped by 6" diffusion pumps equipped with manual 6" gate valves (Varian 1293S). The diffusion pumps are both Varian models (VHS-6) that are equipped with extended (Mexican hat) cold caps. The expansion chamber diffusion pump uses Dow Corning silicone 704 oil while the interaction chamber uses the cleaner, but more expensive Santovac 5 polyphenyl ether fluid. The interaction chamber also is equipped with a long-life cryotrap (Varian 326), which is not used for active condensation and reduces the pumping capacity, but provides a significant decrease in back-streaming of gases and especially the diffusion pump oil. This provides a cleaner environment in the collision region, which is evident compared to

![Diagram](image)

**Figure 4.1** Schematic diagram of the apparatus. PV-pulse valve; EG-electron gun; FC-Faraday cups; MS-mass spectrometer; EM-electron multiplier; CI-ionized clusters; CEM-channel electron multiplier; P-photons; M-metastable fragments. The CEM is located at 45 degrees to the gas beam.
observed minor amounts of oil condensing on the inner chamber walls (near the diffusion pump port) in the expansion region. (It should be stressed that throughout the course of study, no oil was observed in the vicinity of the skimmer and pulsed valve.) Fortunately, however, cluster surface contamination pick-up (using an O₂ “pollutant” with He and Ne clusters) was determined to be insignificant for small amounts of impurities (i.e., low background pressures) [1].

Both diffusion pumps are backed by a forepump, each with a thermocouple gauge (KJL 1518) indicating the foreline pressure upstream from a diaphragm valve. The thermocouple gauges are each separately controlled by appropriate thermocouple gauge controllers (KJL 210). Safety levels of approximately 140 and 80 mTorr (microns) were used for the expansion and collision foreline pressures, respectively. If the foreline pressure increased above this pressure level, then a connected (bypassable) interlock relay box shut off the respective diffusion pump until the pressure returned to a safe level. The chamber pressures were measured by (external glass type) ionization gauges (Bayard-Alpert design; KJL G100F) and suitable high vacuum gauge controllers (typically Veeco RG-1000). The operational chamber pressures were typically around 5×10⁻⁴ Torr (in the worst case) and 5×10⁻⁶ Torr for the expansion and collision regions, respectively. The ion gauge port was baffled so that stray charged particles could not enter the interaction region and interfere with the experiment.

The forepumps consisted of relatively heavy duty Edwards, Varian, or Sargent-Welch direct-drive and belt-driven rotary pumps. The direct drive units were Edwards three-phase (E2M40) and Varian three-phase (DS1002) pumps that were used on the
expansion chamber at separate times during the course of study. A Sargent-Welch single-phase (1374B) vacuum pump was normally used, except when being serviced, on the interaction chamber. The pumping speeds of the foreline pumps matched or exceeded the recommended values for the diffusion pumps. Edwards Ultragrid16 roughing pump oil was normally used. Suitable configurations of Speedivac diaphragm valves enabled roughing of each respective chamber or backing of each respective diffusion pump.

The gas handling system consisted of SS 316/316L tubing joined to other components using Swagelok ferrule-compression (swage) connections. Several Swagelok bellows-sealed valves (Series H, etc.) were used to allow direct access to a total of two gas cylinders and one air purge. The air purge was used, along with an independent connection on the top flange of the main (interaction) chamber, to bring the chamber up to atmospheric pressure if servicing was required. This gas line split to a valved port into the expansion chamber and to gas tubing towards the pulsed valve (see Figure 4.1). The gas line stagnation pressure was monitored using a Honeywell pressure transducer (SA-200PA-1C1DE). This pressure transducer provided an absolute, linear pressure reading (up to 200 psi) indicated by a (0.025 V/psi) voltage output whereby 1-6 V represented 0-200 psi. This output voltage was measured via a standard multimeter. It was found that the gas pressure reading from the pressure transducer indicated slightly different pressure values in the high and low extremes compared to the gas cylinder regulators, thus necessitating attentive care when modifying the stagnation conditions. Additionally, from a practical perspective, it was found that a small amount of SNOOP®
(by Swagelok) served as a much more efficient positive-pressure leak checker compared to "soapy water."

The critical components of the experiments undertaken in this course of study are conceptualized in Figure 4.1. The pulsed valve (PV), located in the expansion chamber, is mounted on a linear pusher and is aligned by a well-constructed cradle. The skimmer separates the expansion and collision chambers and serves to well-collimate the gas beam pulse. Upon the gas beam entering the interaction chamber, a beam of pulsed electrons originating from the electron gun (EG) intersects the collision region. A Faraday cup (FC) is used to monitor the electron current. From the point of collision between the gas and electron beams, two sub-experiments were possible. To monitor and verify the gas constituents and amount of clustering, a linear two-stage time-of-flight (Wiley-McLaren-type) mass spectrometer (MS) was used (see Chapter 3 and Appendix C) inline with the gas beam. The positively ionized clusters (CI) of a particular gas sample were accelerated into the MS flight tube and detected by an electron multiplier (EM). Alternatively, photons (P) and neutral metastable fragments (M) could be investigated from the electron-cluster interactions. In this case, the signal is detected as a function of time at a channel electron multiplier (CEM) located in the scattering plane, at 45 degrees between the gas and electron beams.
4.2 Aspects of the Supersonic Jet Source

4.2.1 Supersonic Expansions

The following discussion is not intended to be a thorough review of aspects of supersonic expansions, but rather a brief introduction. Free jet sources and various issues related to supersonic expansions have been thoroughly reviewed (see, e.g., References [2-14]). Besides, this “ideal” framework—isentropic expansion etc.—is recognized to be an approximation that to some degree fails for real gases, especially in the event of condensation [15]. (Clusters were first observed in gas dynamic expansions at the outset of nozzle beam experiments [16,17].) This implies that the discussion provided below generally falls short for clustered gas expansions. However, it remains a reasonable starting point, leading to a qualitative understanding and some experimental insights.

The method used prior to the supersonic gas flow development was an effusive flow [18]. (This will naturally lead to the definition of a supersonic expansion.) The “effusive flow” developed from a pressure gradient, with the molecular flow through a thin-walled orifice that was much less than the throat size. Furthermore, the thermal equilibrium of the gas source was maintained by the effusing gas particles in the case of a very small orifice cross sectional area relative to the source surface area. In the event that the mean free path (as a function of the average speed and mean free time between successive collisions) was much greater than the orifice throat diameter (i.e., Knudsen
condition), molecular flow developed. This physically means that no collisions occurred in the vicinity of the orifice and in the effusing flow.

However, in terms of the ratio of the directed motion of the flow to the random thermal motion, the effusive source has a small value. Thus the local speed of flow is less than the local sonic speed. At this point the definition of the Mach number becomes relevant:

\[ M_a = \frac{w}{c} = \frac{\text{local flow speed}}{\text{local sonic speed}} \]  \[4.1\]

where \( M_a \) is the Mach number. The local speed of sound is given as:

\[ c = \sqrt{\frac{k T}{m}} \]  \[4.2\]

where the ratio of the specific heats (assumed to be independent of temperature) at constant pressure and volume is \( \kappa = c_p/c_v \), \( m \) is the gas particle mass, \( k_B \) is the Boltzmann constant, and \( T \) is the local temperature. The local temperature (as determined in References [13,14]) is given by:

\[ T = T_0 \left[ 1 + \frac{1}{2} (\kappa - 1) M_a^2 \right]^{-1} \]  \[4.3\]

where \( T_0 \) is the source temperature. Thus,

\[ M_a < 1 \quad \text{subsonic} \]

\[ M_a = 1 \quad \text{sonic} \]

\[ M_a > 1 \quad \text{supersonic}. \]

Furthermore, two other standard concepts deserve mention. A supersonic expansion is normally characterized by the jet boundary, barrel shock, streamline, and zone of silence. The skimmer placement should be sampling the zone of silence, with the
realization that it will modify the ideal expansion characteristics. Also, the nozzle-to-skimmer distance should be less than the distance from the nozzle to the Mach disk \(x_m\):

\[
x_m = 0.67 \frac{p_o d}{\sqrt{p_b}} \tag{4.4}
\]

where \(d\) is the nozzle throat diameter, \(p_o\) is the source pressure, and \(p_b\) is the background chamber pressure. This has been determined from many experiments (see, e.g., Reference [2]). For our typical conditions (e.g., 3.5 atm, 0.25 mm, and \(3 \times 10^{-4}\) Torr), the Mach disk is expected to develop at approximately 500 mm, which is well past our nozzle-to-skimmer distance. In addition, the maximum diameter of the barrel-shaped expansion is around \(0.75 \cdot x_m\) and the Mach disk diameter is around \(0.5 \cdot x_m\), both being ± 25 percent.

Figure 4.2 demonstrates the concept of a free jet expansion: as the gas expands from a high pressure environment to a vacuum through a small orifice, supersonic expansion occurs. Basically, this results from a conversion of the random thermal motion of the particles to a directed flow. The large local flow speed, relative to the speed of sound in the local medium, produces a narrower speed distribution compared to the effusive source. Notice that the maximum tends to shift to larger speeds for the supersonic expansion, as shown in Figure 4.3. Here, \(M=0\) represents a subsonic (effusive) source, while the Mach numbers greater than sonic (i.e., 10 and infinity) indicate the supersonic speed distributions. (It should be noted that as the local flow speed overwhelmingly dominates the local sonic speed, the maximum tends to slightly
Figure 4.2 A conceptual diagram that demonstrates the behaviour of the atoms/molecules prior to and after the supersonic expansion through a small orifice.

Figure 4.3 Theoretical velocity distributions for different Mach numbers. The peaks have been normalized for convenient comparison. See the text for further discussion.
shift back to smaller speeds.) Experimentally, the supersonic expansion followed by skimming results in a very cold gas beam—in both the translational and radial directions (for the cylindrically symmetric beam).

An experimental representation of the supersonic speed distribution is shown in Figure 4.4. The MS was used with a $+5$ V bias on the flight tube (to exclude positive ions) and no accelerating grid voltage. The time-of-flight spectrum of neutral excited argon fragments was produced using a source pressure of approximately 50 psi, room

![Time-of-flight spectrum](image)

**Figure 4.4** Time-of-flight spectrum of neutral metastable Ar fragments detected inline with the gas beam using the mass spectrometer with the flight tube held at $+5$ V. The time scale has been adjusted to show the velocity distribution. The photon signal (at zero time) has been excluded for viewing convenience. See the text for further details.
temperature (~ 295 K), and an electron beam energy of 50 eV. Similar distributions were
obtained for other targets.

A Maxwell-Boltzmann speed distribution (see Appendix B for further discussion)
was used, in terms of the supersonic condition, whereby

\[ f(v) = Av^2 \exp\left(-\frac{m(v-w)^2}{2k_BT}\right) \]  \[4.5\]

represents the signal yield and the flow speed is

\[ w = \sqrt{\frac{k_BT}{m}}M_o. \] \[4.6\]

Fitting Equation 4.5 and the related equations in the time domain resulted in a mean
speed of approximately 600 m/s, with a full-width half-maximum of 85 m/s, for the argon
data in Figure 4.4. The supersonic fitting procedure consistently resulted in mean speeds
within ~ 15 m/s for different data runs. This analysis suggests a Mach number of
approximately 12.7 and an expansion temperature of 6.5 K. A similar analysis of CO\textsubscript{2}
data, using the same approach, generated a mean speed of approximately 585 m/s.

\[ \text{Figure 4.5} \quad \text{Cutaway diagram of the geometry of the orifice indicating a divergent nozzle.} \]
Figure 4.5 represents the type of nozzle (divergent) used in this body of work. The throat size (smallest diameter) was 250 \( \mu \text{m} \) with a full-angle (2\( \theta \)) of 60 degrees. It is known as a conical nozzle and provides a means of generating clusters via the narrow throat and divergent zone. The constrained expansion region allows for more collisions to occur prior to condensation and expansion termination [19]. Other types of nozzles (e.g., sonic) are known to be much less efficient at cluster generation (see Chapter 2) [20-22].

4.2.2 Pulsed Valve

The pulsed valve, shown in Figure 4.1, and related components, is arguably the most important feature of our experiment. Without a properly functioning pulsed valve, generating a well-clustered gas beam, the work presented in the following chapters, discussing aspects of the electron-cluster interactions, would not have been possible. There are several types of pulsed valves commonly used for obtaining pulsed gas beams: current-loop drive, solenoid type, and piezoelectric. A popular piezoelectric pulsed valve was designed by Proch and Trickl [23]. The design being used in this work is a similar, but commercial version of the Proch-Trickl valve. The piezoelectric pulsed valve is an especially practical choice from a magnetic field standpoint: our electron beam is not adversely influenced. Pulsed sources typically have a small pulse duration compared to the interval of interruption. In our case, the choice of a pulsed gas flow is cost effective from a pumping and gas standpoint: typically less gas and smaller pumps are needed.
Furthermore, a pulsed beam, compared to a continuous beam, has a higher beam intensity for a given background chamber pressure. This benefit has the effect of increased signal-to-background ratios for pulsed beams.

The Lasertechnics (model LPV) pulsed valve obtained a pulse profile via a piezoelectric Bimorph® disk. The bimorph was obtained from Morgan Electro Ceramics (60957-1-PZT-5B); practical diagnostic information is included in Appendix D. (In addition, it is strongly urged that any bimorph maintenance should follow the suggestions included in both the Lasertechnics valve manual and the Morgan Electro Ceramics catalogue and users guide.) A Viton tipped poppet, composed of an aluminum rod and Varian TorrSeal epoxy bonding, was mounted and centered on the piezoelectric disk, as

![Exploded diagram of the piezoelectric pulsed valve.](image)

**Figure 4.6** Exploded diagram of the piezoelectric pulsed valve.
Figure 4.7  Bimorph schematic diagram illustrating the effect (dashed line) of applying a positive voltage to the backside. The poppet and tip are shown on the right of the figure (frontside), with the translation induced by the applied potential indicated by the arrow. CLK indicates the master oscillator (clock) assembly (see Section 4.5).

indicated in Figure 4.6.

The bimorph was constrained along its circumference and with an applied voltage between +70 and 120 V, as indicated in Figure 4.7, the electric-field-induced translational motion of the poppet away from the orifice for a positive potential. Thus, for a given input pulse of some characteristic width (150 μs to DC) and potential (as indicated), translational motion of the bimorph-poppet assembly provided the required
pulsed action of the valve. Furthermore, the Lasertechnics manual indicates a maximum repetition rate of 500 pulses per second, though only 200 pulses per second (5 ms period) maximum was ever required. A maximum limit of 10 atm and 50 °C was stated by the manufacturer. The operating temperature was initially at room temperature, but thermal contact with the flange the electron gun was mounted on caused additional heating. This was a problem since an adjustment at room temperature conditions resulted in an improper poppet tip placement against the nozzle after some operation. The proper adjustment of the poppet-orifice distance was determined after trial-and-error.

Figure 4.8 was obtained for a pulse of Ar gas at approximately 50 psi (with a 150 μs wide clock pulse to the PV voltage pulser), a continuous electron beam at about 100 eV and a relatively small current (95 nA), and ± 75 V on the bimorph. Additional bouncing of the poppet and gas intensity (and clustering) can be observed for higher applied bimorph voltages. The observed signal is primarily a result of photon emission from the electron collisions with the gas beam. The intense photon signal at small detection times, as verified for pulsed gas and electron beams, is a convenient artefact of the collision processes. This implies that the signal in time of Figure 4.8 accurately represents the gas beam profile. This profile was observed to be approximately the same for other gas targets. The main feature is peaked at approximately 375 μs, but can possibly shift to larger times with deteriorating valve performance with age. (This is based upon the present experience with aged crystals versus the new bimorph that was used to obtain the data in Figure 4.8.) Therefore, a 375 μs delay to the electron beam, relative to the start of the gas beam pulse, was used with some of the recent
Figure 4.8  Signal versus time at the 45-degree CEM detector using a continuous electron beam and a pulsed Ar gas beam. The peaks indicate a more plentiful gas target. See the text for further details.

measurements. Also, as can be seen in Figure 4.8 (and pressure measurements), there is always some leakage associated with the pulsed valve.

Once the pulsing scheme (cf Figure 4.21) has been established, the choice of gas source conditions must also be determined prior to the intended set of research. Since room temperature is maintained throughout these investigations, the choice of stagnation pressure is the other parameter (besides nozzle geometry) used in determining the degree
of condensation in the gas beam (see the previous subsection and Chapter 2). For a given stagnation pressure, the average cluster size can be determined based upon the empirical cluster condensation parameter scaling laws presented in Section 2.5. For the heavy rare gases (i.e., Ar, Kr, and Xe), a set of average cluster sizes has been presented in Figure 4.9 for changing source pressure. It should be emphasized that the curves of Figure 4.9 are theoretical. Room temperature (~295 K), a nozzle throat of 0.25 mm, and a full-angle of 60 degrees for a conical nozzle were used. The two curves per rare gas represent the standard recommended cluster condensation parameter scaling relations, squares, and the alternate possibility for heavy clustering with conical nozzles, circles, (see Section 2.5). Clearly a significant amount of condensation occurs for Xe compared to Ar for the same stagnation pressures. For a given source pressure of 50 psi, and the other parameters already mentioned, we could expect average cluster sizes of around 100, 400, and 1500 atoms, respectively, for Ar, Kr, and Xe. The visible discontinuity on the Ar data results from different recommended cluster condensation parameter-scaling laws for the particular source conditions (see Section 2.5).

In addition to the pulse timing and source parameters, the positioning of the pulsed valve relative to the skimmer must be considered. A “cradle” assured that the skimmer and pulsed valve were properly aligned in the x-y directions. A linear pusher attached to the pulsed valve allowed the nozzle-skimmer distance to be varied (in the z direction). The choice of a suitable nozzle-to-skimmer distance was not just a function of the supersonic expansion conditions (e.g., Mach disk), as discussed in subsection 4.2.1, but also the degree of clustering being sampled by the skimmer.
Figure 4.9  Mean cluster size versus stagnation pressure for the heavy rare gases. The squares and circles represent different theoretical cluster condensation parameter scaling law relations. See the text for further details.
Figure 4.10 presents a representative sample of measurements for small cluster sizes (N=1-4) of CO₂, for an electron impact energy of 150 eV. It is expected that the large impact energy will induce significant fragmentation. Points were accumulated by integrating the number of counts for specific mass lines within a set run time, while keeping all other experimental conditions constant. The circles (in Figure 4.10) correspond to the main gas peak as in Figure 4.8. The squares represent a similar set of measurements, but for the electron beam coinciding 20 μs prior to the gas pulse maximum; the triangles were for 20 μs after the maximum. The overall trend is that the most intense points (i.e., large number of counts) occur, within the statistical fluctuation, at a 9 mm nozzle-to-skimmer distance. Thus most measurements were performed with this setting.

