2011

Design and Construction of a Reflectron Time of Flight Mass Spectrometer for Multiphoton Ionization and Vibrational Spectroscopic Studies of Mass-Selected Clusters

Matthew Dodd McDowell

University of Mississippi. Sally McDonnell Barksdale Honors College

Follow this and additional works at: https://egrove.olemiss.edu/hon_thesis

Part of the Chemistry Commons

Recommended Citation


https://egrove.olemiss.edu/hon_thesis/673

This Undergraduate Thesis is brought to you for free and open access by the Honors College (Sally McDonnell Barksdale Honors College) at eGrove. It has been accepted for inclusion in Honors Theses by an authorized administrator of eGrove. For more information, please contact egrove@olemiss.edu.
DESIGN AND CONSTRUCTION OF A REFLECTRON TIME OF FLIGHT MASS SPECTROMETER FOR Multiphoton ionization AND VIBRATIONAL SPECTROSCOPIC STUDIES OF MASS-SELECTED CLUSTERS

by
Matthew Dodd McDowell

A thesis submitted to the faculty of The University of Mississippi in partial fulfillment of the requirements of the Sally McDonnell Barksdale Honors College.

Oxford
May 2011

Approved by

Advisor: Professor Nathan Hammer

Reader: Professor Gregory Tschumper

Reader: Professor Susan Pedigo
ACKNOWLEDGEMENTS

Many people in the chemistry and physics departments were of great assistance in the construction of the mass spectrometer. I would like to thank Dr. Hussey for purchasing needed tools and also for allowing me access to the chemistry department’s machine shop. I would like to thank the past and present members of the Hammer group for providing assistance, and especially to my advisor Dr. Nathan Hammer for allowing me to work countless hours in his laboratory and for believing in me as I struggled through the construction.
ABSTRACT

(Under the direction of Dr. Nathan Hammer)

Mass spectrometry is typically employed for the elucidation and identification of elements and compounds. Its ability to select and isolate specific molecular clusters makes it an ideal tool for the fundamental spectroscopic study of the photophysical and geometric properties of molecules and molecular clusters. The design and construction of a reflectron time of flight mass spectrometer (reflectron TOF-MS) as well as its implementation for electronic and vibrational spectroscopic studies of various molecules and molecular clusters is discussed. The first chapter introduces basic theory related to electronic spectroscopy, multiphoton ionization, and vibrational spectroscopy. The second chapter entails the theoretical aspects of mass spectrometry required for the creation of molecular ion beams involved in TOF-MS. The third chapter contains the technical details of the construction and implementation of the many required components in a reflectron TOF-MS. The fourth chapter reports multiphoton ionization spectra of methyl iodide and data obtained while exploring the vibrational study of molecular ion clusters.
# TABLE OF CONTENTS

1. Background ................................................................................................................... 1  
   1.1 Electromagnetic Radiation - Matter Interactions .................................................... 1  
   1.2 Theory of Multiphoton Ionization ........................................................................ 2  
   1.3 Theory of Vibrational Spectroscopy ..................................................................... 4  
   1.4 References ............................................................................................................. 6  

2. Mass Spectrometry ......................................................................................................... 8  
   2.1 Reflectron Time of Flight Mass Spectrometry ......................................................... 8  
   2.2 Molecular Ion Clusters for Study .......................................................................... 10  
   2.3 Laser Interaction with Mass Spectrometry ............................................................ 11  
   2.4 References ............................................................................................................. 12  

   3.1 Basic Design of a Time of Flight Mass Spectrometer ............................................ 14  
   3.2 Interaction with Tunable Dye Laser ....................................................................... 16  
   3.3 Construction of Movable Detector ......................................................................... 16  
   3.4 Construction of a Reflectron .................................................................................. 17  
   3.5 Construction of Ion Optics ..................................................................................... 20  
   3.6 Construction of Ion Optics Controls ....................................................................... 21  
   3.7 Construction of Pulse Valve Controller ................................................................... 21  
   3.8 Construction of Electron Gun ................................................................................ 22  
   3.9 Construction of the Control for an Electron Gun .................................................. 22  
   3.10 References ............................................................................................................ 24
4. Mass Selected Ion Spectroscopy

