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A STUDY OF IONIZATION DYNAMICS IN CLUSTERS

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ABSTRACT

Delayed ionization is a fascinating phenomenon in which the ionization of a cluster is measured on a microsecond time-scale; one billion times slower than prompt ionization described by Einstein’s photoelectric effect. Due to delayed ionization, and a number of other size dependent phenomena, the study of clusters has become a flourishing field providing new information between the realms of the gas and condensed phases. Due to the intrinsic differences of clusters from all other types of materials, clusters have been described as the fifth phase of matter after solid, liquid, gas and plasma. A plethora of new findings have been uncovered over the recent years as those interested look deeper into this medium with an increasing number and variety of methods. Cluster science continues to grow as a vehicle of study providing insight into the molecular world of nanoscale dimensions. Presented herein, are a number of new studies concerning the delayed ionization of metal-carbon cluster species.

A new experimental technique, referred to as the Reverse Field Technique (RFT), for studying delayed ionization of clusters is presented. The RFT enables delayed ionization to be observed at earlier time steps and with better resolution than previous methods allowed. In contrast to previous methods, the RFT requires no modification to the Wiley-McLaren acceleration region of the time-of-flight mass spectrometer (TOF-MS). The thermionic emission model, used to describe delayed ionization of clusters, is presented in terms of the RFT data.

Results of reflectron studies are presented in order to help elucidate the origins of the delayed atomic ion, which appears only in the study of delayed ionization of the
Metallo-carbohedrene (Met-Car) clusters, $M_8C_{12}$, where M is an early transition metal. In addition, a calculation used to determine the mass of daughter ions created during metastable decay in the first field free region of the TOF-MS is presented.

Time-Resolved fluence studies are presented as a method to determine the number of photons absorbed during photoionization in time-resolved experiments, such as a delayed ionization studied with the RFT or a femtosecond pump-probe spectroscopy. A Macro was written in Visual Basic for Applications in order to analyze data collected via the combination of time-resolved studies and fluence studies. These new time-resolved fluence studies provide information with potential to provide further information concerning excited states of individual clusters species as well as their reaction dynamics.
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Chapter 1

Introduction

Fascination with ionization/electricity possibly began in ancient times when the Ionian, Thales of Miletus, rubbed amber with fur and seemed to magically defy gravity by attracting light objects such as feathers.\cite{1} In modern times we understand this “magic” to be due to static electricity and have since used the ability to remove and manipulate electrons in a controlled manner to build our modern technological world. Despite all the knowledge gained, some details of ionization remain hidden. One such process deserving further investigation is delayed ionization of clusters.

Delayed ionization is a fascinating phenomenon in which the ionization of a cluster, consisting of at least seven atoms in the case of the niobium, tantalum and tungsten metal systems, \cite{2} is measured on a microsecond time-scale. Therefore, the time it takes this long-time delayed ionization to occur is approximately one billion times slower than prompt ionization.\cite{3} Due to delayed ionization and a number of other size dependent phenomena, the study of clusters has become a flourishing field providing new information between the realms of the gas and condensed phases. Due to the intrinsic differences of clusters from all other types of materials, clusters have been described as the fifth phase of matter after solid, liquid, gas and plasma. A plethora of new findings have been uncovered over the recent years as those interested look deeper into this medium with an increasing number and variety of methods. Cluster science continues to
grow as a vehicle of study providing insight into the molecular world of nanoscale dimensions.

The determination of the characteristics of clusters is essential for the next phase of modern technology, which presently revolves around buzz words containing the soon-to-be common household prefix: nano. The nanotechnology being developed at today’s forefront of science includes clusters as the building blocks of new materials designed and constructed for new applications ranging from quantum computing [4] to the eradication of cancer during a single visit to the doctor’s office [5]. However, in order to build this new “nanoworld”, the attributes of the clusters must first be studied and understood.

Nearly a century ago, Albert Einstein was awarded the Nobel Prize for his explanation of the ejection of electrons from metal surfaces induced by the appropriate color of incident light, commonly known as the photoelectric effect. Initial rudimentary understandings of photoionization, first understood by Einstein’s photoelectric effect, considered the process to occur promptly. As discussed by Schlag and Levine and references therein, prompt ionization occurs on the femtosecond timescale, which in most cases can be considered instantaneous [3]. Over the past two decades the study of cluster ionization through interaction with laser light has grown into an enormous sub-discipline of nanoscience. In the late eighties Dao and Castleman, [6] and later Nieman et al., [7] discovered that certain clusters do not ionize promptly, but instead the ionization occurs over a significant delay in time. This observation generated a new community of scientists attempting to unravel the mechanism by which a cluster is able to store energy for such long time periods. To this day, the details of delayed ionization remain only partially understood.

In order for a system to require such a long time to ionize when it has sufficient energy to undergo prompt ionization, there must be some general energy storage
mechanism active in the cluster, or a mechanism such as a bottleneck to an energy transfer from the initially excited mode to the mode leading to ionization.[8][9] Attempts to describe the energy storage mechanism responsible for this delay have been centered around the thermionic emission (TE) model, which is a well understood limiting case [10] involving purely statistical processes.[11]

Quantitative consideration of thermionic emission, such as occurs from a heated filament, is usually based on the Richardson-Dushman equation. Derived on the basis of the free electron model, [10] the Richardson-Dushman equation describes the delayed emission of electrons from bulk substances in which there is a small ratio of work function, $W_f$, to cohesive energy per atom, or a small value of $W_f$ in absolute terms. Klots modified the TE model to account for systems of finite size such as clusters.[11] Klots’ model states that the cluster acts as its own temperature bath and the excitation energy is stored in the vibrational modes of the cluster until the vibrations couple to the electronic modes leading to the eventual ejection of an electron. Along with the heat bath capable of storing the excess energy mentioned above, sufficient time [12] must be allowed for all of a cluster’s phase space to be sampled in order for delayed ionization of clusters to conform with the thermionic emission model.

Delayed ionization has been observed in several different cluster systems [6][7][8] in which the binding energy of the cluster is higher than the cluster’s ionization energy. This characteristic allows the cluster to store energy, in excess of its ionization energy, in the vibrational modes without immediately undergoing fragmentation. This is essential for otherwise there is a high probability that the clusters undergo fragmentation before the vibrations have sufficient time to couple with the electronic modes and emit an
electron. The storage of energy in the vibrational modes, eventually leading to ionization, bears the analogy to thermionic emission in bulk metals. In the case where the process is fully statistical and all of phase space is sampled, the delayed ionization can be described by a version of the thermionic emission model that has been adjusted for the finite size of the cluster.[11][13]

Studies have shown that delayed ionization of clusters is a wavelength independent phenomenon, [8] and according to the thermionic emission model, a completely statistical process. However, according to Levine, [8] evidence is accumulating that delayed ionization also can be influenced by the timescale and means of excitation. It is important to note that true thermionic emission would occur only when sufficient time is given for all of phase space to be sampled, e.g., when nanosecond lasers rather than femtosecond lasers are used to ionize the cluster. It has been observed that whereas DI is prominent when strongly bound clusters are excited with nanosecond laser pulses, the same clusters show only prompt ionization with femtosecond laser pulses.[12] This is due to the insufficient amount of time between photon absorptions in the femtosecond pulse, preventing the totality of the system’s phase space to be sampled before ionization occurs. In turn, the excitation energy never has time to “fill” the vibrational levels, thereby saturating the clusters temperature bath and leading to delayed ionization. Essentially, in order to observe photon induced delayed ionization, a cluster with a binding energy higher than its ionization energy must undergo a multiphoton ionization process with a laser-pulse timescale greater than 750 fs [12] depending on the relaxation time of the system. This is due to the fact that thermionic emission in clusters is a multiphoton process where sufficient time between photon absorptions must be given
such that the total energy of the cluster increases up the vibrational ladder until the internal (vibrational) energy reaches a level sufficient for ionization, and the electron is ejected. Determining whether such processes are completely statistical in nature has stimulated the extensive study of DI in several cluster systems. Motivated by our findings of considerable delayed ionization in a unique molecular cluster discovered by Castleman et al. [14] the Metallocarbohedrenes, (Met-Cars, \( M_8 C_{12} \), where \( M \) is a early transition metal) and growing interest in the basic mechanisms of delayed ionization, we developed a method of studying the details of the process in selected short time intervals.

In previous experiments, delayed ionization was measured with an altered Wiley-McLaren time-of-flight (TOF) lens assembly (see Figure 3-1) where the molecular beam was directed parallel to the axis of detection [15][16]. In order enable focus on the delayed ions rather than the prompt ions, a blocking field was applied to the source region for a finite time after the ionization laser interacted with the molecular beam. The blocking field was then removed, resulting in a field free region between the repeller plate, \( R \), and the extractor plate, \( E \), until at some fixed time later (\( \sim 3 \mu s \)) an extraction pulse was applied to accelerate the delayed ions toward the detector.

The new method presented in this dissertation involves a reverse extraction field applied perpendicular to the excited molecular beam. Since this method extracts the ions orthogonal to the molecular beam and eliminates the field free region between the repeller and extraction plate (TOF\(_1\) and TOF\(_2\), respectively), the mass resolution is increased enabling a more facile investigation of the electron emission rate in selected time intervals. The mathematical concepts of the statistical TE model have been used to date to describe two general types of delayed ionization data. The first observations of
DI, [6][7] which were made using techniques that will be referred to here as a passive method of measuring DI. The approach consisted of analyzing long tails to the slow side of cluster peaks observed using a time-of-flight mass spectrometer (TOF-MS).

Researchers who have attempted to describe this type of DI data with the concepts of the TE model have stated that it is necessary to include additional decay channels that reduce the DI signal (i.e. neutral fragmentation and radiative decay of the delayed ionization species) in order to obtain a good fit between the model and data.[17] An additional decay channel (viz. high energy neutral fragmentation) is added to the model at a delay time when the TE model fit becomes inadequate.[17] The addition of a neutral decay channel at the point where the TE model fails to conform to the passive DI data seems to be an insufficient and somewhat random manner to account for the discrepancy between the model and data. However, a decay channel that was not considered but should be taken into account when studying the tail to the slow side of a mass peak in the spectrum is the fragmentation of heavier ionic species that occurs in the time-of-flight acceleration region.

If a species of high mass is ionized and then fragments into a smaller ion after beginning its acceleration toward the detector, then the mass peak representing that ionic fragment will appear in the spectrum as a tail to the slow side of the smaller species (forming a tail that is identical in appearance to that resulting from delayed ionization). This fragmentation then adds to any delayed ionization signal that is present, or even makes it appear that there is a delayed ionization tail when, in fact, it may only be fragmentation of higher mass species in the acceleration region. Also, with regard to problems concerning the passive study of delayed ionization, the concomitant presence of
prompt ions in the mass spectrum disables passive DI studies from revealing the extent of DI at early times after the initial excitation of the studied species. In addition, the analyses of the tails to the slow side of a peak in a mass spectrum can only be easily studied when there are no species of slightly higher mass present in the spectrum such as is the case in studies made utilizing pure C$_{60}$. In the case of the Met-Car, the tail to the slow side is obscured by heavier species. The new technique presented herein allows the analyses of delayed ionization of species regardless of the sample’s purity.

The second type of DI data has been measured via modified Wiley-McLaren TOF lenses through the utilization of an electric-field blocking technique.[15] In this technique, rather than simply studying the peak shape observed in the mass spectrometer, a blocking electric field is utilized to actively block ions created prior to a selected variable time, $t_1$, by deflecting them off axis from the detector. Ions created in the field free region (FFR) at times between $t_1$ and the extraction time, $t_2$, are then sampled. This technique will be referred to herein as the active measurement of delayed ionization. To perform this active blocking field technique (BFT), fast high-voltage transistor (FHVT) switches (a.k.a. Behlke switches) are used to pulse the appropriate voltages at $t_1$ and $t_2$ (see Figure 3-1). These switches enable blocking and extraction fields to be turned on and/or off quickly (see Chapter 3 for details).

This active method of studying DI allows detection of small DI signal in the presence of large prompt ionization and to our knowledge has been implemented by only a few groups, including the Recknagel and Castleman groups. This limited use of the BFT may be a direct result of the need to modify the Wiley-McLaren TOF lens system (i.e., adding the deflector plates) in order to implement the technique. As will be seen in
Chapter 3, no modification of the experimental set-up is necessary to utilize the new active technique presented herein (the only necessary additions to the experiment are a FHVT switch and an additional high-voltage power supply). The Recknagel group, along with Olof Echt, [15] described in detail the process of fitting the TE model to DI data of pure tungsten clusters collected via an active BFT. However, the model used to describe the data collected via the BFT did not account for the longevity of the extraction pulse at the delayed extraction time, $t_2$. The reverse field technique (RFT) mentioned above and described in Chapter 3 accounts for the subtle details of the voltage pulse as well as provides an advanced technique for studying delayed ionization of clusters.

A prominent uncertainty, deserving mention here in brief, concerns the TE model’s vibronic description of delayed ionization and the phenomenon of the delayed atomic ion.[16] The ambiguity involves the delayed ionization of the metallocarbohedrene (Met-Car) discovered in our group in the early nineties.[14] In the past, [16][18] and more recently, [19] the Met-Car family has been observed to display the characteristic of delayed ionization common to several cluster systems (including the fullerenes [20] and refractory metal clusters) that possess a higher binding energy than ionization energy. There appears a delayed atomic ion (DAI), to the best of our knowledge, observed solely in the presence of the Met-Car. Since the atomic ion, e.g. Zr$^+$, obviously has no vibrational modes to store its ionization energy, its appearance in the delayed ionization spectrum was totally unexpected and has led to a search for reasons explaining this behavior. Evidence has accumulated revealing that the Met-Car’s presence and subsequent fragmentation is responsible for the appearance of the delayed...
atomic ion; however, some questions concerning this issue remain unanswered and are discussed in Chapter 5.[21]

The study of metastable decay has been used extensively in order to examine the fragmentation pathways of clusters in time-of-flight mass spectrometry and provide information about the binding energy of clusters [22][23][24] as well as the kinetic energy released (KER) during their fragmentation.[25][26][27] The metastable decay processes, which are observable in the time windows accessible by this technique, are ones which occur after neutral clusters are ionized in a Wiley-McLaren TOF lens assembly and thereafter accelerated into the first FFR. Ions possessing sufficient internal energy following the ionization process can undergo cluster rearrangement and/or a cluster fragmentation analogous to evaporation. These “hot” ion clusters, referred to as parent ions, which have a sufficient amount of energy to undergo fragmentation, lose neutral \( n \)-monomer units (where \( n \) is an integer) to become daughter ions. Rearrangement of the excited ion clusters can occur without fragmentation; however, daughter ions are not produced in this situation and are therefore not included in the study of metastable decay.

Some examples of cluster systems that undergo the process of metastable decay are: protonated water clusters, \( (H^+(H_2O)_n) \), [28] protonated methanol clusters, \( (H^+(CH_3OH)_n) \) [29], protonated ammonia clusters \( (H^+(NH_3)_n) \), [25] rare gas clusters such as \( \text{Ar}_n^+ \) [27] and metal carbon clusters such as the Met-Car. A number of properties of clusters can be determined from studying the unimolecular reaction processes such as the binding energy and KER as mentioned above, and the rates of the unimolecular reaction. [30] However, according to theoretical predictions made by Klots considering metastable
decay as an evaporative ensemble model [31] and experimental verifications, [22][25][32][33][34] no cluster ion ensemble may be assigned a unique lifetime due to the fact that the reaction rates are not inherent to the ions, but are caused by an ensemble of clusters having a range of internal energies (temperatures) after the ionization event. In the experiments of Märk et al., [32][33][34] the voltage of the acceleration region was scanned. As the voltage of TOF1 was decreased, the rates of reaction of the metastable decay also decreased by factors as large as 10, proving that the MSD did indeed occur over a statistical range as Klots predicted.

However, no theoretical treatment has been derived to determine the loss of mass due to the fragmentation of the parent ion clusters into daughter ion clusters. Previously, the only effective method of determining the mass of the daughter ions (md) was to perform a time intensive cut-off study using the reflectron as an energy analyzer. Presented in Chapter 6 is a method to determine md using the difference in time (Δt) between the arrival of the parent and daughter ions at the detector without the tedious process of performing a reflectron cut-off study.

Previously, the metastable unimolecular dissociation channels and decay fractions of M_mC_n+ (where M = Ti, V, and Nb) were investigated; [35][36] however, Zr_xC_y+ was neglected, due in part to the difficulty in assigning masses in the system with five naturally occurring isotopes of zirconium. With recent studies of the delayed ionization of the zirconium Met-Car, Zr_xC_{12}, [19] it is necessary to uncover more information concerning the decay channels of the zirconium-carbon species. Therefore, the task of interpreting the metastable dissociation (presented in Chapter 5), regardless of the
difficulties involved with the presence of the five isotopes, was undertaken in order to ascertain more information concerning the production of the DAI.

As stated above, delayed ionization of clusters is observed when a cluster possessing a binding energy higher than its ionization energy is excited with a multiphoton process via a laser pulse greater than 750 fs in duration. Multiphoton ionization (MPI), first predicted independently by Geltman [37] and Keldysh [38] in the early 1960s and first observed shortly thereafter by Voronov and Delone [39] in 1965, has continued to be of interest to the laser community since its discovery. The investigation of the phenomenon pertaining to gas phase dynamics and the study of clusters has lead to the discovery of a multitude of other phenomenon all of which cannot be listed here. A few examples, however, are isotope separation, [40] laser induced nuclear fusion, [41] coulomb explosion [42] and the production of multiply charged ions.[43]

Due to the process of MPI itself as well as these additional phenomena, the subject of ionization and fragmentation has continued to attract interest due to the challenges posed to both the experimental and theoretical communities. In the study of multiphoton processes, information pertaining to the number of photons absorbed during the photoionization of the system can be determined by varying the intensity of the ionization laser. The rate of ionization, $I$, for a non-resonant MPI with a coherent (time independent) laser pulse is given by Eq. 1.1

$$I = \sigma_N F^N$$

1.1
where \( \sigma_N \) is the ionization cross-section for \( N \) photons, \( F \) is the ionization laser fluence and \( N \) is the number of photons necessary to reach the ionization continuum. Taking the natural logarithm of both sides of equation 1 yields the following equation, analogous to that of a straight line:

\[
\ln I = N \ln F + \ln \sigma_N
\]

where \( N \), the number of photons, has become the slope of the natural logarithm of the ion intensity as a function of the natural logarithm of the laser fluence. Fluence study experiments can be performed where the quantity of ions created can be measured while varying the ionization laser fluence. The natural logarithm of this data can then be plotted such that the slope of the line can be obtained. This slope, representing the number of photons necessary to reach the ionization continuum, should be an integer within experimental error. Due to several circumstances, it has been observed, however, that this is not always the case.

For example, Lightstone et al., [44] observed non-integer values for the photon order, \( N \), from their measurements of the ionization of MoC. They attributed these non-integer values to fragmentation occurring in the ionization region and described the fragmentation with a rate equation. Their rate equation relates the non-integer photon order to the fragmentation of the parent ions [45] under study, as well as the fragmentation of larger species into the parent ion.[46] In addition to fragmentation processes contributing to non-integer values, Eq. 1.1 is meant to describe ionization occurring in an ideally monochromatic, uniform field; therefore, any divergence from ideality will contribute to the non-integer values. Several additional factors, such as near
resonant excited states, contribute to the non-integer photon order.[47] With all of these conditions, the difficulty in obtaining integer values of photons absorbed in the ionization process is quite obvious; however, all circumstances are constant for each species in the same system and therefore, information may be garnered from the change in relative trends of the system constituents.

In order to further study the MPI process involved during delayed ionization, fluence studies were performed where the ionization laser intensity was varied in order to determine the effect of laser fluence on delayed ionization. It has been shown in the past that fluence is a factor in the production of delayed ions.[8] The delayed ionization was observed using the reverse field technique [13] developed in our laboratory while varying the fluence at each delay time. While performing these studies a new data analysis technique was developed to study the time-resolved fluence effect of delayed ionization. The resulting new technique that we refer to as a “time-resolved fluence study,” enables the measurement of the fluence dependence at the incremental times of delayed ionization. This new technique can be applied to delayed ionization fluence studies as well as femtosecond pump-probe fluence studies.