A recent investigation of CO₂ free jet expansion for changing source pressures (using a nozzle diameter of 300 μm, but an unidentified geometry, and 300 K) indicated that condensation reaches a maximum after approximately 2.5 nozzle diameters (0.75 mm) downstream [15]. It was also found that condensation was noticeable after 1 nozzle diameter (0.30 mm) and ceased after approximately 9 nozzle diameters (2.70 mm) for a stagnation pressure of 500 kPa, though smaller source pressures appeared to delay the condensation completion. Another interesting bit of information provided by Reference [15] was, for a source pressure of 203 kPa of CO₂ and the other conditions as above, the maximum number density occurred at approximately 9 nozzle diameters downstream (in the “zone of silence”). Considering the general lack of details included on their nozzle, these results seem consistent with our measurements. Further, the average cluster size for
Figure 4.10 Intensities of \((\text{CO}_2)_N\) clusters, for \(N=1, 2, 3,\) and 4, using the mass spectrometer, versus the nozzle-to-skimmer (N-S) distance. The intensities have been recorded under the same conditions, while varying the N-S distance and the delay between the gas and electron pulses. The circles correspond to the main peak in the gas pulse (see Figure 4.8), while the squares and triangles represent data taken 20 \(\mu\)s before and after, respectively, relative to the maximum. See the text for further details.
CO₂ clusters (at 50 psi, etc.) was based upon similar mass spectra with the rare gases (thus being around 100 atoms), rather than the cluster condensation parameter scaling laws. This was due to uncertain molecular cluster condensation parameter scaling relations since molecules like CO₂ have been observed to obey slightly different cluster condensation parameter scaling relations compared to the rare gases, but have not been as well studied [24,25].

An experimental mass spectrum, based upon the optimized conditions (including other parameters discussed in Section 3.3 and Appendix C), is shown in Figure 4.11. The abundance of mass lines was recorded as a function of flight time for electron impact energy of approximately 40 eV and a source pressure of 50 psi. Figure 4.11 shows several layers. The small inset layer shows the cluster distribution out to large masses. The large inset and the main figure show the mass distribution in better resolution. The large inset (up to 250 μs) is simply an expanded view of the main bottom mass distribution. Complex mass bunching is often a feature of heavily clustered gas beams.

From the cluster condensation parameter scaling law results of Figure 4.9, a mean cluster size of around 400 atoms in the original neutral beam would be expected. However, electron impact ionization of clusters is well known to dramatically skew the detected mass distributions to smaller average sizes compared to photoionization methods [26]. Figure 4.11 demonstrates a complex mass distribution, where certain peaks (e.g., N=13, 16, 19, etc.) are expected to be more abundant than others. This is based upon shell-closing arguments involved with cluster growth and evaporation, briefly discussed in Section 2.4. The abundant lines essentially are indicators of stable, favoured
geometries. A similar increase in abundance around 35-40 Kr atoms was observed in Reference [27]. In any case, Figure 4.11 indicates obvious clustering in our supersonically expanded gas beam, which provides a source for the subsequent cluster investigations.

Alternatively, various experimental parameters (e.g., pressure, bimorph voltage, etc.) could be tweaked to generate an insignificantly clustered beam for comparisons. From the cluster concepts considered in Chapter 2, the cluster formation is proportional to $p_0^2 d$ and the beam intensity is proportional to $p_0 d^2$. This implies that it is possible to increase clustering by decreasing the nozzle diameter, $d$, and increasing the source pressure (for a fixed source temperature, etc.), $p_0$. Alternatively, for equal beam intensities, a decrease in the source pressure and increase in the throat size produces a decrease in condensation.
Figure 4.11  Positively ionized krypton cluster signal as a function of time. The top scale indicates the number of Kr atoms in the cluster. The top (small) inset shows (with poor resolution) the Kr cluster mass spectrum up to large numbers of constituents. The large inset shows an expanded view of the main mass spectrum.
4.3 Electron Gun

The electron gun was originally designed by Dr. P. Hammond (during the mid-to-late 1980s) and discussed in B. Karras’ thesis [28]. As shown in Figure 4.12, it consists of an electron emitter normally composed of a two percent thoriated tungsten wire, 0.005” in diameter (A. D. MacKay Inc.), that is spot welded onto two terminals into a V-shape (hence pointed). Extreme care was necessary during the welding process since improper filament handling and misalignment was unacceptable. The filament support rods were mounted through an insulating, Macor rod. This was secured into a Wehnelt cylinder by adjustable setscrews, which provided a means of careful alignment of the filament point into the Pierce cavity of the filament housing (i.e., grid). (It was found that alignment of the filament posts in the vertical plane provided a situation that extended filament life and alignment. Sagging was apparently not a problem in this case.)

![Figure 4.12](image-url)  
**Figure 4.12** A cut away representation of the electron gun.
A current of 2.3 A was normally supplied to the filament (via an in-house unit).

The electron gun also consisted of two aperture lens elements and five other lens elements. The electrons were extracted from the filament using a Pierce diode extraction scheme. The first aperture (E1; see Figure 4.13) was used as the positive anode in conjunction with the Wehnelt filament housing, which received a pulse (via the pulser of Jet Propulsion Laboratory design) to extract the filament emitted electrons. The E1 and E2 lens elements each had apertures 1 mm in diameter, whereby the second aperture aided in skimming any excessively divergent electrons upon exiting the E1 anode. Furthermore, the three sets of overlapping three element stacks (E3-E5, E4-E6, and E5-E7, thus totalling to five lens elements) provided a means of beam focusing within different energy ranges. In practice, for convenience and due to the automated excitation function technique (see Section 4.5), E3-E5 (including E1 and E2) were fixed at around +240 V (relative to grid earth), while E6 was adjusted to obtain a practical current distribution over the required energy scale (see Figure 4.14) and reasonable focusing. E6 was normally set at around +80 V, while E7 was grounded such that the zero volt bias corresponded to the target region. Lambda Power Supplies were used to supply lens element voltages and to define the electron-beam energy. (Note that the resistors shown in Figure 4.13 were R1=10k\(\Omega\) and R2=50k\(\Omega\).) The electron beam power supply (Lambda LQD-425; rigged in series) provided 0-500 V electron beam energy.

The inner Faraday cup (IFC) had a +18 V bias applied while the outer Faraday cup (OFC) had no applied bias. They were electrically isolated from each other. A reasonably deep IFC/OFC length ratio of approximately 1/10 (along with the applied IFC
Figure 4.13  Schematic diagram of the experimental circuitry used for the electron gun (EG) and Faraday cups (FC). FS represents the filament supply; LS is the lens supply; EXF indicates excitation function (optional: depending on use). The other components are discussed in the text.
Figure 4.14  A plot of current entering both the inner Faraday cup (IFC) and outer Faraday cup (OFC) versus the calibrated electron energy. Kr was used as the calibrating gas. See the text for further details.

bias) ensured that surface reflected electrons were not likely to escape. The zero volt bias on the OFC provided (along with the grounded E7 lens element) a zero volt target. Two sensitive ammeters (Keithley 414A picoammeters) were used to monitor the collected current. Figure 4.14 shows an example of an energy calibrated current distribution (using Kr at 3.5 atm, etc.) where the total current is composed of the sum of the currents on the IFC and OFC. The current measurements are integrated over the duty cycle of the experiment (typically a 1.6 µs electron pulse width and a clock period of 15 ms).
Without steering plates or magnetic focusing methods, the current clearly changes focusing conditions for different electron beam energies. (It is possible that surface scattered or secondary electrons were collected by the OFC, thus providing the relatively large contribution at smaller energies.) Modifying each lens element bias for different energies is unfortunately impractical considering the automated energy sweep during excitation function measurements (see Section 4.5).

The calibration of the electron beam energy was necessary because of potentially energy modifying phenomena like space charge effects and contact potentials. Several approaches throughout the course of study were utilized to assure calibrated energy scales. Using the mass spectrometer, the abundance of a known ion line could be monitored as a function of impact energy, thus providing a calibration standard using the known ionization energy. For the rare gases, useful articles covering various sized and charged clusters include, for example, References [29-31]. Alternatively, the known thresholds of various excitation functions (photons or metastables) were used for energy calibration. Electron gun performance appeared rather uniform for various targets (e.g., helium or some other target of choice), so that calibration via a target different than that which was primarily being studied was possible. Helium was a suitable calibration standard, though the vacuum ultraviolet resonance lines of the studied rare gases (e.g., Ar, Kr, and Xe) were often used (see Chapters 6-8). The energy calibration, combined with the spread in electron energies from the hot filament source, resulted in an estimated electron energy uncertainty of ± 1 eV.
4.4 Detectors

As introduced above (cf Figure 4.1), several types of detector arrangements were utilized throughout this work. In the case of mass measurement (and cluster verification), a mass spectrometer was used, as shown in Figure 4.15, to observe the mass bunches at the detector as a function of flight time—heavier masses (and less charged) arrived at later times. Following electron impact ionization, a positively charged cluster was attracted by an accelerating grid (using a homemade pulsing device and a standard 40 V max power supply by Harrison Laboratories Inc., Model 865B) towards the flight tube. The accelerating grid was pulsed-off (grounded to target) prior to and during the electron pulse (see Figure 4.21), while a constant voltage, < 500 V (Fluke 412B Power Supply), was applied to the flight tube. Either an EMI venetian blind multiplier or a channel electron multiplier (CEM) was used for detection.

The CEM (Burle/Galileo 4773) detector configuration is illustrated in Figure 4.15. This type of CEM contains the standard cone and tube, but also a grid and dynode. The grid and conversion dynode were wired together in vacuum (via the available number of electrical feedthroughs) and supplied by a maximum voltage of -5 kV (Ortec 659). Incoming positive ions would strike the conversion dynode, and then emit secondary electrons, which would then be attracted to the CEM cone. The cone of the CEM was biased at typically -3.2 kV (Tennelec TC-945), always less than the dynode, and the output (amplified secondary electrons, via a zero bias back-end) was picked-up by a preamp prior to further data acquisition units.
Figure 4.15  Simplified schematic diagram of the relevant components utilized in the mass spectrometer (MS). The CEM detector is shown. EG is the electron gun; FC is the Faraday cups; CLK indicates the clock pulse; CI represents positively ionized clusters. Other elements are discussed in the text.
Figure 4.16  Simplified schematic diagram of the relevant components utilized in the time-of-flight, fluorescence, and excitation function studies. EG is the electron gun; FC is the Faraday cups; P represents photons, M indicates neutral metastable fragments. Optional filters (OF) are indicated and placed in front of the CEM. See the text for additional details.
As discussed previously, once a clustered beam was verified, the "real" experiment was performed. In this case, the clustered beam was impacted by an electron beam of a particular energy and the resultant vacuum ultraviolet (VUV) fluorescence and neutral metastable fragments were probed by the CEM (Burle/Galileo 4039) at the 45 degree detector position. As shown in Figure 4.16, appropriate biasing of the CEM cone and meshes in front of the CEM excluded charged particles (i.e., ions or electrons) from being detected. The mesh nearest the interaction region was held at the interaction region potential (i.e., grounded).

To lower the work function of the photon detector, the CEM was coated with a thin layer of CsI using a commercial coating unit (Edwards 403A). Rejuvenation of a CEM was accomplished by filling the CEM channel with acetone and heating it rapidly with a heat gun. The resulting minor explosions, which were observed to occur, had the effect of removing the contaminated surface layer and exposing a fresh surface. Once rejuvenated, the CEM cone was recoated with CsI and the CEM returned to use.

Furthermore, an optional optical filter could be placed in front of the CEM assembly, which would physically block incoming metastable fragments, but provide a means of separating the observed fluorescence into wavelength intervals. While the CsI-coated CEM provided the upper wavelength cut-off around 180 nm [28,32,33], the particular VUV compatible optical filter provided the lower wavelength limit. As demonstrated in Figures 4.17-20, several VUV wavelength cut-offs are available for use [34].
Figure 4.17 Transmission spectra of a LiF optical filter in the VUV for various temperatures.

Figure 4.18 Transmission spectrum of a MgF$_2$ optical filter in the VUV for room temperature.
**Figure 4.19** Transmission spectra of a CaF$_2$ optical filter in the VUV for various temperatures.

**Figure 4.20** Transmission spectra of a BaF$_2$ optical filter in the VUV for various temperatures.
4.5 Data Acquisition

Standard nuclear instrumentation modules (NIMs) processed the detected pulses from the preamp (homemade; 10 times gain) that was attached to the detectors used for the mass spectra, time-of-flight, photon decay, and excitation function observations. Figure 4.21 represents the relevant timing between aspects of the experiment discussed above. A 150 μs pulse from the internal gate and delay unit P1 (see, e.g., Figure 4.22) of the master oscillator (clock) was provided to the voltage pulsing unit of the pulsed valve (PV). As indicated, a pulse from the internal gate and delay unit P2 of the clock (CLK) to the JPL electron gun pulsing unit followed approximately 225 μs after the end of the PV pulse. In other words, the electron gun beam was activated approximately 375 μs after the CLK triggers a new repetition. The delay between the gas and electron pulses was determined as discussed in Section 4.2.2. In practice, this setting slowly increased near to the end of the bimorph lifetime (e.g., up to 550 μs for a very worked-over crystal). An electron pulse width of approximately 1.6 μs was used for collision events. This pulse width could be decreased to approximately 1 μs by suitable use of an external (relative to the CLK) NIM unit. In the case of a mass spectroscopic measurement, a pulse was sent to the accelerating grid, just before (1 μs) the electron pulse, to temporarily (~ 2.6 μs) turn off the ion extraction voltage so as not to disturb the electron beam. This represents the simplest timing sequence used in the present body of work. Slightly more elaborate schemes were employed (via NIM units) in certain special cases as discussed below.
Figure 4.21  Time sequence of the pulses applied to the different elements of Figure 4.1. As discussed in the text, the pulse of electrons coincides with the center of the gas pulse as it traverses the interaction region.

Figure 4.22 shows the data acquisition scheme used for mass spectroscopy. A CLK master pulse (typically a 15 ms period, $p$) started the internal clock gate and delay units ($p1$-$p3$) that had some set delay ($d1$-$d3$), relative to the CLK start event, and pulse width ($w1$-$w3$). $p1$ was always used to trigger the PV pulser by applying a 150 $\mu$s pulse coincident with the CLK trigger. $p3$ was used to trigger the accelerating grid of the mass spectrometer, according to the timing sequence example in Figure 4.21. $p2$ was used to trigger multiple devices. The $p2$ output could be used to directly trigger the EG pulser.
(leading to a 1.6 μs pulse width) or it could be fed into an Ortec (416A) gate and delay NIM. In the case of the external Ortec gate and delay unit being used, an electron pulse width down to approximately 1 μs could be obtained, which also resulted in a slightly decreased beam current.

The P2 output was also used to trigger the multichannel scaler (MCS)—the main data acquisition workhorse. This MCS was a homemade unit with 511 usable channels (the 512th stored the runtime) with a minimum channel width of 200 ns. (Other channel increments were, for instance, 500 ns/ch, 1 μs/ch, 2, 5, 10 μs/ch, etc.) An integrating time window could be set-up allowing mass abundances to be probed without requiring data transfer to the PC. Output from the EM (or CEM) mass spectrometer detector was amplified by the preamp and then amplified again (1 times coarse gain, full scale 12.5 times fine gain) by the main data acquisition amplifier (Ortec 474 timing filter amplifier). The preamp essentially acted as an inexpensive fuse between the detector and NIMs. The amplifier output was directed into a discriminator (Canberra 1428A constant fraction discriminator), with an appropriate lower voltage cut-off, that outputted to several devices. A counter (Ortec 719 timer and Canberra 892 timer/scaler) was connected to the discriminator as a diagnostic tool; the observed number of counts per second was useful in setting CEM voltages, etc. The discriminator also connected to the MCS input, thus providing a mass distribution as a function of flight time (channel number). An RS232 output connected from the MCS to a data dump PC. The MCS output was also connected to an analog oscilloscope (CRO) for real-time monitoring of the accumulated signal.
A diagram illustrating the typical electronic modules required for mass spectroscopic investigations. MCS indicates multichannel scalar; CRO is cathode ray oscilloscope; PC is personal computer; CLK is clock; PV is pulsed valve; EG is electron gun; EM is electron multiplier (see Figure 4.1); see the text for more details.

A similar data acquisition scheme was used for time-of-flight (neutral metastable fragment) and fluorescence studies. P1 was again used to trigger the gas pulse. P2 was used to trigger the MCS data accumulation and the gate and delay NIM or EG pulser directly. Another optional gate and delay NIM (Ortec 416A) could be used to start the time-to-amplitude converter (TAC; Ortec 567).

The first gate and delay NIM was used to decrease the electron pulse width, while the second gate and delay NIM was either bypassed (with the same pulse triggering both
the EG pulser and TAC) or included to insert a delay between the EG pulse and TAC data accumulation start time. Use of the additional time delay in triggering the TAC relative to the EG pulse had the effect of circumventing the possibly undesirable, intense photon signal at the shortest times. This provided a well-resolved method to detect very fast metastable fragments or longer lifetime photon contributions without a significant saturation effect on the TAC. The stop pulse on the TAC was provided by the detector

![Diagram](image)

**Figure 4.23** A diagram illustrating the typical electronic modules required for TOF and fluorescence investigations. MCS indicates multichannel scalar; MCA is multichannel analyzer; PHA is pulse height analyzer; TAC is time-to-amplitude converter; CLK is clock; PV is pulsed valve; EG is electron gun; CEM is channel electron multiplier (see Figure 4.1); see the text for more details.
output, via the data accumulation scheme discussed above. The output from the TAC was accumulated on an external (Quantum 8) multichannel analyzer (MCA) operating in the pulse-height analysis (PHA) mode. The MCA had 1024 channels available and the TAC settings used were typically either a 5 or 10 µs range. (Calibration of the TAC time-scale was performed by triggering the TAC start from the CLK P2 and sending a pulse from the CLK P3 into the stop of the TAC. By changing the delay between the TAC trigger pulse and the data pulse, a well-defined, repeatable timing pattern developed, such that the time scale increment could be determined.) After sufficient data accumulation (determined by the required statistics on features of interest), the acquired data from the TAC was transferred to a PC for further analysis.

It is fair to say that the main experimental focus was on neutral metastable fragment detection, rather than the VUV fluorescence. From a practical matter, a few revealing comments should be made. It was normal for the VUV photon signal to heavily dominate the metastable signal at the 45 degree CEM detector. This prompt photon signal, coincident with the electron pulse, was used to determine the zero on the time axis. Furthermore, it was not feasible (or desirable) to somehow physically gate-out the incoming photon flux and the MCS data intake was not an issue (as it is for TACs). Therefore, an approach based upon possible photon saturation was employed when required for good metastable accumulation. (Too high of a count rate on the CEM can lead to destructively high secondary electron production rates. If the ability of the CEM to replenish its electron supply is surpassed by secondary electron production, then "dead time" can occur. This can, in principle, generate false output either by the dead time or
by ion backflow from the backend of the CEM.) Possible saturation of the CEM was not observed to occur beyond the prompt photon signal. Not even on the photon tails were any “fake” valleys or peaks observed throughout the large amounts of accumulated data. Consequently, possible saturation of the prompt photon signal was not observed to be detrimental (in our experimental investigations) to the metastable yield. Further, no apparent variation was observed for the metastable peaks (e.g., from rare gas clusters) as a function of electron beam current. A lower current simply had the effect of decreasing the count rate and prolonging data accumulation. This was an obvious disadvantage for expensive gases and metastable fragments with relatively low internal excitation energies. From these perspectives the metastable accumulation at the expense of the photon yield was justified.

The data acquisition set-up for excitation function measurements is rather similar to the schemes outlined above. Again, the PV pulser is triggered via P1. P2 again triggered the MCS and gate and delay NIM or EG pulser directly (as discussed above). P2 also triggered a dual channel counter (SR400) that accumulated counts for set time windows as a function of electron impact energy. The data resulting from the 45 degree CEM was processed (as outlined above) and inputted into the SR400. An included computer program (written in DOS BASIC) was used to control the SR400 by an interfaced PC. The SR400 excitation function program provided control over the time windows for data accumulation, the number of sweeps (and the time per channel via the SR400 interface), the number of channels (typically 100), the refresh time between sweeps (which was important to make sufficiently long to ensure that the voltage dropped
to zero prior to running a new sweep), and the voltage increment. The SR400 was able to control the stepping of the applied electron energy by a small incremental voltage output that was inputted into the control of a 1 kV max Tenneelee power supply. The output from this was then connected to the electron beam power supply, as in Figure 4.13. SR400 data was transferred to the PC RAM after each channel increment and saved to the hard drive or floppy drive after each sweep.