4.1 Multiphoton Ionization of Methyl Iodide

4.2 Water Cluster Precursor for Vibrational Spectroscopy

4.3 Conclusion

4.4 References
1 Background

Spectroscopy is the study of the interaction between matter and electromagnetic radiation. Electromagnetic radiation can be used to probe a system (a molecule or group of molecules) and a subsequent response can be measured. Alternatively, a system is stimulated and the emitted electromagnetic radiation can be measured. These interactions can reveal many of the system’s photophysical properties and are the subject of this thesis.

1.1 Electromagnetic Radiation - Matter interaction

Spectroscopy had been employed by scientists even before the development of quantum mechanics. The emission line spectra of many atoms had already been utilized for the identification of certain elements. However, it was not until the advent of quantum mechanics that the physics behind the occurring phenomena was known. One of the most fundamental concepts from quantum mechanics that makes spectroscopy possible is the quantization of energy. For a transition to occur, the energy of a photon, or group of photons, must exactly match the difference in the initial and final energy states of a molecule. There are four types of energy transitions that can occur in a molecule. They are, in decreasing energy: electronic, vibrational, rotational, and translational. From this, the total energy associated with a molecule can be written as (Eqn. 1).

\[
E_{Total} = E_{Electronic} + E_{Vibration} + E_{Rotation} + E_{Translation}
\]  

(1)
Taking into account a single molecule, the Born-Oppenheimer approximation is used and the nucleus is fixed in place. This approximation allows the Schrödinger equation to be more easily solved and is one of the fundamental approximations implemented in quantum chemistry. Because the types of spectroscopies performed neglect rotational and translational energy transitions, very little will be discussed regarding them. Electronic and vibrational spectroscopy are the two main types that are performed with a reflectron TOF-MS.

1.2 Theory of Multiphoton Ionization

Photoionization is a process that readily occurs in nature. It is very similar to the photoelectric experiment that Einstein theorized. In this experiment a light was directed onto a metal surface and ejected electrons were detected. During this experiment he concluded that the energy of the ejected electrons were proportional to wavelength of light, not intensity as described by classical physics. This showed that light had particle like nature. This is the same experiment that supported Planck’s hypothesis and led to the field of quantum mechanics. In multiphoton ionization the photons are interacting with the molecules instead of metal surface, but the same principle is used. It is defined as (Eqn. 2).

\[ T_{\text{max}} = h\nu - w \]  

In this equation “\(T_{\text{max}}\)” is the kinetic energy of the ejected electron, “\(h\nu\)” is the energy of a photon and “\(w\)” is the binding energy of the electron. By setting the kinetic energy term to zero, one obtains the minimum amount of energy a photon requires to remove one electron (ionization). In processes that have an intense source of photons, such as a
pulsed laser, molecules can be excited and ionized by the addition of multiple photons. In the late 1970's this was accomplished in a time of flight mass spectrometer (TOF-MS). These were some of the first studies where laser-molecular cluster interactions occurred in a TOFMS.\textsuperscript{4-6} When an intense monochromatic light source that is lower than the binding energy interacts with a molecule, it transitions to a metastable excited state. There are many of these virtual states differing in different amounts of energy. If multiple photons interact with the molecule in a short period of time it can transition from one excited state to another. If the photons interact with the molecule quickly enough the molecule can transition from an excited state to another excited state until it reaches the ionization potential. If a molecule needs one 300 nm photon to eject an electron, then two 600 nm photons can do the same. Since a molecule normally relaxes from an excited state to its ground state in the order of $10^{-8}$-$10^{-15}$ seconds, the interaction with photons must be performed quickly.\textsuperscript{7} Alternatively, this can also be accomplished by an intense light source where there are many photons in an area small enough to interact with the same molecule, e.g., a laser beam. Also, the sum of the photon’s energies used to eject the electron do not have to match exactly. The reason is that the excess energy of the final photon that transitions the molecule to the ionization potential is transferred to the ejected electron in the form of kinetic energy. In fact, this is one of the basic principles that drives the field of photoelectron spectroscopy.