1.1 References

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Chapter 2

Experimental

2.1 Introduction

The majority of the experiments presented in this thesis were performed on a reflectron time-of-flight mass spectrometer (R-TOFMS) coupled to a laser vaporization (LaVa) source where neutral atoms and clusters were ionized via a nanosecond XeCl Excimer laser (~10 ns pulses, 308 nm). However, the experiment presented in Chapter 6 was performed on a R-TOFMS where non-metal neutral atoms, molecules and clusters were ionized with femtosecond laser pulses (~150 fs pulses, 620 nm) generated by a Colliding Pulse Mode-Locked (CPM) ring dye laser system. Each system will be described in detail below.

2.2 Nanosecond Laser System Coupled to R-TOFMS (LOLA)

A schematic of the laser vaporization (LaVa) source can be found in Figure 2-1. A schematic of the apparatus used with the nanosecond laser system is presented in Figure 2-2. The LaVa source consists of machined Teflon containing a metal rod, 0.635 cm in diameter. The metal rod, as it rotates and translates, is ablated by the second harmonic of a Nd:YAG laser (532 nm, ~10 ns pulse width, ~50 mJ/pulse, 30 Hz), focused with a 70 cm focal length lens. The Nd:YAG laser is externally triggered by a 16
Figure 2-1: Schematic of LOLA’s source
Figure 2-2: Schematic of LOLA
channel analog pattern generator, designed and built by the research electronics group at Penn State. The Pattern Generator is the clock that controls the timing of all equipment in the experiment. As the ablation laser impinges on the metal rod, creating a plasma, a reactant gas (generally CH₄ gas) seeded in helium passes through a pulsed nozzle and over the ablation point. The high energy plasma removes the hydrogen atoms from the hydrocarbon and the remaining carbon reacts with the hot metal ions. The hot gas travels through the nozzle of the Teflon source and expands (supersonically) into high vacuum. Upon expansion, cooling occurs and the metal and carbon atoms cluster together. Ionic species are accelerated off axis by a deflection rod placed after the source (275 V/cm), while neutral species continue through the skimmer which collimates the expansion into a molecular beam. The neutral molecular beam passes between two time-of-flight (TOF) grids where it is intersected with a XeCl Excimer ionization laser, ~10 ns pulses, 308 nm (see Figure 2-2). TOF₁ generally possesses a potential of 4500 V unless it is set to pulse from 1000 V to 4500 V as is the case during delayed ionization experiments (see Chapters 3 and 4 as well as Section 2.2.1 below). TOF₂ is held constant at 3500 V.

Upon ionization of the neutral species, cations are accelerated through the potential field created by the voltages placed on the TOF grids. The potential field accelerates the cations toward or away from the detector, depending on the settings of the experiment. If the cations are accelerated away from the detector they are lost as they pass through TOF₁, whereas if they are accelerated towards the detector, they enter the first field free region (FFR). After the cations pass through the first FFR, they enter the reflectron where a reflecting electric field turns the cations toward the second FFR which ends with the microchannel plate (MCP) detector.
The reflectron can be operated in two modes: soft reflection and hard reflection. In soft reflection, the second grid of the reflectron, \( U_r \), located 1.5 cm beyond the first (grounded) grid of the reflectron is held at 2800 V, and the last grid of the reflectron, \( U_h \), 10.8 cm beyond \( U_r \) is held at a potential of 4600 V. The soft reflection mode enables a greater separation of species differing in mass, charge, or kinetic energy. The separation of ions that differ in kinetic energy due to fragmentation in the field free region enable the study of metastable decay (see Chapters 3 and 4 as well as Section 2.2.4 below). In hard reflection, the reflectron acts as an ion mirror. The second grid, \( U_r \), is held at a high voltage of 4600 V so that ions are reflected toward the detector with separation between species of differing mass and charge; however, little to no separation is achieved between species of differing kinetic energy due to fragmentation in the field free region.

Once the cations have been accelerated away from the reflectron, they enter the second FFR and collide with the MCP detector which possess a front plate after a grounded grid, held at a potential of -2100 V, and a second plate, held at a potential of -500 to -100 V. Upon impact with the front MCP, a cascade of electrons is accelerated to the second plate, causing a second cascade which is then detected as a voltage on the collector plate which is held at ground potential. This voltage signal is amplified and then recorded on a digital oscilloscope (DSO-2100) which is averaged over at least 300 laser shots.
2.2.1 Delayed Ionization: Reverse Field Technique

Delayed ionization (DI) is a phenomenon that will be discussed in more detail in Chapters 3 and 4. In previous experiments, a passive technique was originally employed to study DI, whereas the tail to the slow side of the mass peak within the mass spectrum was analyzed. Later experiments used an active technique where a modified Wiley-McLaren time-of-flight lens system applied a blocking field to the acceleration region, perpendicular to the path of the mass spectrometer (see Chapter 4). The blocking field was applied for a variable period of time, $t_1$, after the ionization laser interacted with the neutral molecular beam in order to remove prompt ions as well as delayed ions. The blocking field was then turned off creating a field free region between the acceleration grids until a time, $t_2$, when a potential was applied to the extraction grids, accelerating the ions toward the detector. This method had its faults in that the neutral molecular beam was parallel to the axis of the mass spectrometer, which diminished the resolution. In addition, in order to sufficiently remove the prompt ions, the blocking field was applied for approximately 0.2 $\mu$s, hindering the observation of early delayed ionization behavior.

The reverse field technique (RFT) presented herein (Chapters 3 and 4) is a new active technique to study delayed ionization that eliminates the two issues of the blocking field technique (BFT) mentioned above. The issue of resolution is alleviated by directing the neutral molecular beam perpendicular to the axis of the mass spectrometer. Also, by placing the point of ionization, i.e., the point at which the ionization laser interacts with the neutral molecular beam close to TOF$_1$, the RFT allows the delayed ionization to be observed in the first 50-100 ns after interaction with the ionization laser. In addition, it is
unnecessary to modify the Wiley-McLaren TOF grids that are utilized in most TOF mass spectrometers. Rather than using additional deflector plates to remove unwanted ions, as was done in the BFT, a simple pulsing scheme of the potentials already applied to the TOF grids is used. This pulsing scheme invokes the use of a fast high voltage transformer (FHVT) switch such as those produced by Behlke USA Inc.

Generally a potential of ~4500 V is applied to TOF$_1$ and a potential of ~3500 V is applied to TOF$_2$. This creates a potential field that accelerates cations toward the reflectron and detector. The RFT applies a potential of ~1000 V to TOF$_1$ for a period of time, $t_I$, which is determined with respect to the interaction of the ionization laser with the neutral molecular beam. With the potential on TOF$_1$ at 1000 V and the potential on TOF$_2$ at 3500 V, there is a reverse potential field that accelerates all ions (prompt and delayed) away from the detector (toward TOF$_1$) until the time, $t_I$. At that time, the potential on TOF$_1$ is pulsed, through the use of the FHVT Behlke switch, from 1000 V to 4500 V. Ions created at $t_I$ are accelerated toward the reflectron and detector. Ions continue to be accelerated to the detector after $t_I$ due to the persistence of the voltage present on the acceleration grid after the Behlke switch has opened, i.e., the voltage on TOF$_1$ remains high enough to accelerate the ions for ~50 μs due to the time it takes for the potential on TOF$_1$ to drain to ground. In this way, prompt ions, as well as prompt and delayed ions, can be removed from the spectrum as the time, $t_I$, is increased relative to the time at which the ionization laser interacts with the neutral molecular beam. By increasingly removing ions from the spectrum in 50 ns time steps, the amount of delayed
ionization created during those specific time intervals after the interaction of the ionization laser with the neutral molecular beam, can be measured.

2.3.2 Automation of the Reverse Field Technique

Due to the analog nature of the 16 channel pattern generator used to control the timing of the reverse field technique, it was necessary for the experimenter to manually complete the following steps in order to acquire data at one particular delay time: start the oscilloscope, wait approximately two minutes, save the acquired data to a file, advance the pattern generator 50 ns and repeat for several hours for a complete study. It was recognized early on that this process could be automated; however, the analog pattern generator could not be computer controlled. Therefore, the research electronics group (REG) at the Pennsylvania State University constructed a digital first in-first out (FIFO) pattern generator that could be programmed through the RS-232 serial port of a PC. The program supplied by the REG was a low level, non-user friendly program written in Visual C++. In order to suitably control the FIFO Pattern Generator such that the delayed ionization experiments could be automated, it was necessary to create a virtual instrument (VI) program in LabVIEW.

This undertaking required many months of programming as well as debugging. Documentation concerning this FIFO pattern generator will be stored on the Castleman group web-site at http://research.chem.psu.edu/awcgroup/Home/Lola/Lola.htm. In addition, the recent purchase of a 12-bit Gage Compuscope 12100 data acquisition
system will allow the full automation of the delayed ionization experiments performed on the time-of-flight mass spectrometer known as LOLA.

In order to control the delayed ionization experiment with a PC, a larger VI will be created in LabVIEW that starts the data acquisition, saves the data to a file, advances the FIFO pattern generator and repeats. This VI will allow the operator to set-up the experiment, start the experiment, and then concentrate on something other than turning a control knob every two minutes. This VI will also be documented on the web-site provided above.

2.3.3 Time-Resolved Fluence Study

Fluence studies were performed in order to determine the number of photons absorbed during the ionization process of species that display delayed ionization (see Chapter 7 and Appendix C). The fluence of the excimer ionization laser was decreased by placing metal screens in the beam bath before the laser entered the ionization region via the Brewster’s window. The ionization laser power was measured via a Molelectron, PowerMax 500A power meter affixed at a location prior to the Brewster window. Ionization intensity was then measured as a function of laser power. Delayed ionization experiments were performed at different ionization laser powers and the photon absorption was determined as a function of time (see Chapter 7 and Appendix C) according to the process detailed in Appendix A. This new technique of time-resolved fluence studies can also be used to determine the photon absorption as a function of time in femtosecond pump-probe spectroscopy. Knowledge of the number of photons
absorbed as a function of time may provide further information concerning energy states as well as lifetimes in reaction dynamics.

2.2.4 Metastable Decay: Reflectron Study

Metastable decay is a process where cluster ions, hot from the ionization event, exhaust their excess energy by evaporating monomers from the cluster. This process can be measured if the hot species are stable enough to undergo the evaporation after they have entered the field free region (FFR) of the mass spectrometer; ergo the species is considered to be metastable.

As stated in Newton’s second law, an object in motion stays in motion unless acted upon by an outside force. This statement expresses the principle which makes possible the detection of metastable decay. Once the hot cluster ion, or parent ion, enters the field free region, there are no longer any forces/fields acting on it. If the metastable parent ion loses mass though the evaporation of a monomer, the ion (as well as the evaporated neutral species) continues to travel at the same velocity as the unfragmented parent ion; however, the product of the metastable decay, otherwise know as the daughter ion, contains less mass and therefore less kinetic energy (KE) than the parent ion even though they are traveling at the same velocity. Since the daughter ion possesses less KE than the parent ion, it is turned by the reflectron (operating in soft reflection) at a lower voltage, i.e., it does not penetrate the reflectron as deeply as does the parent ion. Therefore, the daughter ion travels a shorter path than the parent ions that did not undergo metastable decay and is detected at a slightly earlier time than the parent ion.
Whereas the mass of the parent ions can be determined according to their time-of-flight, the mass of the daughter ions created in the FFR cannot. In order to determine the mass of the parent ions, the kinetic energy equation,

\[
KE = \frac{1}{2} mv^2 \tag{2.1}
\]

must be solved for mass, \( m \), such that

\[
m = \frac{2(KE)}{d^2}. \tag{2.2}
\]

If \( 2(KE)/d^2 = c \), then Eq. 2.2 simplifies to

\[
m = ct^2. \tag{2.3}
\]

Eq. 2.2 is applicable to time-of-flight mass spectrometry because all of the parent ions are created with the same birth potential (BP). The BP is the point in the potential field at which the neutral species are ionized which can be determined if the point of ionization between TOF\(_1\) and TOF\(_2\), as well as the voltages on the TOF grids, are known. As the ions are accelerated to TOF\(_3\), which is held at ground potential, the birth potential is converted to kinetic energy. The mass of the parent species is then directly proportional to the time-of-flight squared. The daughter ions, however, no longer have the same kinetic energy due to their loss of mass and therefore, the mass of the daughter ions cannot be easily determined according to their time-of-arrival at the detector. In order to determine the mass of the daughter ions, a reflectron study must be performed. (For a rudimentary treatment of calculating the mass of the daughter ion according to their time-of-flight, see Chapter 6).
A reflectron study utilizes the reflectron as an energy analyzer (see Chapter 5 and 6). This is done by lowering the reflectron’s “reflecting potential” until the species in question is no longer observed in the mass spectrum. As the potential on the back grid of the reflectron (see Figure 2-2) is lowered, eventually the potential of the reflectron will be too low to turn the ions around toward the detector and the ions will pass through the reflectron. The potential on the back grid of the reflectron at the point when the parent ions pass through the reflectron is equal to the birth potential of the parent ions. Since the daughter ions have less kinetic energy than their parent ions, due to the evaporation of mass in the first field free region, the parent ions pass through the reflectron as the daughter ions continue to be turned around by the reflectron. Eventually, as the potential on the final grid of the reflectron continues to be lowered, the daughter ions will also pass through the reflectron and the potential on the reflectron at which this happens is equal to the kinetic energy of the daughter ions. The mass of the daughter ions can then be determined by the following equation:

$$m_d = \left( \frac{U_d}{U_o} \right) m_p,$$

where $m_d$ is the mass of the daughter ion, $m_p$ is the mass of the parent ion, $U_d$ is the potential equal to the kinetic energy of the daughter ions (determined by the potential on the last grid of the reflectron when the daughter ions pass through the reflectron) and $U_o$ is the birth potential of the parent ions (i.e., the potential on the last grid of the reflectron when the parent ions pass through the reflectron).

In the above description of reflectron studies, the reference to a specific grid of the reflectron used to determine the kinetic energy of an ion in question was left
intentionally vague. This is due to the fact that reflectron studies can be performed in either the soft or hard reflection mode. The chosen mode directly affects which grid of the reflectron receives the focus of the study. If the resolution of the mass spectrometer is high enough to separate the parent and daughter ions in soft reflection mode, then the most common way of performing the reflectron study is in soft reflection (as was the case in Chapter 6.1). In this mode, the disappearance of the individual ions from the mass spectrum, used to determine the kinetic energy of the species, can be observed directly while the potential of $U_k$ is lowered (see Figure 2-2). However, if the parent and daughter ions cannot be resolved in the mass spectrum, then a reflectron study may be performed with the reflectron in hard reflection mode (as was done in Chapter 5.1).

While using the reflectron as an energy analyzer in the hard reflection mode, the potential on $U_i$ is lowered (see Figure 2-2). In hard reflection, the daughter ions are not separated in time from the parent ions; therefore, the daughter and parent ions arrive at the detector simultaneously, creating one mass peak in the spectrum. The daughter and parent ions, however, still possess different quantities of kinetic energy and therefore will pass through the reflectron at different reflecting potentials. The potential on $U_i$ at which the different species pass through the reflectron can be determined by plotting the integration of the area under the peak of the parent/daughter species in question versus reflectron voltage ($U_i$). The potential at which the parent ions pass through the reflectron will appear in the graph as a large drop in peak intensity and the potential at which the daughter ions pass through the reflectron will appear as a smaller, yet significant, drop in intensity at those potentials equal to the kinetic energy of the daughter ion species.
Figure 2-3: Absorption and fluorescence diagram of rhodamine 590 tetrafluoroborate gain dye
2.4 Femtosecond Laser System Coupled to R-TOFMS (Phoenix)

The ionization laser used to perform the experiment reported in Chapter 6 is an amplified Colliding Pulse Mode-locked ring dye laser (CPM). In this arrangement, a gain jet containing rhodamine 590 tetrafluoroborate is pumped by a continuous wave Coherent Innova 305 argon ion laser (5W, all lines visible) causing the dye to fluoresce. More recently, the argon ion laser was replaced with a Coherent Verdi V diode-pumped Nd:YVO₄ laser (4W, 532 nm). The diode-pumped solid state laser is much more stable and greatly resists laser beam drift. The absorption and fluorescence of the gain dye is shown in Figure 2-3. Pumping with the Nd:YVO₄ laser is much more efficient than with the argon ion laser as can be seen by the absorption curve. The absorption maximum of the rhodamine dye is much closer to 532 nm than that of the most intense line in the argon ion distribution (514.5 nm). As a result, less strenuous pumping of the dye is necessary to obtain the same amount of fluorescence. It must be noted, however, that the experiments presented in Chapter 6 were performed with the argon ion laser and the addition of the more stable Nd:YVO₄ laser to the femtosecond system will serve to benefit future experimentation discussed in Section 2.4.

A basic illustration of the CPM dye laser and amplification scheme is given in Figure 2-4. Figure 2-5 shows the pump laser impinging upon the gain dye jet after redirection by a pump-steering mirror, M1. The gain dye is kept at a relatively constant temperature by domestic water cooling and remains at a constant pressure of 40 psi which is further aided by a pulsation dampener to minimize pressure fluctuations. The ethylene
glycol/rhodamine dye enters the laser cavity through a nozzle to produce a broad, flat ribbon bound by two cylindrical edges at Brewster’s angle.

The gain dye is surrounded by three laser optics. The pump laser is redirected by a concave reverse D-cut mirror (M2, 10 cm focus, 0.5” diameter, 0.38” thick, coated for high energy broadband) and focused into the gain dye. Optic M3 (D-cut, 10 cm focus, 0.5”x 0.38”, coated for HeNe, 633 nm) is located to the left of the gain dye and is situated to collect the fluorescence from the excited gain dye. Optic M4 is identical to M3 with the exception that M4 is not D-cut but is rather a whole circular optic. The colliding pulse ring dye laser gets its name because two counterpropagating pulses are present. The counterpropagating pulses are a result of the fluorescence from the gain jet traveling both clockwise and counterclockwise around the laser cavity. Mirror M3 collects the clockwise fluorescence while M4 collects the counterclockwise fluorescence. The fluorescence overlaps in a seven mirror laser cavity forming a continuous wave laser. The continuous wave lasing from the gain jet is interrupted by a saturable absorber jet containing DODCI. The saturable absorber, acting as an organic optical shutter, creates laser pulses, generated at 90 MHz, on the order of 100 fs with pulse energies of ~200 pJ.

Amplification of the laser pulses is achieved in four stages through the use of a six-pass bowtie amplifier (BTA) and three successive Bethune cells in which the beam is progressively expanded from a 2 mm initial diameter to a final beam diameter of 12 mm. All amplification is achieved by transverse pumping of sulphorhodamine 640 in a 50/50 mixture of methanol and water by the second harmonic (532 nm) of a 10 Hz Nd:YAG laser (Spectra Physics GCR-4). The system is Q-switched to produce 5 ns laser pulses of
Figure 2-4: Schematic of the CPM Ring Dye Laser and Amplification System
Figure 2-5: Schematic of the CPM Ring Dye laser
up to 775 mJ in the second harmonic. This energy is too high to be useful in performing experiments and thus is reduced to roughly 450 mJ of energy. 90% of the beam is steered through a series of optics to be used as the pump for the Bethune cells. The remaining 10% percent beam is focused with a 60 cm lens and is used to pump the BTA. Recompression of the femtosecond laser pulse is performed using a prism pair to compensate for group velocity dispersion. The amplified laser pulse is 120-150 fs in duration, possesses ~1.5 mJ of energy and has a wavelength centered at 620 nm. The laser is focused into the mass spectrometer with a 40 cm optical lens.