Figure 4.24 A diagram illustrating the typical electronic modules required for excitation function studies of the photon and neutral metastable fragmentation. MCS indicates multichannel scalar; SR400 Counter is a two-channel computer controlled counter; CLK is clock; PV is pulsed valve; EG is electron gun; CEM is channel electron multiplier (see Figure 4.1); see the text for more details.
4.6 References:


Chapter 5

Molecular Cluster Results

5.1 Nitrous Oxide Clusters

5.1.1 Introduction

Interactions between electrons and N₂O molecules have been widely studied over the years. Interest has been sustained because of the need for cross section and other spectroscopic data to help explain the possible importance of this gas in various atmospheric situations [2] or the relevant mechanisms occurring in the N₂O laser [3]. Because it is known to produce a wide range of metastable fragments upon dissociation (see, e.g., References [4,5]), N₂O can be a very active species in any discharge situation.
Most of the main gas-phase electron impact cross sections were established some decades ago. Thus Mark and Dunn [6] listed partial and total ionization cross sections, Latimer and McConkey [7], Gerzanich et al. [8], and van Sprang et al. [9] measured various excitation cross sections involving emissions in the visible and near ultraviolet (UV), while Sroka and Zietz [10] extended this work to cover the vacuum UV spectral region.

Elucidation of the various dissociation mechanisms that can occur has been the subject of much effort. LeClair and McConkey [11] used a fragment-specific detection technique to study the channel involving $O^1S$ atoms. A paper by Furuhashi et al. [12] in this area gives reference to other earlier work. Very recently (Matsuo et al. 1999 [13]), coincidence techniques have been applied to investigate dissociation pathways where ionization has also occurred.

Electron impact on N$_2$O clusters has also received considerable attention, particularly by the group at Novosibirsk. Vostrikov [14] studied the formation and properties of N$_2$O clusters, Vostrikov et al. [15] investigated ion ejection from ionized clusters, and Vostrikov et al. [16,17] studied electron-induced fluorescence. The latter work was done at a constant electron impact energy of 90 eV and spectroscopic observations were confined to the visible and near UV. They also made observations of metastable particles ejected from the clusters following electron impact.

Vostrikov and colleagues suggested that the main contribution to the fluorescence intensity comes from excited molecules that have been ejected from the clusters. This conclusion was supported by Khmel and Sharafutdinov [18,19] using high-current, high-
energy (20 keV) electron beams. If this is the case then there is a serious question regarding the validity of using electron impact excitation techniques to extract expansion jet temperatures and densities. Such techniques are widely used (see, e.g., Muntz [20], Beylich [21], Holland et al. [22]). Recently, we have studied VUV and metastable emission from CO₂ cluster beams and concluded that the excited molecules are essentially decoupled from the cluster during the fragmentation process in disagreement with the conclusions of the earlier Russian work.

Electron-impact dissociative excitations of carbon dioxide clusters were investigated by photon decay, time-of-flight, and excitation function techniques [1]. An investigation of both CO₂ clusters and non-clustered gaseous CO₂ provided a means of evaluating the results from the molecular cluster work. An extensive comparison to previous metastable fragmentation and fluorescence work from electron collisions with gaseous carbon dioxide was provided.

The CO₂ clusters were generated in a typical manner (3.5 atm, with other details in Chapter 4) for this assembled equipment. Measurements of the vacuum ultraviolet fluorescence, using optical filters or no filter in-place, and a pulsed electron beam, enabled measurements of the lifetimes of the main spectral contributions. The variations of the spectral emissions as a function of electron energy were also probed. Furthermore, emissions of metastable fragments were observed as a function of time from the electron impact events. The main point to mention is that there was a significant degree of similarity between the clustered and non-clustered data. This led the authors to suggest that, following the initial interaction with the cluster in which a molecule of CO₂
becomes excited, effective decoupling of CO\textsubscript{2}\textsuperscript{*} from the cluster exists during fragmentation. Photon decay emissions and metastable and Rydberg fragments were also identified with various excited fragments from molecular carbon dioxide. The present work is an extension of these studies to the case of N\textsubscript{2}O clusters.

The experimental arrangement has been discussed in detail in Chapter 4, so only a brief outline will be included here. Clusters were produced at room temperature and typically a stagnation pressure of 3.5 atm. Under these conditions an average cluster size of approximately 100 molecules was estimated by van der Burgt and McConkey [23] for (Ar)\textsubscript{n} beams using the procedure outlined by Wormer et al. [24]. A very similar mass distribution was recorded here for N\textsubscript{2}O beams and so a similar cluster size distribution seems reasonable. Alternatively, the valve could be operated under conditions where insignificant clustering, as demonstrated by the time-of-flight (TOF) mass spectrometer in-line with the gas beam, occurred. Additionally, the electron energy scale was calibrated using the onset for N\textsubscript{2}O\textsuperscript{+} production at 12.89 eV [25]. During this calibration, which was made using the mass spectrometer, all parameters were maintained as close as possible to the values used during the excitation function measurements. Hence changes in contact potentials were avoided. The accuracy of the energy scale is estimated as ±1 eV.
5.1.2 Time-of-Flight Data

Figure 5.1 shows the signal recorded at the detector as a function of time during and following the 1.6 $\mu$s electron pulse. Suitable biasing of the detector housing and of the CEM itself excluded any scattered electrons or other charged particles. Only minor differences in this time-of-flight curve were observed when a heavily clustered or non-clustered target beam was used. A prompt photon peak, coincident with the electron pulse, is evident followed by a ‘tail’ extending for many microseconds. This indicates that some of the fragments are quite long lived as discussed in more detail later. To highlight the contribution to Figure 5.1 of metastable atoms and molecules from the target, a second curve is shown (displaced downwards from the first) which was taken with a LiF filter in front of the detector. As expected it is seen to be structureless and to fall monotonically to negligible values at longer times. A detailed analysis of this curve is given later.

Removal of the background photon component allows the details of the metastable spectrum to be seen. This is shown in Figure 5.2 where a number of structures are evident. The broad structure observed at the longest flight times is due to metastable $\text{N}_2$ molecules, probably mainly a $^1\Pi_g$ since the CEM detector will be more sensitive to this species than to $A\ ^3\Sigma_u^+$ (see Barnett et al. [5]). This feature has been widely observed and discussed by Freund and Klemperer [26], Clampitt and Newton [27], Alcock and McConkey [4], Mason and Newell [28], and Barnett et al. [5], so no further discussion will be added here except to emphasize that no significant differences
Figure 5.1  Detector signal as a function of time after a 100 eV electron beam pulse. Zero time marks the nominal start of the electron pulse. The upper curve is displaced upwards for clarity and was taken with no filter in front of the detector. The lower curve was taken with a LiF filter and thus represents photon signal only. The full curve through the photon data represents a fitted curve as discussed in the text. Note the natural log scale on the intensity axis. N₂O clusters were used.
Figure 5.2  Metastable signal as a function of time after the 100 eV electron beam pulse. The data have been retrieved from those of Figure 5.1 (N$_2$O) as discussed in the text.
in production were observed when using clustered or unclustered target beams.

The second peak has also been widely studied and is due to metastable O(^3S) or O(R) and N(R) Rydberg atoms. The peak is clearly composite in nature and its structure was observed to change with increase in incident electron energy. For example, the position of the peak maximum shifts from 13 to 10 µs after the end of the electron pulse as the electron energy changes from 50 to 100 eV. These findings, which are in accord with the earlier work of Allcock and McConkey [4] and others, indicate the existence of new production channels as the energy is increased.

The third feature, which appears at the shortest flight times, is observed as a shoulder on the photon decay, but is clearly evident as a peak in Figure 5.2 at flight times around 4 µs. This structure is barely visible on the 50 eV data and so the threshold must be close to this energy. These fragments are very energetic (> 15 eV) and must originate in steeply repulsive curves in the Franck-Condon region. (See Section 3.2.4 for discussion of possible errors involved with the released kinetic energies of this fast metastable fragment.) Earlier works deliberately suppressed the trailing edge of the photon peak and so this structure seems to have been overlooked.

5.1.3 Kinetic Energy Analysis

The TOF data presented in Figure 5.2 (and similar data obtained at other electron energies) may be readily converted to fragment kinetic energy (FKE) data knowing the distance from the source to the detector, assuming that the mass of the detected fragment
Figure 5.3  Fragment kinetic energy spectra at 50 eV (lower curve) and 100 eV (upper curve) incident electron energies. The fragment is assumed to be oxygen (see text; N₂O was used).
is known. In our case we assume that the detected fragments are oxygen atoms because they must be either $\text{O}^2(\text{S})$, which is most likely, or O(R) or N(R). Also, since the masses of O and N are similar there will only be a small modification to the calculated energy spectrum if the fragment happens to be N. The proper conversion procedure has been discussed widely (see Chapter 3).

Figure 5.3 gives fragment kinetic energy data at incident electron energies of 50 and 100 eV. This corresponds to the TOF data of Figure 5.2 where the broad feature at the longest flight times (cf. Figure 5.1) has been suppressed. The main feature on the 50 eV curve is a peak just below 5 eV. This is in very good agreement with the results of Mason and Newell [28]. At 100 eV the spectrum has become dominated by the peak at 7 eV and a broad shoulder is apparent at higher energies above 10 eV and extending to higher than 20 eV. This shoulder is the result of the peak near 5 μs in Figure 5.2 and, as stated elsewhere, represents excitation to a highly repulsive surface in the parent molecule.

5.1.4 Photon Decay Analysis

The photon decay curve shown in Figure 5.1 was fitted by a combination of four exponential decays. The fitted curve is shown as a full curve through the data points. The four lifetimes extracted from the fit are indicated in Table 5.1, in addition to the apparent lifetimes from fitting the non-clustered case. Because these data were obtained with a homemade multichannel scaler where the minimum channel width was 200 ns, the
0.12 μs lifetime of the fastest component should be taken as an upper limit to the actual lifetime. The longer lifetime components were relatively minor contributors to the total photon signal except at very long times after the initiating electron pulse. A similar analysis carried out on a decay curve obtained when there were no clusters in the target beam yielded identical curve parameters within the errors of the fitting routine for the three shortest lifetimes. The longest lifetime was measured to be 16.1 ± 2.1 μs, some 30% longer than in the clustered case. The higher density of target particles, which are present in the interaction region when clustering is present, leads to enhanced absorption or collisional deactivation of the radiating molecule. These data emphasize the fact that similar spectral emissions are obtained from clustered and non-clustered molecular beams. This is consistent with our previous findings with CO₂ beams (Kedzierski et al. [1]) and with earlier work by Khmel and Sharafutdinov [18,19].

<table>
<thead>
<tr>
<th>Clusters (μs)</th>
<th>No Clusters (μs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12±0.01</td>
<td>0.15±0.07</td>
</tr>
<tr>
<td>0.68±0.05</td>
<td>0.6±0.2</td>
</tr>
<tr>
<td>2.69±0.14</td>
<td>2.8±0.6</td>
</tr>
<tr>
<td>12.0±0.3</td>
<td>16.1±2.1</td>
</tr>
</tbody>
</table>

**Table 5.1** Lifetimes (in μs) extracted from photon decay fitting for both clustered and non-clustered N₂O impacted by 100 eV electrons and using the LiF optical filter (see text).
The longer decays are due to Rydberg atoms, O(5S) atoms, and N2(a 1Πg) molecules, all of which are known to radiate in the spectral region in which our detector is sensitive. O(5S) and N2(a 1Πg) are known to have long lifetimes; 185 µs for the former (Mason and Newell [30]) and 115 µs for the latter (Mason and Newell [31]). There does not appear to be any published data for electron-impact-induced N2O radiation covering the complete VUV spectral region. The only information available seems to be that of Sroka and Zietz [10], who show a spectrum (see Figure 5.4) that extends down to the LiF cut-off at 105 nm. Lines of atoms and atomic ions, principally nitrogen, dominate this region. It is expected that these will also be the main features below 105 nm. Other features, which may be present, are molecular bands of N2 and NO. Ajello et al. [32,33] have studied electron impact excitation of these molecules in the VUV spectral region above 40 nm and list the various spectral features, both atomic and molecular, that result. Some of these features will undoubtedly be excited in the electron-N2O interaction. The very short (< 120 ns) decay time is quite consistent with the lifetimes that would be expected from the excited N or O fragments that are being observed.

The O(5S) atoms from the dissociation process are known to be energetic and so would be lost quickly from the field of view of the detector in a few microseconds. Kedzierski et al. [1] identified a long-lived component in their study of electron-CO2 cluster interactions as being due to this species. Judging by the flight times involved, the fast metastable O atoms from N2O and CO2 would produce photons of very similar apparent ‘lifetimes’. Since the N2(a 1Πg) molecules are moving much slower (Figure 5.1) they will not disappear from the field of view as quickly and thus their apparent lifetime
Figure 5.4  Fluorescence from gaseous N$_2$O excited by 158 eV electrons. The data and designations are taken from Reference [10]. The approximate low-wavelength cut-off of our available, relevant optical filters is indicated.

will be longer. Hence we can identify the longest (12 μs) decay component with this species.

5.1.5 Excitation Functions

Figure 5.5 shows a series of excitation functions taken using different TOF windows as discussed in the experimental section. Details are given in the caption. The windows are chosen to highlight the different features in Figure 5.1. For each window
Figure 5.5  Excitation functions appropriate to different TOF windows (see Figure 5.1): (A) 0–3 μs, photons only; (B) 4–10 μs; (C) 11–21 μs; (D) 25–100 μs. The bold curves represent data taken using heavily clustered N₂O target gas beams, while the lighter curves represent data taken with no clusters present. See the text for a discussion.
Figure 5.6  Excitation functions near threshold appropriate to different TOF windows (see Figures 5.1 and 5.5): (A) 0–3 μs, photons only; (B) 4–10 μs; (C) 11–21 μs; (D) 25–100 μs. See the text for a discussion. N₂O clusters were used.
two curves are shown corresponding to clustered and non-clustered beams. These have been normalized at 200 eV in each case to highlight the differences (or lack of them) between the two situations. The curves have been corrected for variations of electron beam current with energy. An expanded view of near threshold features is shown in the series of excitation functions of Figure 5.6, corresponding to Figure 5.5.

The bottom curve represents the excitation function of the prompt photons emitted coincident with or shortly after the exciting electron beam pulse. We note that the excitation function is broad, indicating an optically allowed transition in the parent molecule. In the intermediate energy range between 30 and 140 eV, emission from the clusters is somewhat suppressed from the non-clustered case. The threshold is close to 20 eV and a clear plateau is observed near 40 eV. This region of the curve resembles the curve shown by Sroka and Zietz [10] for the single N emission at 120 nm thus supporting the suggestion given above that our prompt photons were predominantly from dissociative excitation of atoms. They suggest the process:

\[
\begin{align*}
\text{N}_2\text{O}(X^1\Sigma^+)+e & \rightarrow \text{N}_2\text{O}^+(\Sigma^+ \text{ or } \Pi) + e^+ \\
& \rightarrow \text{N}^+(3s\text{ }^4\text{P}) + \text{NO}^+(a^4\Pi_1 \text{ or } b^4\Sigma^-) + e^+ \\
& \rightarrow \text{N}(2p^3\text{ }^4\text{S_o}) + h\nu \text{ (120 nm)}. \tag{5.1}
\end{align*}
\]

They were able to show, using synchrotron radiation rather than electrons to carry out the initial excitation in the molecule, that the threshold for this process occurred at 20.5 eV. In a similar way they showed that the threshold for the total fragmentation process in which ground state O and N atoms were produced in addition to \(\text{N}^+(3s\text{ }^4\text{P})\) was 27 eV.
Closer examination of our near-threshold excitation function reveals clear discontinuities at 16, 21, and 27 eV. The latter two thresholds may be identified with the same or similar processes as were discussed by Sroka and Zeitz [10]. The 16 eV threshold is almost certainly due to two-fragment break-up of the parent molecule in which a ground state NO(X 2Π) or N 2(X 1Σg⁺) molecule is formed in conjunction with an excited N or O atom. The N atom would have to be in a doublet state and the O atom in a singlet state in order that excitation of a singlet state in the parent was assured. This is necessary because of the optically allowed nature of the initial excitation. The shoulder at 40 eV indicates the opening of new photon-producing channels. These will probably involve total fragmentation of the parent molecule with simultaneous excitation and or ionization of more than one fragment.

The second excitation function, for the time window 4–10 µs after the electron pulse, is seen (Figure 5.5) to be independent of whether the target gas beam is clustered or not over the whole energy range studied. The main threshold here is at 12 eV with subsidiary thresholds at 24 and 44 eV. The existence of the first threshold strongly supports the assignment that a major contribution to the ‘tail’ of the prompt photon pulse must be due to the in-flight decay of N 2(a 1Πg) molecules. The process:

\[ \text{N}_2\text{O}(X \ 1\Sigma_g^-) + e \rightarrow N_2O^*(1\Sigma^- \text{ or } 1\Pi) + e^* \]
\[ \downarrow \text{N}_2(a \ 1\Pi_g) + O(1S \text{ or } 1D) \]  \[ \text{[5.2]} \]

gives an appearance energy in very good agreement with our measurements. This is justified by the sharply peaked shape of the N 2(a 1Πg) excitation function as discussed
later in connection with the top curve of Figure 5.5. The existence of the other thresholds at 24 and 44 eV supports the contention given earlier that many different species and processes contribute to the photon flux.

The third excitation function, for the time window 11–21 µs, is again seen to be independent of the clustering or otherwise in the beam. Its initial threshold is at 12 eV and this is due to the underlying molecular component, especially at the upper end of the time window. These and additional data indicate that there are other thresholds at 24, 32, and 42 eV. These are due to processes that produce the fast atomic fragments, which make up the peak close to 10 µs (see Figure 5.1). Mason and Newell [28] show an excitation function for O(5S) from N₂O which has a threshold in very good agreement with the value of 24 eV in our data and some further structure around 50 eV. Our three thresholds may be connected with the three processes that have been identified as producing fast atoms. Allcock and McConkey [4] identified a process which led to O(5S) and an excited N₂ molecule. They first observed this at an energy of approximately 33 eV, quite close to the value which we observe. The 42 eV threshold which is also apparent in the data for the 4–10 µs window (Figure 5.5) represents the threshold for production of the very fast fragments (Figure 5.2) that have been discussed previously. We note that if the initial excitation processes in the parent molecule are optically allowed and if an O(5S) atom is one of the decay fragments then any companion excited N₂ molecule would also have to be in a quintet state so that correlation to a parent, singlet state would occur. It is more likely that total fragmentation of the molecule will result.
The final (top) excitation function shown in Figure 5.5 represents the excitation of the slow metastable molecules shown as the broad peak at long flight times in Figure 5.1. As discussed previously, these are \( \text{N}_2(a^1\Pi_g) \) with an observed threshold of 12 eV.

5.1.6 Conclusions

A detailed investigation has been carried out using TOF, kinetic energy, and excitation function analyses of the break-up of \( \text{N}_2\text{O} \) molecules and clusters following electron impact over the energy range from threshold to 200 eV. The data obtained are relatively insensitive to the degree of clustering in the target beam with only minor differences being observed between heavily clustered and non-clustered beams. Metastable fragments and VUV photons are used as diagnostics. The findings are consistent with the conclusion that when a molecule in the cluster interacts with an electron and fragments, the dissociation occurs as though the molecule was decoupled from the cluster. This is reasonable given the strength of the interatomic bonds in the molecule compared with the weak van der Waals bonds that hold the molecules in the cluster.