A nomenclature system is used to describe the the different states in a transition. The ground state is referred to as the $X$ state and the subsequent excited states are denoted by letters, beginning with the letter $A$. They are then increased to describe all the inter-
mediate metastable excited states until the ionization potential is reached. Figure 1-1 is an energy level diagram of methyl iodide that visually demonstrates the principle of multiphoton ionization. In Figure 1-1 the different colored lines demonstrate the different amounts of energy for the photons of different wavelengths and how many photons were needed to ionize methyl iodide.

![Energy Level Diagram of CH₃I Demonstrating the Process of Multiphoton Ionization where IP designates the ionization potential.](image)

**Figure 1-1** - Energy Level Diagram of CH₃I Demonstrating the Process of Multiphoton Ionization where IP designates the ionization potential.

### 1.3 Theory of Vibrational Spectroscopy

All molecules are in constant motion and all of these motions contribute to a molecule’s total energy. Both periodic and non-periodic motions exist. Most molecular vibrations and rotations fall into the category of periodic motions. They involve the movement of
the atoms connected by a bond either by the rotation about a bond (rotational), or by the change in bond length or bond angle relative to an internal coordinate system (vibrational). In simple diatomic molecules the only motions that occur are rotational and stretching motions. Rotations also occur in larger molecules, but are of small concern in vibrational spectroscopy since they are difficult to resolve. Vibrational spectroscopy is predominantly concerned with all the motions that occur in a molecule except rotations. Depending on the symmetry of a molecule many vibrations can occur. The total number of vibrations can be described by 3N-6 for all molecules, except linear molecules which is described by 3N-5, where N is the number of atoms and the 3 is for the total number of directions (x,y,z) the molecule can move. The last number describes all the motions that result in translational and molecular rotations. When the correct amount of energy is added to a molecule that corresponds to a specific motion, a vibration occurs. The major vibrations that occur can typically be described by one of the following motions: symmetric stretching, anti-symmetric stretching, wagging, rocking, twisting, and scissoring. The stretching motions involve the changing of bond lengths, and all the others involve movement of the atoms relative to each other. The effect of bond length on the required amount of energy needed to vibrate can be analogized by two socket wrenches with different length handles tightening the same bolt. Which would be easier to tighten with? Obviously the longer one is easier to move, the same is true for a vibration and the effect of bond length. Intermolecular forces such as hydrogen bonding affect the vibrations of a molecule as well and could be analogized in a similar manner.
The preceding discussion is the basic principle of IR spectroscopy. Molecules strive to be at the lowest energy level attainable. An excited molecule will radiatively and non-radiatively lower its energy to the lowest possible state. In fact, this is the principle that drives chemical reactions. It also occurs in molecular clusters. Groups of molecules will rearrange to the lowest energy conformations possible.

Another important thing to point out is that in infrared spectroscopy, as well as all other types of bulk measurement techniques, the fundamental molecular information attained is skewed by the bulk interactions. This means that all spectroscopic data obtained is a compilation of the individual molecular information plus all other effects such as solvent effects, hydrogen bonding, van der Waals forces and so on. This makes it difficult to retrieve the fundamental information from a molecule, let alone any conformational information.

1.4 References


(2) Hecht, E. Optics; Fourth ed.; Addison Wesley, 2002.


2 Mass Spectrometry

Mass spectrometry is the study of the separation of molecular species based on their mass to charge ratio. It is typically thought of as an analytical tool used to assist in the elucidation of a compound or mixture of compounds. However, the application of mass spectrometry in spectroscopy is sometimes used as a platform to study charged molecular clusters of interest or the products formed through a spectroscopic process.