Water clusters were generated via supersonic expansion of room-temperature water vapor seeded in helium at a pressure between 1.7 and 2.4 bar. The molecular beam produced in this fashion was skimmed and then ionized between the cation TOF grids with femtosecond laser pulses. Methanol clusters were generated in a similar fashion.

Under typical operating conditions, a potential of 4600 V was applied to TOF\textsubscript{1} while the potential applied to TOF\textsubscript{2} was 2980 V. Upon ionization between TOF\textsubscript{1} and TOF\textsubscript{2}, the ionic clusters are accelerated into the first field free region (FFR) of the mass spectrometer before entering a reflectron. For the studies presented in Chapter 6, the reflectron was operated in an even gradient/soft reflection mode with a potential of 530 V applied to $U_i$ and a potential of 4600 V applied to $U_k$. The potentials applied to the grids of the reflectron, necessary to attain an even gradient, depend on the characteristics of the reflectron. The process used in order to determine the correct voltages is described in more detail in Chapter 6. The ions are reversed in the reflectron and accelerated towards the detector, which employs a pair of microchannel plates coupled to an oscilloscope (Agilent Technologies 54820A) for detection (see Figure 2-6).
Figure 2-6: Reflectron time-of-flight mass spectrometer coupled with a reflectron used to analyze the cationic clusters created in the field of the time-of-flight (TOF) grids via the CPM Ring Dye laser
A reflectron study, as described above (Section 2.2.4), was performed in order to experimentally determine the masses of daughter ions formed via evaporative cooling in the first field free region of the mass spectrometer. The experimental findings were compared to theoretical calculations, both of which are presented in Chapter 6.

2.5 Femtosecond Tandem Time-of-Flight Mass Spectrometer

The study of clusters generally involves the ionization of a cluster distribution ensemble in the gas phase. Upon ionization of the cluster distribution several observable events occur and are able to be studied, e.g., Coulomb explosion of clusters, cluster reactions, cluster fragmentation, etc. The study of certain processes, in particular Coulomb explosion, where fragmentation is the main focus of the study, can be difficult due to the fact that the origin of the fragmentation cannot be traced as a result of the presence of the entire distribution of clusters. The only way to be absolutely certain of a mechanistic assignment originating from an individual cluster size is through mass selection.

Beginning in 1999, modifications were made to the femtosecond (fs) time-of-flight mass spectrometer (TOF-MS) described in the previous section. A second TOF-MS, equipped with a new filament source as well as a new laser vaporization (LaVa) source, was added to the original mass spectrometer in order to enable mass selection of clusters via tandem TOF-MS (see Figure 2-7). The fs Tandem TOF-MS entered the testing phase in the spring of 2004 and is designed to work as described below.
Figure 2-7: Schematic of the tandem TOF-MS
Figure 2-8: Close up of the source region of the tandem TOF-MS displaying the anion TOF grids and Einzel lenses.
In order to mass select individual cluster masses, the clusters must possess an electrical charge so that they may be manipulated via electrostatic lenses. The clusters produced in the source of the fs Tandem TOF-MS are created as anions by either the filament or the LaVa source. Once the anionic clusters are created, they pass through a skimmer to create a molecular beam which is focused by an Einzel lens as it enters the anionic TOF acceleration region (see Figure 2-8). A voltage pulse is applied to the TOF lenses (present preliminary test values have been set at -4900 V and -2500 V on TOF$_1$ and TOF$_2$, respectively, with TOF$_3$ held at ground) which accelerate the negatively charged clusters through a second Einzel lens and then into a meter long field free region (FFR). While traversing the FFR, the packet of accelerated clusters separate in time and space according to mass. At the end of the FFR there is a mass gate (MG) and momentum decelerator (MD) used to bring about the mass selection and deceleration of the desired ions, respectively. The set-up is similar in design to one used by L. S. Wang et al.[1]

The mass gate consists of three parallel grids orthogonal to the time-of-flight axis. The first grid of the mass gate (MG$_1$) is grounded, the second grid (MG$_2$) possesses a potential greater than or equal to the birth potential of the anions (≥ -3700 V) and the third grid (MG$_3$) is grounded. Using a push-pull Behlke switch (Behlke 61-03-GSM) the voltage of MG$_2$ is pulsed from -3700 V to ground potential at the appropriate time to facilitate the mass selection of a specific cluster species. Once the desired cluster has been selected, the negative voltage is restored in order to continue the diversion of unwanted cluster species. The velocity of the selected cluster species is reduced upon entering the MD.
The MD consists of 10 stainless steel grids resistively connected (20 ohms) to create a uniform gradient of increasing potential. After passing the first, grounded grid of the momentum decelerator (this grounded grid is the third, grounded, grid of the mass gate, MG₃), the voltage of the last grid of the MD is pulsed to a voltage capable of slowing the mass selected cluster while at the same time minimizing the deterioration of the space focusing of the anion packet. Before exiting the MD, the voltage on the last grid is pulsed back to ground. The magnitude and timing of the voltage pulse on the last grid of the MD will be determined experimentally. After exiting the MD, the cluster packet then passes between the second (original) set of TOF grids where it can be intersected with a fs or ns laser pulse. In order to determine that the appropriate anionic cluster has been mass selected, an MCP detector, configured to detect anions, has been placed beneath the original set of TOF lenses.

Once it has been confirmed through detection at the anion MCPs that the appropriate cluster size has been selected, as well as decelerated, the approximate time at which the ions pass through the second set of TOF grids can be determined. The timing of the pulsed nozzle, Nd:YAG ablation laser, the anion TOF voltage pulse, the mass gate and the momentum decelerator (essentially the first of the two tandem TOF-MS’s) will be controlled via a 16 channel analog pattern generator (PG) designed and built by the research electronics group at Penn State University (PSU). The 16 channel PG will be externally triggered by a 4 channel digital pattern generator (Stanford Research Systems, Inc., Model DG535) which will also control the timing of the cation TOF grids as well as Oscilloscope. Due to the nature of the CPM Dye laser, the amplification Nd:YAG laser is the master clock that begins the timing cycle by externally triggering the Stanford PG.
Since the Stanford PG is directly controlled by the master clock of the amplification
Nd:YAG laser, the external trigger of the analog PSU pattern generator will be adjusted
in time in order to intersect the mass selected, momentum decelerated anionic cluster
with the femtosecond laser pulses.

Once the tandem TOF-MS facility is online, a number of new experiments will be
possible. In addition to experiments as rudimentary as determining the size dependence
of Coulomb explosion by “Coulomb exploding” mass selected clusters of different size,
more elaborate experiments such as negative-neutral-positive, or NeNePo, spectroscopy
[2] can be performed. NeNePo spectroscopy, where a neutral species is created by
removing the electron from the negative ion with a pump laser pulse and then ionizing
that neutral species with a probe laser pulse to form a cation, can be used to study the
time dynamics of reactions that occur only as neutral species (such as the cluster reaction
of transition metal oxides with hydrocarbons presently undergoing study to determine
catalytic information.) [3]. Since it is not possible to mass select neutral cluster species,
these neutral reaction dynamics have yet to be studied in such detail as will be possible
with this new apparatus. The Tandem TOF-MS is presently ongoing preliminary testing.
Niobium oxide anions have been detected at the first set of MCPs below the original
(cationic) TOF lenses.

2.6 References


   (1997) 6688.
Chapter 3

Reverse Field Technique to Study Delayed Ionization in Time-of-Flight Mass Spectrometry*

3.1 Introduction

Delayed ionization of clusters in the gas phase is a form of ionization that occurs over a time-scale that is approximately a billion times slower than standard, or prompt, ionization. Since first observations of delayed ionization [1][2], attempts have been made to describe the mechanism in terms of the thermionic emission model developed for electron emission from bulk metals [3][4]. The thermionic emission model was adapted by Klots to account for systems of finite size [5]; however, according to Levine [6], there is evidence accumulating that delayed ionization can also depend on the timescale and means of excitation. Stimulated by our findings of extensive delayed ionization in Met-Cars and growing interest in the basic mechanisms, we developed a method of studying the details of the process in selected short time intervals.

In previous experiments, delayed ionization was measured with an altered Wiley-McLaren time-of-flight (TOF) lens assembly (see Figure 3-1) where the molecular beam was directed parallel to the axis of detection [3][7]. In order to prevent prompt ions from being detected, a blocking field was applied to the source region for a finite time after the ionization laser interacted with the molecular beam. The blocking field was then removed, resulting in a field free region between the reflector plate, R, and the extractor
Figure 3-1: a) Altered Wiley-McLaren time-of-flight set-up used in prior work [3, 7] to study delayed ionization. b) Potential difference between D₁ and D₂ “blocks” prompt ions from detection until time, t₀, while no potential difference exists between R (TOF₁) and E (TOF₂). Then, after t₀, a field free region (FFR) exists until the extraction time, tₑ, when the voltage on R pulses up and the voltage on E pulses down to accelerate the ions to the detector.
plate, E, until at some fixed time later (~3 μs) an extraction pulse was applied to accelerate the delayed ions toward the detector.

The method described here involves a reverse extraction field applied perpendicular to the excited molecular beam. Since this method extracts the ions orthogonal to the molecular beam and eliminates the field free region between the extraction and repeller plate (TOF$_1$ and TOF$_2$, respectively), the mass resolution is increased. In addition, the reverse field technique enables the investigation of the ionization rate in selected time intervals, including early time intervals never before investigated.

3.2 Experimental

A reflectron time-of-flight mass spectrometer (R-TOFMS) equipped with a laser vaporization (LaVa) source was employed to study delayed ionization (Figure 3-2). The LaVa source consisted of a rotating and translating 6.35 mm diameter zirconium rod (99.9% purity, Aldrich) which was laser ablated using the second harmonic (532 nm) of a Nd:YAG laser (Spectra Physics GCR-150) focused by a lens of 70 cm focal length. A mixture of 15% CH$_4$/He ultra-high purity gas was pulsed through a nozzle (General valve 99-43-900; a modified version of a standard General Valve Series 9 with short pulse duration [8]) with a backing pressure of 4.9x10$^3$ torr over the metal rod at the point of ablation. The mixed vapor was then supersonically expanded into the source chamber at a pressure of 6x10$^{-5}$ torr to form various zirconium-carbon clusters. In order to study only neutral species, ions created in the plasma of the LaVa source were prevented from
reaching the ionization region by use of a deflection rod located approximately 10 cm from the source, to which was applied a potential of ~275 V. The molecular beam was then skimmed and an Excimer XeCl laser (308 nm, Lambda Physik EMG 201 MSC) with a pulse width of ~10 ns was used to ionize the Zr₃C₈ species. The power of the Excimer laser was measured to be 9.46 mJ/pulse at the Brewster’s window. In this set-up, the molecular beam was perpendicular to the axis of detection for increased mass resolution and only cations were detected. The pressure of the detection chamber was 9x10⁻⁷ torr. The source chamber and detection chamber were pumped with a total of four Alcatel oil diffusion pumps backed by mechanical pumps.

In order to remove the prompt ions and observe the delayed ion species, a fast high voltage transistor switch (Behlke switch, Eurotek, Inc. USA) was used to pulse the voltage, \( U_1 \), on TOF₁. Figure 3-3 shows a schematic of the high voltage pulsing. The Behlke switch possesses a rise time of ~30 ns and a total fall time of ~75 μs. The voltage, \( U_2 \), on TOF₂ (see Figure 3-4), was held constant at 3500 V so that initially, before TOF₁ was pulsed from 1000 V to 4500 V, there is an electric field that accelerates the prompt ions away from the detector towards TOF₁, where they collide with TOF₁ and become undetectable.\(^9\) At some variable delay time, \( \Delta t \), after the ionization laser interacts with the molecular beam, the voltage on TOF₁ was pulsed to 4500 V. The voltage of TOF₁ was maintained higher than TOF₂ for 50 μs so that any delayed ions created after the voltage on TOF₁ was pulsed, were accelerated towards a reflectron and ultimately to a microchannel plate (MCP) detector (Galileo).
Figure 3-2: Schematic of ion source for R-TOFMS.
Figure 3-3: New technique to study delayed ionization. From $t_o$ to $t_b$, the potential on TOF$_1$, U$_1$, is 3000 V and the potential, on TOF$_2$, U$_2$, is 4125 V causing ions created in that time to be accelerated into TOF$_1$. Then, at $t_a$, U$_1$ pulses up to 4500 V and ions created after that time are accelerated towards the detector. Notice that in the new technique, $t_b$ and $t_c$ are approximately the same time.
Figure 3-4: Schematic of the TOF acceleration region. X is the point at which the ionization laser interacts with the molecular beam. The curved arrow represents the path of the ion that theoretically does not get accelerated into TOF$_1$. The first bar across the ion path represents the point at which the U$_1$ pulses from 3000 to 4500 V. At this point the ion has to slow down, stop (at the second bar where $v = 0$) and turn around. The calculations represent the distance the ion travels during these two segments of the ion path. If $d_1 + d_2 \geq 0.675$ cm, then the ion collides with TOF$_1$. 

\[
d_1 = \frac{1}{2} a t^2
\]
\[
d_2 = \frac{v^2}{2a}
\]
\[
v = \sqrt{2a_d}
\]
The entire system runs at 30 Hz. Data are collected and averaged over 300 scans on a digital oscilloscope (Link Instruments, DSO-2100).

3.3 Discussion

Calculations utilizing the kinematic equations were performed to determine whether or not the electric field required to remove the prompt ions was effective. As mentioned in Chapter 2, the distance between TOF$_1$ and TOF$_2$ is 1.35 cm. With $U_1$ at 1000 V and $U_2$ at 3500 V, a potential difference of 2500 V was created giving rise to an electric field of -1852 V/cm (the negative sign is inserted here to represent the reverse field’s direction for cations towards TOF$_1$). Since $F=Eq=ma$, the acceleration specific to individual masses can be calculated, where E is equal to 1852 V/cm. The time interval, $\Delta t$, between the instant when the ionizing laser interacts with the molecular beam and when $U_1$ is pulsed can be changed by increments of 0.05 $\mu$s. Using the time interval for which the field is -1852 V/cm, and the acceleration determined from the field ($a_1$), the distance that the mass will travel towards TOF$_1$ can be determined (see Figure 3-4). If that distance is greater than half of the distance between TOF$_1$ and TOF$_2$ (0.675 cm), assuming that the ions are created at the half-way point between these two grids, then the ions will collide with TOF$_1$ and will not be detected. Notice in Figure 3-4 that $a_1$ represents the acceleration before TOF$_1$ pulses ($U_1 = 1000$ V) and $a_2$ is the acceleration after TOF$_1$ pulses ($U_1 = 4500$ V).

Hence, after substitution of the values stated above and 0.05 and 0.1 $\mu$s for $t$, masses up to 447 amu are calculated to be removed in the first time increment while
masses up to 1788 amu will be removed by the second time increment. Also, keep in mind that these calculations were done with the assumption that the ions are created at the half-way point between TOF₁ and TOF₂. In actuality, the ionization point was more likely closer to TOF₁. While preparing for the experiment, the ionization laser was lowered until it was confirmed through observation of an enormous baseline jump on the oscilloscope, that the ionization laser was striking TOF₁. The ionization laser was then elevated until adequate ZrₓCᵧ signal was achieved, therefore placing the ionization event as close to TOF₁ as possible, and decreasing the time it takes for ions to travel the distance to collide with TOF₁. Through these calculations it can be seen that the method is theoretically valid.

3.4 Results

Delayed ionization studies were carried out on zirconium carbide clusters including the Met-Car, Zr₈C₁₂ (see Figure 3-5 for a spectrum taken with no time delay). The delay between the laser pulse interacting with the molecular beam and the pulsing of U₁ was increased for the majority of the experiment in increments of 0.05 μs. At times when all clusters were absent from the spectra and only the delayed atomic ion remained, steps of 0.20 μs were taken (see Figure 3-6).

After integrating the area under the peaks of the Met-Car, the atomic ion, Zr⁺, (which is seen to undergo a substantial delayed emission process) and a peak with m/z ~27, the resulting intensity was plotted versus the delay time (Figure 3-7). Several things can be seen from Figure 3-7. It is evident from the spectra that the marker peak (which is
most likely an impurity in the methane) has no delayed ionization. The intensity for this peak is constant and within one 0.05 \( \mu \)s increment, the intensity falls to zero (see Figure 3-7). Since methane impurity has no delayed ionization, the last point in time at which this peak has a detectable intensity is considered to be time zero, \( t_o \). That is, \( t_o \) is considered to be the point at which the ionization laser is interacting with the molecular beam at the same time that \( U_1 \) is pulsing and accelerating ions towards detection. For this reason the peak with \( m/z \sim 27.5 \) (possibly \( N_2, \) \( CO, \) or \( Al \)) is referred to as the marker peak. Also at this time, peaks with \( m/z \) 1, 4, and 14-16 display anomalous behaviors as can be seen in Figure 3-8. At the same range of time at which the marker peak is no longer detected, the referred to peaks appear to split into two peaks one of which is detected at slightly earlier times. These split peaks then dominate the spectrum as the original peaks disappear. The peak splitting is a result of the prompt ions that are accelerated towards \( TOF_1 \).

These prompt ions that experience the reverse field crash into \( TOF_1 \). That ensuing impact ejects particles that were adsorbed onto \( TOF_1 \). When \( U_1 \) pulses to send ions towards the detector, these ejected particles are “born” at \( TOF_1 \). Since they are born at \( TOF_1 \), they possess a higher birth potential (BP) as they are accelerated towards the detector. From this higher BP, the ejected particles accrue a higher kinetic energy and therefore reach the detector at a slightly earlier time. These particles ejected from \( TOF_1 \), represented by the slightly faster “split” peak, remain in the spectrum while the prompt ions themselves are no longer detected because of their impact with \( TOF_1 \). The time at which the daughter peaks dominate the spectrum and the parent peaks disappear, coincide with the time at which the marker peak is no longer detected. This anomalous behavior
Figure 3-5: Time-of-flight mass spectrum showing the m/z ~27 “marker” peak, the zirconium monomer (Zr⁺) and the Met-Car (Zr₈C₁₂⁺). Spectrum was taken with U₁ = 4500 and U₂ = 4125 V.
Figure 3-6: 3-D plot of zirconium carbide clusters spectra at increasing delay time from top to bottom (0.05 µs, 0.20 µs steps). The last spectrum displaying the marker peak is the zero time. Note the long delay of the met-car and the atomic ion, Zr⁺.
Figure 3-7: Plot of normalized intensity (integrated peak area) vs. delay time for the marker peak, atomic ion and the met-car. Inset shows behavior of the Met-Car between 0.35 and 0.65 μs.
Figure 3-8: a) Peaks representing m/z 1, 4, and 14-16. b) Satellite peaks grow into the spectrum as prompt ions collide with TOF₁ detaching species adsorbed onto TOF₁. When U₁ pulses from 3000 V to 4500 V, these detached ionic species are then accelerated to the detector at higher kinetic energies causing them to appear in the spectrum slightly before their “parent” ions. c) These satellite peaks dominate over the original parent peaks at the time delay when all prompt ions are accelerated into TOF₁. This happens at time 0.05 µs and coincides with the time when the marker peak is no longer detected.
further validates that the marker peak can be used experimentally to determine the $t_o$ in the delayed ionization experiments. This anomaly was eventually eliminated by replacing the solid TOF\textsubscript{1} plate with a TOF\textsubscript{1} grid so that the ions removed in the reverse field passed through the screen of TOF\textsubscript{1} rather than crash into it.

Once the zero time delay between the laser interaction with the molecular beam and the pulsing of TOF\textsubscript{1} was determined, an interpretation of the data collected by means of this technique was necessary and is as follows. At the $t_o$, the laser ionization interacts with the molecular beam at the same time that the voltage on TOF\textsubscript{1} pulses to 4500 V, therefore, prompt ions are detected. However, since TOF\textsubscript{1} possesses a potential higher than TOF\textsubscript{2} for 50 $\mu$s after the pulsing event, prompt ions as well as any delayed ions formed in that 50 $\mu$s time span are detected at $t_o$. Since delayed ionization commonly occurs in a few microseconds [1-7], 50 $\mu$s is ample time to sample all ions created after photoexcitation. The quantity of ions detected at time zero then represents the integral, or sum, of all ions created.