Three main interactions were observed to yield fast atomic fragments, most likely \( \text{O}(^5\text{S}) \). In each case the original transition in the parent molecule was optically allowed. The first process with the lowest excitation threshold resulted in two-fragment break-up with an \( \text{N}_2 \) molecule being the other fragment. Processes with higher thresholds involved total fragmentation of the molecule, probably accompanied by ionization as well as
excitation of the resultant fragments. The channel producing the very fastest fragments had not been reported previously.

Production of metastable N₂(a \( ^1\Pi_g \)) molecules manifested itself in two ways. Detection of the Lyman-Birge-Hopfield emission from their in-flight decay was evidenced as a long ‘tail’ on the prompt photon decay pulse and they were also detected directly when no filter was placed in front of the detector. This gave an additional broad feature on TOF curves at long times.

5.2 Other Molecular Work

5.2.1 Water Clusters

Water has been identified as a “benchmark” molecule for comparisons between theory and experiment [34]. Furthermore, electron interactions with water are significant for a multitude of subjects including radiation chemistry, environmental chemistry (for example, in the upper atmosphere, especially around the polar regions), stability of radioactive waste containers, and even in the life sciences [34]. Secondary electrons are known to be produced by high energy particles (for example, X-rays) entering the body. In particular, water clusters are being investigated since most secondary electron effects occur beyond the gas phase. It is probable that water-bonding networks would have a cluster-like geometry in and on the surface of biologically relevant molecules. Also, most secondary electrons have energies below 20 eV [34], which is within our range of
detection. This water cluster research will eventually involve isotope comparisons between H$_2$O and D$_2$O, though this work focuses on H$_2$O. The choice of water as a target is keeping to the goal of making water studies one of the research pinnacles from this group (see, e.g., References [35-39]). This molecular cluster work will also complement the CO$_2$ and N$_2$O molecular cluster research previously investigated in our laboratory.

From a practical standpoint, water is difficult to work with in a vacuum environment, compared to other non-condensable gases, especially at higher flow rates. Normally the approach of heating the sample is employed [39,40], though this causes pumping troubles due to the large water throughput. Ironically, a cold valve head (and stagnation temperature) is normally a major influence on forming large clusters. The high stagnation temperature can be an issue for cluster size determination. The alternative approach normally employed is to utilize a carrier gas. Besides using less water in the total throughput, the carrier gas normally provides a significant cooling sink for the heat of condensation (i.e., formation) of the water clusters. (However, average cluster size determination or estimation based upon scaling laws—see Chapter 2—is quite difficult and generally unreliable in this case.) Helium is a suitable choice for a carrier gas since it is known to generate water clusters [41].

Other research has demonstrated the ability of other carrier gases (e.g., CH$_4$, Ne, N$_2$, Ar), besides He, to generate water clusters [42]. It was determined that, of the carrier gases tested, Ar induced the largest average cluster size of water (about seven times greater than He). However, mixed (i.e., heterogeneous) clusters were alluded to be a possible problem for certain size ranges. In our case, Ar clusters easily form in our set-up
(see Chapter 6). Unfortunately only content fractions for water (and the carrier gas) were provided in Reference [42]. From this it is not clear if a very small Ar pressure could be used to induce significant clustering, but experience with homogeneous Ar clustering and the He carrier suggests otherwise.

Figure 5.7 demonstrates successful generation of water clusters. A helium carrier gas pressure of approximately 5 atm was used. The helium mass line is not shown. (Further “engineering” is needed to determine the optimal stagnation conditions, especially for the pressure, for generating various average sized water clusters in the current or updated apparatus.) The mass spectrum suffered from poor focusing conditions, which induced the mass “spreading” as the number of constituents increased. This was an unfortunate artefact of the accelerating grid and flight tube potentials used. Anything larger resulted in water mass bunching and resolution problems. This could be circumvented by updating the MCS timing resolution, decreasing the electron pulse width, etc. The other benefit to a system upgrade would be the determination of whether the observed water clusters are \((\text{H}_2\text{O})_N^+\), which was assumed for mass calibration purposes, or \((\text{H}_2\text{O})_N^+\cdot\text{H}^+\). This was not obvious with the present resolution.

Though it was alluded to in the introduction, water clusters will make for a wonderfully rich platform for future heterogeneous work, either by co-expansion or a pick-up technique. It is envisioned that good control over the water cluster size and the amount of dopant will allow for surface and bulk studies of various sorption and chemical processes. Significantly new and pertinent information ranging from atmospheric
processes (e.g., cloud physics and chemistry) to pharmaceutically relevant drug-water-bio-uptake is anticipated.

![Graph](image)

**Figure 5.7** Positively ionized water (H$_2$O) cluster mass signal as a function of time. A carrier gas of He at approximately 5 atm was used. See the text for further discussion.
5.2.2 Methanol

Besides targets of CO$_2$, N$_2$O, and H$_2$O, other molecular clustering was also attempted. Methanol (CH$_3$OH) was determined to be a poor candidate in terms of the current equipment. Condensed methanol in the pulsed valve head was responsible for dissolving the bonding agent (TorrSeal vacuum epoxy by Varian) holding the Viton poppet onto the aluminium rod that was attached to the piezoelectric bimorph (see Chapter 4). The rod-bimorph bonding was also compromised. Another type of pulsed valve, such as a solenoid driven design (e.g., General Valve), that does not require epoxy-bonded components, is the style to use in any future methanol cluster work. Furthermore, in the limited time window of operation, clusters of methanol were not observed. Perhaps a helium carrier gas (as used with our water cluster work), or a proper heating system, would provide some amount of condensation. Previous cluster investigations of methanol have typically involved adsorption or embedding in water clusters or various types of rare gas clusters [43-46, and references therein]. Free clusters of methanol have also been studied [44,47, and references therein], but in relatively small average sizes, which have focused on bonding and geometrical structure.

5.2.3 Methane

The motivation for investigating methane clusters was recent observations of methane condensation with cloud formation on Saturn’s moon Titan (south pole) [48,49].
Electron collisions, due to Saturn's plasma sheet, could be an interesting mechanism with the methane clouds of the N$_2$ rich Titan atmosphere. (An obvious possible by-product of the plasma sheet interaction with the Titan atmosphere would be HCN.) Previous methane cluster work has involved, for example, (inner shell) electronic and geometric structure [50]. A carrier gas of Ne was used to induce CH$_4$ condensation [50].

The attempted methane (CH$_4$) cluster investigation was not fruitful since it was not found to cluster with free expansion at room temperature up to a stagnation pressure of approximately 8 atm with our piezoelectric pulsed valve. A carrier gas, like He, would possibly provide a condensation mechanism for CH$_4$, though it was not attempted in this body of work. In this case, a pre-mixed He and CH$_4$ source or a gas diffuser would be required. Alternatively, a low temperature valve head could provide a successful way of clustering methane. The difference between water clusters and methane clusters is the difference between a hydrogen-bonded network and a van der Waals rare-gas-like bonding situation. While the water molecule has a charge polarization associated with its planar structure, the symmetry of the methane molecule precludes any significant hydrogen bonding (utilizing a charge representation) with other methane molecules nearby.

Excited neutral and ionized fragments and fluorescence following electron or photon impact on molecular methane has been well studied in the gas phase [51-62, and references therein]. Our preliminary TOF investigation of the non-clustered methane appeared to coincide with the results of Finn et al. [63]. These references are included for the curious reader.
5.3 References:


Chapter 6

Argon Cluster Results

6.1 Review of Previous Group Work

As a first attempt at a cluster experiment, van der Burgt and McConkey [1] investigated electron impact excitation of argon clusters. Besides experimental diagnostics, the main objective of this neutral argon cluster study was the investigation of neutral metastable fragments from the collision events using time-of-flight, kinetic energy, and excitation function techniques. The cluster beam was generated at room temperature using a stagnation pressure of 3.5 atm. Measurements were undertaken with a channel electron multiplier (CEM) detector located at 90 and 45 degrees in the scattering plane with the same flight distance. It was found that the detector positioned at 45 degrees was more receptive to obtaining separated processes in time, thus providing
better resolution. This can be understood from simple momentum-scattering arguments. All comparable measurements in following studies used the 45-degree arrangement (see Chapter 4). However, in order to make a comparison between the data obtained at the two detector locations, a mathematical exercise was required. A transformation from the lab frame to the center-of-mass frame provided the necessary transformation procedure (see reference [1] and Chapter 3 for a full discussion).

Using these methods, van der Burgt and McConkey were able to identify at least four different metastable production processes. An extensive discussion of the observations in the context of related cluster and condensed matter experiments was provided. The faster fragments (with 0.2 to 1.5 eV kinetic energy) were argued to be produced by \( n=2 \) excitons, which localize on an excimer or an excited trimer within the cluster and upon dissociation cause the ejection of a metastable atom. The slower fragments (less than 0.2 eV kinetic energy) were produced by \( n=1 \) excitons, which tend to localize in an excited dimer on the periphery of the cluster, leading to the ejection of a metastable atom due to weak repulsive forces with neighbouring atoms.

A second study of argon clusters, by Kedzierski and McConkey [2], investigated the fluorescence following electron impact excitation. The same piezoelectric pulsed valve used in the current body of work was used in this case, at room temperature and with a stagnation pressure of 3.5 atm. Optical filters were utilized in the vacuum ultraviolet spectral region along with time-resolved photon decay measurements. Excitation function techniques were also exploited in order to ascertain how the observed photon processes evolved with increasing electron impact energy. The electron energy
was calibrated using the onset for $\text{Ar}^+$ formation at 15.76 eV. Long lived fluorescence transitions from excited $\text{Ar}_2$ and emissions from excited atoms and ions were identified. Numerous excitation processes identified with initial excitation of $n=1$ (according to the Wannier notation) and higher $n$ excitons within the cluster were observed. For sufficiently large electron impact energies, evidence for two-center excitations was presented. These fluorescence investigations from electron-impact excitation of argon clusters were noted to closely parallel similar work from solid argon targets.

6.2 Metastable Yield

The metastable time-of-flight (TOF) results of van der Burgt and McConkey [1] were repeated using the same stagnation temperature and pressure (see Figure 6.1). A discussion of the features of Figure 6.1 has been thoroughly presented in reference [1], including fragment kinetic energy analysis and excitation function results. The motivation for repeating some of the argon cluster results, shown in Figure 6.1, was to have a set of metastable yields for convenient electron impact energies that could be used to directly compare with other TOF results from other targets (see Section 6.4 and Chapter 7).

In terms of the experimental conditions that determine relative yields for metastable fragments and photons, repeatability is an issue. Factors such as the detector sensitivity and quantum yield are difficult to control for our detection technique, which can be observed in comparing the results of Figure 6.1 with the TOF spectra of reference
Though the peak locations and features are virtually identical, relative intensities are slightly varying. Likely reasons are different piezoelectric bimorph performance and channel electron multiplier (Csl-coated) surface quality. Thus, future multi-target comparisons should use a relative flow technique, whereby experimental uncertainties are cancelled out as much as possible. The general concepts are to calibrate the experimental conditions using a previously studied target (and one that is intended for direct comparison), and then repeat the experiment immediately after, using the new target. As a consistency check, it is generally good practice to take measurements with the known target (i.e., previously studied target) both before and after the measurements on the new target.

In the case of a heterogeneous cluster investigation, a convenient order would be $A_N$, $(A_xB_y)_N$, and $B_N$ targets, while taking into account the stagnation pressures and average cluster sizes. See Section 6.4 for further discussion. Furthermore, the distinct TOF spectra of the homogeneous cluster targets could be scaled to the heterogeneous TOF results, such that new processes would become evident. A specific methodology, due to possible relative intensity and cluster size issues, would need to be developed. This would naturally follow the abovementioned work.
Figure 6.1  Detector signal as a function of time (Ar clusters were used). The incident electron beam energies are: A 20 eV; B 30 eV; C 40 eV; D 50 eV; E 100 eV; F 200 eV. All time-of-flight curves are displaced upwards except for the 20 eV curve.
6.3 Variation with Pressure

6.3.1 Time-of-Flight

As further continuation of the results of van der Burgt and McConkey [1], the TOF yield of metastable fragments was investigated for various stagnation pressures and thus average cluster sizes. This work was actually suggested in reference [1]. A series of papers [3-7] investigated fluorescence excitation spectra via synchrotron excitation from various average-sized rare gas clusters. The present work looks at non-radiative decay channels that were seemingly overlooked in the aforementioned series of articles. It is also worthwhile noting that in these articles, the sputtering channels were assumed to be of minor importance (see, e.g., Reference [8]). Latter work by some of the same authors [9] suggested that the sputtering channels were possibly more important than was previously thought and a need for kinetic energies was stated.

The variation of metastable fragment yield in time as a function of average cluster size was investigated using several electron impact energies. All work in this section was recorded using constant experimental conditions and within a short time frame. The empirical cluster scaling laws presented in Section 2.5 and the experimental parameters discussed in Chapter 4 (cf. Figure 4.9) provide the required considerations for the data presented in Table 6.1. Table 6.1 indicates the approximate average neutral argon cluster size for varying stagnation pressures. The mean cluster sizes in parentheses represent an alternate possibility (see Equation 2.11 and the included discussion).
<table>
<thead>
<tr>
<th>Pressure (psi)</th>
<th>Mean Cluster Size</th>
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<tbody>
<tr>
<td>15</td>
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<td>20</td>
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<td>177 (148)</td>
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<td>70</td>
<td>255 (197)</td>
</tr>
<tr>
<td>80</td>
<td>349 (252)</td>
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</table>

Table 6.1  Average cluster sizes determined for Ar, based on the experimental parameters (see Chapter 4) and cluster scaling laws (see Chapter 2).

Figure 6.2 shows TOF data, with the stagnation pressures indicated in the figure caption, taken at an impact energy of approximately 25 eV. The TOF curves are all displaced upwards, except for the 15 psi data. The overall fragmentation pattern is quite similar over the studied pressure range. There are, however, several features to note. First, the two obvious peaks do not appear to shift in time for different pressures. Also, the relative intensity of the fast peak is strikingly out of proportion relative to the slow peak for stagnation pressures of 20 and 40 psi compared to the other TOF curves. This likely indicates that there is an efficient production mechanism at the pressure values for the fast peak. The fast peak is also observed to broaden with increasing average cluster
Figure 6.2 Metastable signal as a function of time after the 25 eV electron beam pulse. The Ar stagnation pressures are: A 15 psi; B 20 psi; C 30 psi; D 40 psi; E 50 psi. All time-of-flight curves are displaced upwards except for the 15 psi curve. See text for further details.
size, with possibly new structure contributing as the shoulder, near 70 μs, that is observable at larger pressures.

Furthermore, as the average cluster size increases, so too does the structure between the two peaks. This increase near 100 μs is most noticeable in the 50 psi TOF data of Figure 6.2. A comparison of the 50 psi (curve E) data at 25 eV of Figure 6.2 with curves A and B of Figure 6.1 demonstrates the elevated level, but also a change in relative heights (discussed above) of the various TOF features. This is probably due to different detector sensitivities in the two data sets.

Figure 6.3 shows the TOF metastable yield at various stagnation pressures (indicated in the figure caption) for an electron impact energy of approximately 105 eV. The TOF spectra have been shifted upwards, except for the 20 psi curve. Further, the photon decay has been suppressed for the convenience of viewing the metastable signal, while noting that no observable fragments were excluded at these impact energies (cf. Figure 6.4). Some of the structure at the longest flight times is due to randomly directed background argon atoms that have been excited into metastable states as they pass through the electron beam. It is clear that additional processes are contributing to the TOF signal since the structure near 210 μs is observed to broaden and shift to shorter times with increasing stagnation pressure. Furthermore, the structure at short flight times (less than 100 μs) is observed to increase in complexity and change significantly over the pressure range.
Figure 6.3  Metastable signal as a function of time after the 105 eV electron beam pulse. The Ar stagnation pressures are: \( A \) 20 psi; \( B \) 30 psi; \( C \) 40 psi; \( D \) 50 psi; \( E \) 60 psi; \( F \) 70 psi, \( G \) 80 psi. All time-of-flight curves are displaced upwards except for the 20 psi curve. See text for further details.
Figure 6.4  Metastable signal as a function of time after the 105 eV electron beam pulse. The Ar stagnation pressures are: A 15 psi and B 20 psi. The 20 psi curve is displaced upwards. The insert shows a magnified view of the features near 100 μs. See text for further details.
Moreover, as discussed with Figure 6.2, the TOF structure of Figure 6.3, near 100 µs, is observed to broaden and increase in relative height as the average cluster size increases. At this impact energy, a feature at approximately 100 µs is actually more apparent for smaller stagnation pressures (i.e., 15 and 20 psi) as shown in Figure 6.4. A very fast fragment peaked at approximately 16 µs, also becomes evident in Figure 6.4. It is not observable in the 25 eV impact energy TOF data. Additionally, a shoulder is apparent between the 16 and 55 µs peaks.

6.3.2 Kinetic Energy Analysis

The TOF data of Figures 6.2-4 can be readily converted to fragment kinetic energy (FKE) data via the procedure described in Chapter 3. In this case, the flight distance was taken as 122 mm and the atomic mass of argon (40 amu) was used assuming a two-body dimer break-up. This assumption is reasonable based upon our group experience with the heavy rare gases (Ar, Kr, and Xe).

Figure 6.5 represents the FKE transformation of the TOF data of Figure 6.2. The insert shows structure at small kinetic energy values. This mainly is due to the random background argon gas that happens to pass through the electron beam and reaches the CEM detector. For room temperature (~ 295 K), a most probable kinetic energy of approximately 0.013 eV is expected, which is consistent (via extrapolation) with our results. Anything less than 0.037 eV must be due to the background monomer
contribution since momentum arguments rule out dimer fragments, from the cluster beam with energies below 0.037 eV, from reaching the detector.

The most interesting feature of Figure 6.5 is the peak at approximately 1 eV (~ 55 μs). It appears to shift to smaller kinetic energy values with increasing stagnation pressure. Perhaps the most remarkable point to note is the characteristic Gaussian shape of the 1 eV FKE process in curve A, which falls mostly within 0.5 to 1.5 eV. This shape corresponds to fragmentation from a purely repulsive state (see Chapter 3) for an Ar dimer.

Previous Ar cluster work [1], using a stagnation pressure of 3.5 atm (~ 50 psi), identified a dimer fragmentation process with a FKE of approximately 1 eV that was essentially due to the bulk or surface n=2 exciton (see Figure 6.8 and Reference [1] for a full discussion), which was not distinguishable within the experimental energy resolution. The feature in Figure 6.5 may very well be this process. Moreover, the increase of structure at lower FKEs, compared to the 1 eV peak, as the stagnation pressure (cluster size) is increased, may be due to sputtering from deeper layers in the clusters. Perhaps the surface sputtering results in the 1 eV peak, while the bulk contribution progresses to smaller FKEs, via elastic scattering and structure deformation losses, as the surface depth increases. Additionally, the higher-pressure curves (20 psi and larger) indicate a tail extending to larger kinetic energies. The small TOF structure near 100 μs is not obvious in Figure 6.5, though it would be at about 0.3 eV. Figure 6.6 represents the FKE transformed data of Figure 6.3 (see the figure caption for further details). The small TOF structure, greater than about 85 μs, appears as a shoulder at approximately 0.3 eV. This
Figure 6.5  Fragment kinetic energy spectra derived from the time-of-flight (TOF) data of Fig. 6.2 (see text). The incident electron energy is 25 eV with Ar stagnation pressures of $A$ 15 psi, $B$ 20 psi, $C$ 30 psi, $D$ 40 psi, and $E$ 50 psi. All curves are displaced upwards except for the 15 psi curve. Some TOF times are indicated under their corresponding kinetic energies.