2.1 Reflectron Time of Flight Mass Spectrometry

There are five major types of mass spectrometers: quadrupole, sector, ion trap, time of flight (TOF), and ion cyclotron resonance (ICR). All mass spectrometers work by separating charged particles based on their masses. When ions are exposed to an electrostatic field, the force exerted on them is displayed in (Eqn. 3), also known as Coulomb’s law.¹

\[ F = \frac{1}{4\pi\varepsilon_0} \frac{q_1q_2}{r^2} \]  

(Eqn. 3)

TOF-MS’s work by accelerating charged particles a given distance. In mass spectrometry all particles are imparted with the same kinetic energy. The separation occurs because the given kinetic energy is proportional to the charge of the ion (or +/- charge of an electron) times the applied electrostatic field. In this case, the basic kinetic equation becomes (Eqn. 4).¹

\[ Ve = \frac{1}{2}mv^2 \]  

(Eqn. 4)

Where \( e \) is the charge of the electron and \( V \) is applied voltage used for the electrostatic
field. Eqn. 4 can then be simply rearranged to show that particles of different masses will have different speeds. By using a specific flight distance, also known as drift length, the time it takes an ion to reach the detector can then be determined. This is the basis of mass separation in TOF-MS. When a sample is inserted into a mass spectrometer, the molecules will quickly expand in all directions. When this occurs some ions with the same mass will be exposed to the electrostatic field for different amounts of time thus two particles with the same mass can have different kinetic energies. This effect is seen as a broadening of the peak. A reflectron can then be implemented to correct this problem. A reflectron is an electrostatic mirror. It is created by a gradient electrostatic field of the same polarity as the particle being detected. When the particle enters the field it is slowed, turned around, and then accelerated back the direction whence it came. Similarly to the reflection principle in geometric optics, the angle of incidence from the normal is equal to the angle of reflection. By slightly angling the reflectron, the ions can be reaccelerated to a detector slightly offset from the initial ion beam path. When particles of the same mass, but different kinetic energies, enter the reflectron they are slowed. Particles with more kinetic energy will enter further into the reflectron, while particles with less kinetic energy will not traverse as far. Because the time spent in the reflectron is less for the particle with lower kinetic energy, both particles will exit the reflectron in the reverse order of how they entered. By placing a detector at a given distance from the reflectron, both particles with the same mass will reach the detector at the same time. Many of the time of flight designs used today have spawned from a simplistic design described by Wiley and McLaren in 1955. Figure 2-1 is a basic diagram of the molecular...
cluster flight path for a reflectron TOF-MS.

**Figure 2-1** - Basic Flight Path for a reflectron TOF-MS.

### 2.2 Molecular Ion Clusters for Study

The ability to isolate molecular clusters in the environment is a very difficult process. To be able to study any small molecular cluster one must remove any external interactions. This can only be performed in an environment where very few molecules exist such as in a vacuum. By performing this experiment in a vacuum, many of the external interactions that contribute to the bulk sample spectra are removed. However, a problem still exists. How does one know which molecule or molecular cluster you are studying? This is the main reason that mass spectrometry is used as the platform to study molecular clusters because of the ability to mass select. This also has its disadvantages. In order to perform mass spectrometry the cluster must be charged. This is performed by ionizing the sample. If the molecule has weak bonds when ionization occurs, it may fragment. This has
lead to the development of a plethora of different ionization sources including matrix assisted laser desorption ionization (MALDI) and electrospray. The difficulty in the ability to ionize certain molecules also hinders the types of systems that can be studied.