As the time at which TOF\textsubscript{1} pulses from 1000 to 4500 V is delayed relative to the ionization laser, more ions are sent towards TOF\textsubscript{1} rather than the detector. Delaying the extraction time (0.05 $\mu$s) that accelerates the ions to the detector effectively removes any ions that were created in a given 0.05 $\mu$s increment of time, thereby reducing the overall quantity of ions detected. If the difference in ion intensity from one delay time to its subsequent longer delay time is taken, then slices in time of the delayed ionization process can be studied. These data and their implications are discussed in Chapter 4.
The plot in Figure 3-7 shows that the Met-Car has a delayed ionization with a large decrease of intensity at 0.35 μs. With closer inspection (see inset in Figure 3-7) it can be seen to have a finite intensity above the baseline until 0.65 μs. Interestingly, the atomic ion undergoes delayed ionization until 1.95 μs.

The delayed atomic ion was also observed by May et al. [7] and was proposed to have a connection to the presence of the Met-Car. These delayed ionization experiments were repeated with conditions altered to suppress the formation of the Met-Car as can be seen in Figure 3-9. To prevent the formation of the Met-Car, 100% He was used rather than the 15% CH₄/He mixture that was used to produce the Met-Car [10]. When the Met-Car was not present, there was a drastic decrease in delayed atomic ion emission, providing strong supporting experimental evidence for the earlier conjecture.

### 3.5 Conclusion

A technique to study delayed ionization was presented. The zirconium Met-Car, a species known to display delayed ionization, was investigated. Delayed ionization of the Met-Car and of the atomic ion was successfully observed and reported. Chapter 4 delves deeper into the intricacies of the data obtained using this technique and the phenomenon of delayed ionization.
Figure 3-9: Delayed ionization experiment with conditions set so that no Met-Cars are present. Notice that without Met-Cars present there is greatly reduced delayed atomic ion emission. Inset shows intensity of Zr$^+$ and Zr$_9$C$_6^+$ versus delay time.


3.6 References


9. E. E. B. Campbell, G. Ulmer and I. V. Hertel, Phys. Rev. Lett. 67 (1991) 1986. Although this technique is similar to that used by Hertel et al. the use of the fast high voltage transistor Behlke switch, allows one to observe events that occur on a faster time-scale than what Hertel was able to study.

10. There was, however, still some carbon present on the zirconium rod which resulted in zirconium clusters that contained small amounts of carbon. As can be seen in Figure 9, there is still a peak present approximately where the Met-Car would be observed, but slightly later in time. This peak corresponds to the Zr$_9$C$_6$ cluster (m/z = 891 amu). The inset plot in Figure 9 represents the intensity of this peak versus time delay. This peak shows interesting delayed ionization behavior. The intensity stays the same until ~0.40 μs. Since, the potential on TOF$_1$ remains higher than that of TOF$_2$ for ~48 μs after the pulse as described above, all ions that are born after the pulsing event are detected. Keeping this in mind one can see by the inset in Figure 9 that no Zr$_9$C$_6$ ions are formed until ~0.40 μs.
Chapter 4

Delayed Ionization of the Zirconium Met-Car, Zr₆C₁₂*

4.1 Introduction

Delayed ionization (DI) of clusters is a fascinating phenomenon that has attracted extensive attention over recent years and has been observed in several systems. [1][2][3] Initial rudimentary understandings of photoionization, first understood by Einstein as the photoelectric effect, considered the process to occur promptly. As discussed by Schlag and Levine and references therein, prompt ionization occurs on the femtosecond timescale.[4] Delayed ionization, on the other hand, is measured on a microsecond timescale; therefore, the time it takes long-time delayed ionization to occur is approximately one billion times slower than prompt ionization, with varying scales in between.[5] In order for a system to require such a long time to ionize when it has sufficient energy to undergo prompt ionization, there must be some general energy storage mechanism active in the cluster, or a mechanism such as a bottleneck to an energy transfer from the initially excited mode to the mode leading to ionization.[1][6] Thermionic emission (TE) is a well understood limiting case, [7] which involves purely statistical processes that account for an energy storage mechanism.[8]

Quantitative consideration of TE, such as occurs from a heated filament, is usually based on the Richardson-Dushman equation. Derived on the basis of the free electron model, [7] the Richardson-Dushman equation describes the delayed emission of
electrons from bulk substances where there is a small ratio of work function, $W_f$, to cohesive energy per atom, or a small value of $W_f$ in absolute terms. Klots modified the TE model to account for systems of finite size such as clusters.[8] Thermionic emission occurs in bulk metals due to the bulk’s ability to store vibrational energy in the form of heat. Therefore, Klots adjusted the model so that the clusters acted as their own heat bath in which the energy could be stored. Along with the heat bath capable of storing the excess energy mentioned above, sufficient time [9] must be allowed for all of phase space to be sampled in order for delayed ionization to conform with the thermionic emission model. Recknagel and coworkers state that TE is a good model for metal clusters, but point out that the nature of DI of the fullerenes remains a controversial issue.[1][10]

The concepts of the statistical TE model have been used to describe two different types of delayed ionization data. The first observations of DI, [2][3] which were studied using techniques that will be referred to here as a passive method of measuring DI, consisted of long tails to the slow side of cluster peaks observed using a time-of-flight mass spectrometer (TOF-MS). These tails were analyzed to extract information concerning the phenomena. Researchers who have attempted to describe this type of DI data with the concepts of the TE model, have stated that it is necessary to include additional decay channels (i.e. neutral fragmentation and radiative decay) in order to obtain a good fit between the model and data.[11] An additional decay channel (viz. high energy neutral fragmentation) is added to the model at a delay time when the TE model fit becomes inadequate.[11] Due to the concomitant presence of prompt ions in the mass spectrum, passive DI studies could not reveal the extent of DI at early times following the initial excitation of the studied species. In addition, the analyses of the tails to the slow
side of a peak in a mass spectrum can only be easily studied when there is mass selection or when there are no species of slightly higher mass present in the spectrum such as is the case in studies made utilizing pure C$_{60}$. However, in the case of the Met-Car, the tail to the slow side is obscured by heavier species. The new technique presented herein allows the analyses of delayed ionization of species regardless of the sample’s purity.

The second type of DI data has been measured via modified Wiley-McLaren TOF lenses which utilized an electric-field blocking technique.[Figure 3-1, 10] In this technique, rather than simply studying the peak shape observed in the mass spectrometer, an electric field is utilized to block ions created prior to a selected variable time, $t_1$, by deflecting them off axis from the detector. Ions created in the field free region (FFR) at times between $t_1$ and the extraction time, $t_2$, are then sampled. This form of technique will be referred to herein as the active measurement of delayed ionization. To perform this active blocking field technique (BFT), fast high-voltage transistor (FHVT) switches (a.k.a. Behlke switches) are used to pulse the appropriate voltages at $t_1$ and $t_2$. These switches enable blocking and extraction fields to be turned on and/or off quickly.

This active method of studying DI allows detection of small DI signal in the presence of large prompt ionization and to our knowledge has been implemented by only a few groups studying DI, including the Recknagel and Castleman groups. This limited use of the BFT may be a direct result of the need to modify the Wiley-McLaren TOF lens system in order to implement the technique. As will be seen below, no modification of the experimental set-up is necessary to utilize the new active technique presented herein to study DI (the only necessary additions to the experiment are a FHVT switch and an additional high-voltage power supply). The Recknagel group along with Olof Echt,[10]
described in detail the process of fitting the TE model to DI data of pure tungsten clusters collected via an active BFT; however, the model used to describe the data collected via the BFT did not account for the longevity of the extraction pulse at the delayed extraction time, $t_2$.

The TE model, described in section 4.4, assumes that when the blocking time, $t_1$, is equal to the extraction time, $t_2$, the probability of electron emission is zero and DI is no longer observable (see Eq. 4.4). It can be seen from results employing the blocking field technique that experimentally this is not the case and that delayed ions continue to be observed when $t_1$ is equal to $t_2$. The continued presence of signal is due to the decay of the extraction pulse applied at $t_2$, during which time delayed ions continue to be formed.

In other words, when the FHVT switch (in this case a Behlke HTS 31) that provides the extraction field is pulsed on, the voltage rises in a matter of nanoseconds; however, the pulse then decays over a finite amount of time (about 50-75 μs). Hence an extraction field continues to be present and, therefore samples ions created after $t_2$. Leisner et al. [10] (with $t_2 = 5$ μs) compensated for this by using an experimentally determined absorption cross-section of a single tungsten atom chosen to ensure that the model and the cluster data point coincided at 2 μs, while Kooi and Castleman [12] normalized the data to zero when $t_1$ equaled $t_2$. In order for the model presented by Leisner et al. to more accurately describe the BFT experiment, a “push-pull” Behlke switch, ideally consisting of an infinitely short pulse with both a fast rise-time and a fast fall-time, would be required at $t_2$. Using a push-pull switch with these characteristics, the extraction field would collect only the ions created prior to $t_2$ (during the blocking field techniques field free region), and therefore not collect any ions created after $t_2$. However, this must be
noted as a fictionally ideal situation since an infinitely short extraction pulse would not accelerate the ions sufficiently in order to procure a time-of-flight mass spectrum. In order for a TOF-MS to operate properly, the extraction field must be on until the ions have exited the acceleration region (i.e., so all the potential energy has time to be converted to kinetic energy). Therefore, an alternative method is necessary to resolve this problem. In developing the reverse field technique used to collect the data presented herein, much consideration was given to the characteristics of the voltage pulse used to create the extraction field and its role in the TE model. It was soon realized that when implementing the BFT without the utilization of a “push-pull” voltage switch, a modification in the assignment of $t_2$ was necessary in order to appropriately apply the TE model to the experimental set-ups used to actively study DI via blocking field techniques. This modification, i.e. the assignment of $t_2$ to the time at which delayed ionization no longer occurs, is described in the Section 4.4 “Thermionic Emission Model and Data Analyses.” In addition, the form of the TE model necessary to describe the new RFT is discussed.

In this chapter, the delayed ionization data for the heterogeneous molecular cluster known as the Met-Car is presented. Throughout the chapter the process of applying the TE model to the data presented herein is described. The TE model-fits of the Met-Car, as well as a description of the new assignment of the extraction time, $t_2$, are presented.
4.2 Experimental

The apparatus used in this study is a reflectron time-of-flight mass spectrometer (TOF-MS) described in detail elsewhere. [Section 2.2, 13] Hence, only a brief description is given here. A zirconium rod is ablated by the second harmonic of a Nd:YAG (50 mJ/pulse, 532 nm) in a laser vaporization (LaVa) source while a mixture of 15% CH₄/He gas is pulsed over the point of ablation. ZrₓCᵧ clusters are formed in a supersonic expansion. Ions created directly in the LaVa source are deflected with a potential of ~275 V/cm. The expansion is skimmed and the neutral clusters and ensuing molecular beam are directed between two grids, TOF₁ and TOF₂, to which are initially applied potentials of 1000 and 3500 V, respectively. Thereupon, the cluster species are intersected with a ~10 ns pulse of an Excimer XeCl laser (4 mJ/pulse, 308 nm) and, after a variable delay time, the potential on TOF₁ is pulsed up to 4500 V using a fast high voltage transistor switch (Behlke switch HTS 31, Eurotek, Inc., USA; rise time = 15 ns). Ions formed at this time, and thereafter (i.e. the voltage on TOF₁ continues to extract any ions present for at least 50 µs after the initial pulse) are accelerated perpendicular to the molecular beam through a 1.275 m field free region (FFR) toward a reflectron. In order to ensure that the early application of the blocking field serves to remove the prompt ions, the point of ionization, i.e. the point where the ionization laser interacts with the molecular beam, is positioned close to TOF₁. The reflectron is operated in hard reflection mode with the front grid grounded and the second grid, 1.5 cm beyond the first grid, maintained at a potential of 4600 V. Ions that are turned around by the reflectron
thereafter travel through a second 0.4 m FFR and are detected with microchannel plates. Each experiment was averaged from 300 TOF spectra acquired on a digital oscilloscope.

4.3 Results

The reverse field technique (RFT) is described in detail elsewhere; [Chapters 2 and 3, ref 13] however, the concepts are reviewed here for clarity. To study delayed ionization using the RFT, a fast high voltage transistor (FHVT) switch is applied. As stated above, the voltage that is initially applied to TOF$_1$ is 1000 V. This creates a reverse field that accelerates all prompt cations toward TOF$_1$. The FHVT switch then pulses the voltage on TOF$_1$ to 4500 V, creating a forward field that accelerates cations toward the detector. The time at which this high voltage pulse is applied to TOF$_1$ is changed by increments of 50 ns. The reverse field removes all ions (prompt ions and eventually prompt as well as delayed ions) created during the time prior to the application of the voltage pulse.

This method of removing ions from the acceleration region is similar in concept to the blocking field technique in which ions are removed by deflection; however, the reverse field technique eliminates the field free region that occurs in the acceleration region before the extraction pulse. In addition, the early versions of the BFT employed a deflection field oriented perpendicular to the time-of-flight axis, thereby requiring ~0.2 μs to remove the prompt ions. It is worthy of note that the experiments in which delayed ionization was passively studied via peak shape were unable to observe the DI for the first several hundred nanoseconds. This inability was found to be due to the presence of
the prompt ions in the acceleration region since there was no active attempt to remove them. Due to the nature of the RFT, (viz. removal of ions via acceleration over a short distance to the side of TOF₁ opposite the detector) ions are removed from the acceleration region within the first 50 ns time interval after laser excitation, allowing the detection of early delayed ionization. With this set-up (i.e. a FHVT switch connected to TOF₁) DI is studied by incrementally removing additional 50 ns time slices after the laser-cluster interaction, until ions are no longer detectable. Campbell et al. [14] used a similar experimental set-up to study C₆₀; however, then did not incrementally increase the time at which the reverse field pulsed to a forward field. Instead, Campbell et al. passively analyzed the DI tail to the slow side of three mass spectra with delays between the laser and the voltage pulse of 0, 2 and 8 μs.

Figure 4-1 shows a 3-dimensional plot of the delayed ionization data of the zirconium-carbon system and displays pictorially the change in the spectra as the delay time is increased in 0.05 μs time increments. Figure 4-2 is a natural log-linear plot of the temporal behavior of the Met-Car shown in Figure 4-1, displayed in 2-dimensions. The delayed ionization data at early times are important. Figure 4-2 presents data displaying a somewhat different trend than data collected in past experiments made using the modified Wiley-McLaren BFT, or ones employing the passive method. This different result is a consequence of measuring the DI at early times, and is observable in Figure 4-2 as the rapid drop in intensity that occurs directly after the clusters interact with the ionization laser.

This quick drop in intensity results from the removal of the prompt ions within the first time increment. It can be seen that the TE model fit to the data, also presented in
Figure 4-1: 3-D data from delayed ionization study of the zirconium-carbon system. The delay time between the interaction of the ionization laser with the molecular beam and the extraction pulse is increased from the top spectrum to the bottom spectrum. The delay time step is 0.05 μs. The last spectrum to contain the impurity peaks is considered the time zero at which the ionization laser interacts with the molecular beam.
Figure 4-2: Natural log-linear plot of the delayed ionization of the Zr Met-Car (integrated peak area vs. delay time) shown with the thermionic emission model fit. Due to the long extraction time (50 μs), each data point represents the summation of ions created at that time step and thereafter. Inset: Linear-linear plot of data.
Figure 4-2, and discussed in detail below, accounts for this removal of the prompt ions. Furthermore, when comparing the data in Figure 4-2 to the thermionic emission model fits presented by Leisner et al., [10] it can be seen that the shape of the fits that Leisner deemed as inadequate (i.e. the model fits for small tungsten clusters, n<40) in fact do follow the same general trend as the data presented in Figure 4-2. So whereas Leisner et al. had judged the thermionic emission model to fit the data inadequately, due to the steep initial drop of the model, data recorded using the RFT (including the early delay times) shows that the steep initial drop of the thermionic emission model does indeed represent reality when early delayed ionization is included.

Leisner et al. had fit the model to the data by adjusting their absorption cross section (σ) in order to force convergence of the model and data at a delay time of 2 μs. This was required to compensate for the extraction time, t2, which inadequately described the experimental set-up as mentioned above. It would be interesting to see how the TE model would fit the data from the Leisner paper if the adjustments to t2, suggested in this paper to account for the long arbitrary decay of the extraction pulse, were made. Observation of this trend of the data, (i.e. the steep initial drop of DI that then levels off to the familiar steady decay of DI) is enabled by the ability to now observe the ionization at much earlier times. Significantly the trend is in accord with the TE model.

Since, as stated above, the extraction pulse provided by the Behlke HTS-31 FHVT switch remains active for at least 50 μs, each point in the data (Figure 4-2) represents the sum of ions created at that specific time and thereafter. Each additional delay in time of the extraction pulse removes ions created in the 0.05 μs time slice that is no longer sampled. Therefore, in order to determine how many ions were created during
Figure 4-3: Histogram of the difference in intensity of delayed Zr Met-Car ions created at specific time intervals. Since each point in the data (Figure 2) represents the summation of ions created after that time, the difference in adjacent data points is taken to determine the amount of ions created at each time increment (0.05 μs) relative to the amount of ions created at adjacent times. Inset: Expanded view of y-axis.
the specific time intervals, the difference between adjacent data points was taken. The results are displayed in Figure 4-3. Once the characteristic details of the collected data were determined, it was necessary to ascertain the exact nature of the information that the TE model, as applied to the BFT experiments, was providing. From consideration of the equations provided by the Recknagel paper, [10] it was determined that the probability of electron emission calculated for each time, \( t_i \), was also the probability of electron emission at that time and thereafter. It can be seen from Figure 4-3 that the ions created during the 0.05 \( \mu s \) time increments follow a progressively decreasing electron emission process which is consistent with the TE model.

Using the fitting procedure described below, it can be seen (Figure 4-2) that the TE model, (which had been modified by Klots, [8] and previously applied by Leisner \textit{et al.} [10] to the tungsten system) modified to more accurately describe the present delayed ionization experiments, provides a very good fit to the delayed ionization data of the Met-Car. Fitting the data with the model yielded the following values for the adjustable parameters: the absorption cross section was 9.6x10^{-18} \, \text{cm}^2, which gave the average number of 308 nm photons absorbed by the Met-Car as 1.99, and the initial internal energy was 0.14 eV. For comparison, Leisner \textit{et al.} [10] used an absorption cross-section for a single tungsten atom, with a value of 2x10^{-17} \, \text{cm}^2 while Kooi and Castleman [12] fit delayed ionization data for the titanium Met-Car using an experimental best-fit absorption cross-section of 1x10^{-17} \, \text{cm}^2. The values obtained in our study and the excellent model fit to the data lead to the conclusion that our application of the thermionic emission model is a sound description of the delayed ionization of the Met-Car as studied by the RFT.
4.4 Thermionic Emission Model and Data Analysis

Previously, the thermionic emission model, adapted by Klots to account for systems smaller than bulk, [8] has been used to model DI of metal clusters. This model assumes that the energy absorbed upon radiation is immediately distributed over all the degrees of freedom of the cluster. In this section, the model is re-examined in detail and applied to the Zr Met-Car.

The TE model, as used to describe the blocking field technique, determines the theoretical probability of electron emission between two times, $t_1$ and $t_2$. In previous experiments, [10][12] $t_1$ represented the time at which the blocking field was turned off and $t_2$ represented the time at which the extraction field was turned on. The TE model applied to this previous experimental set-up accounted for delayed ions created in the FFR at times between $t_1$ and $t_2$; however, it did not account for any ions that may have been born after the extraction field was turned on at $t_2$.