Figure 6.6  Fragment kinetic energy spectra derived from the time-of-flight (TOF) data of Fig. 6.3 (see text). The incident electron energy is 105 eV with Ar stagnation pressures of \( A \) 20 psi, \( B \) 30 psi, \( C \) 40 psi, \( D \) 50 psi, \( E \) 60 psi, \( F \) 70 psi, and \( G \) 80 psi. All curves are displaced upwards except for the 20 psi curve. Some TOF times are indicated under their corresponding kinetic energies.
Figure 6.7  Fragment kinetic energy spectra derived from the time-of-flight (TOF) data of Fig. 6.4 (see text). The incident electron energy is 105 eV with Ar stagnation pressures of A 15 psi and B 20 psi. The 20 psi curve is displaced upwards. Some TOF times are indicated under their corresponding kinetic energies.
structure is likely the same identified in Reference [1] as process 3. In such a case, arguments in Reference [1] indicate that this is possibly due to the n=1 exciton (see Figure 6.8), with an onset near 11.6 eV. In addition, the 70 μs shoulder on the 55 μs (~1.0 eV) TOF peak emerges as a significant contributor to the FKE spectra, which is peaked at approximately 0.7 eV. Again, as the stagnation pressure increases, the distinct FKE structure becomes more complex.

The resolution of Figure 6.6 has been extended in Figure 6.7 (see the figure caption) for stagnation pressures of 15 and 20 psi. The 0.7 eV and 1.0 eV FKE peak structures (with a hint of the 0.3 eV contribution) are observable, as are several new structures. The TOF structure near 35 μs appears in the FKE distributions peaked at approximately 2.2 eV with a tail to larger kinetic energies. The fast TOF peak (~16 μs) is observable in Figure 6.7 as a very broad structure with a maximum near 9 eV. This is less obvious in the 15 psi data. Energetic considerations (see Figure 6.8) indicate that these fast neutral fragments (~16 μs and 35 μs) likely originate from a dimer that has been simultaneously ionized and excited. It is noted that Ar₂⁺ is well known to form in argon clusters [10].

Though the results of this section are exciting and reveal new experimental paths for future investigations, a comprehensive investigation will take a lot of time and effort! Also, a fluorescence study of the evolution of exciton energy values for n≥2 excitons has shown a blueshift compared to the bulk values [6]. The blueshift increases with decreasing cluster size. Excitation function and TOF techniques can be applied to this interesting problem, but to do so at each stagnation pressure would involve an enormous
Figure 6.8  (Left) Location of excitons in solid argon. Numbers indicate principle quantum numbers of bulk excitons; \( L \) is a longitudinal excitation; \( s \) is a surface exciton; \( E_g \) is the energy of the band gap. (Right) Schematic diagram of Ar\(_2\) potential energy curves. Only two of the repulsive potential energy curves leading to \( \text{Ar}^* (3p^5 4s) + \text{Ar}(1S_0) \) are shown. Arrows indicate a possible sequence of steps occurring in electron-impact fragmentation of argon clusters (assuming the localized exciton is an excimer; see discussion of process 1 in the Reference [1]). This figure has been taken from Reference [1].
amount of work.

It is not immediately clear whether the results of this section warrant such a comprehensive investigation. (Perhaps with a next generation cluster experiment, using better resolved electron energies and narrower pulses, the exact energy pathways will become tangible.) What is clear, however, is that the metastable fragmentation dynamics vary greatly with not only changing electron impact energy, but also with cluster size. From other results in this body of work at a given stagnation pressure, the impact energy influences the TOF metastable fragmentation yields via the accessible energy levels and potential energy curves. On the other hand, the pressure effect on the TOF distributions is essentially a different process. This is understandable in terms of the larger fraction of dimers, trimers, and other small clusters in the composite cluster beam at smaller pressures. Alternatively, part of the explanation may be due to the greater significance of surface, as compared to volume, effects for the smaller clusters. Thus different investigated average cluster sizes have, in general, different available energy and dissociation dynamics.

6.4 Heterogeneous Argon-Krypton Clusters

The TOF spectra presented in Figure 6.9 should be considered as a “proof-of-principle.” The intended study was that of a co-expanded heterogeneous mixture of Ar and Kr. However, as it turned out, the precise control of the gas mixture ratio was not easily obtained with the available equipment. Future work would most reliably utilize
“factory mixed” gas cylinders of specific proportions. For instance, heterogeneous cluster studies of Ar and Xe mixtures [11] have determined that for concentrations greater than 3% of Xe in the co-expanded mixture, only pure Xe clusters are formed.

The experimental setup was modified between data runs, such that curves B and C used a crude mixing chamber (see Chapter 4), while curve A was acquired from an in-house, premixed bottle of Ar and Kr at roughly a 50-50 content ratio (via pressure). Though specific and quantitative results are not considered reliable in this case, the TOF data of Figure 6.9 certainly demonstrate that this is a promising area for further study. A direct comparison with the TOF data at comparable electron impact energies of Ar clusters (see Figure 6.1 and Section 6.3) and Kr clusters (see Figure 7.2) shows that there are peaks (e.g., at about 40 µs) in Figure 6.9 that presumably are due to the ArKr dimer. (However, the results of Section 6.3 could indicate that cluster size effects are contributing.) These ArKr excimer TOF peaks are not present in the homogeneous Ar and Kr cluster TOF data. Furthermore, the prominent feature peaked near 60 µs in Figure 6.2 is noticeably absent from the data of Figure 6.9.
Figure 6.9    Metastable signal as a function of time. The incident electron beam energies are: $A$ 20 eV; $B$ 50 eV; $C$ 100 eV. All time-of-flight curves are displaced upwards except for the 20 eV curve. The insert shows a magnified view of the features between 25-125 µs for curve $A$. See text for further details. A heterogeneous mixture of Ar and Kr was used.
6.5 References:


Chapter 7

Krypton Cluster Results

7.1 Introduction

Krypton is a valuable continuum light source in the vacuum ultraviolet (VUV) [1,2]. Pulsed lasing in the VUV has also been observed via Kr excimers [3] and various non-linear techniques [4-6]. Situations involving relatively high pressure can generate clusters that have even been shown to increase harmonic radiation yields when using xenon [7]. In addition, there has been considerable interest in the excitation of Kr clusters, in the various mechanisms that can occur, in the different possible decay channels, and in how the size of the cluster influences the outcome. Much of the experimental work has involved synchrotron radiation [8-17]. Recently, site-specific inner shell excitation in Kr clusters was studied using synchrotron radiation [12]. In
many cases in the study of neutral Kr clusters the total unresolved fluorescence was observed as a function of incident photon wavelength, so-called fluorescence excitation spectroscopy [13,14]. In some cases [14], the fluorescence was wavelength analyzed and in others [15], the temporal behaviour of the fluorescence was investigated.

Electron impact excitation (1 keV) has been used by Verkhovtseva et al. [18] to investigate rare gas clusters. In these studies, Kr cluster fluorescence in the VUV was wavelength-resolved. The VUV spectrum from reference [18] shows several features, in addition to the atomic resonance lines, resulting from cluster effects. (See Figure 7.1.) Bondarenko et al. [19] later re-examined the VUV spectrum of the rare gas clusters by electron impact (same conditions) as a function of mean cluster size. For Kr clusters, an additional feature peaked at 159 nm was observed with larger mean cluster sizes. The spectral peak at 159 nm was attributed to radiative decay of Kr excimers formed in ionic Kr clusters. Karnbach et al. [17] observed a broad continuum between 126 and 142 nm for small (N<50) Kr clusters (using synchrotron radiation), which was not identified in Refs. [18,19]. This continuum is attributed to the decay of krypton excimers desorbing from the cluster surface. Interestingly, Gerasimov et al. [2] show several data plots with this 126-142 nm continuum, though no distinct identification was made.

The present work involving electron beam excitation of Kr clusters is a continuation of previous argon cluster studies [20,21, and see Chapter 6]. A variety of techniques have been used to probe the electron-cluster interaction, to obtain spectroscopic information on the potential energy curves of the Kr dimer and to obtain
Figure 7.1  Fluorescence from Kr clusters excited by 1 keV electrons. The data and designations are taken from Ref. [18]. The approximate low-wavelength cut-off of the filters used in the present work is indicated.

significant new information on the cluster dissociation dynamics. The work complements the wealth of information that is currently available from photon impact studies.

The experimental details have been discussed in Chapter 4, so only a brief outline will be included here. Clusters are produced at room temperature typically at a stagnation pressure of 3.5 atm. Under these conditions, an average cluster size in the
hundreds was estimated using the procedure in references [24,25] (and see Chapter 2). The upper wavelength cut-off of the CEM was determined by the CsI coating and was approximately 180 nm though, from the work of Bondarenko et al. [19] and Möller et al. [26], insignificant VUV emissions from the clusters at wavelengths longer than 180 nm should be expected. The electron energy was calibrated using the onset for Kr$^+$ formation at 14.00 eV (88.59 nm) [8-10]. During this calibration, which was made using the mass spectrometer, all parameters were maintained as close as possible to the values used during the excitation function measurements. The accuracy of the energy scale is estimated as 1 eV. The onset for Kr ($^2P_1 \rightarrow ^1S_0$) VUV fluorescence at 10.03 eV was also used for energy calibration [27]. (Note that here and elsewhere we use this simple L-S nomenclature for the $^3P_1$ state. More rigorously, because of the intermediate coupling situation it should be described as the $5s[3/2]_J=1$ state).

7.2 Time-of-Flight Data

Figure 7.2 shows the signal recorded at the detector as a function of time during and following the 1.6 μs electron pulse. Several time-of-flight (TOF) curves are shown (displaced upwards) at various electron energies for the clustered beam. The series of TOF curves taken at different electron-impact energies show the cluster fragmentation pattern and signal intensity varying significantly. Suitable biasing of the detector housing and of the CEM itself excluded any scattered electrons or other charged particles. A prompt photon peak, coincident with the electron pulse, is the suppressed structure on the
**Figure 7.2** Detector signal as a function of time. The incident electron beam energies are A: 20 eV, B: 30 eV, C: 40 eV, D: 50 eV, and E: 100 eV. All time-of-flight curves are displaced upwards except for the 20 eV curve. Kr clusters were used.
**Figure 7.3** Detector signal as a function of time taken with an electron impact energy of approximately 14 eV. Kr clusters were used.
Figure 7.4  Metastable signal, indicating at least four contributing processes, as a function of time after the electron beam pulse at 20 eV. The solid curve (4) with a maximum at 320 μs is representative of a process identified using lower incident electron energies (see text; Kr clusters were used). Subtraction of this curve from the 20 eV data in Figure 7.2 yields the data set shown. The dashed curves represent an approximate deconvolution into three separate structures, 1-3.
left of Fig. 7.2. It exhibits a characteristic tail extending for many microseconds. This feature indicates that some of the excited Kr atoms or molecules are rather long lived. The TOF data demonstrate increasing signal intensity for the two peaks at intermediate flight times (referred to as the 75 µs and 112 µs peaks, respectively from the left) relative to the broad peak at longest flight times (referred to as the 320 µs peak). These peaks are due to the detection of metastable Kr atoms. At higher electron impact energies, the two peaks (75 µs and 112 µs) at intermediate flight times merge into a single peak. We note that because of its heavier mass and hence longer flight times, better resolution of these structures is achieved than was achieved for Ar [20].

Some of the structure observed at the longest flight times is due to randomly directed background krypton atoms which have been excited into metastable states as they pass through the electron beam. However, most of the structure is due to additional processes. That additional processes are present is evident from the observation that the maximum of the structure at the longest flight times (320 µs peak) shifts to shorter times with increasing electron beam energy. To illustrate the compound nature of this structure we follow the procedure outlined in reference [20]. We assume that the TOF distribution from a single process should be independent of incident electron energy and also that the TOF distribution taken at the lowest incident energy (~ 14 eV; see Figure 7.3) should be representative of just a single process. Thus we take the shape of the feature peaked at 320 µs and scale it suitably so that it matches the trailing edge of the feature taken at 20 eV incident energy. This fit is represented by the solid curve in Fig. 7.4. Subtraction of this scaled data from the original 20 eV data results in the data set shown in Fig. 7.4.
Deconvolution of these data into three separate structures is shown by the dotted lines on Fig. 7.4. All of this reveals that at least four processes (numbered 1-4 on Fig. 7.4) are contributing to the observed spectrum. Excitation function observations (discussed later) will include further details on the indicated processes.

Removing processes 3 and 4 from the data of Fig. 7.2 using a velocity distribution fit (see reference [28]) allows us to zero in on processes 1 and 2. The result is shown in Fig. 7.5. Additional TOF data (not displayed) demonstrate that the 75 μs and 112 μs peaks appear at approximately the same onset energy, within the energy resolution of our system. This is consistent with excitation function observations discussed later. The maxima of the two metastable peaks appear not to shift with increasing energy, though the first peak, which appears at the shortest flight times, is observed to broaden.

7.3 Kinetic Energy Analysis

The TOF data displayed in Fig. 7.5 can be converted readily to fragment kinetic energy (FKE) data knowing the distance from the source to the detector, assuming that the mass of the detected fragment is known (see reference [29] and Chapter 3 for details). In this case, we assume that a krypton metastable atom is detected which originates from an excited dimer. This is reasonable based upon previous argon results [20].

Figure 7.6 presents fragment kinetic energy data at incident electron energies of 20, 30, and 40 eV obtained using the data of Fig. 7.5. The main feature at all displayed electron energies is peaked at roughly 0.5 eV. This corresponds to the peak near 112 μs
Figure 7.5  Metastable signal due to processes 1 and 2 as a function of time after the electron beam pulse at incident energies of A: 20 eV, B: 30 eV, and C: 40 eV. The data have been retrieved from those of Figures 2 and 4 as discussed in the text (Kr clusters were used). All curves are displaced upwards except for the 20 eV curve.
Fragment kinetic energy spectra derived from the time-of-flight (TOF) data of Figure 7.5 (see text; Kr clusters were used). Incident electron energies are A: 20 eV, B: 30 eV, and C: 40 eV. All curves are displaced upwards except for the 20 eV curve. Some TOF curves are indicated in parentheses under their corresponding kinetic energies.
from the TOF data. As the incident electron energy increases, the maximum appears to shift slightly, from approximately 0.5 eV at 20 eV impact energy to approximately 0.4 eV at an impact energy of 40 eV. This 0.4 eV fragment kinetic energy value is fortuitously similar to the reported value of 0.4 eV obtained with solid targets using high energy (2.5 keV) electron impact [30]. The solid target observation was argued to be the result of the repulsion of ground-state atoms after radiative decay of vibrationally relaxed dimers (M band) [30]. The M band is recognized as the second continuum of the cluster fluorescence, which results from strongly bound states, i.e., $^{1,3}\Sigma_u^+$ [17].

The other metastable peak near 75 µs (in Fig. 7.5) gives rise to the FKE shoulder at energy slightly greater than 1 eV. This is clearly a minor feature relative to the first FKE peak. As the incident electron energy increases, the shoulder around 1 eV becomes less prominent. The long tail to the FKE spectrum, which extends to higher values as the incident electron energy is increased, suggests that the inner repulsive wall of the parent-potential energy curve is being accessed or that new production channels are opening up. This is consistent with the slight broadening observed in the fastest metastable peak (near 75 µs), Fig. 7.2. It should also be noted that the 215 µs metastable peak (process 3; see Figure 7.4) corresponds to a fragment kinetic energy of about 0.14 eV. This peak was not transformed into a FKE curve because of poor signal-to-noise. This becomes particularly significant at longer times because of the $r^3$ factor that appears in the transformation (see reference [29] and Chapter 3). We note that the 320 µs peak corresponds to a fragment kinetic energy of 0.06 eV, significantly higher than thermal.
7.4 Excitation Functions

Figure 7.7 shows a series of excitation functions taken using different TOF windows as discussed in the experimental section. The curves are displaced upwards for clarity with additional details given in the caption. The windows are chosen to highlight the different features in Fig. 7.2.

The bottom curve of Figure 7.7 represents the excitation function of the prompt photons, without the use of an optical filter, emitted coincident with or up to 5 μs after the exciting electron beam pulse. We note that the excitation function is broad with a maximum near 75 eV, indicating that the excitation process is optically allowed. The threshold is in the vicinity of 10 eV and a distinct shoulder is observed around 25 eV, which indicates that a new excitation channel is opening. This additional photon-producing channel possibly involves simultaneous excitation and ionization or possibly sequential excitation of two atoms in the cluster. The 10 eV onset is consistent with the threshold for exciting the atomic resonance lines, $^1P_1 \rightarrow ^1S_0$ and $^3P_1 \rightarrow ^1S_0$, within the energy resolution of our set-up. Lifetime fitting, not presented here, involving the trailing edge of the prompt photon peak, Fig. 7.2, suggest that at least three different decays are contributing, one as long as 3.5 μs. Some of these will be due to decay of excimers within the cluster [15,18,19,32].

Figure 7.8 shows two excitation functions for photon emission, with the time windows indicated in the caption, taken using a BaF$_2$ optical filter. With the BaF$_2$ filter installed, the only emissions that are detectable are those above about 135 nm. From
Figure 7.7  Excitation functions appropriate to different time-of-flight windows (see Figure 7.2): A 0-5 μs, photons only; B 50-90 μs; C 90-150 μs; D 150-850 μs. All curves, except A, are displaced upwards for clarity. See the text for further discussion. Kr clusters were used.
**Figure 7.8** Excitation functions, taken using a BaF$_2$ filter (see Figure 7.1), appropriate to different photon decay time windows (see Figure 7.2): A 0-5 μs and B 3-9 μs. Curve A is displaced upwards for clarity. See the text for further discussion. Kr clusters were used.
Figure 7.1, this appears to be a structureless, low relative intensity continuum stretching past 160 nm. As discussed in Section 7.1, the later work by Bonderanko et al. [19] demonstrated an additional feature peaked at 159 nm for large average sized clusters of Kr. A comparison of curves A from Figures 7.7-8 clearly indicates a change in observed optical processes, as evident from Figure 7.1. Using similar arguments that were utilized by this group for Ar clusters [21], the shoulder in curve A of Figure 7.8, near 35 eV (and peaking at roughly 55 eV), could have a possible origin as simultaneous ionization and excitation of Kr atoms within the cluster. This would then be identified with the feature peaked at 159 nm. The feature at lower energies (i.e., the shoulder near 25 eV) in curve A seems to be present in curve B, with little relative contribution from the more energetic features of curve A, such that both curves appear to have the same onset energy (~ 10 eV). If this is the case, then the main contributor of curve A has relatively fast fluorescence decay compared to what is contributing to curve B of Figure 7.8. From Figure 7.1 and the comparable Ar cluster fluorescence study [21], curve B is possibly mainly due to radiative emission from the $^3\Sigma_u^+ \rightarrow ^1\Sigma_u^+$ transition, with some overlap from the longer lifetime tail of the processes giving rise to curve A. Furthermore, this assignment is consistent with a 3.5 $\mu$s apparent lifetime, discussed above, for Kr$_2$ radiative emission.