2.3 Laser Interaction with Mass Spectrometry

Mass spectrometry is used to isolate molecular clusters of a given mass. In order to be able to perform electronic, multiphoton ionization, or vibrational studies on these molecules an interaction with a laser must occur. This is performed by two different methods. The first method is to employ the laser as an ionization source. This is predominantly only used in multiphoton ionization. In this type of spectroscopy, the laser utilizes photons of specific energies to electronically excite molecules to the point of ejecting an electron. The charged particles are then accelerated in the same manner as in mass spectrometry. The individual mass peaks are then integrated as a function of wavelength. This allows the determination of the amount of energy required to ionize a molecule at differing energy photons. The second method involves interacting a photon with a particle during flight. This is performed by accelerating a particle towards the detector and then calculating the location of the interaction point. The timing of the laser is then adjusted to allow the photon to interact with the molecule or molecular cluster during flight. The method of detection in this interaction is determined by a few methods. The first method discussed is performed by attaching an argon atom to the cluster. When interaction with a laser occurs, depending on the binding energy of the charged species, the argon can be lost preferentially in the interaction. The argon then departs with some of the molecular clusters kinetic energy. The cluster is then re-weighed for the new lower mass
and the creation of a new peak, with the new total mass is created. The area under the peak is then integrated and the vibrational spectra of the molecular cluster obtained. Another approach can be used if the electron is bound to the molecule. A photon of given energy can then be used to remove the excess electron and the spectra can be determined by the integration of either the neutral, if the detector is in the initial line of flight, or inversely by the loss of intensity of the molecular clusters peak. If fragmentation occurs during the interaction it also allows the ability to study fragments that could be created. Conversely, if cationic clusters are being studied this can be accomplished similarly to the methods described previously except for the loss of an electron method and detecting the neutral. When dealing with cations a proton is attached and then the cluster is accelerated. A proton can then be removed and the neutral detected. This type, as well as binding an excess electron, can be difficult due the binding energy being larger than the energy of the photons used to study these clusters. The mass spectrums described in this thesis has been specifically designed to carry out the above spectroscopic experiment.

2.4 References


3 Construction of a Reflectron Time of Flight Mass Spectrometer

In the first two chapters, the basic theory behind different types of spectroscopy, time of flight mass spectrometry, and the interaction of the two are discussed. The following are the details of the construction and implementation of a reflectron time of flight mass spectrometer for the spectroscopic study of molecular clusters. Many aspects are involved in the design of a mass spectrometer. Certain types of equipment will only be mentioned and not fully discussed. The basic design follows one introduced by Wiley and McLaren.¹

3.1 Basic Design of a Time of Flight Mass Spectrometer

The construction of a mass spectrometer has many different aspects that have to be taken into account. The first is the vacuum system. Because the average mean free path for most molecules is less than 100 nm in air, a vacuum system is required to perform mass spectrometry.² Figure 3-1 is a basic diagram of the vacuum system of a TOF-MS. They are based on a basic design created by Lineberger at University of Colorado.³⁴ All chambers were mounted on aluminum supports and leveled to allow connection of the three chambers. Once connected, the system was in need of a second diffusion pump due to the total volume of the mass spectrometer. The second diffusion pump was acquired from a retired HP quadrupole mass spectrometer and then fitted to the flight chamber. A
photograph of this assembly is shown in figure 3-2.

**Figure 3-1** - Basic Block Diagram of the Vacuum Systems on a Time of Flight Mass Spectrometer.

**Figure 3-2** - Photograph of Diffusion Pump and Power Supply.
A turbomolecular pump was connected to the detector chamber. The power supply that powered the second diffusion pump was also taken from the retired HP quadrupole mass spectrometer. Once all the chambers were sealed the mass spectrometer was evacuated to determine the location of any leaks. This process continued until it was able to maintain a suitable vacuum. Once this was complete, methyl iodide was used to optimize and fine tune the operation of existing components.