In order to describe the experimental set-up of the BFT with the model presented below and by Leisner et al., [10] it would be necessary to make adjustments to either the experiment or the model. In order to use the blocking field technique thermionic emission model, the extraction field should be pulsed on at a time, $t_2$, at which the extraction field is no longer actively sending ions to the detector, i.e. when the delayed ionization events cease to occur. This could prove difficult since the prior blocking field technique used a molecular beam path parallel to the mass spectrometer’s axis of detection. Therefore, the time, $t_2$, at which the extraction field is turned on, must be prior to the time when the ions exit the Wiley-McLaren ion lens assembly in order to ensure
that no ions born after \( t_2 \) are detected. Then, only ions created in the FFR between \( t_1 \) and \( t_2 \) would be sampled.

In the new RFT experimental set-up [13] used to produce the data presented herein, \( t_1 \) is again the point at which the blocking field is turned off. However, it is also effectively the time at which the extraction field is turned on since these two events are only separated by the 15 ns rise time of the voltage pulse on TOF\(_1\). (Note that the molecular beam is perpendicular to the axis of the TOF). Therefore, if one wishes to use this form of the thermionic emission model, it is necessary to assign \( t_2 \) differently than in past blocking field technique experiments. Since the extraction time in the reverse field technique, which in the BFT experiments was referred to as \( t_2 \), is essentially equal to the time \( t_1 \) at which the reverse/blocking field turns off, and since the extraction field is active for a duration of time much longer than the time for which delayed ionization is observed (i.e. 50 \( \mu \)s vs. 1-2 \( \mu \)s, respectively), \( t_2 \) for the reverse field technique is assigned to the first delay time in the experiment at which delayed ionization is no longer observed. Assigning \( t_2 \) to this value results in an equation (Eq. 4.4, below) that acts as a “killer function”, essentially bringing the probability of thermionic emission to zero at the time at which delayed ionization is no longer experimentally observed. This modification resulted in successful fits of the model to the data without the need to alter the data in any manner or consider any additional decay channels.

Within this time period, between \( t_1 \) and \( t_2 \), the probability of electron emission, \( P \), for \( n \) number of clusters is as follows

\[
P(n, t_1, t_2) = \int_{E=0}^{\infty} \rho(m, m, E) \cdot p(n, E, t_1, t_2) dE,
\]

4.1
where the integral is over all possible energies, $E$, in the cluster ensemble, where $n$ is the number of atoms in the cluster, $\bar{m}$ is the average number of photons absorbed by the cluster, $m$ is the number of photons and $E$ is the energy of the clusters in the ensemble. The term, $\rho(n, \bar{m}, m, E)$, which hereafter will be referred to simply as $\rho(E)$, is the distribution of internal energies, and $p(n, E, t_1, t_2)$ is the microcanonical probability of electron emission.

### 4.4.1 Microcanonical Probability of Electron Emission

The microcanonical probability is the probability that an electron will be emitted between times $t_1$ and $t_2$ is defined as

$$p(n, E, t_1, t_2) = \exp[-k(n, E) \kappa] \cdot \{1 - \exp[-k(n, E) \cdot (t_2 - t_1)]\}, \quad 4.2$$

where the first term is the probability that an excited neutral cluster will survive until after $t_1$ and the second term is the probability that an excited neutral cluster will ionize between $t_1$ and $t_2$. As stated above, it can be seen from Eq. **4.4** that when $t_2$ is equal to $t_1$, then the probability of electron emission is zero. By assigning $t_2$ as the first time delay at which delayed ionization is no longer detected, the zero probability of electron emission when $t_1$ equals $t_2$ causes the intensity of thermionic emission to go to zero at the same time delay at which the delayed ionization is no longer observed. The adjustable parameters are then solved to fit the model to the data. The microcanonical probability of electron emission involves the thermionic electron emission rate $k(n, E)$, which is accounted for employing the modified Richardson-Dushman relation presented by
Klots.[8] Neglecting the difference in the partition functions prior to and following electron emission, \( k(n,E) \) is taken to be

\[
k(T_b) = (2k_BT_b / h) \cdot \exp\left[-\frac{IP}{k_BT_b}\right] \cdot \left[2(r/a_o) + 2(Q_{surf}\pi/4)^{1/2} + Q_{surf}\right].
\]  

where \( a_o \) is the Bohr radius, and \( h \) is the Planck constant. The ionization potential, IP, may be determined empirically if no experimental data are available.[15] The partition function, \( Q_{surf} \), is defined as

\[
Q_{surf} = \left(\frac{2me^2r^2\cdot k_BT_b}{\hbar^2}\right).
\]

where \( m_e \) is the mass of an electron, \( r \) is the cluster radius, and \( \hbar = h/2\pi \). The rate of electron emission is now given as a function of the isokinetic temperature, \( T_b \), which is related to the energy and the number of clusters in the following manner

\[
E = (3n-6)k_BT_b \cdot \left\{ 1 + \frac{IP}{2CT_b} + \frac{1}{12} \left(\frac{IP}{CT_b}\right)^2 + \cdots \right\}.
\]

wherein \( C = (3n-7)k_B \). Only the first three terms were used since the other terms are insignificant in this application. For every energy in the cluster ensemble there will be a different isokinetic temperature; hence, the microcanonical probability of electron emission will change with both \( t_1 \) and \( E \).

### 4.4.2 Distribution of Internal Energy

The distribution of internal energies is defined as

\[
\rho(E) = \sum_{m=0}^{\infty} \left\{ \frac{(m)^m}{m!} \cdot \exp(-m) \cdot \delta\left[E - E_i - m \cdot h\nu\right] \right\}.
\]
where $m$ is the number of photons, $\bar{m}$ is the average number of photons defined below, $\nu$ is the frequency of the ionization laser, and $E_i$ is the initial internal energy of the cluster system after collisional cooling in the expansion beam but before the cluster/laser interaction. Due to the nanosecond time-scale of the laser pulse, the energy imparted to the cluster by the ionization laser has ample time to distribute evenly throughout the cluster, possibly sampling all of phase space.[1,12] This process causes the cluster to essentially “forget” how it received the energy. Therefore, it is unimportant in the process of thermionic emission how the energy is supplied to the system, as long as there is ample time for all of phase space to be sampled. As a side note, it is significant that employing excitation via femtosecond pulses less than 750 fs, delayed ionization is not observed for C$_{60}$, [9] evidently due to the fact that there is insufficient time for the totality of phase space to be sampled.

The initial energy of the system, $E_i$, though unknown is relatively low due to cooling.[12][16] As stated by Campbell and Levine, [1] lack of knowledge of $E_i$ is one of the TE model’s weak points. Due to the uncertainty of this value, a best fit value is employed in the present work. Once $E_i$ is determined by the model, a range of energies, $E$, where $E = E_i - m \hbar \nu$, is utilized since the delta function only allows these values to be significant; therefore, the range of energy values is chosen in order to make the terms inside the delta function zero. Eq. 4.6 is to be summed from $m = 0$ to $\infty$ for every value of $E$. However, due to the delta function, for every value of $E$, there is only one $m$ from 0 to $\infty$ that gives a non-zero number in the summation. Accordingly, for every chosen energy term making the delta function equal to 1, there is one value of $m$ from 0 to $\infty$ that
Table 4-1: Numerical example of choosing energy values, $E$, in order to determine the internal energy distribution of the cluster ensemble, $\rho(E)$, see text. $E_i$ is the best fit for the initial energy of the cluster, and $m$ is the number of photons, $h\nu$.

<table>
<thead>
<tr>
<th>$E_i = 0.492$ eV</th>
<th>$m$</th>
<th>$E$ (eV)</th>
<th>$E-E_i-h\nu$</th>
<th>$\rho (n,m,E,\nu)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.492</td>
<td>0</td>
<td>0.062</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>4.517</td>
<td>0</td>
<td>0.172</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>8.542</td>
<td>0</td>
<td>0.239</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>12.568</td>
<td>0</td>
<td>0.222</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>16.593</td>
<td>0</td>
<td>0.155</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>20.619</td>
<td>0</td>
<td>0.086</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>24.644</td>
<td>0</td>
<td>0.040</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>28.670</td>
<td>0</td>
<td>0.016</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>32.695</td>
<td>0</td>
<td>0.006</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>36.721</td>
<td>0</td>
<td>0.002</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>40.746</td>
<td>0</td>
<td>0.000</td>
</tr>
</tbody>
</table>
gives a value other than zero for the internal energy distribution summation, \( \rho(E) \). For a clarification via a numerical example see Table 4-1.

The average number of photons is determined based on the following equation

\[
\bar{m} = I_L \cdot \sigma / h\nu
\]

where \( I_L \) is the laser fluence of the ionization laser and \( \sigma \) is the absorption cross-section. In the final step, once that both components of Eq. 4.1 have been determined (i.e. \( \rho(E) \) and \( p(n,E,t_1,t_2) \)), each value of the \( \rho(E) \) is multiplied by each value of the microcanonical probability term, \( p(n,E,t_1,t_2) \), that is also determined at each energy. These products are then summed over all energies at each \( t_1 \) to obtain the final probability at each time step. This sum is the probability of electron emission between \( t_1 \) and \( t_2 \).

4.4.3 Adjustable Parameters

The adjustable parameters in the model were as follows: 1) the absorption cross-section, which directly affects the average number of photons absorbed, and 2) the initial internal energy, \( E_i \).

4.5 Discussion

As mentioned above, the blocking field technique would best be described by the model presented here if the extraction pulse was applied at a time, \( t_2 \), when there was no longer any delayed ionization events. However, the blocking field techniques used in the past employed a molecular beam parallel to the axis of the time of flight mass
spectrometer. Therefore the pulsed extraction field was always applied at times before the neutral excited species exited the acceleration region. In general, when studying the phenomenon of delayed ionization in a TOF-MS coupled with a molecular beam, the fact that the neutral excited ions might exit the acceleration region before ionization occurs is a significant issue when considered by any method, be it passive or active. To determine whether this issue would be a major difficulty in our experimental set-up, we estimated that the excited neutral species would remain in the acceleration region for approximately 50 µs giving us ample time to observe the phenomenon of delayed ionization. This is longer than the values determined for \( t_2 \).

Another issue that warrants some discussion is that the absorption cross section obtained from the model fit to the data, reported above, is noticeably small. Generally, when multiple photons are absorbed there is a first absorption cross section, \( \sigma_1 \), in units of \( \text{cm}^2 \) and then a much smaller valued second absorption cross-section, \( \sigma_2 \), in units of \( \text{cm}^4 \text{.s} \) for the absorption of the second photon. The absorption cross sections (\( \sigma_m \text{ cm}^{2m} \text{.s}^{m-1} \) for each additional \( m \)-photons absorbed) become increasingly smaller in value for each additional photon absorption. However, the thermionic emission model contains only one variable for the absorption cross-section which must account for any and all multiple photon processes that are occurring. It should be noted that the thermionic emission model gives a value of the average number of photons absorbed that is, in this case, greater than 1. Based on this logic that one absorption cross section is accounting for the absorption of multiple photons, it is reasonable to accept a relatively small value for the absorption cross-section that is obtained from the thermionic emission model fit. It is
interesting to note that the value determined here for the $\text{Zr}_8\text{C}_{12}$ $(9.6 \times 10^{18} \text{ cm}^2)$ is virtually identical to that determined for the titanium Met-Car by Kooi and Castleman.[12]

4.6 Conclusion

We have presented a slightly modified thermionic emission model description of the blocking field technique used to actively study delayed ionization, which more accurately describes the experimental set-up. Our new reverse field technique allows delayed ionization to be observed starting from the time of laser/cluster interaction. These early-time data have not been observed by either the passive or active BFT methods used in the past. Whereas the passive technique used to study delayed ionization can most easily be put into service when the species being analyzed is from a pure sample, this new method also allows one to study delayed ionization of a cluster species in the presence of other neighboring clusters. In addition, the only requirements necessary to implement the RFT are a fast high-voltage transistor switch (a.k.a. Behlke switch) and an additional high-voltage power supply, so, therefore, no modifications to the mass spectrometer are necessary.

The TE model fits very well to these new early data, accounting for the first time step at which the prompt ions are removed leaving only delayed ions (i.e. the initial quick drop shown in Figure 4-2). In fitting the thermionic emission model to the delayed ionization of the zirconium Met-Car, we obtain reasonable values for the internal energy of the cluster and the number of absorbed photons. The absorption cross section obtained
from the model is smaller than one would expect from a molecular cluster such as the Met-Car; however, it was noted that the thermionic emission model contains only one absorption cross section to account for both single and multi-photon ionization. It was also noted that the absorption cross section value obtained for Zr₆C₁₂ was virtually identical to the value obtained by Kooi and Castleman for Ti₆C₁₂.[12] A forthcoming publication will further address the issue of describing delayed ionization as a thermionic process, focusing particularly on the effect of fluence along with the modifications presented here.

4.7 References


Chapter 5

Metastable Dissociation of the Zirconium Met-Car, Zr₈C₁₂, and Connections to the Production of the Delayed Atomic Ion*

5.1 Introduction

Previously, the metastable unimolecular dissociation channels and decay fractions of MₙCₙ⁺ (where M = Ti, V, and Nb) were investigated; [1][2] however, Zr₃C₇⁺ was neglected, due in part to the difficulty in assigning masses in the system with five naturally occurring isotopes of zirconium. With recent studies of the delayed ionization of the zirconium Met-Car, Zr₈C₁₂, [Chapters 3, 4 and ref 3] it is necessary to uncover more information concerning the decay channels of the zirconium-carbon species. Therefore, the task of interpreting the metastable dissociation, regardless of the difficulties involved with the presence of the five isotopes, was undertaken.

In the past, [4][5] and more recently, [3] the Met-Car family has been observed to display the characteristic of delayed ionization common to several cluster systems, such as the fullerenes [6] and refractory metal clusters, [7] that possess a higher binding energy than ionization energy. Delayed ionization has been modeled with the thermionic emission model, [7] which was adapted by Klots [8] to enable treatment of systems of size smaller than bulk. This model takes into account the randomization of electronic energy over vibrational modes of the cluster, and assumes that all of phase space is accessed. Since the atomic ion, Zr⁺, obviously has no vibrational modes, its appearance in the delayed ionization spectrum was totally unexpected and has led to a search for
reasons for this observed behavior. Presented herein is evidence pertaining to the source of the delayed atomic ion, along with some detailed as well as general (due to the five isotopes) decay channels of the Zr,C system.

5.2 Experimental

The apparatus used in this study is a reflectron time-of-flight mass spectrometer (R-TOFMS) described in section 2.2.[3] Hence, only a brief description is given here. A zirconium rod is ablated by a 532 nm YAG in a laser vaporization (LaVa) source while a mixture of 15% CH₄/He gas is pulsed over the point of ablation. Zr,C clusters are formed in a supersonic expansion. Ions created directly in the LaVa source are deflected with a potential of ~275 V. The expansion is skimmed and the neutral metal-carbon clusters and ensuing molecular beam is directed between two grids, TOF₁ and TOF₂, to which are applied potentials of 4500 and 3500 V, respectively. Thereupon the cluster species are intersected with a ~10 ns pulse of an Excimer XeCl laser (308 nm). Ions are formed and accelerated perpendicular to the molecular beam through a 1.275 m field free region (FFR) towards a reflectron (see Figure 5-1). For the studies shown here the reflectron was operated in hard reflection mode with the front grid grounded and the second grid, Uᵣ, 1.5 cm beyond the first grid, initially at a potential of 4600 V. The reflectron was used as an energy analyzer to perform a reflectron study by reducing the potential on Uᵣ in increments of ~12 V. Ions that were turned around by the reflectron traveled through a second FFR 0.4 m long and were detected with microchannel plates (MCPs). Data was averaged over 300 spectra on a digital oscilloscope.
**Figure 5-1:** Schematic of the R-TOFMS. The ionization laser interacts perpendicularly with the molecular beam. Ions created between TOF \(_1\) and TOF \(_2\) are accelerated through a field-free region (FFR) after which they encounter the reflectron where they are turned around toward the detector.
### 5.3 Results

Generally, a reflectron study is performed with the reflectron in soft reflection mode. This ensures that the parent and daughter masses are separated in time, resulting in parent and daughter peaks that are fully resolved. The voltage of $U_b$ (see Figure 5-1) is lowered until the parent ions are no longer turned around towards the detector, but instead pass through the reflectron. The potential on the reflectron when this occurs is equal to the birth potential (BP) of the ions. The BP of the ion is a result of where the ion was created in the potential field of the acceleration region. As the ion accelerates to ground (TOF$_3$), the potential energy is fully converted to kinetic energy.

In accordance with Newton’s second law, the daughter ions created in the first FFR travel at the same velocity as their respective parent ions, but have less kinetic energy due to the loss of mass in the fragmentation process. Therefore, the disappearance of the daughter peaks from the mass spectrum follows the disappearance of the parent peaks, and occurs at a lower potential on the reflectron. The voltage at which the daughter peaks disappear is then used to determine the mass of the daughter ions ($m_d$) according to the following equation:

$$m_d = \left( \frac{U_d}{U_o} \right) m_p$$  \hspace{1cm} \text{(5.1)}

where $U_d$ is the potential at which the daughter ion passes through the reflectron, $U_o$ is the birth potential and $m_p$ is the mass of the parent ion.
Since zirconium exists as five naturally occurring isotopes, it is not possible to fully resolve all of the daughter peaks that may be present in the mass spectrum. Therefore, the reflectron study was conducted in the hard reflection rather than soft reflection mode. By conducting the study in this manner, several things must be considered in the data analysis. In hard reflection, the parent ion and daughter ions are not separated in time. This means that a parent ion and any daughter ions that are generated, arrive at the detector at the same time. Therefore, there is no discernible difference between the parent and daughter ions in the mass spectrum, though the presence of daughter ions can lead to an increase in peak width corresponding to any kinetic energy release associated with the dissociation process. However, as the voltage is lowered on $U_t$ (see Figure 5-1), the parent ions begin to pass through the reflectron when $U_t = U_o$, but the daughter ions continue to be turned around and detected as species arriving at the original parent time. By plotting the intensity versus the reflectron voltage, drops in intensity are observed.

The drops in intensity represent voltages at which a species, such as the parent ion, passes through the reflectron and is no longer detected. The first drop in intensity occurs at the voltage equal to the birth potential (BP) (see Figure 5-2). If the intensity falls to zero at the BP, then there is no fragmentation of the parent ion. Since the zirconium monomer cannot fragment into a daughter ion, the intensity of the monomer versus the voltage of the reflectron (Figure 5-2) was used to determine the BP of the parent ions. The value of $U_o = 4220$ V was used as the BP in all calculations of daughter masses. The BP was chosen as the voltage halfway between the peak intensity and zero intensity.
Figure 5-2: Intensity of $\text{Zr}^+$ versus voltage of $U_i$ in the reflectron. The point half-way between the maximum intensity and zero intensity was determined to be the birth potential (i.e. 4220 V).
Figure 5-3: Intensity of Zr$_8$C$_{12}^+$ versus voltage of $U_r$ in the reflectron. Notice that after the initial decrease in intensity representing the birth potential (BP) of the parent ion (Zr$_8$C$_{12}^-$), there is a shoulder indicating the loss of a neutral species (i.e. Zr) that originated from Zr$_8$C$_{12}^+$. 
Furthermore, if the intensity does not immediately drop to zero after the BP, but instead continues with a finite intensity plateau until dropping to zero intensity at a lower voltage, then the original parent ion is identified to have undergone fragmentation (see Figure 5-3). The voltage at which the intensity plateau drops following the drop at the BP can be substituted into Eq. 5.1 as $U_d$ to determine the mass of the daughter ion. By utilizing the reflectron as an energy analyzer in hard reflection mode, the details of the decay channels of particular clusters may be determined as well as how many decay channels are available to the cluster. Figure 5-5 and Figure 5-4 are examples of a parent ion fragmenting into more than one daughter species.