The second excitation function (curve B, Figure 7.7), for the time window 50-90 $\mu$s after the electron pulse, relates to process 1 (see Figure 7.4) and is seen to be broad with a maximum around 135 eV (with a small local maximum near 20 eV), and a threshold at 11-12 eV. Note that this excitation function has a TOF window that includes
a portion of the other metastable signal from process 2 (peaked near 112 μs). An additional appearance energy was observed at about 27 eV, indicating the presence of an additional process which we will refer to as process 1a. This onset at approximately 27 eV possibly corresponds to simultaneous excitation and ionization based upon similar argon results [20]. Process 1a yields fragments with kinetic energies of approximately 1 eV, similar to process 1 but with a relatively larger full width half maximum.

The third excitation function in Figure 7.7, for the time window 90-150 μs, is also broad with a maximum around 100 eV (with a local maximum near 20 eV). Clearly, different processes are dominant for this curve compared to the second excitation function. The mean kinetic energy of these fragments is around 0.5 eV (see Fig. 7.6) which is about half that of the fragments resulting from process 1. The process 2 threshold is observed near 11.5 eV with additional processes appearing at higher energies. As in the second excitation function, a second onset at approximately 27 eV was identified (process 2a), again with a fragment kinetic energy in the range of the FKE of process 2. The excitation functions have significant overlap with respect to the TOF peaks (see Figs. 7.2-5). The reason for the 27 eV onset of process 2a is probably similar to that for the sister excitation (process 1a) discussed above. Given the different excitation function shapes of processes 1a and 2a, and the different energies of the resulting fragments, different parent excited states must be involved.

The final (top) excitation function displayed in Fig. 7.7, with a threshold near 10 eV, represents the excitation mainly of process 4. This is shown as the broad peak at long flight times in Fig. 7.2. Because these atoms are being detected hundreds of
microseconds after the exciting electron pulse, they must be metastable in character, most possibly the lowest lying metastable states, $5s[1/2]_{J=0}^3P_0$ and $5s[3/2]_{J=2}^3P_2$ states. The sharply peaked nature of the excitation function, with a maximum near 20 eV, indicates initial excitation via an exchange process to a state of different multiplicity to the ground state. Since krypton has a singlet ($^1S_0$) ground state, the detected excited state must have a strong triplet contribution. It is well known that the lowest lying excited metastable states of Kr have a strong triplet component [1,31,32]. Because the 320 µs peak dominates the signal in the lower energy region, an identification of the onset energy for the 215 µs peak (process 3) using excitation function data is not possible. However, TOF data suggest a threshold between 14 eV and 20 eV (certainly above 10 eV).

Figure 7.9 shows some potential energy curves for Kr$_2$ and indicates the known energy positions of the Kr atom and exciton energies. Data from references [8,13,16,27,31,33-36] have been used to produce this figure. Excitation function and FKE observations along with Fig. 7.9 indicate that the two fastest metastable fragments originate via a bound state of a manifold above the 5s states followed by decay to a repulsive state that leads to fragmentation. Interestingly, an infrared fluorescence experiment [37] on xenon dimers has recently demonstrated a broad continuum (centered at about 0.95 eV) that is possibly produced by a bound-repulsive transition within the excited state manifold. A similar process may be occurring here. The 11-12 eV onsets of processes 1 and 2, yielding the two fastest metastable fragments, suggest that these were possibly produced via initial excitation of excitons in the cluster. Though our energy resolution does not allow for an exact exciton identification, it is known that Kr dimers
Figure 7.9 (Left) Location of excitons in solid krypton [8,13,16,33,34]. Surface excitons are indicated by s (broken line) and solid lines are for bulk excitons (transverse and longitudinal). (Right) Schematic diagram of Kr₂ potential curves adapted from References [31,35,36] with atom energy positions from References [27,35]. The arrows indicate a possible excitation scheme, such as that discussed in the text, for fast metastable atom production.
undergo desorption from small Kr clusters (our clusters being somewhat larger, hundreds of atoms) only after excitation of surface states [14]. It should be noted that this Kr situation is different than the Ar case (see references [14,20,21]) in that bulk excitons can cause Ar₂ desorption from cluster surfaces. An onset of 11 eV (with small Kr clusters) possibly corresponds to the excitation of surface excitons close to this energy [8,13,16,33,34]. The approximately 27 eV threshold (processes 1a and 2a) is possibly due to simultaneous ionization (14 eV) and excitation (around 13 eV), paralleling our previous Ar work [20]. The 10 eV threshold of the slowest fragments (process 4) indicates that here the excitation of the small cluster proceeds via a surface exciton near 10 eV, though an exact exciton identification cannot be made within our energy resolution.

7.5 Conclusions

Time-of-flight and excitation function measurements of the fragmentation of neutral krypton clusters following electron impact have been presented. At least six different production mechanisms for metastable neutral fragments have been identified in addition to three different channels leading to prompt photon production.

The metastable neutral fragments were ejected from the cluster with energies in the range 0.06 to 1 eV. The particular energy distribution obtained depended on the excitation energy. The fragments with the highest kinetic energy resulted from the population and subsequent dissociation of repulsive states of Kr₂. Measured thresholds
were in the neighbourhood of 10-12 eV suggesting that exciton production was occurring. Secondary thresholds at 27 eV possibly involved simultaneous excitation and ionization or possibly two sequential excitations within the cluster.
7.6 References:


Chapter 8

Xenon Cluster Results

8.1 Introduction

Rare gases have traditionally been explored in the solid [1-8] and gaseous [9-19] states. However, in order to bridge the gap in our understanding of these two realms, investigations of the properties of the evolution from the atomic to condensed states are necessary. The majority of homogeneous heavier rare gas cluster (RGC) investigations have focused on either optical issues, such as high-harmonic generation [20], X-ray production [21], and absorption and fluorescence [22-28], or various topics involving ionized products [29-36]. The ionized RGC studies are popular since the charge makes for reasonable experimental control and manipulation. Neutral cluster investigations are more challenging due to, for instance, the general lack of control of the investigated
cluster size. Recently, neutral RGC research has increased in complexity by way of inventive, sequential, pick-up techniques (see, for example, references [27,37,38]) allowing for richer RGC research in the future.

There have been some studies, in addition to standard mass spectrometry, of RGCs utilizing electrons as probes. Verkhovtseva et al. [39] used 1 keV electrons to probe RGCs via a wavelength-resolved study of the resultant vacuum ultraviolet (VUV) fluorescence. Bondarenko et al. [40] extended the investigations of reference [39] to include xenon clusters as a function of average cluster size and to longer VUV wavelengths. Kovalenko et al. [41] studied the structure of medium to large xenon clusters by way of electron diffraction, determining that xenon clusters with an average size of 2,000 or more have an fcc structure with “deformation”-type stacking faults. Allan [42] investigated small xenon clusters by way of electron energy loss spectroscopy and observed weak satellite bands of the two lowest excited states (\(^3\)P\(_2\) and \(^3\)P\(_1\)). Information for energy losses larger than approximately 9 eV does not seem to be available.

The present investigation of electron impact of xenon clusters is a continuation of previous RGC studies by our group involving argon [43,44] and krypton [45] clustered targets. This work utilizes an assortment of methods to explore the electron-cluster interaction, to investigate the potential energy curves of the xenon dimer, and to provide considerably new information on the dynamics of cluster dissociation. Further, this body of work directly addresses a data need for released kinetic energy distributions of excited fragments from rare gas clustered targets [37].
Discussions of our experimental details have already been presented in Chapter 4, so only salient information follows. Xenon clusters were generated at room-temperature (295 K) and a stagnation pressure of 3.5 atm, corresponding to an average cluster size in the thousands. If necessary, the system could be operated under conditions where negligible clustering occurred. Furthermore, the coated CEM was limited to detection of neutral metastable species with internal energies above about 7 eV [43]. We note that this resulted in relatively poor detection efficiency for xenon metastable fragments and some optical emission compared to our previous rare gas cluster studies where fragments with more internal energy were being considered. The electron energy was calibrated using the onset for Xe$^+$ ($^3P_{3/2}$) formation at 12.13 eV [9,23,30,50,51]. During this calibration, which was made using the mass spectrometer, all parameters were maintained as close as possible to the values used during the excitation function measurements. Hence changes in contact potentials were avoided. The onset for Xe ($^3P_1 \rightarrow ^1S_0$) VUV fluorescence at 8.44 eV was also used for energy calibration [51-53]. The calibrations were consistent to within 1 eV. (Note that here and elsewhere we use this simple L-S nomenclature for the $^3P_1$ state. More rigorously, because of the intermediate coupling situation, it should be described as the $6s[3/2]_{\pi \downarrow}$ state.) The accuracy of the energy scale is estimated as $\pm 1$ eV.
8.2 Time-of-Flight Data

Figure 8.1 shows the signal collected at the CEM detector as a function of time during and following the 1.6 μs electron pulse. The series of photon decay and TOF curves, taken with different incident electron energies, are displaced upwards, except for the bottom (10 eV) signal. A prompt photon peak (not displayed), coincident with the electron pulse, is followed by a long tail extending towards the neutral metastable signals, which appear at later times. The photon decay has been suppressed, particularly with the 10 eV and 20 eV TOF curves, for the convenience of viewing the metastable signal, while noting that no fragments were excluded at these impact energies. The neutral metastable data displayed in Figure 8.1 illustrate an increase in complexity as the incident electron energy is increased. This is a consequence of additional parent potential energy curves becoming available with increase in energy. Metastable structure is apparent at flight times greater than approximately 60 μs at the highest electron impact energies, while at the lowest incident energies (∼20 eV), structure occurred only after about 75 μs. The TOF data demonstrate increasing signal intensity for the features at intermediate flight times (60-200 μs) compared to the structure at longest flight times (> 300 μs). Though the larger atomic mass of xenon, compared to the other clustered rare gases that our group has studied [43,45], allows for better separation of processes in time, the many features in the Xe TOF of similar intensity make the deconvolution somewhat challenging.

Metastable peaks are identifiable at various times in the TOF data of Figure 8.1.
Figure 8.1  Detector signal as a function of time. The incident electron beam energies are: $A$ 10 eV; $B$ 20 eV; $C$ 30 eV; $D$ 50 eV; $E$ 100 eV. All time-of-flight curves are displaced upwards except for the 10 eV curve. Xe clusters were used. The photon peak at short times (< 80 µs) has been suppressed for clarity in curves A and B.
A 65 μs peak is already noticeable in TOF data taken with an incident electron beam energy of 40 eV (not shown), and there is even an indication that this peak is developing in the 30 eV TOF data. It is not apparent in the 20 eV data. Thus the onset energy for the 65 μs peak (identified as process 6) is only approximately known.

TOF structures at intermediate flight times (60-200 μs) clearly increase with increase of the electron-beam energy as additional processes become active and/or broadening of the existing processes occur. Some of the structure at the longest flight times (> 300 μs) is due to randomly directed background xenon atoms that have been excited into metastable states as they pass through the electron beam. It is clear that additional processes are contributing to the TOF signal since the structure near 300 μs is observed to broaden and shift to shorter times with increasing electron-beam energy (see Figure 8.1). Using a similar TOF method, a study of high-Rydberg states from electron-impact excitation of xenon atoms [12] observed a distribution peaked at approximately 605 μs. Correcting this for the different source-detector distances and temperatures in their experiment and ours, reduces this to a value of 446 μs, which is the value we obtain (cf. Figure 8.3).

A VUV photon decay curve (Figure 8.2) generated using a LiF optical filter, with about a 105 nm (~ 11.8 eV) lower wavelength cut-off that excluded metastable fragments, was fitted using a combination of exponential functions. The largest fitted lifetime was approximately 14.7 μs, which contributed greatest to the photon signal at the longest times. The fitted, statistically smooth curve was used to remove the photon contribution from the time data of Figure 8.1 (see below) at the lowest energies. Besides
Figure 8.2 Time-resolved emission from Xe clusters taken using a LiF optical filter and an electron impact energy of approximately 10 eV. See the text for further discussion.
metastable levels (e.g., \( ^3\text{P}_{0,2} \)), the only observable emissions from gaseous xenon that we are aware of, that are comparable to the long (fitted) lifetime, come from observations of atomic xenon. Lifetimes ranging from 0.0034 to 8.3 \( \mu \text{s} \) for the \( ^3\text{P}_1 \rightarrow ^1\text{S}_0 \) transition [54-57, and references therein] have been reported, where the largest lifetimes have been attributed to radiation trapping [56]. (Additional information on relevant lifetimes can be found in references [58-61].) Alternatively, measurements on cold (\( \sim 6 \text{ K} \)) solid xenon have yielded lifetimes of approximately 15 \( \mu \text{s} \) [62]. The largest lifetimes in the solid case are likely due to the metastable \( \text{A}_u \) level (\( \sim 7.2 \text{ eV} \) emission band) at low temperature that results from the crystal-field splitting of the \( ^3\Sigma_u^+ \) state [62]. A direct comparison of results in terms of the cluster temperature was not possible, though it is possible that the larger xenon clusters in the supersonic beam were in excess of 60 K [63] due to the large number of vibrational degrees of freedom. (This note also applies to any comparisons with temperature specific results that follow.) However, it is possible that the observed long lifetime of 14.7 \( \mu \text{s} \) implies that the large clusters were significantly cooler than what the results of [63] suggest.

The TOF curve produced using 20 eV incident electrons is the focus of Figure 8.3. The dashed curve (MB) represents a scaled Maxwell-Boltzmann curve [64] (and see Appendix B) for atomic xenon at room temperature (for a random, three-dimensional gas). The scaling was such as to match the experimental data at the longest flight times where this component will dominate. Subtraction of this scaled curve from the experimental data allowed the randomly directed atomic xenon contribution at the longest flight times to be removed from the data. Similarly the photon decay curve obtained
Figure 8.3  Metastable signal, indicating at least six contributing processes, as a function of time after the electron beam pulse at 20 eV. The dashed curve (MB) and dotted curve (P) subtracted from the 20 eV data (see text) of Fig. 8.1 yields the data set shown (open circles). The other labelled solid curves represent an approximate deconvolution into five separate structures, 1-5. The solid curve passing through the data points corresponds to the superposition of the five separate structures. Xe clusters were used.
using the LiF filter was scaled to fit the prompt photon peak, P, which was then also subtracted from the data. The resultant data, minus the photon (P) and Maxwellian (MB) contributions, shown in Figure 8.3, represents the metastable contribution to the TOF signal that is a consequence of the cluster fragmentation processes.

Five features are evident in the 20 eV data set shown in Figure 8.3. A similar number of features were evident on other data sets obtained at energies of 10 and 30 eV. Hence, as a first approximation to the actual make-up of the data, we show in Figure 8.3 a deconvolution into five separate Gaussian peaks. These are the solid curves labeled 1 to 5. Their widths and heights are chosen so that their sum closely approximates to the experimental data points in Figure 8.3. All five were necessary to give a good overall fit. Approximate fitted peak locations for the scaled Gaussian distributions for processes 1 to 5, respectively occurred at 99 µs, 114 µs, 152 µs, 219 µs, and 303 µs. The superposition of processes 1-5 resulted in an excellent fit to the metastable data, shown as the solid line through the data points.

We note that the choice of Gaussian distributions for the fitting procedure was somewhat arbitrary at larger impact energies. However, given the complicated nature of the excitation processes involved (see later), use of more involved functions seemed an unnecessary and unjustified complication. Additional processes are required for identification of structure shown in the TOF data of Figure 8.1 at larger impact energies.

This deconvolution process was repeated for the 10 eV TOF data and the same number of processes at the same times (with some being slightly narrower), as in the 20 eV case, were found to be present. Process 5 is observed to dominate the TOF
Figure 8.4  Metastable signal, indicating at least six contributing processes, as a function of time after the electron beam pulse at 10 eV. The dashed curve (MB) and dotted curve (P) subtracted from the 10 eV data (see text) of Fig. 8.1 yields the data set shown (open circles). The other labelled solid curves represent an approximate deconvolution into five separate structures, 1-5. The solid curve passing through the data points corresponds to the superposition of the five separate structures. Xe clusters were used.
Figure 8.5  Metastable signal, indicating at least six contributing processes, as a function of time after the electron beam pulse at 30 eV. The dashed curve (MB) and dotted curve (P) subtracted from the 30 eV data (see text) of Fig. 8.1 yields the data set shown (open circles). The other labelled solid curves represent an approximate deconvolution into six separate structures, 1-6. The solid curve passing through the data points corresponds to the superposition of the five separate structures. Xe clusters were used.
deconvolutions at 10 and 20 eV, though it rapidly falls-off in intensity relative to the other deconvoluted processes at higher impact energies. This is consistent with excitation function results presented in Section 8.4. At 30 eV the TOF data could be deconvoluted in a similar fashion, but now a new process (namely process 6 at approximately 65 µs) had to be considered. Some broadening of existing processes (1-5) was apparent also. TOFs at larger impact energies were not deconvoluted due to the uncertainties involved and the relatively rich structure. Further discussions of the details of these processes are presented in later sections.

8.3 Kinetic Energy Analysis

The TOF data of Figure 8.1 can be converted to fragment kinetic energy (FKE) data via the procedure described in reference [65] and Chapter 3. In order to make the transformation from the time domain to the FKE domain, the following information must be known: the distance from the interaction region to the CEM detector and the mass of the detected fragment. The source to detector distance used in this xenon cluster investigation was 122 mm, while the mass was assumed to be that of atomic xenon. The assumption of the detected mass is reasonable based on previous investigations with argon [43] and krypton [45] clusters, where the metastable atom was determined to result from dimer fragmentation.

Figure 8.6 is the result of the FKE transformation on the TOF data of Figure 8.1. A series of FKE curves are shown for different incident electron energies (corresponding
Figure 8.6  Fragment kinetic energy spectra derived from the time-of-flight (TOF) data of Fig. 8.1 (see text). Incident electron energies are A 10 eV, B 20 eV, C 30 eV, D 50 eV, and E 100 eV. All curves are displaced upwards except for the 10 eV curve. Some TOF times are indicated in parentheses under their corresponding kinetic energies. Xe clusters were used.
to Figure 8.1) where all FKE curves, except for the 10 eV impact energy, are displaced upwards. The most intense feature, at the smallest fragment kinetic energies that results from the TOF feature at the longest displayed flight times (process MB), is not fully displayed in Figure 8.6. Velocity distribution data for metastable xenon atoms were provided in reference [11] via TOF beam measurements. These indicated a kinetic energy of 0.062 eV (from the most probable speed). However, it should be noted that this 0.062 eV corresponds to about 302 m/s or about 479 K (using $v_{\text{max}} = \sqrt{\frac{3k_B T}{m}}$ as the most probable beam speed). This is well above room temperature and, unfortunately, no details were given in [11] of their experimental temperature. Our most probable speed was approximately 193 m/s (0.025 eV), which is based on our TOF peak time (using $v_{\text{max}} = \sqrt{\frac{2k_B T}{m}}$ and room temperature for a (random) three-dimensional gas). The second feature to be appreciated in our FKE data is the visible shoulder between approximately 0.5 eV and 1.5 eV. This FKE range corresponds to the intermediate flight-time TOF data of Figure 8.1 and is largely due to processes 1 and 2 (cf. Figure 8.3). FKE data (not shown) suggest that fragments with larger kinetic energies, even in excess of 3 eV, are being produced for 30 eV and higher impact energies. This is consistent with the TOF data displayed in Figure 8.1.