3.2 Interaction with a Tunable Dye Laser

The doubled output from a Continuum Surelight I-10 Nd:YAG laser was employed as the pump laser for a ND6000 tunable dye laser. The output from the dye laser was then directed to the entrance window in the mass spectrometer using turning prisms. A ten centimeter focusing lens was then used to focus the laser beam in the center of the source chamber directly below the pulse valve. During the methyl iodide studies, multiple fluorescent dyes were used to access the required laser wavelength ranges. Different types of dyes that fluoresce at different wavelengths are used in the oscillator and amplifier stages of the dye laser. Each dye was used in the range that it fluoresces. The spectra was obtained during that range and the dye was changed until all regions studied were performed. This is shown in Figure 3-3 from a Continuum ND6000 tunable dye laser for the different dyes used for their fluorescing ranges. During operation with the tunable dye laser the delay between the pulse valve and the laser is varied to optimize peak intensity.

3.3 Construction of a Moveable Detector

The initial detector received for the reflectron TOF-MS was inadequate for use with a re-
flectron due to its fixed location. A moveable detector was then constructed using micro
channel plates according to drawing. Figures 3-4 and 3-5 are the moveable microchannel
plate detector and its circuitry used in the reflectron TOF-MS.  

![Graph showing Power vs. Wavelength scans performed from a Continuum ND6000 tunable dye laser](image)

**Figure 3-3** - Power vs. Wavelength scans performed from a Continuum ND6000 tunable dye laser

### 3.4 Construction of a Reflectron

A reflectron ion mirror was constructed from stock aluminum plates. The UM physics
machine shop assisted in the machining. After the plates were machined the reflectron
was assembled by equally spacing the eight plates. The first plate and last plate were de-
dsigned to be supports and not electrically isolated to create a gradient field. 1 MΩ resis-
tors were used to create the voltage network for the electrostatic field gradient. Then one
side is attached to a variable high voltage power supply and the other side is connected to
ground. Figure 3-6 is a basic diagram of a reflectron showing the required arrangement
and the required electrical circuit.
**Figure 3.4** - Moveable Detector and its wiring

**Figure 3.5** - Photograph of the Moveable Detector
Figure 3-6 - Diagram of an Electrostatic Mirror (Reflectron) and its Electrical Circuit.
3.5 Construction of Ion Optics

Two major types ion optics, other than the reflectron, are commonly employed in mass spectroscopy. The first is ion deflectors. Ion deflectors work by creating an electrostatic gradient that ions pass through orthogonally to their direction of flight. When the ions pass through this electrostatic field, a small amount of kinetic energy is imparted to the ions as they pass through. This is best described by a Cartesian coordinate system where the flight path is defined as being along the $z$-direction and the deflector creating electrostatic fields in the $x$, and $y$-directions. This effectively adjusts the flight path of the ions. The second type is an Einzel lens. An Einzel lens lens works by three concentric hollow cylinders with a voltage placed on the center cylinder and the remaining two grounded. The field lines created are in a cylindrical fashion from the charged cylinder to the grounded cylinders. Since the weakest of the field lines are in the center of the cylinder an ion traversing through will be acted upon by the field lines. A particle located near the side will be pushed toward the center. Since it is symmetrical about the center, all particles will be moved toward the center. The exiting paths of all of the ions will then intersect at a given point down the flight path (focal point) depending on the strength of the electrostatic field. Adjusting the voltage applied to the center ring adjusts the electrostatic field and the focal point of the ions. This device acts is similarly to a convex lens in geometric optics.\(^6\) Figure 3-7 is a basic diagram of an Einzel lens showing the electrostatic field lines and their interaction with traversing ions.
3.6 Construction of Ion Optics Controls

Because each of the optics requires only a fixed voltage for a given optic, a simple DC voltage divider network was designed and implemented for this purpose. A field switching device was also employed to change the direction of the deflector field lines from +X to -X and from +Y to -Y to allow the trajectory of the ion in flight to be manipulated in the (+) and (-) X and Y directions. The einzel lens is simply controlled by a fixed DC voltage and did not require a custom control circuit.