The metastable decay data, e.g. the data in Figure 5-4 and Figure 5-5, were utilized to calculate the decay fractions of daughter ions to their respective parent ions. Figure 5-6 is a plot of the decay fraction, $D = I_d/I_p$, where $I_d$ is the intensity of the daughter ion, which is determined as the height of the fragment’s intensity plateau, and $I_p$ is the intensity of the parent ion, determined as the maximum before the BP. A minimum in the plot of the decay fraction represents a cluster ion with exceptional stability whereas a maximum represents a metastable cluster ion that decays into the more stable structures. The decay channels of $\text{Zr}_x\text{C}_y$ are listed in Table 5-1. Notice that there is evidence that clusters larger than the Met-Car, such as $\text{Zr}_9\text{C}_{16}^+$ and $\text{Zr}_{10}\text{C}_{15}^+$, metastably decay into the exceptionally stable Met-Car. Also there is evidence of $\text{Zr}_3\text{C}_6^+$ and $\text{Zr}_3\text{C}_8^+$ decaying into the “half-cage” of the Met-Car, $\text{Zr}_4\text{C}_6^+$. Furthermore, there is an additional point of interest in the data that is, as of yet, unexplained.

Figures 5-2 to 5-5 display an increase in intensity at the voltage corresponding to the onset of the BP. Upon first consideration, it was proposed that as
Figure 5-4: Intensity of ZrC$_2^+$ versus voltage of $U_l$ in the reflectron. The inset shows the decrease in intensity corresponding to two decay channels; ZrC$_2^+$ → ZrC$^+$ + C and ZrC$_2^+$ → Zr$^+$ + C$_2$. 
Figure 5-5: Intensity of Zr$_{10}$C$_{13-18}^+$ versus voltage of $U_f$ in the reflectron. Notice two additional shoulders after the BP representing two different decay channels: The first shoulder; Zr$_{10}$C$_{13-18}^+ \rightarrow$ Zr$_8$C$_{10-15}^+$ + Zr$_3$C$_3$ and the second shoulder; Zr$_{10}$C$_{13-18}^+ \rightarrow$ Zr$_9$C$_{11-16}^+$ + ZrC$_2$. 
the reflectron voltage is lowered, the point at which the ions are turned around moves deeper into the reflectron and that at a certain point the ions are interacting with the grid on $U_r$. This interaction might have an effect on the ion intensity. However, it was noticed that at the voltages where the daughter ions pass through the reflectron, the interaction of the ions with the grids would also take place as the ions were turned around toward the detector. At the voltages where the daughter ions were no longer detected, there was no increase in intensity. There is, therefore, something special about the specific voltage on the reflectron when this abrupt increase in intensity occurs, namely at the BP. However, we cannot totally rule out the possibility that the effect is an instrumental artifact.

5.4 Discussion

In studies of the delayed ionization of Met-Cars, [3][5] a delayed atomic ion was observed. It was proposed that the Met-Car played a role in the production of this delayed atomic ion and evidence was seen to support this conjecture.[5] It can be seen from Table 5-1, as well as in the literature, [1][2] that the Met-Car, in addition to other metal-carbide species, undergoes the loss of a metal atom in the field free region (FFR). However, it must be noted that this metal atom is neutral and therefore does not contribute to the delayed atomic ion observed. Table 5-1, however, displays the decay channel of $\text{ZrC}_2^+$ which at first glance seems as if it could be a source of the delayed atomic ion signal.
Figure 5-6: Decay fractions ($D=I_d/I_p$) versus cluster mass where $I_d$ is the height of the intensity plateau of the fragment and $I_p$ is the maximum intensity before the birth potential (viz. the intensity of the parent ion). Minimum points represent the most stable clusters whereas maximum points in the graph represent the least stable clusters.
Table 5-1: Decay channels of Zr$_x$C$_y$.

<table>
<thead>
<tr>
<th>Parent Mass (amu)</th>
<th>Assignment</th>
<th>Daughter Ion</th>
<th>Neutral Lost</th>
</tr>
</thead>
<tbody>
<tr>
<td>114-120</td>
<td>ZrC$_2^+$</td>
<td>ZrC$^+$</td>
<td>C</td>
</tr>
<tr>
<td>114-120</td>
<td>ZrC$_2^+$</td>
<td>Zr$^+$</td>
<td>C$_2$</td>
</tr>
<tr>
<td>416</td>
<td>Zr$_5$C$_4^+$</td>
<td>Zr$_7$C$_4^+$</td>
<td>Zr</td>
</tr>
<tr>
<td>428</td>
<td>Zr$_5$C$_6^+$</td>
<td>Zr$_7$C$_4^+$</td>
<td>C</td>
</tr>
<tr>
<td>428</td>
<td>Zr$_5$C$_6^+$</td>
<td>Zr$_7$C$_2^+$</td>
<td>C$_3$</td>
</tr>
<tr>
<td>464</td>
<td>Zr$_5$C$_8^+$</td>
<td>Zr$_7$C$_2^+$</td>
<td>C$_3$</td>
</tr>
<tr>
<td>522-600</td>
<td>Zr$_5$C$^{6-10}$</td>
<td>Zr$_5$C$^{6-10}$</td>
<td>Zr</td>
</tr>
<tr>
<td>522-600</td>
<td>Zr$<em>5$C$</em>{6-10}$</td>
<td>Zr$<em>5$C$</em>{4-8}$</td>
<td>ZrC$_2$</td>
</tr>
<tr>
<td>612-720</td>
<td>Zr$<em>5$C$</em>{6-12}$</td>
<td>Zr$<em>5$C$</em>{5-11}$</td>
<td>ZrC</td>
</tr>
<tr>
<td>878</td>
<td>Zr$<em>5$C$</em>{12}^+$</td>
<td>Zr$<em>7$C$</em>{12}^+$</td>
<td>Zr</td>
</tr>
<tr>
<td>978-1068</td>
<td>Zr$<em>5$C$</em>{14-17}^+$</td>
<td>Zr$<em>5$C$</em>{10-13}^+$</td>
<td>ZrC$_4$</td>
</tr>
<tr>
<td>1056-1176</td>
<td>Zr$<em>{10}$C$</em>{13-18}^+$</td>
<td>Zr$<em>5$C$</em>{10-15}^+$</td>
<td>Zr$_3$C$_3$</td>
</tr>
<tr>
<td>1056-1176</td>
<td>Zr$<em>{10}$C$</em>{13-18}^+$</td>
<td>Zr$<em>5$C$</em>{11-16}^+$</td>
<td>ZrC$_2$</td>
</tr>
<tr>
<td>1170-1272</td>
<td>Zr$<em>{11}$C$</em>{15-18}^+$</td>
<td>Zr$<em>{10}$C$</em>{13-16}^+$</td>
<td>ZrC$_2$</td>
</tr>
<tr>
<td>1272-1404</td>
<td>Zr$<em>{11}$C$</em>{16-21}^+$</td>
<td>Zr$<em>{11}$C$</em>{16-21}^+$</td>
<td>Zr</td>
</tr>
<tr>
<td>1398-1548</td>
<td>Zr$<em>{12}$C$</em>{19-25}^+$</td>
<td>Zr$<em>{12}$C$</em>{17-23}^+$</td>
<td>ZrC$_2$</td>
</tr>
</tbody>
</table>

* Exact masses could not be determined for all species due to poor resolution of the five isotopes

** Since exact masses could not be determined, exact assignments could not be made

*** Calculated neutral lost for average mass of unresolved peak
From Table 5-1, it can be seen that ZrC\textsubscript{2}\textsuperscript{+} has two decay channels. The first decay channel is the loss of a carbon resulting in a daughter ion of ZrC\textsuperscript{+}. The second channel is the loss of mass equal to two carbons (probably C\textsubscript{2} since consecutive daughter losses are unlikely [9]) which leads to a Zr\textsuperscript{+} daughter ion. However, this fragmentation occurs in the first field free region and therefore, any atomic ions created by this decay channel appear in the spectrum as a daughter species to ZrC\textsubscript{2}\textsuperscript{+} and not as the (delayed) atomic ion, Zr\textsuperscript{+}. From this point of fact, it is important to recognize that the delayed atomic ion must be created before TOF\textsubscript{2}, in the acceleration region. However, according to Klots, [9] the metastable decay process occurs over a statistical range and therefore, processes that occur in the field free region of the time-of-flight mass spectrometer, can begin to occur in the acceleration region.

If an ion larger than the atomic ion was born in between the time-of-flight grids where the laser interacts with the molecular beam, then that ion would begin to accelerate towards the reflectron (see Figure 5-7a) according to the equation:

\[ a = \frac{(TOF_1 - TOF_2)}{d} \times \frac{q}{m} \]  

\[ \text{(5.2)} \]

where \( a \) is the acceleration felt by the ion between TOF\textsubscript{1} and TOF\textsubscript{2}, \( q \) is the charge of a proton, \( m \) is the mass of the ion in kg, TOF\textsubscript{1} and TOF\textsubscript{2} are the potentials on each grid and \( d \) is the distance between them. The first term on the right hand side of Eq. 5.2 represents the electric field in the acceleration region between TOF\textsubscript{1} and TOF\textsubscript{2}. If the larger ion were to lose a Zr\textsuperscript{+} at some point before TOF\textsubscript{2} (see Figure 5-7b), then the acceleration of the newly formed atomic ion would greatly increase (compared to that of its heavier mass
parent) due to the inverse relation of the mass to acceleration in Eq. 5.2. This would result in a daughter atomic ion arriving at the detector at the same time as atomic ions that were created from neutral Zr. However, since the daughter atomic ion was originally accelerated as a larger ion at a slower rate, the daughter atomic ion would arrive at a slightly slower time than atomic ions born of neutral atoms. Since this fragmentation happens at statistically different times, the end result would be a Zr peak with a tail to the slow side similar to a tail from delayed ionization.[10]

In Figure 5-8, the Zr$^+$ peak is shown as the reflectron voltage is lowered. As the zirconium ions that were born at the birth potential, i.e. from neutral atoms, begin to pass through the reflectron, a tail to the slow side of the Zr$^+$ peak becomes more visible. The times-of-flight of daughter atomic ions (born from fragmentation at TOF$_2$ in the acceleration region from species of mass greater than or equal to that of ZrC$_2$) were calculated. These calculated times corresponded to the times observed experimentally in the tail to the slow side of the Zr$^+$ peak. Also, since these atomic ions were created statistically over time via fragmentation in the acceleration region, they would have a distribution of slightly lower velocities than the Zr$^+$ born from neutral Zr atoms, and therefore lower kinetic energies, and would therefore be detected as an unresolved hump at reflectron voltages below the birth potential as displayed by Figure 5-8. With this evidence, it can be put forward that the observation of the tail to the slow side of the atomic ion in the reflectron-study data can be attributed to the fragmentation of larger cluster species into Zr$^+$ in the acceleration region (after the ionization event but before reaching TOF$_2$).
Figure 5-7: a) After the molecular beam interacts with the ionizing laser between TOF$_1$ and TOF$_2$, unstable ion clusters are formed (Zr$_x$C$_y^+$ with $x > 1$, $y \geq 0$) and begin accelerating towards ground. b) Over a statistical ensemble of points, after acceleration begins but before TOF$_2$ (represented in the figure as point X), the cluster fragments and loses a Zr$^+$ which arrives at the detector slightly later in time compared to atomic ions that were generated from neutral Zr.
Figure 5-8: As the reflectron voltage is lowered toward and beyond the BP (4220 V), a tail can be seen to the slow side of the atomic ion, Zr\textsuperscript{+}. This tail indicates the detection of Zr\textsuperscript{+} born from fragmentation of larger clusters in the acceleration region. Since the Zr\textsuperscript{+} born from fragmentation has less kinetic energy than Zr\textsuperscript{+} born from neutral Zr (see text), the tail is detected as an unresolved hump at voltages below the BP.
This process of fragmentation after ionization in the acceleration region, supported by the data presented herein, may be utilized to further understand the production of the delayed atomic ion observed exclusively in the Met-Car system. From delayed ionization experiments of zirconium-carbon species, [3][5] it is known that a number of larger cluster species, including the zirconium Met-Car, show delayed ionization behavior. If these species undergo delayed ionization, begin accelerating and then lose a zirconium ion in the acceleration region, then the zirconium ion would be observed as a delayed atomic ion. These peaks, representing the delayed atomic ion, observed in the delayed ionization experiments, referenced above, should then also display tails to the slow side. Figure 5-9 displays zirconium monomer data from a delayed ionization experiment presented in Chapter 3.[3] As the pulsing of the acceleration grids is delayed in time by increments of 50 ns, the prompt ions disappear and the delayed atomic ion, with a tail to the slow side, can be observed.

With the evidence presented in Figure 5-8, it can be seen that zirconium ions are indeed born from larger ions in the acceleration region. In a cluster system such as titanium-carbon [4], there are only two observed delayed ions, i.e. the Met-Car and the atomic ion. Therefore, if the delayed atomic ion is coming from fragmentation of larger ions in the acceleration region, then in the case of the titanium system, the delayed atomic ion must be coming from the Met-Car. Like the zirconium Met-Car, as a result of metastable decay, the titanium Met-Car loses a neutral metal atom in the field free region.[11]

Since the delayed atomic ion is coming from larger clusters (i.e. the Met-Car) the ionization potential (IP) of M_7C_{12} must be higher than the IP of the atomic ion in order for the atomic ion to obtain the charge from the cluster. However, when the
Figure 5-9: 3-D arrangement of multiple spectra from a delayed ionization study. As the delay time for observation is increased by increments of 50 ns, the prompt ions disappear from the spectrum and only the delayed atomic ion remains. A tail to the slow side of the delayed atomic ion peak can be seen, just as in the reflectron-study data presented in Figure 8.
Met-Car ion fragments in the field-free-region, the metal atom is lost as a neutral (See Table 1). Therefore, the question as to how the atomic ion obtains the charge is as of yet unanswered and requires further study.

5.5 Conclusion

Presented here is a reflectron study of the zirconium Met-Car performed in hard reflection mode. Decay channels of Zr$_3$C$_{12}^+$ are observed as well as a tail to the slow side of the zirconium monomer, indicating fragmentation in the acceleration region. This fragmentation indicates a source of the previously observed delayed atomic ion emission.

Although it is not yet known in complete detail which species in the zirconium-carbon system decay into the delayed atomic ion, evidence has been collected pointing toward cluster species larger than the monomer in the acceleration region of the TOF-MS. In the case of the titanium-carbon system, the candidacy of the Met-Car as the source of the delayed atomic ion has been further supported.

5.6 References


Chapter 6

Calculation to Determine the Mass of Daughter Ions in Metastable Decay*

6.1 Introduction

The study of clusters has become a flourishing field providing new information between the realms of the gas and condensed phases. A plethora of new phenomena has been uncovered over the recent years as those interested look deeper into this medium with an increasing number and variety of methods. Cluster science continues to grow as a vehicle of study providing insight into the molecular world of nanoscale dimensions.

Previous studies of clusters, focusing on the study of unimolecular reactions in the form of metastable decay (MSD) during cluster fragmentation in the first field free region (FFR) of a reflectron time-of-flight mass spectrometer (R-TOFMS) (see Figure 6-1), have provided information about the binding energy of clusters [1][2][3] and the kinetic energy released (KER) [1][4][5]. The metastable decay processes, which are observable in the time windows accessible by this technique, are ones which occur after neutral clusters are ionized in a Wiley-McLaren TOF lens assembly and thereafter accelerated into the first FFR. Ions possessing sufficient internal energy from the ionization process can undergo cluster rearrangement and/or a cluster fragmentation analogous to evaporation. These “hot” ion clusters, referred to as parent ions, which have a sufficient amount of energy to undergo fragmentation, lose neutral n-monomer units, where n is an integer, to become daughter ions. Rearrangement of the excited ion clusters can occur without
fragmentation; however, daughter ions are not produced in this situation and therefore these are presently not included in the study of MSD.

Some examples of cluster systems that undergo the process of metastable decay are protonated water clusters, \((\text{H}^+\text{(H}_2\text{O})_n)\) [6], protonated methanol clusters, \((\text{H}^+\text{(CH}_3\text{OH})_n)\) [7], protonated ammonia clusters \((\text{H}^+\text{(NH}_3)_n)\) [8], and rare gas clusters such as \(\text{Ar}_n^+\) [9]. A number of properties of clusters can be determined from studying the unimolecular reaction processes such as the binding energy and KER as mentioned above, and the rates of the unimolecular reaction [10]. However, according to theoretical predictions made by Klots considering metastable decay as an evaporative ensemble model [11] and experimental verifications [1][8][12][13][14], no cluster ion ensemble may be assigned a unique lifetime due to the fact that the reaction rates are not inherent to the ions, but are caused by a particular range of internal energies (temperatures) after the ionization event. In the experiments of Märk et al. [12-14], the voltage of the acceleration region was scanned. As the voltage of TOF\(_1\) was decreased, the rates of reaction of the metastable decay also decreased as large as a factor of 10, proving that the MSD did indeed occur over a statistical range as Klots predicted.

In Chapter 5 an investigation employing a reflectron study, where the reflectron was used as an energy analyzer in order to determine the products of the metastable decay process. However, no theoretical treatment has been derived to determine the loss of mass due to the fragmentation of the parent ion clusters into daughter ion clusters. Previously, the only effective method of determining the mass of the daughter ions \((m_d)\) was to perform a time intensive cut-off study using the reflectron as an energy analyzer. Presented herein is a method to determine \(m_d\) when the mass spectrometric resolution is
high enough to distinguish between parent and daughter ions (e.g., when ions are created with femtosecond laser pulses). This method uses the difference in time ($\Delta t$) between the arrival of the parent and daughter ions at the detector without the tedious process of performing a reflectron cut-off study.

### 6.2 Experimental

Water clusters were generated via supersonic expansion of room-temperature water vapor seeded in helium at a pressure between 1.7 and 2.4 bar. The molecular beam produced in this fashion was skimmed and then ionized between the TOF grids with femtosecond laser pulses. The methanol clusters were generated in a similar fashion.

Under typical operating conditions, a potential of 4600 V was applied to TOF$_1$ while the potential applied to TOF$_2$ was 2980 V. In the studies presented here, the reflectron was operated in an even gradient/soft reflection mode with a potential of 530 V applied to $U_i$ and a potential of 4600 V applied to $U_k$. The potentials applied to the grids of the reflectron necessary to attain an even gradient, depend on the characteristics of the reflectron. The process used in order to determine the correct voltages is described in more detail below. The ions are turned around in the reflectron and accelerated towards the detector, which employs a pair of microchannel plates coupled to an oscilloscope (Agilent Technologies 54820A) for detection.

The ionization laser is an amplified colliding pulse mode-locked ring dye laser (CPM). In this arrangement, a gain jet containing rhodamine 590 tetrafluoroborate is pumped by a continuous wave argon ion laser (Coherent Innova 305). Continuous wave
lasing from the gain jet is interrupted by a saturable absorber jet containing DODCI. Laser pulses on the order of 100 fs are generated at 90 MHz with pulse energies of ~200 pJ. Amplification of the laser pulses is achieved in four stages using a six-pass bowtie amplifier and three successive Bethune cells where the beam is progressively expanded from a 2 mm initial diameter to a final beam diameter of 12 mm. All amplification is achieved by transverse pumping of sulphorhodamine 640 by the second harmonic of a 10 Hz Nd:YAG laser (Spectra Physics GCR-4). Recompression is performed using a prism pair to compensate for group velocity dispersion. The amplified laser pulse is 120-150 fs in duration, possesses ~1.5 mJ of energy and has a wavelength centered at 620 nm. The laser is focused into the mass spectrometer with a 40 cm optical lens to yield a final focused beam diameter of ~6.6 μm, which was calculated according to the equation [15]:

\[ \omega_{0,2} = \frac{\lambda f}{\pi \omega_{0,1} \left[ 1 + \left( \frac{\lambda f}{\pi \omega_{0,1}^2} \right)^2 \right]^{1/2}} \]

where \( \omega_{0,2} \) is the beam diameter at the focal point, \( \lambda \) is the wavelength (620 nm), \( f \) is the focal length of the focusing lens (40 cm), and \( \omega_{0,1} \) is the initial beam diameter (12 mm). With a focused beam diameter of this size the peak power was ~10^{16} W/cm^2.