The data of Figure 8.3 (8.4) were used to produce the FKE transformed data shown in Figure 8.7 (8.8). Here we have shown the adapted FKE data from curve B of Figure 8.6, where an incident electron energy of 20 eV was used. (This process was repeated for the 10 eV TOF data with very similar results as in the 20 eV case.) The labelled processes 1-5 in Figure 8.7 correspond to the same processes as in Figure 8.3.
Figure 8.7  Fragment kinetic energy spectra resulting from the 20 eV time-of-flight data of Fig. 8.3 (see text). As in Fig. 8.3, the experimental data (open circles) have been approximated by the solid curve passing through the data points. The labelled solid curves, 1-5, are the transformed curves (1-5) of Fig. 8.3. The insert shows an expanded version to highlight the contributions of processes 1-4. Xe clusters were used.
Curve MB in Figure 8.3 is not shown in Figure 8.7 since it was removed from the TOF signal. Its approximate peak FKE was 0.013 eV. Processes 1 to 5, respectively, had the following approximate FKE peaks: 1.01 eV, 0.73 eV, 0.38 eV, 0.18 eV, and 0.08 eV. The peaks corresponding to processes 1-5, are observed to shift to slightly smaller FKEs and broaden slightly with increasing electron impact energy.

The FKE of process 3, with a peak at approximately 0.38 eV, is fortuitously similar to the reported value of 0.36 eV obtained with solid Xe targets (15 K, ~ 1 μm thick) using high energy (2.5 keV) electron impact [66]. The solid target observation was argued to be the result of the repulsion of ground state atoms after radiative decay of vibrationally relaxed dimers (M band) [66]. The M band (molecular self-trapped excitons) is recognized as the second continuum, in the gas phase, of the cluster fluorescence that results from strongly bound states, i.e., \( ^1\Sigma_g^+ \) [13,22]. (In large clusters, these emissions are the dominant radiative relaxation channels [22].) In addition to the 0.36 eV feature, reference [66] observed other (non-identified) lower energy fragments that seem compatible with our observations. It is not clear from the published figures whether the data displayed in reference [66] contain any higher energy (> 0.36 eV peak) features. From Figure 8.7, it can be seen that most of the processes are reasonably narrow in the FKE scale. This indicates that the inner repulsive-walls of the potential energy curves, which are responsible, are fairly shallow.

Process 6, shown in Figure 8.9, corresponding to the peak near 65 μs (cf. Figure 8.1), is responsible for a FKE that is peaked at 1.6 eV and extends past 3 eV, with increasing impact energy. Process 6 involves a wide distribution of higher fragment
Figure 8.8  Fragment kinetic energy spectra resulting from the 10 eV time-of-flight data of Fig. 8.4 (see text). As in Fig. 8.4, the experimental data (open circles) have been approximated by the solid curve passing through the data points. The labelled solid curves, 1-5, are the transformed curves (1-5) of Fig. 8.4. The insert shows an expanded version to highlight the contributions of processes 1-4. Xe clusters were used.
Figure 8.9  Fragment kinetic energy spectra resulting from the 30 eV time-of-flight data of Fig. 8.5 (see text). As in Fig. 8.5, the experimental data (open circles) have been approximated by the solid curve passing through the data points. The labelled solid curves, 1-6, are the transformed curves (1-6) of Fig. 8.5. The insert shows an expanded version to highlight the contributions of processes 1, 2, and 6. Xe clusters were used.
kinetic energies. This indicates that a steep inner repulsive-wall of the parent potential energy curve is being accessed. Further details of this are considered in the next section.

8.4 Excitation Functions

Excitation functions were performed by ramping the electron-beam energy while collecting the signals arriving in various TOF intervals. The results of the excitation function studies are displayed in Figure 8.10, where all data have been displaced upwards, except for the bottom curve A. Further details of Figure 8.10 are provided in the caption. The windows were chosen to emphasize particular features of the TOF data in Figure 8.1. Furthermore, the excitation functions corresponding to Figure 8.10 have been investigated near threshold, as shown in Figure 8.11. Onset energies have been determined from the normalized excitation functions in Figure 8.11.

The bottom curve A of Figures 8.10 and 8.11 represents the prompt VUV photon signal collected at the CEM from 0 to 10 μs. (Recall that the nominal start of the electron pulse set the zero on the time scale). The broad shape of curve A with a maximum around 115 eV indicates that the photon signal was primarily due to optically allowed excitations. The threshold appears at approximately 8.5 eV with a distinct shoulder emerging at about 16 eV, suggesting the possibility of a new excitation channel opening-up. The prompt photon excitation function has a change in slope close to (and following) 35 eV, which may indicate another excitation channel. These additional photon-producing channels likely involve simultaneous excitation and ionization or possibly
Figure 8.10  Excitation functions appropriate to different time-of-flight windows (see Fig. 8.1):  A 0-10 µs, photons only; B 3-10 µs, photons only; C 80-150 µs; D 150-850 µs. All curves, except A, are displaced upwards for clarity. See the text for further discussion. Xe clusters were used.
Figure 8.11  Excitation functions near threshold appropriate to different time-of-flight windows (see Fig. 8.1): A 0-10 μs, photons only; B 3-10 μs, photons only; C 80-150 μs; D 150-850 μs. See the text for further discussion. Xe clusters were used.
sequential excitation of two atoms in the cluster. (Luyken [67] found the optical emission cross section of the 1100 and 1245 Å resonance lines of the xenon ion (Xe II) to peak at approximately 38 eV with an onset near 23.4 eV.) The 8.5 eV onset is consistent with the threshold for exciting the atomic resonance lines [9,51-53], \(^1\text{P}_1\rightarrow^1\text{S}_0\) and \(^3\text{P}_1\rightarrow^1\text{S}_0\), within the energy resolution of our setup. Because of the onset and rapid rise of the excitation function near threshold, exchange excitation seems to be the major contributor in this energy region. Emission from the first or second continua could also be contributing [56,68].

Karnbach et al. [22] investigating the photo-excitation (via synchrotron radiation) of small xenon clusters observed and discussed what was ascribed to be an efficient population of excited atomic xenon in the \(^3\text{P}_1\) (n=1 exciton) state following excitation energetically close to the \(^1\text{P}_1\) (n=1' exciton) state (via a bound-repulsive excimer curve crossing). Furthermore, the excited \(^3\text{P}_1\) atomic xenon were stated to be ejected from the cluster and emitted after the desorption had occurred. Steeg and coworkers [2,4] observed and discussed structure (up to 26 eV) with onsets at approximately 16.3 eV and higher via time-resolved excitation spectra from solid xenon, which was attributed to variations (free and/or bound) of an electronic polaron complex (simultaneous excitation of a free exciton (i.e., a bound electron-hole pair) and a free electron-hole pair).

Another counting channel was used to simultaneously collect the prompt photons over an integration window from 0 to 3 μs (not shown in Figures 8.10 and 8.11). Subtraction from the 0 to 10 μs excitation function curve yields the photon contribution from 3 to 10 μs. This relatively small difference in signals is shown scaled and shifted
upwards as curve B in Figure 8.10. The threshold of this feature is also displayed in Figure 8.11. The 3 to 10 µs excitation function data has a threshold at approximately 8.5 eV. It comes to a sharp peak at approximately 16 eV with a fall-off in intensity that indicates excitation by way of an exchange process to a state of different multiplicity to that of the ground state. An identification of the specific fluorescence transition(s) is not obvious due to the rather large lifetime lower bound, though (see Section 8.2) it could be a result of the fluorescence from the $^3\Sigma_u^+ \rightarrow ^1\Sigma_g^+$ transition, analogous to the solid Xe system [62]. Correspondingly, a localized bulk exciton (caged excited xenon) would progress into a non-sputtering (non-desorption) channel due to the larger xenon cluster size and inelastic collisions with the surrounding bulk [37], thus tending to radiate within the cluster. Radiation trapping could be occurring [56], especially considering our medium-to-large average cluster size. This would have the effect of delaying the photon detection.

A third excitation function, curve C, for the time window of 80 to 150 µs, is shown in Figures 8.10 and 8.11. The statistics are relatively poor because of the low count rate for this time window. A threshold of approximately 10 eV was observed with a sharp peak following at about 16 eV and another maximum at approximately 130 eV. The onset energy is consistent, within the context of the FKE analysis, with the metastable states 6s'[$1/2]_0 \ 3P_0$ and 6s[$3/2]_2 \ 3P_2$. The time window for curve C includes mainly contributions from processes 1-3 (see Figures 8.3 and 8.7), though with some underlying contributions from the tails of the processes 4 and 5 (evident from the shoulder near 8.5 eV).
Figure 8.12  Relative excitation function points representing the contributions of processes 1-5 contained in the TOF data of Figures 8.3-8.5. Processes 1-5, respectively, are represented by the following symbols: 1 □, 2 ▲, 3 ◀, 4 ●, and 5 ■. The dotted lines help indicate the excitation function shape for processes 4 and 5. Processes 1-3 have shapes similar to process 5. See the text for further discussion. Xe clusters were used.
Figure 8.12 shows points at 10, 20, and 30 eV of the relative excitation functions that represents the integrated intensity of processes 1-5. The deconvoluted TOF curves, which are representative of processes 1-5, of Figures 8.3-8.5, were used to obtain the integrated, relative intensities at each energy value. The dotted lines (see the figure caption) assist in demonstrating the general shape of the excitation function of each respective process. Processes 1-3 and 5 appear to be optically forbidden excited states, likely with electron exchange involved. They all appear to peak around 20 eV, which is consistent with excitation function observations (i.e., Figures 8.10-11), with onsets at 10 eV or less. However, process 4 is observed to steadily rise from threshold towards some maximum value above 30 eV. This possibly indicates that the peak near 130 eV (curve C of Figure 8.10) results from process 4. In this case, the peak near 130 eV would be expected to contribute to curve D (Figure 8.10), due to the time window overlap. It is not clearly observable within our statistics, though the slight change in slope near 130 eV (curve D of Figure 8.10) hints at some contribution.

Curve D of Figures 8.10 and 8.11 appears similar to features in curves B and C, but represents the excitation function for the 150-850 μs time window. The observed threshold was at approximately 8.5 eV and the excitation function peaked at approximately 15 eV. The integrated time window corresponds mostly to processes 4 and 5, in addition to some random metastable background (MB) and a portion of process 3 (see Figures 8.3 and 8.7). The long time delay between excitation and detection suggest the detected species were most likely the lowest lying metastable states: 6s'[1/2]_0 \(^3P_0\) or 6s[3/2]_2 \(^3P_2\). Furthermore, the excitation function and threshold energy suggests
that the $^3P_2$ metastable was more strongly excited than the $^3P_0$ metastable state. A possible excitation route would be an initial excitation of a low-lying exciton in the cluster (excitation energy $\sim 8.5$ eV) followed by localization into a dimer state (see Figure 8.13, lower arrow) and subsequent decay into the $^3P_2$ channel with very little excess kinetic energy. Furthermore, a possible route for metastable ejection from the cluster would be from the surface exciton ($\sim 9$ eV), which is energetically feasible within our onset and fragment kinetic energy observations (and resolution). The excess energy ($\sim 0.2$ eV) could go towards exciting vibrational modes in the cluster and/or ejection of neutral ground state fragments.

The deconvolution method (see Figure 8.3) suggests that process 5 dominates the signal in the lower energy region, and likely leads to $^3P_2$ metastable atoms. The onset energy for process 4 could not be determined accurately, though it was observed to be contributing to the TOF spectra at 10 eV. Possibly the mechanism of excitation of process 4 is similar to that of process 5 but with production of $^3P_0$, rather than $^3P_2$, metastable atoms.

Reference [15] investigated total cross sections for metastable excitation of xenon gas by way of electron impact. A similar excitation function also peaking at 15 eV, with about the same full-width half-maximum, was observed. Furthermore, a study [12] of high-Rydberg states (most probable $n=43\pm4$) from electron-impact excitation of xenon atoms found an excitation function peaking at approximately 16 eV with an onset at about 12 eV.

Figure 8.13 shows some potential energy curves for Xe$_2$ and indicates the known
Figure 8.13 (Left) Location of excitons in solid xenon (at 10 K) [2]. Surface excitons are indicated by s (dotted line) and solid lines are for bulk excitons (transverse, using the Wannier notation, and longitudinal, L). (Right) Schematic diagram of Xe₂ potential energy curves adapted from [70] with atom energy levels from Refs. [9,52,69]. The arrows indicate possible excitation schemes, (see text) for fast metastable atom production. The numbers, 1-5, refer to the processes discussed in the text.
energy positions of the Xe atom and exciton energies. Data from references [2,9,52,69-71] have been used to produce this simplified figure. (For a recent comparison, potential energy curves for the xenon dimer have been calculated in detail by Jonin and coworkers [52]. Additional information on relevant potential energy curves can be found in references [50,72,73].) It is worth noting that "cluster" excitons have been observed between 8.975 and 9.239 eV for medium size XeN (N=50-500) clusters [25], via absorption band studies. These were not reported in condensed xenon [2,4,5,8].

Recently, an infrared fluorescence experiment [71] on xenon dimers has demonstrated a broad continuum (centered at about 0.95 eV energy difference) that is likely produced by a bound-repulsive transition within the excited state manifold. A similar process may be occurring here leading to the observation of fast metastable fragments (processes 1-3). Iannuzzi and coworkers [71] have observed a number of emissions from the xenon dimer. They identify an emission (in the dissociation limit) as 6p' (or 5d') to 6s' transition via radiative decay. Another transition was the 6p to 6s via direct excitation, cascading from higher levels, and/or predissociation. Furthermore, 6p' bound state(s) to 6s repulsive state(s) are shown to lead to excimer radiation [71]. The total metastable excitation cross section would be dominated by cascade contributions several electron-volts above onset.

Steeg and coworkers [2,4], using synchrotron radiation on solid xenon, observed a 10.85 eV excitation (absorption) peak by way of photon-stimulated luminescence spectroscopy, but provided no specific identification. For the case of our medium-to-large clusters, Verkhovtseva et al. [39] found (using argon and krypton clusters) that the
importance of ejected excited particles decreases such that the major contributor to the VUV photons was the radiative decay of self-localized excitons created inside the cluster. Our energy resolution does not allow for exact exciton identifications, however, the fastest metastable fragments (curve C in Figures 8.10 and 8.11) likely originated via an excitation (e.g., 10.85 eV) above the band-gap energy followed by localization to an excited dimer state and subsequent (radiative) decay to a repulsive state. This yields metastable atoms with relatively large kinetic energies.

TOF and FKE observations along with the data in Figure 8.13 indicate that the 65 μs peak (process 6) originates via initial excitation of a bound state manifold above the 6s' states followed by radiative decay to a repulsive state leading to fragmentation. The appearance threshold occurred above 20 eV, which likely corresponds to the fragmentation of a simultaneously excited and ionized xenon dimer.

8.5 Conclusions

Time-of-flight and excitation function measurements of the fragmentation of neutral xenon clusters using electron-impact have been presented, along with VUV fluorescence observations. At least six processes leading to neutral metastable fragments and also additional channels leading to prompt photon production have been identified. Metastable fragments with most probable kinetic energy values between 0.08 and 1.6 eV have been observed. These processes have been discussed in terms of known dimer potential energy curves and other data obtained using various techniques.
In summary, processes 1-3 have been determined to have most probable fragment kinetic energy values of 1.01, 0.73, and 0.38 eV, respectively, with an onset observed at approximately 10 eV. Excitation above the band-gap energy, ensuing localization to an excited xenon dimer, and subsequent decay (primarily infrared fluorescence) to a repulsive state led to metastable production (likely the $6s[1/2]_0 \ ^3P_0$ and/or $6s[3/2]_2 \ ^3P_2$ states). A 8.5 eV threshold energy corresponded to processes 4 and 5 with maximum fragment kinetic energies of 0.18 and 0.08 eV, respectively. Processes 4 and 5 likely originated via an exciton (possibly the surface exciton at $\sim$ 9 eV), followed by localization into a dimer state belonging to the 6s manifold and successive fragmentation with the production of the metastable $6s[3/2]_2 \ ^3P_2$ state. Process 6 had a wide distribution of fragment kinetic energies that were peaked at 1.6 eV, even extending past 3 eV, and an appearance energy above 20 eV. This likely resulted from fragmentation of a simultaneously excited and ionized xenon dimer. The VUV fluorescence was primarily due to transitions from the 6s to ground atomic transition ($^3P_1 \rightarrow ^1S_0$) and from the second continuum emission ($^{1,3}\Sigma^+_0 \rightarrow ^1\Sigma^+_g$).
8.6 References:


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Chapter 9

Overall Summary and Suggestions for Future Cluster Studies

A comprehensive investigation of neutral metastable fragments following electron collisions with clustered targets has been undertaken. Vacuum ultraviolet fluorescence was probed by electron collisions, in addition to the study of the neutral metastable fragments. Combinations of vacuum based techniques—fluorescence and translational spectroscopies and mass spectrometry—were used to explore the electron-cluster interaction, to investigate the potential energy curves (where available) and to provide considerably new information on the cluster dissociation dynamics. The majority of clustered targets were van der Waals bound. Results from investigations by our group on clusters composed of covalent molecules (CO$_2$, N$_2$O) have determined that neutral
metastable fragmentation patterns mirror their molecular counterparts. Radiative emission is also essentially unaffected by clustering, with variations in intensity and slight lifetime differences being observed. This is understandable in light of the significant difference between the molecular bond strength (covalent) and the relatively weak van der Waals cluster bonds.

Homogeneous heavy rare gas (Ar, Kr, Xe) cluster investigations have demonstrated complex neutral metastable fragmentation patterns. Photon decay has also been found to be rich in structure compared to, especially, the atomic rare gas. Figure 9.1 shows time-of-flight spectra for metastable fragments resulting from electron collisions (at 20 eV) with clustered targets of Ar, Kr, and Xe. The series of curves demonstrate complex fragmentation behaviour that results from excited dimer cores being formed in the cluster via the electron interaction. The lighter rare gases (He and Ne) were not found to cluster in our experimental setup.

Preliminary work on the variation of metastable fragmentation with changing stagnation pressure, and hence average cluster size, using clustered argon, has demonstrated very exciting time-of-flight spectra for smaller pressures. The time-of-flight spectra and associated kinetic energy distributions at relatively small pressures indicated generally few fragmentation channels compared to ‘heavily’ clustered targets, but quite well resolved. The complex processes at larger pressures indicated that more fragmentation channels were accessed and possible bulk-sputtered fragments were impeded by elastic scattering. The assortment of techniques used for the homogeneous
rare gas cluster investigations can be utilized for a comprehensive study with changing stagnation conditions. Furthermore, a beginning survey of heterogeneous clustering,

![Graph](image)

**Figure 9.1** Time-of-flight data for rare gas clusters impacted by 20 eV electrons. The curves are for Xe (bottom), Kr (middle), and Ar (top) clusters. The curves are not normalized and the Ar and Kr data have been shifted upwards for clarity of presentation.

using a mixture of argon and krypton, found this to be an interesting area of study. Novel time-of-flight features were observed, compared to the homogeneous cases, though better control over the Ar/Kr-gas-mixture ratio will be required for characterization of these features.
Additionally, a carrier gas of He was used to generate water clusters as evident by mass spectra. Further comprehensive investigations of the photon decay and time-of-flight of metastable fragments resulting from the electron impact of the water clusters is planned. It is expected that this research will provide for interesting results considering the relatively comparable bond strength between the cluster constituents and the molecular hydrogen-bonds. Questions like “will the hydrogen-bonded cluster network suppress metastable fragmentation?” or “will the water cluster generate more energetic fragments compared to the molecular case?” beg to be answered.
Appendix A

Conversion Factors and Other Constants

The purpose of this appendix is to facilitate required unit conversions within this body of work and for the reader. CODATA 1998 recommended values have been used where applicable.