### 6.3 Results and Discussion

The majority of detected ions are created in the ~6.6 μm focal point of the laser positioned between the repeller plate (TOF₁) and the accelerating plate (TOF₂). The potential on these two plates is applied in order to accelerate the parent ions toward the
Table 6-1: Mass of methanol daughter ions (loss of one monomer unit) determined experimentally through a reflectron study compared to masses of daughter ions determined via this new technique.

<table>
<thead>
<tr>
<th>m_p (amu)</th>
<th>m_d (amu) refl. study</th>
<th>calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>97</td>
<td>65.7</td>
<td>66.6</td>
</tr>
<tr>
<td>129</td>
<td>97.0</td>
<td>97.6</td>
</tr>
<tr>
<td>161</td>
<td>128.8</td>
<td>129.3</td>
</tr>
<tr>
<td>193</td>
<td>160.7</td>
<td>160.9</td>
</tr>
<tr>
<td>225</td>
<td>192.9</td>
<td>192.8</td>
</tr>
<tr>
<td>257</td>
<td>225.9</td>
<td>224.3</td>
</tr>
</tbody>
</table>
FFR. Since all clusters are ionized in a very confined region within the potential, the charged clusters have a very narrow kinetic energy distribution (± 1.1 V). Therefore, the velocity of each parent ion, once it is accelerated into the FFR, is proportional to the inverse square of the ions mass:

\[
V_o = \frac{2V_a q}{m_p},
\]

where \( V_o \) is the ion birth potential (BP), \( q \) is the charge of an electron and \( m_p \) is the mass of the parent ion.

In accordance with Newton’s second law, velocity is conserved when a parent ion fragments in the FFR. The daughter ion that is formed after a parent ion loses \( n \)-neutral monomer units has the same velocity as the parent ion; however, it has less mass and therefore less kinetic energy. The daughter ions, therefore, have less momentum and do not penetrate the reflectron as deeply as the parent ions that did not fragment. The daughter ions reach the detector at a time (\( \Delta t \)) before their respective parent ions. Since the loss of mass occurred in the FFR, the mass of the daughter peak cannot be assigned in the typical manner used in R-TOFMS and typically a reflectron cut-off study is performed.

As a means of comparison to the method developed here, a reflectron cut-off study was performed. The reflectron was set in soft reflection mode and the potential of \( U_k \) (see Figure 6-1) was lowered until the parent ions were no longer detected. The potential at which the parent ion peaks disappear is the BP of the ions (see Figure 6-2). After the parent ions were no longer detected, \( U_k \) was continually lowered until the
Figure 6-1: Schematic diagram of the R-TOFMS displaying the source/acceleration region, the first field free region, the reflectron, the second field free region and the MCP detector. Note the first field free region where metastable decay occurs.
daughter ion peaks were no longer detected. The potential at which the daughter and parent ions disappear is:

\[ U_i = V_i q, \]

where \( U_i \) is the energy of the ion in Joules and \( V_i \) is the potential at which the ion was no longer detected. It is important to note that all of the parent ions disappear at approximately the same voltage, the birth potential, but daughter peaks disappear over a range of potentials with the heavier daughter ions disappearing at the higher potentials (see Figure 6-3). Because the ions were all born at the same potential (±1.1 V) the parent ions are all turned around at approximately the same point in the reflectron. The differences in times-of-arrival of the parent ions are due to the differences in velocity according to Eq. 6.2. Once the potential at which the ions disappear is determined the mass of the daughter ions are then calculated as:

\[ m_d = \left( \frac{U_d}{U_o} \right) m_p, \]

and are reported in Table 6-1.

A new method is presented below to calculate the mass of the daughter ions using the difference in time-of-arrival (\( \Delta t \)) between the daughter and parent ions. Since the difference in time is a result of the daughter ion being turned around in the reflectron earlier than the parent ion, the \( \Delta t \) is directly related to the loss of mass. In order to obtain the \( \Delta t \) in a manner that facilitates the calculation of the \( m_d \), the reflectron was set in a soft reflection mode where the reflecting electric field is an even gradient. That is, the
Figure 6-2: The reflectron study on methanol used to determine the birth potential (BP) of the parent ions. The potentials on $U_k$ range from 3580 V (the front spectrum) to 3200 V (the back spectrum). The parent ion peaks (dimer to octamer) all disappear by $\sim$3545 V while the daughter ions continue to be detected. The broad peaks that continue after the parent ions disappear are parent ions that underwent fragmentation in the acceleration region.
potential on the second grid in the reflectron, \( U_t \) (see Figure 6-1), is set according to the equation:

\[
U_t = \left( \frac{U_k}{l_{\text{ref}}} \right) * l_{U_t},
\]

where \( l_{\text{ref}} \) is the length of the reflectron and \( l_{U_t} \) is the distance between the grounded grid of the reflectron and \( U_t \) (see Figure 6-1).

Once the uniform gradient is established, the electric field of the reflectron is represented as

\[
E = \frac{U_k}{l_{\text{ref}}} C_r,
\]

where \( l_{\text{ref}} \) is the length of the reflectron and \( C_r \) is a reflectron constant specific to the reflectron, that is used to fit the data.

Once the field of the reflectron has been modeled, the acceleration of the parent ion in the reflectron can be determined. Since the force of the electric field is

\[
F = Eq = ma,
\]

Eq. 6.7 can be solved for the acceleration of the parent ion, \( a_p \). After substitution of Eq. 6.6, Eq. 6.7 becomes

\[
a_p = C_r \left( \frac{U_kq}{l_{\text{ref}} m_p} \right),
\]

where \( m_p \) is the mass of the parent.

Using the kinematic equation for motion in a straight line under constant acceleration, the velocity as a function of time is:
Figure 6-3: A portion of the reflectron study used to determine the daughter masses showing the result of the decrease in potential on $U_k$ from 3150 V to 2900 V. The peaks represent the daughter ions from the methanol tetramer up to the methanol octamer. Notice that the heavier daughter ions pass through the reflectron at higher potentials.
\[ v = v - at. \quad 6.9 \]

However, the final velocity, \( v \), at the turning point in the reflectron is equal to zero. Taking this into account and solving for time gives:

\[ t_{ir} = \frac{2v_o}{a_i}, \quad 6.10 \]

where \( t_{ir} \) is the total time an ion spends in the reflectron, \( a_i \) is the acceleration of that ion and \( v_o \) is from Eq. 6.2.

The time of the parent ion in a reflectron, set to hard reflection, has been determined previously by Wei, Tzeng and Castleman [1] as

\[ t_{pr} = C \left[ \frac{U_o}{m_p} \right] \frac{1}{2} \frac{m_p}{U_i}, \quad 6.11 \]

where \( U_o \) is the birth potential, \( C \) is a proportionality constant equal to \( \frac{2.88L}{\sqrt{q}} \) and \( L \) is the length (1.5 cm) between the ground plate of the reflectron and \( U_i \). Substituting Eq. 6.2, and Eq. 6.8, into Eq. 6.10 gives

\[ t_{pr} = C_s \left[ \frac{U_o}{m_p} \right] \frac{1}{2} \frac{m_p}{U_k}, \quad 6.12 \]

where \( C_s = \frac{1.63l_{ref}}{\sqrt{q}} \) and \( l_{ref} \) is the length of the reflectron (13.0 cm). The difference in the proportionality constants (\( C \) and \( C_s \)) is due to the fact that the equation derived by Wei et al. is for hard reflection whereas the one derived in this paper is for soft reflection.
Table 6-2: Differences between calculated $m_d$ and ideal $m_d$ values for Figure 6-4 and Figure 6-5.

<table>
<thead>
<tr>
<th>Parent mass (amu)</th>
<th>Daughter mass (amu)</th>
<th>Loss of $\text{H}_2\text{O}$</th>
<th>Loss of $(\text{H}_2\text{O})_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>Ideal</td>
<td>Calculated</td>
</tr>
<tr>
<td>73</td>
<td>54.9</td>
<td>55</td>
<td>38.4</td>
</tr>
<tr>
<td>91</td>
<td>72.9</td>
<td>73</td>
<td>56.2</td>
</tr>
<tr>
<td>109</td>
<td>90.8</td>
<td>91</td>
<td>73.9</td>
</tr>
<tr>
<td>127</td>
<td>108.7</td>
<td>109</td>
<td>91.7</td>
</tr>
<tr>
<td>145</td>
<td>126.6</td>
<td>127</td>
<td>109.5</td>
</tr>
<tr>
<td>163</td>
<td>144.5</td>
<td>145</td>
<td>127.3</td>
</tr>
<tr>
<td>181</td>
<td>162.5</td>
<td>163</td>
<td>145.1</td>
</tr>
<tr>
<td>199</td>
<td>180.4</td>
<td>181</td>
<td>162.8</td>
</tr>
<tr>
<td>217</td>
<td>198.3</td>
<td>199</td>
<td>180.6</td>
</tr>
<tr>
<td>235</td>
<td>216.2</td>
<td>217</td>
<td>198.4</td>
</tr>
</tbody>
</table>
Since the $\Delta t$ between parent and daughter ions occurs in the reflectron, then

$$\Delta t = t_{pr} - t_{dr} . \tag{6.13}$$

After substitution of Eq. 6.10,

$$\Delta t = 2v_o \left( \frac{1}{a_p} - \frac{1}{a_d} \right). \tag{6.14}$$

Solving for the acceleration of the daughter ion, $a_d$, gives:

$$a_d = \frac{2a_p v_o}{2v_o - a_p \Delta t}. \tag{6.15}$$

Since the force of the electric field ($F = Eq$) in the reflectron is constant for species of the same charge, $q$, the accelerations of ions in the reflectron, $a = F/m$, differ only when the mass of the ions are different. The daughter ion has less mass than the parent ion, and hence the daughter ion experiences a larger acceleration that is inversely proportional to the difference in mass such that:

$$a_p - a_d = \frac{F}{m_p - m_d}. \tag{6.16}$$

Therefore, after substitution and rearrangement, the mass of the daughter ion, $m_d$, is determined to be:

$$m_d = m_p - \left[ \left( C_r \frac{U_k q}{l_{ref}} \right) \left( \frac{a_d - a_p}{a_p a_d} \right) \right], \tag{6.17}$$

where the term in brackets represents the mass of the neutral fragment ($n$-monomer units) lost in the metastable decay.
Table 6-3: Differences between calculated $m_d$ and ideal $m_d$ values for Figure 6-6 and Figure 6-7.

<table>
<thead>
<tr>
<th>Parent Mass (amu)</th>
<th>Daughter Mass (amu)</th>
<th>Loss of $\text{CH}_3\text{OH}$</th>
<th>Loss of $(\text{CH}_3\text{OH})_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Calculated</td>
<td>Ideal</td>
</tr>
<tr>
<td>97</td>
<td></td>
<td>66.6</td>
<td>65</td>
</tr>
<tr>
<td>129</td>
<td></td>
<td>97.6</td>
<td>97</td>
</tr>
<tr>
<td>161</td>
<td></td>
<td>129.3</td>
<td>129</td>
</tr>
<tr>
<td>193</td>
<td></td>
<td>160.9</td>
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</tr>
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</tr>
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<td></td>
<td>318.5</td>
<td>321</td>
</tr>
<tr>
<td>385</td>
<td></td>
<td>350.3</td>
<td>353</td>
</tr>
</tbody>
</table>
The validity of the calculation was confirmed with water clusters and methanol clusters. As mentioned earlier, a reflectron cut-off study was performed to determine the daughter ion masses (Table 6-1). Then, with the reflectron set to an even gradient, the masses of the parent ions and the difference in time between the parent and daughter ions were noted and used in the calculation above to determine the mass of the daughter ions.

Figure 6-4 plots the parent masses of water clusters on the x-axis and the daughter masses for a loss of one monomer unit (m=18) along the y-axis. Also, Figure 6-5 plots the daughter masses versus the parent masses for the loss of two monomer units (m=36) from water cluster parents. Figure 6-6 and Figure 6-7 display plots of the methanol cluster results in a similar manner. The dark line represents the ideal daughter masses confirmed experimentally via the reflectron cut-off study, while the white line represents the daughter masses determined by the calculation derived above. Values for Figure 6-4 to Figure 6-7 can be seen in Table 6-2 and Table 6-3. The marked agreement is considered to be indicative of the validity of the calculation.
Figure 6-4: Mass of daughter ions plotted vs. mass of parent ions for loss of one H₂O monomer from (H₂O)ₙH⁺ clusters. The dark line represents ideal masses of the daughter ions confirmed experimentally (refl. study) while the light line represents masses determined with the technique presented herein.
Figure 6-5: Mass of daughter ions plotted vs. mass of parent ions for loss of two H$_2$O monomer units from (H$_2$O)$_n$H$^+$ clusters. The dark line represents ideal masses confirmed experimentally (refl. study) while the light line represents masses determined with the technique presented herein.
Figure 6-6: Mass of daughter ions plotted vs. mass of parent ions for loss of one CH$_3$OH monomer from (CH$_3$OH)$_n$H$^+$ clusters. The dark line represents ideal masses confirmed experimentally (refl. study) while the light line represents masses determined with the technique presented herein.
Figure 6-7: Mass of daughter ions plotted vs. mass of parent ions for loss of two CH$_3$OH monomer units from (CH$_3$OH)$_n$H$^+$ clusters. The dark line represents ideal masses confirmed experimentally (refl. study) while the light line represents masses determined with the technique presented herein.
6.4 Conclusions

Presented in this chapter is a new, less demanding experimental method, to
determine the mass of daughter ions that form when parent cluster ions fragment in an
evaporative metastable decay process. This process occurs in the first FFR of a R-
TOFMS and generally, the parent and daughter ions are able to be resolved when
ionizing isotopically pure neutral species with femtosecond laser pulses. Previous studies
of metastable decay (MSD) have provided information concerning binding energy of
clusters, kinetic energy released (KER) during fragmentation and rates of decay which
are not inherent to the ions, but are caused by a particular range of internal energies
(temperatures) after the ionization event as predicted by Klots. However, to our
knowledge, no theoretical method has been employed to calculate the mass of the
daughter ions using the difference in time ($\Delta t$) between the parent and daughter ions. As
a result, the work presented here provides a useful new tool for the study of metastable
decay.

6.5 References

* J. R. Stairs, T. E. Dermota, E. S. Wisniewski and A. W. Castleman, Jr., *Int. J. of
Chapter 7

Time Resolved Fluence Studies and Delayed Ionization of the Niobium-Carbon Cluster System

7.1 Introduction

Delayed Ionization has been observed in several different cluster systems [1] where the binding energy of the cluster is higher than the ionization energy of the cluster. This characteristic allows the cluster to store the ionization energy in the vibrational modes without immediately undergoing fragmentation. The storage of energy in the vibrational modes, eventually leading to ionization, bears an analogy to thermionic emission in bulk metals. In the case where the process is fully statistical in nature and all of phase space is sampled, the delayed ionization can therefore be described by a version of the thermionic emission model that has been adjusted for the finite size of the cluster.[2][3] According to the thermionic emission model, the vibrational modes of the cluster acts as a temperature bath and eventually, after all of phase space has been sampled, the vibrational modes couple to the electronic modes ejecting an electron on the microsecond time-scale. This ionization time-scale is a billion times slower than prompt ionization described by the photoelectric effect. It is important to note that true thermionic emission would occur only when sufficient time is given for all of phase space to be sampled, e.g., when nanosecond lasers rather than femtosecond lasers are used to ionize the cluster. This is due to the fact that thermionic emission in clusters is a multiphoton process where sufficient time between photon absorptions must be given
such that the total energy of the cluster increases up the vibrational ladder until the internal (vibrational) energy reaches a level sufficient for ionization, and the electron is ejected. In order to ascertain more information concerning this process, fluence studies were performed in an attempt to determine the degree of multiphoton ionization/absorption.

Multiphoton ionization (MPI), first predicted independently by Geltman [4] and Keldysh [5] in the early 1960s and first observed shortly thereafter by Voronov and Delone [6] in 1965, has continued to be a fascination in the laser community since its early discovery. The study of the phenomenon, pertaining to gas phase dynamics and the study of clusters, has lead to the discovery of a multitude of other phenomenon all of which cannot be listed here. A few examples, however, are isotope separation [7], laser induced nuclear fusion [8], coulomb explosion [9] and multiply charged ions [10].

Due to these additional phenomena as well as to the process of MPI itself, the subject has continued to attract interest due to the challenges posed to both the experimental and theoretical communities. In the study of multiphoton processes, information pertaining to the number of photons absorbed during the photoionization of the system can be determined by varying the intensity of the ionization laser. The rate of ionization, \( I \), for a non-resonant MPI with a coherent (time independent) laser pulse is then given by

\[
I = \sigma_N F^N, \tag{7.1}
\]

where \( \sigma_N \) is the ionization cross-section for \( N \) photons, \( F \) is the ionization laser fluence and \( N \) is the number of photons necessary to reach the ionization continuum. Taking the
natural log of both sides of Eq. 7.1 gives the following equation, analogous to that of a straight line:

\[
\ln I = N \ln F + \ln \sigma_N,
\]

where \(N\), the number of photons has become the slope of the natural log of the ion intensity as a function of the natural log of the laser fluence. Fluence study experiments can be performed where the quantity of ions created can be measured while varying the ionization laser fluence. The natural logarithm of this data can then be plotted such that the slope of the line can be obtained. This slope, representing the number of photons necessary to reach the ionization continuum, should be an integer within experimental error. Due to several circumstances, it has been observed, however, that this is not always the case.

For Example, Lightstone et al. [11], observed non-integer values for the photon order, \(N\), determined from their measurements of the ionization of Mo\(_x\)C\(_y\). They attributed these non-integer values to fragmentation occurring in the ionization region and described the fragmentation with a rate equation. Their rate equation relates the non-integer photon order to the fragmentation of the parent ions [12] under study, as well as the fragmentation of larger species into the parent ion. [13] Several additional factors contribute to the non-integer photon order [14].

In performing the so-called fluence study mentioned above to determine the quantity of photons absorbed during delayed ionization, it was natural step to combine the fluence study with the study of delayed ionization. The delayed ionization was observed using the reverse field technique [3][15] described in Chapter 3, while also
varying the fluence at each delay time. The resulting new technique that we refer to as a “time-resolved fluence study”, enables the measurement of the fluence dependence at the incremental times of delayed ionization, and is presented herein.

7.2 Experimental

The apparatus used in this study is a reflectron time-of-flight mass spectrometer (TOF-MS) described in detail elsewhere (see Chapter 2). Hence, only a brief description is given here. A niobium rod is ablated by the second harmonic of a Nd:YAG (50 mJ/pulse, 532 nm) in a laser vaporization (LaVa) source while a mixture of 15% CH₄/He gas is pulsed over the point of ablation. Nb₃C₃ clusters are formed in a supersonic expansion, and ions created directly in the LaVa source are deflected with a potential of ~275 V/cm. The expansion is skimmed and the neutral clusters in the ensuing molecular beam are directed between two grids, TOF₁ and TOF₂, to which are initially applied potentials of 1000 and 3500 V, respectively. Thereupon, the cluster species are intersected with a ~10 ns pulse of an Excimer XeCl laser (308 nm) focused with a 60 cm lens and, after a variable delay time, the potential on TOF₁ is pulsed up to 4500 V using a fast high voltage transistor switch (Behlke switch HTS 31, Eurotek, Inc., USA; rise time = 15 ns). Ions formed at the time of the voltage pulse, and thereafter (i.e. the voltage on TOF₁ continues to extract any ions present for at least 50 μs after the initial pulse) are accelerated perpendicular to the molecular beam through a 1.275 m field free region (FFR) toward a reflectron. In order to ensure that the early application of the blocking field serves to remove the prompt ions, the point of ionization, i.e. the point
where the ionization laser interacts with the neutral molecular beam, is positioned close to TOF$_1$.

The pulsing of the voltage on TOF$_1$ at increasing delays in time as compared to the pulsing of the ionization laser (0.05 µs steps), allows the amount of ionization to be measured at specific times throughout the delayed ionization process. The reflectron is operated in soft reflection mode with the front grid grounded, the second grid, 1.5 cm beyond the first grid, maintained at a potential of 2800 V, and the third grid, positioned 10.5 cm beyond the second grid, held at a potential of 4600 V. Ions that are turned around by the reflectron thereafter travel through a second 0.4 m FFR and are detected with microchannel plates. The power of the Excimer ionization laser is decreased by placing metal screens in the beam path prior to the focusing lens. The Excimer laser power is measured (Molelectron, PowerMax 500A) before the Brewster window. The delayed ionization studies are then performed at five different laser powers: 9.175x10$^4$, 7.075x10$^4$, 4.175x10$^4$, 2.5x10$^4$, 1.67x10$^4$ and 1.25x10$^4$ W/cm$^2$ (3.7, 2.8, 1.7, 1.0, 0.7, 0.5 mJ/pulse, respectively). Each experiment is averaged from 300 TOF spectra acquired on a digital oscilloscope.

**7.3 Results and Discussion**

The reverse field technique used to study delayed ionization of clusters is described in Chapter 3. [3][15] Figure 7-1 shows the delayed ionization of the Nb$_x$C$_y$ system at an ionization laser power of 9.175x10$^4$ W/cm$^2$. As the delay time between the laser pulse and the voltage pulse is increased on the x-axis (labeled “Delay time, µs”), the
Figure 7-1: Delayed ionization of the Nb$_x$C$_y$ cluster system with the ionization laser power at $9.175 \times 10^4$ W/cm$^2$ (3.7 mJ/pulse).
intensity of the ion signal decreases as fewer excited neutral molecules are present and able to undergo delayed ionization. Figure 7-2 shows a fluence study of the NbxCy system at a zero delay time, that is, when the ionization laser interacts with the neutral molecular beam coincidentally with the voltage pulse on TOF1, sending all ions created to the detector. The integer values on the x-axis represent the number of screens placed in the path of the ionization laser, thereby lowering the fluence of the ionization laser and incrementally covering the range of powers listed above. As can be seen in the Figure 7-2, as the power of the ionization laser is lowered, the ion peak intensities also lower. The area under the peaks is integrated and the natural logarithm of that area is plotted versus the natural logarithm of the ionization laser power. Figure 7-3 displays the resulting analysis where the slope of the line is the photon order according to Eq. 7.2 above.

The time resolved fluence study is carried out by performing delayed ionization studies at different ionization laser powers. The slope of the natural logarithm of the ion intensity as a function of the natural logarithm of the ionization laser power is then determined at each time increment of the delayed ionization experiments. (The Visual Basic for Applications program used to determine the slope/photon order, can be found in Appendix 1). Worthy of note is that when determining the photon order, the unit of ionization laser power are inconsequential due to the fact that the slope is a rate of change which is the same regardless of what units are applied to laser intensity, only a constant may arise in Eq. 7.2 to convert laser power to fluence. The resultant plot, displayed in Figure 7-4, is the photon order versus time. Each point in the plot represents the slope of the fluence study at that particular time which is illustrated by the slopes in the insets (see Figure 7-4). Each of these slopes represents the number of photons absorbed in the
Figure 7-2: Fluence study of the Nb\textsubscript{x}C\textsubscript{y} cluster system at zero delay time between ionization laser and extraction pulse on TOF\textsubscript{1}.
ionization process; however, the photon interaction with the neutral molecular beam occurs only at the zero time delay. Therefore, the slopes determined after the zero time delay cannot represent the number of photons absorbed at that time. Instead they must be representative of the amount of energy stored in the vibrational modes from the initial photon absorption that ultimately leads to the delayed ionization of the neutral molecule.

In order to determine whether the position of the ionization laser focal point in the molecular beam affected the ion intensities, the focusing lens, with a long focal length of 60 cm, was translated over a 5 cm range giving no change in the ion distribution. Moreover, since the clusters whose photon orders are being compared differ in mass by a miniscule amount compared to the total weight of the clusters (12 amu vs. approximately 752 amu), cluster size dispersion in the beam should be minimal. Hence, the use of the long focal length would ensure that the clusters in comparison are seeing an equivalent flux of photons.

Figure 7-5 shows an example of the different amount of energy storage between clusters varying in size. Displayed in the figure are the photon orders versus time for Nb$_7$C$_{7,10}$. It can be seen from Figure 7-5 that the Nb$_7$C$_{9,10}$ clusters follow similar trends in the amount of energy stored in the clusters whereas the Nb$_7$C$_8$ cluster displays a slightly different trend accounting for the storage of more energy prior to the ionization event. In contrast the Nb$_7$C$_7$ cluster has the lowest values indicating the least amount of energy storage. Presently the only theoretical calculations of structure available to us are those calculated by Harris and Dance [16] who calculated the structure of Nb$_7$C$_9$; however, the structures of the Nb$_7$C$_{7,8}$ and Nb$_7$C$_{10}$ were not calculated. Therefore, we can as of now only conjecture that there is something unique about the cluster of Nb$_7$C$_8$
Figure 7-3: Natural logarithm of the ion intensity for Nb₃C₃ as a function of the natural log of the ionization laser power. The slope of the line is equal to the photon order according to Eq. 7.2 (see text).
Figure 7-4: Time resolved fluence study: photon order as a function of delay time between the ionization laser pulse and the extraction pulse on TOF₁. As is illustrated in the insets, each point in the figure represents the slope of the natural logarithm of the ion intensity as a function of the natural logarithm of the ionization laser power at that specific time interval, i.e. the photon order at each delay time.
Figure 7-5: Time resolved fluence studies of Nb7C7-10. Note that the Nb7C8 species shows a time resolved fluence trend indicating that it is capable of storing more energy than the Nb7C7-8,10 clusters.
that allows it to store more energy than the clusters with plus or minus one or two carbon atoms.

7.4 Conclusion

A technique of data analyses combining the study of delayed ionization and the effect of fluence on multiphoton ionization resulting in a new method that we refer to as a time-resolved fluence study was presented. In regards to the study of delayed ionization, this new technique allows the amount of energy stored in a cluster to be quantitatively measured and compared to the energy storage of clusters that differ in stoichiometry. Additional analysis will be carried out in order to determine the relevance of the non-integer photon data that results from the ionization fluence effect. Nevertheless, the relative intensities of the time-resolved photon orders may be compared as well as the relative trends between different cluster sizes in the same cluster system.

7.5 References

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Appendix A

Multisolver Program to Analyze Time-Resolved Fluence Data

The following Multisolver Template program was written in Excel 2002 Visual Basic for Applications (VBA), in order to analyze the data for the time-resolved fluence study presented in Chapter 7 and Appendix B.

A.1 Installation

The Multisolver Template Program (MSTP) uses Microsoft (MS) Excel’s Solver function to automatically solve a number of iterations for a range of cells, one after the other, rather than just solving one problem at a time. In order to use the MSTP for the first time on a particular PC, the Solver function must first be installed and referenced in Excel. In order to determine whether the Solver function is installed on your computer, open MS Excel, and pull down the Tools menu. If there is no Solver option in the Tools menu, then it is necessary to install the Solver Add-in. To install the Solver function, go to the Tools menu and select Add-ins. Under Add-ins, select Solver Add-in and click OK. You will be requested to insert the MS Office installation CD. Upon doing so, the Solver Add-in will be installed. Once the Solver is successfully installed, it must be referenced in the Visual Basic (VB) editor.

Once again, pull down the Tools menu, select Macro and open the VB editor, or, while in Excel, hit ALT-F11. In the editor, select Tools from the Toolbar and click on
References. Under References, click Browse. In the drop down menu, click on "*.* All Files." and find the following path, "C:\program files\microsoft office\office 10\library\solver\solver." Click on Solver, not the solver.dll file! Upon installing the Solver function for the first time, it is necessary to use the Solver function in Excel before the Multisolver program will run properly. Run the solver in Excel by going to Tools → Solver. Enter cells into the appropriate fields and click on solve. Once Solver is run in excel then the Multisolver should run as well. In order to produce the time-resolved fluence data, the Multisolver program automatically sets the conditions that normally are set manually in the Solver window.

A.2 Multisolver Code

The Solver, once installed in MS Excel, changes the value of one cell in order to solve for a certain user-determined value in another cell, via iteration. Due to the nature of the Time-Resolved Fluence Study, both the slope and the intercept of the equation of a line must be solved at each time-step of the experiment in order to determine the number of photons absorbed in real time by the species under study. In a time-resolved experiment, such as a femtosecond pump-probe experiment, data from hundreds of time steps may require the slope of the line to be determined. It is unwieldy and time consuming determining this information “by hand”, i.e., using the built in Solver function manually in MS Excel to calculate each individual slope at each time step. The following simple code allows the entire range of slopes at each time step, to be
determined in seconds. Text that comes after an apostrophe are comments that solely provide information to the reader and do not effect the function of the program.

    Sub multisolver()
    
    ' multisolver Macro
    ' Macro recorded 11/6/2002 by Jason Stairs
    
    ' Keyboard Shortcut: Ctrl+Shift+S
    
    ' In order for the multisolver to run on your computer
    ' you must make sure that the SOLVER library is referenced.
    ' To do this, goto tools--->references. In references, click
    ' Browse. In the drop down menu, click on "*. All Files."
    ' Find the following path, "C:\program files\microsoft office\office 10\library\solver\solver." Click on Solver, not the
    ' solver.dll file.
    
    ' If the solver starts to run and then says that there is another
    ' problem such as not enough memory, then run the solver once in
    ' Excel by going to tools--->solver. Enter cells into the appropriate
    ' fields and click on solve. Once Solver is run in excel then
    ' the multisolver should run as well.

    On Error GoTo ErrorHandler

    Dim myLast As Integer  ' declaring variables
    Dim myCheck As VbMsgBoxResult
    Dim myRange As Range
    Dim myEnd As VbMsgBoxResult

    myCheck = MsgBox _
        ("Are you sure you want to run the multisolver?", vbYesNo)

    If myCheck = vbNo Then
        Exit Sub
    End If

    myLast = Range("A1").CurrentRegion.Rows.Count  ' counts the # of time-steps
    Set myRange = Range("B:C")  ' sets the range to be solve, i.e. the slope and
        ' intercept
    Do
        For rwIndex = 2 To myLast
            SolverReset
SolvOptions Derivatives:=2 ' sets solver options
SolvOk SetCell:=Cells(rwIndex, 4), _
  MaxMinVal:=2, ValueOf:="0", _
  ByChange:=myRange.Rows(rwIndex)
SolvSolve UserFinish:=True
SolvFinish KeepFinal:=1

Next rwIndex

myEnd = MsgBox("Multisolver has finished. Would you like to run _
multisolver again?", vbYesNo)
  If myEnd = vbNo Then
    Exit Sub
  End If

Loop

ErrorHandler: MsgBox "Please notify Jason Stairs of error" _
  & Err.Number & vbCrLf & vbCrLf _
  & Err.Description

End Sub

In order for this code to run properly, the data must be inserted into the worksheet
according to a certain format. This format is established by running the MSTemplate
Macro in the Multisolver Template.xls workbook. This necessity is due to the fact that
the Multisolver code is written in such a manner as to solve for the cells in columns B
and C, the slope and intercept, respectively, such that a natural logarithm of the ion
intensity, \( \ln I \), is calculated to match the natural logarithm of the measured intensity with
minimal error between the two values. The calculated \( \ln I \) is determined via the
following equation:

\[
\ln I = N(\ln F) + \ln \sigma 
\]

where \( N \) is the slope (photon order), \( F \) is the fluence and \( \sigma \) is the photoionization cross
section. Column D of the multisolver worksheet, which is labeled Error, takes the
difference between the calculated value of ion intensity and the measured value of ion
intensity, and squares that difference. This is done for each laser fluence and the squared difference of each laser fluence is summed. The slope and intercept are then determined so that this error is minimized.

**A.3 MTemplate Macro**

Before opening the Multisolver Template.xls, make sure that the security setting in Excel, under Tools → Macro → Security is set to Medium. After opening the Multisolver Template.xls, click on the “enable macros” button and insert the fluences used in the experiment under the green columns labeled mJ/pulse. Then run the MTemplate Macro according to the instructions provided. A window will open asking for the first and last time-step of the experiment as well as the time-step interval (see Figure 1-1). The “species” tab provides the option of inputting the number of species to be analyzed (Figure 1-2), i.e., how many clusters are to be analyzed via the multisolver, and therefore, how many worksheets are necessary. When the above information is provided, hit OK and the Template will provide the required worksheets. Input your raw data into the appropriate columns and label all columns appropriately with the proper fluence and cluster names.
Figure 1-1: Screen shot of the MSTemplate Macro.
Figure 1-2: Species Tab for the MSTemplate Macro.
A.4 Preliminary Determinations

Before running the Multisolver, the data itself must be taken into consideration. After the data has been added to the worksheet and the appropriate fluence values have been added, preliminary charts must be graphed on the far right side of the worksheet (see Figure 1-3). The far right side of the worksheet provides the natural logarithm of fluence data and the natural logarithm of intensity data for several time-steps. For each time-step provided, charts must be plotted in terms of \( \ln I \) vs. \( \ln F \). The data points should fall on a straight line. Note that some low fluences provide data that do not fall on the straight line due to the low intensity of the ionization laser. In addition, some high fluences provide data points that do not fall on the line due to saturation of the ionization process. Note the fluences that provide data that do not fall on the straight line, making sure that at least three data points do fall on the straight line (see Figure 1-4). Remove the high and low fluences that do not fall on the line from the error column, column D.

Then run the Multisolver program. After running the multisolver program, the plot will show the slope, \( m \), (column B) versus the delay time (column A).

A copy of the Multisolver Template file (MSTemplate.xls) will be saved on the Castleman group web-site at:

http://research.chem.psu.edu/awcgroup/Home/Lola/Lola.htm
Figure 1-4: Points taken out so only a straight line on at least three data points is left.
Appendix B

Additional Time-Resolved Fluence Study Data: Does One Atom Matter?

B.1 Introduction

Further analysis of the data presented in Chapter 7 uncovered some interesting results that will be presented herein. Theoretical calculations are currently underway in order to understand the following results.

B.2 Data

As stated in Chapter 7, fluence studies that measure the relationship of ionization intensity versus ionization laser power can provide the number of photons absorbed during photoionization by determining the slope of the natural logarithm of the ionization intensity versus the natural logarithm of the ionization laser power. The slope of this line is equal to the photon order, $N$, as stated in Eq. 7.2. Figure 2-1 and Figure 2-2 present the photon order versus delay time for Nb$_6$C$_{4-8}$ and Nb$_8$C$_{6-12}$, respectively. An obvious separation of the data can be observed in both figures. In Figure 2-1 the Nb$_6$C$_4$ and Nb$_6$C$_5$ clusters are seen to absorb two photons while the addition of one more carbon atom to the Nb$_6$C$_5$ cluster to form Nb$_6$C$_6$ causes the photon absorption to rise from a photon order of two to three photons. The clusters Nb$_6$C$_7$ and Nb$_6$C$_8$ are also seen to absorb three photons indicating a clear transition of photon order from two photons to three photons due to the addition of a single carbon atom to Nb$_6$C$_5$. 
Figure 2-1: Photon order vs. delay time for Nb₆C₄₋₈. Note the jump from two photons to three photons with the addition of a single carbon to the Nb₆C₅ cluster to form Nb₆C₆.
Figure 2-2 also shows a clear separation due to the addition of a single carbon atom, in this case to the cluster Nb₈C₁₀. As can be observed in Figure 2-2, the following clusters, Nb₈C₆₋₁₀, have photon orders ranging from one to two photons, respectively. However, upon addition of a single carbon atom to Nb₈C₁₀ to form Nb₈C₁₁ there is a jump from a two photon order to a three photon order. The Met-Car, Nb₈C₁₂, follows suit with Nb₈C₁₁ as shown in Figure 2-2 below.

Harris and Dance [1] calculated the ionization potentials (IPs) of niobium-carbon clusters of this size regime to be ~5 eV with slight variations between the different cluster sizes. The ionization laser used in this initial study was a 308 nm XeCl Excimer laser with photons on the order of 4.02 eV. According to the data presented in the Figure 2-2, the Nb₆C₆₋₈ clusters and Nb₈C₁₁₋₁₂ clusters photoionize with three photons, or ~12 eV, whereas their IPs were calculated (as mentioned above) to be only ~5 eV. Therefore, according to the calculations by Harris and Dance, the Nb₆C₆₋₈ clusters and Nb₈C₁₁₋₁₂ clusters would require only two photons to reach the ionization continuum. Initial assumptions, that differences in the IPs between the Nb₆C₅₋₆ clusters as well as the Nb₈C₁₀₋₁₁ clusters are responsible for the jump in photon order, seem unlikely due to the discrepancy between the theoretical calculations and the experimental evidence presented in this appendix. Calculations are presently being performed in order to determine the IPs for clusters that were not calculated by Harris and Dance (i.e., Nb₆C₄₋₆, Nb₆C₈, and Nb₈C₆₋₁₁) as well as to determine the density of states of the clusters and band gap energies. It is expected that these calculations will shed some light on this exciting preliminary evidence that corroborates with the well known theme in cluster science that the addition of a single atom to a cluster greatly affects the properties of the cluster. This
Figure 2-2: Photon order vs. delay time for Nb₈C₆₋₁₂. Note the jump in photon order from two to three photons with the addition of a single carbon atom to the Nb₈C₁₀ cluster to form Nb₈C₁₁.
work is ongoing and additional experimental evidence will be collected in order to confirm these preliminary results.

**B.3 References**

VITA

Jason Robert Stairs

HIGHLIGHTS
- Awarded the International Journal of Mass Spectrometry’s Best Student Paper Award for 2002
- Selected by the Department of Energy as one of 36 students nation-wide to attend the 52nd meeting of the Nobel Laureates in Lindau, Germany
- Developed the Reverse Field Technique to measure delayed ionization of clusters
- Developed the Time-Resolved Fluence Study method to measure the relative capability of clusters to store energy
- Design of a tandem time-of-flight mass spectrometer facility
- Communication skills developed through numerous research presentations

EDUCATION
Ph.D. Candidate Chemistry, the Pennsylvania State University, University Park, PA
B.S. Chemistry, Saint Joseph’s University, Philadelphia, PA, 1999

RESEARCH EXPERIENCE
- Created a Virtual Instrument in LabVIEW to automate a mass spectrometric facility
- Wrote programs in Visual Basic for Applications (VBA) to create templates for data analysis
- Designed and constructed a new tandem time-of-flight mass spectrometer
- Developed a new method to measure the relative capability of clusters to store energy
- Developed a new technique to study delayed ionization in clusters
- Developed a calculation to determine the mass of metastable ion decay products
- Participated in developing a new technique used to study Coulomb explosion
- Contributed in the investigation of the ultrafast dynamics of molecular systems

1999 Summer Research Internship, Rhone-Polene Rhorer R&D, Collegeville, PA
- Participated in the multi-step synthesis of anti-coagulation drugs

1999-1997 Research Assistant, Saint Joseph’s University. Advisor: Mark A. Forman
- Lead investigator for the successful synthesis of pentacyclo[4.3.0.0^2,4.0^3,8]non-(4)5-ene
- Developed the synthesis of diiodopentacyclo[4.3.0.0^2,4.0^3,8]non-(4)5-ene

AWARDS
- Awarded the International Journal of Mass Spectrometry’s Best Student Paper Award for 2002
- Awarded the Lubrizol Fellowship; funding for 2002-2003
- Awarded the Roberts Fellowship, 2002
- Selected by the Department of Energy to attend 52nd Meeting of the Nobel Laureates, 2002
- First prize in Graduate Research Exhibition, 2002 and 2003
- Research Equipment Grant from Sigma Xi, 1999
- ACS Young Chemist Award, 1995