**Constants and Units**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric constant $\varepsilon_0$</td>
<td>$8.85418781700000\times10^{-12}$ F m$^{-1}$</td>
</tr>
<tr>
<td>Electron mass $m_e$</td>
<td>$9.10938188000000\times10^{-31}$ kg</td>
</tr>
<tr>
<td>Elementary charge $e$</td>
<td>$1.60217646200000\times10^{-19}$ C</td>
</tr>
<tr>
<td>Planck constant $h$</td>
<td>$6.62606876000000\times10^{-34}$ J s</td>
</tr>
<tr>
<td>Speed of light $c$</td>
<td>$2.99792458000000\times10^{10}$ m s$^{-1}$</td>
</tr>
<tr>
<td>Boltzmann constant $k_B$</td>
<td>$1.38065030000000\times10^{-23}$ J K$^{-1}$</td>
</tr>
<tr>
<td>Avogadro constant $N_A$</td>
<td>$6.02214199000000\times10^{23}$ mol$^{-1}$</td>
</tr>
<tr>
<td>Molar gas constant $R$</td>
<td>$8.31447200000000\times10^{-2}$ J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>Atomic mass constant $amu$</td>
<td>$1.66053873000000\times10^{-27}$ kg</td>
</tr>
</tbody>
</table>

**Pressure Units**

1.0 Pa equals ...
- $14.50\times10^{-5}$ psi
- $0.9869\times10^{-5}$ atm
- $0.750\times10^{-2}$ Torr
- $0.750\times10^{-1}$ mTorr
- $1\times10^{-5}$ bar
- $1\times10^{-2}$ mbar

**Energy Units**

1.0 J equals ...
- $6.2415\times10^{18}$ eV
- $1.0\times10^{17}$ erg
- $2.294\times10^{17}$ hartree
- $5.035\times10^{22}$ cm$^{-1}$
- $7.2439\times10^{22}$ K
- $1.4395\times10^{20}$ kcal mol$^{-1}$
Appendix B

Maxwell-Boltzmann Distribution

The well-known Maxwell-Boltzmann (MB) distribution normally describes the random motion of a gas in three dimensions. Other forms have been adapted for the description of constrained geometries, such as in a beam. In terms of the speed of the gas particles in a random, three-dimensional system, the following describes the Maxwellian distribution:

\[ f(v) = A v^2 \exp \left( - \frac{mv^2}{2k_B T} \right) . \]  \hspace{1cm} \text{[B.1]}

Here, the distribution has a physical interpretation of representing the intensity, or number of gas particles, having a particular speed \( v \). The distribution is also in terms of the mass \( m \), temperature \( T \), and Boltzmann's constant \( k_B \) (1.38 \times 10^{-23} \) J/K). The quantity \( A \) is simply an experimentally practical and convenient scaling factor, though, for a random three-dimensional gas, the proper relationship is

\[ A = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} . \]  \hspace{1cm} \text{[B.2]}

The speed form of the MB distribution requires modification for a direct comparison to our experimental data. Since we perform time-of-flight (TOF)
measurements, it makes sense to convert from the speed (v) domain to the time (t) domain:

\[ f(t)dt = \left( -\frac{D}{t^2} \right) f(v)dv, \quad [B.3] \]

where the derivative of \( v = D/t \) with respect to time has been utilized. Inserting the speed version (Equation B.1) of the MB distribution into Equation B.3 generates a form of the MB distribution in the time domain:

\[ f(t) = \frac{C}{t^4} \exp\left( -\frac{\alpha}{t} \right), \quad [B.4] \]

where \( C \) is a scaling factor and \( \alpha \) is represented by

\[ \alpha = mD^2/2k_BT. \quad [B.5] \]

In our set of experiments, it was very normal to have some contribution of the TOF data at the largest flight times due to some of the random background gas in the vacuum chamber. Equation B.4 was very useful for deconvoluting the MB distribution (at room temperature) from experimental data and aiding the interpretation of complex TOF spectra.

Alternatively, the speed form (Equation B.1) of the MB distribution can be converted to the kinetic energy (\( T_E \)) domain using the derivative of \( T_E = \frac{1}{2}mv^2 \) with respect to the kinetic energy and re-arranging:

\[ f(T_E)dT_E = \left( 2mT_E \right)^{-1/2} f(v)dT_E. \quad [B.6] \]

The result of substituting in the speed distribution (Equation B.1) into Equation B.6 produces the kinetic energy version of the MB distribution:
\[ f(T_E) = B \sqrt{T_E} \exp\left( -\frac{T_E}{k_B T} \right), \]  \[ \text{[B.7]} \]

where $B$ is a scaling factor. Figure B.1 illustrates the peak locations and (normalized) distributions of Equations B.1, B.4, and B.7.

![Graph showing normalized intensity vs. speed](image)

**Figure B.1** A comparison of the Maxwell-Boltzmann distribution in the speed domain, based upon the presented transformations (see text).

The various forms of the Maxwell-Boltzmann distribution presented above are necessary depending on the domain being used and if conversions between domains are required. The typical expressions for the most probable ($mp$), average ($ave$), and root-mean-square ($rms$) values of the MB distribution are presented in the speed domain. These expressions are as follows, with their respective locations illustrated in Figure B.2.
\[ v_{mp} = \sqrt{2k_B T/m} \quad \text{[B.8]} \]
\[ v_{ave} = \sqrt{8k_B T/\pi m} \quad \text{[B.9]} \]
\[ v_{rms} = \sqrt{3k_B T/m} \quad \text{[B.10]} \]

Any basic thermodynamic textbook shows the derivations of these expressions. However, it is worth noting that the rms speed \( v_{rms} \), not the average or most probable, in the standard kinetic energy formula \( T_E = \frac{1}{2}mv^2 \) is related to the well-known expression
\[ T_E = \frac{1}{2}k_B T. \quad \text{[B.11]} \]

![Graph of speed distribution with labels for most probable, average, and root-mean-square speeds.](image)

**Figure B.2** A comparison of the most probable, average, and root-mean-square speed locations for the Maxwell-Boltzmann distribution in the speed domain, based upon the derived expressions (see text).
The most probable value is also known as the maximum or peak value. This peak value quantity is most often used in experiments since it is easily extractable from a data curve. Caution must be used when comparing peak values from different domains since the conversion process causes the peaks in different domains to shift. An example would be an experiment that shows a speed distribution and states a peak kinetic energy, where, in fact, the kinetic energy value is not $T_{Emp}$, but rather the kinetic energy corresponding to the peak speed ($v_{mp}$). The most probable kinetic energy ($T_{Emp}$) is given by Equation B.13 (see below), while the kinetic energy from the speed distribution is actually $T_{Emv} = \frac{1}{2} m v_{mp}^2$. This is obviously an issue that could easily cause confusion in the literature if care is not taken. Consequently, it is worthwhile to consider the peak values properly derived in the time and kinetic energy domains. Taking the derivative of the MB distribution in a particular domain (e.g., $f(t)$) with respect to the corresponding variable (e.g., $t$), setting it equal to zero, and solving produces the most probable value:

$$t_{mp} = \frac{\sqrt{m D}}{\sqrt{k g T}}$$  \hspace{1cm} [B.12]

$$T_{Emp} = k_{\mu} T / 2.$$  \hspace{1cm} [B.13]

These expressions have been used in the analysis and comparison of data within this body of work.
Appendix C

Wiley-McLaren Spatial Focusing Conditions

The original two-stage linear time-of-flight (TOF) mass spectrometer (MS) was first used by Wiley and McLaren in 1955 [1]. In order to help obtain narrow mass lines, the following analysis provides a footing for obtaining conditions that improve the TOF-MS spatial focusing. Figure 3.4 shows the relevant variables and layout of the two stage linear TOF-MS. (See reference [2] for further discussion.) The following discussion has been developed for a given set of experimental distances, such that the ideal conditions for spatial focusing can be addressed in terms of the two applied potentials ($U_d$ and $U_L$). There are many factors, like space charge and fringing fields, which are not being incorporated in this classical analysis, however, these results serve as a fine starting point.

The total flight time of a detected charged particle (mass $m$), in this case a positively charged ion, which has been produced in the interaction volume centered at $s$, is given by

$$t(s) = t_1 + t_2 + t_3.$$  \[C.1\]

For convenience, let the initial starting location ($s_o$) equal zero and the initial beam speed is negligible in the limit of relatively large accelerating potentials. (The following expressions can be adapted with relative ease if the initial velocity, following ionization,
is an issue.) Region 1 occurs between two plates, with meshed holes in the centers, separated by distance \( b \) and with potentials as indicated in Figure 3.4. The charged particles (of charge \( q \)) are accelerated by the electric field \( E_1 \) associated with the potentials of region 1, as given by the Lorentz force law (for a zero magnetic field):

\[
\vec{F} = m\ddot{a} = q\vec{E}.
\] [C.2]

Solving the speed and displacement integrals for the distance that experiences field \( E_1 \) and re-arranging in terms of the flight time of region 1 gives

\[
t_1 = \frac{\sqrt{2ms}}{qE_1}.
\] [C.3]

Here we have assumed that the electric field does not have explicit time dependence, though our experimental situation actually uses a pulsed extraction field (off when the electron beam is on). Region 2 experiences the fields associated with potentials \( U_d \) and \( U_i \). The two potentials, having the same polarity (negative in order to attract positive charge), produce oppositely directed electric fields between the plates separated by distance \( d \). The same arguments used for region 1 (\( t_1 \)) apply in this accelerating case, resulting in a flight time of

\[
t_2 = \frac{\sqrt{2m}}{qE_2} \left[ \sqrt{U - sqE_1} \right]
\] [C.4]

for region 2. Here, the "potential" \( U \) is given by

\[
U = sqE_1 + dqE_2 = -\frac{sqU_d}{b} - q(U_i - U_d),
\] [C.5]

and represents the total energy after acceleration. Similarly, the flight time for region 3 is given as
\[ t_j = \frac{L \sqrt{2m}}{2 \sqrt{U}}. \]  

[C.6]

The difference in this case, for region 3, is that the conductive tube of length \( L \) results in a “field-free” region whereby the charged particles experience no acceleration. Relating the kinetic energy to the “potential” \( U \) and the speed-distance relationship generates Equation C.6. This section (region 3) is commonly known as a “drift tube.” Here the difference in speed between particles of different masses (and for the sake of simplicity, the same charge) results in a longer flight time for larger masses over the same distance. The different arrival times at the detector of the spatially separated mass bunches provides the ability of mass analysis.

In order to obtain an expression for first order spatial focusing in terms of the applied voltages, it is necessary to consider the finite volume of the interaction region and the flight time resulting from this spread in starting locations. A Taylor expansion of the flight time about the center of the interaction volume \( (s_o) \) results in

\[ t(s_o \pm \Delta s) = t(s_o) \pm \left( \frac{dt}{ds} \right)_{s_o} \Delta s + \frac{1}{2!} \left( \frac{d^2 t}{ds^2} \right)_{s_o} (\Delta s)^2 \pm \cdots. \]  

[C.7]

The condition for first order spatial focusing corresponds to setting the derivative of time with respect to the interaction distance at \( s_o \) equal to zero:

\[ \left. \frac{dt}{ds} \right|_{s_o} = 0. \]  

[C.8]

Physically, this corresponds to ions of the same mass (and charge) arriving at the detector (or some other chosen distance) at the same time, but with different speeds. Evaluating the derivative of the total flight time, setting it equal to zero, and re-arranging produces
\[ L = \frac{2s_o E_1}{E_2} \left( 1 + \frac{d \cdot E_2}{s_o \cdot E_1} \right) \left( 1 - \left( 1 - \frac{E_2}{E_1} \right) \sqrt{1 + \frac{d \cdot E_2}{s_o \cdot E_1}} \right), \]  

which indicates the required distance \( L \), for the other known conditions, to obtain a spatially focused mass bunch. The electric field can be related to the potential by \( \vec{E} = -\nabla V \) for a given distance and substituted into Equation C.9. This is the typical expression derived for first order spatial focusing of the Wiley-McLaren MS design. It is obvious that the two stages provide better means of tuning the system. However, in the case of a large accelerating potential for region 1 and the requirement of temporal focusing (see Section 3.2) via a large flight path, Equation C.9 no longer is valid. Interestingly, Equation C.9 reduces to the single stage TOF-MS case when \( d \) equals zero and the ratio of electric fields equals one, where: \( L = 2s_o \). This is a physically impractical spatially focused design for cluster studies. Generally, an \( n \)-stage TOF-MS with ‘\( n-1 \)’-order focusing would provide the most flexible and tuneable system [3].

Alternatively, the first order spatial focusing condition can be solved similar to Equation C.9, but in terms of the drift tube voltage, which makes for a convenient comparison with our experiment. Knowing the distances and the applied accelerating grid voltage allows the other applied drift tube voltage to be solved. An analytical solution is rather challenging and labour intensive, though a numerical solution using, for example, Maple was quite easy. This was utilized as a starting point for obtaining suitable accelerating voltages.

In addition, a fourth region was investigated, using the same methods as above, in order to ascertain the significance of the distance between the detector and the end of the
flight tube ($t$). This was equivalent to solving for the first order spatial focusing conditions for a three stage linear TOF-MS. In this case, the flight time for the fourth region was

$$t_4 = \frac{\sqrt{2m}}{qE_4} \left[ \sqrt{U + \ell qE_4} - \sqrt{U} \right].$$

[C.10]

Using a numerical solution, taking account of the acceleration due to the detector resulted in approximately a two-volt shift in the worse case. Generally, the closer the detector is to the end of the flight tube, the smaller the perturbation on the total flight time (excluding fringing fields). Consequently, the fourth region, resulting from the detector positioning, was insignificant in terms of the overall tuning of our TOF-MS.

Furthermore, the resolution of a particular TOF-MS depends on many factors, such as accelerating potentials, spatial focusing, gas beam temperature and collimation, excitation pulse width, among others. By taking a derivative of Equation 3.24, with subsequent manipulation, an expression relating the uncertainty in the mass to the uncertainty in the time scale follows:

$$\frac{m}{\Delta m} = \frac{t}{2\Delta t}.$$  

[C.11]

The physical consequence of Equation C.11 is that for a given set of at least two mass bunches the mass resolution of the TOF-MS is ultimately limited by the minimum time step (i.e., the "uncertainty" in time, $\Delta t$) that the electronics can handle. In our case, the microsecond pulse width of our electron beam is normally the limiting factor in terms of the mass resolution (i.e., temporal effect). However, in some cases where the mass separation is an issue (e.g., when the masses of adjacent peaks are relatively similar), the
minimum time width of our data acquisition electronics (i.e., spatial effect) is our limiting factor. In this case, the acceleration potentials can be decreased to increase the flight time, but then the decrease in spatial focusing and mass bunching (via the temporal spread) limits the overall mass resolution.

Additional factors include the size of the interaction volume, which could be improved by skimming the ionized beam, and the initial velocity distribution of ionized masses. The velocity distribution of the incident neutral beam (prior to electron-impact) and the ionized fragment energy distribution can be corrected by spatial and temporal techniques. Spatial focusing was discussed above. Temporal focusing is achieved by techniques such as time-lag-focusing, impulse-field-focusing, rapid field reversal, among others, in combination with fast ionizing pulses. For a fast ionisation pulse, temporal uncertainty is essentially due to the finite turn-around-time experienced by ions in the interaction volume. The time-lag-focusing method normally makes use of a finite delay in a pulsed extraction field on the first ion lens (i.e., accelerating grid). Alternatively, a large drift tube flight distance can provide some relief. Ultimately, however, linear TOF-MS devices are limited by interplay between good temporal focusing and poor spatial focusing, and vice versa, due to the coupling of $L$ with the electric field ($E_i$) associated with $U_d$ (see Figure 3.4 and Equation C.9). Though very interesting and useful with dramatic improvements in resolution, reflectrons will not be discussed within the context of this work.
Appendix C References:

Appendix D

Piezoelectric Bimorph® Considerations

The purpose of this appendix is to provide a limited and basic introduction to some properties of the double plate ceramic Bimorph® used in the piezoelectric driven pulsed valve. As stated in Section 4.2, the bimorph supplied by Morgan Electro Ceramics (60957-1-PZT-5B) was 1.350±0.005” outer diameter (D) and 0.021±0.002” thick (T). There are many issues associated with a bimorph, and piezoelectric materials in general, to consider for various applications. A more comprehensive discussion is included in, for example, the Morgan Electro Ceramics catalogue and users guide. In order to obtain movement of the bimorph, and pulsing of the gas load through our valve, a voltage (\(V\)) is applied in series across the two sides of the bimorph, which is constrained along its circumference. The piezoelectric charge constant (\(d_{31}\)) also must be known, which is related to the piezoelectric voltage constant (\(g_{31}\)) by

\[
d_{31} = g_{31} \varepsilon_{33}^m,
\]  

[D.1]  

where \(\varepsilon_{33}^m\) is the permittivity of the material. This material permittivity is related to both the permittivity of free space (\(\varepsilon_0\)), 8.85\times10^{-12} \text{ F/m}, and the dielectric constant of the material (\(k_{33}^m\)) by the usual electrostatic relation
\[ k_{33}^m = \frac{\varepsilon_{33}^m}{\varepsilon_o}. \]  

[D.2]

Thus, the PZT-5B charge constant is approximately \(-185 \times 10^{-12}\) m/V. (Note that the subscripts associated with \(d\) and \(g\) etc. indicate the perpendicular electrode configuration and the direction of translation, respectively, for the first and second subscript. For instance, "31" specifies the electrodes connected perpendicular to axis 3 and indicates that the piezoelectric induced initial translation is in direction 1.)

It must be cautioned that this discussion is valid for quasi-static operation only. In other words, as long as the applied frequency is less than the characteristic resonant frequency of the material \(f_r\), then the following holds true. The following expression relates the resonance frequency to the frequency constant \(N_i\) of the bimorph:

\[ N_i = \frac{8.4 f_r D^2}{T}. \]  

[D.3]

The frequency constant for the PZT-5B bimorph is 1420 Hz-m, implying a characteristic material frequency of approximately 77 Hz (\(\sim 13\) ms). (Our typical experimental period is 15 ms.) The equations for dynamic operation are considerably more involved and, with the arguments given in Section 4.2 and in this appendix, do not need to be considered for a comparison with "push-rod" measurements of the bimorph translation. Of course, it must be understood that this discussion then does not apply to the exact performance of the bimorph under typical dynamic experimental pulsing conditions. Rather, this method is a means of diagnosing the "health" of a bimorph using a pseudo-continuous (low frequency and/or large pulse width) pulse in conjunction with a push-rod caliper (Mitutoyo Digimatic Caliper) that can measure linear distance changes of at least
0.01 mm. Finally, the (static) displacement resulting from an applied voltage across the bimorph discs (in series) is given by

\[ \Delta T = \frac{3d_{33}VD^2}{8T^2}. \]  

These considerations result in a (static) displacement ranging from approximately 0.020 to 0.034 mm for an applied voltage from 70 to 120 V, respectively. This translational distance corresponds to the open-close distance the poppet travels that is driven by the rod attached to the bimorph. It is expected that the static displacement is an upper bound to the dynamical displacement experienced during normal operation.
Vita Auctoris

Charles Patrick Malone was born July 20, 1976 (the day of the first Mars landings!), in Windsor, Ontario, but moved to Tecumseh, Ontario, in grade seven. He graduated from St. Anne’s High School in 1995. Immediately following high school, Charles entered into the Physics Program at the University of Windsor and graduated in 1999 with a B.Sc. (Hons.) and a Minor in Mathematics. He was the grateful recipient of three Nicholas Copernicus Scholarships while working on his Undergraduate Degree in Physics. Straight out of his undergraduate schooling he entered into the Masters Program in Physics at the University of Windsor and after a year was switched over to the Doctorate Program. He was the thankful recipient of the NSERC Postgraduate Scholarships and University of Windsor Tuition Scholarships, and attained the degree of Ph.D. in 2003.