3.7 Construction of Pulse Valve Controller

Initially an Iota One pulse valve controller from Parker Hannefin was used to control the duration of the pulse valve. Due to the cost of the Iota One controller and the desire for greater control over experimental parameters, a newly designed pulse valve controller was created. This simple design also affords the ability for future experiments involving multiple pulse valves and multiple pulse valve controllers. The basic electrical circuit is one that was modified from a design used at Yale University.5
3.8 Construction of Electron Gun

Multiphoton ionization is a great method for ionizing samples with a weak chromophore, but for systems that are harder to ionize a Pierce type electron gun was created. An electron gun employs the same types of ions optics discussed earlier. A heavy metal filament, in this case a thoriated iridium filament from discarded ion gages, is employed for this electron gun. The filament is floated to ~1000Vdc and a current is passed across the filament to cause the thermionic emission of electrons. Once the electrons are “boiled off”, a Pierce cavity that is relatively more positive is placed close to the filament causing the electrons to be accelerated towards it. A small hole in the center allows a beam of electrons to emerge. Once the electrons pass through the pierce cavity they are focused on the pulse valve where the sample is emitted. By adjusting the pierce cavity voltage, filament current, Einzel lens voltage, and deflector voltages the ion beam intensity and focusing can be controlled. Figure 3-8 is a block diagram of an electron gun and its required components.

3.9 Construction of the Controls for an Electron Gun

An electron gun can be controlled by only a few power supplies. However, due to the nature of floating power supplies an insulated system must be used to prevent electric shock. A 1.5m x 1m x .75m box of plexiglass was constructed to house the floated power supplies. This enables a safe method for controlling the electron gun. Figure 3-9 is a picture of the insulated power supplies used to control the electron gun.
1.3.6 are Connected to Low Voltage Power Supplies
2,3,5,7 are Connected to Ground
8 is connected to a HV power supply
9,10 are the sides of the filament and are connected to a high current power supply that is floated to -1000Vdc

**Figure 3-9** - Basic diagram of a Pierce-type Electron Gun and the Required Electronic Components
3.10 References


(5) Ph.D dissertation Deluca at Yale.


(7) Ph.D Dissertation, Deluca, M.D., **1990**. Yale University.

(7) Pierce, J. R. *Theory and Design of Electron Beams*. D. Van Nostrand, **1949**.
4 Mass Selected Ion Spectroscopy

As previously discussed, this thesis is concerned with the construction of a reflectron TOF-MS for the intentional purpose of vibrational spectroscopic studies of molecular clusters of interest. The following are the projects performed and the data obtained while building, modifying, and tuning the mass spectrometer for its intended purpose.

4.1 Multiphoton Ionization of Methyl Iodide

Methyl iodide is a well-studied molecule \(^1\text{--}^{40}\) that was initially chosen to assist in the tuning of the reflectron TOFMS. Over the years there have been many conflicting conclusions about the photofragmentation pathways as well as whether photodissociation or photoionization occurs first. This led to the multiphoton ionization of methyl iodide using 1.67 to 2.2 eV photons or wavelengths of 550-740nm,\(^{41}\) an area not previously studied. Methyl iodide has a very weak chromophore which leads to both photodissociation as well as photoionization processes. Photodissociation is the process in which a photon excites a molecule and it subsequently breaks apart. However no one has been able to definitively identify which process comes first.\(^8\text{--}^{11,17,25-27,29,33,34,38,39,41,43}\) Because of its weak chromophore and symmetry alkyl halides, such as methyl iodide, are ideal candidates for studying fragmentation pathways. In this experiment, methyl iodide was pressurized with two atmospheres of argon gas. The argon also acts as a coolant for the methyl iodide. When the methyl iodide was supersonically expanded by pulsing it into
the vacuum chamber collisions would occur with the argon allowing the temperature to be less than 10K. This allowed for a cleaner spectra due to a smaller distribution of kinetic energies. The sample was then excited by multiple photons to the point of ionization and then accelerated down the flight path to be detected. An alternative pathway would be the methyl iodide ion would fragment leaving different charged species. Figure 4-1 is a mass spectrum showing the different fragments that occur from the photoionization/fragmentation of methyl iodide. Even though this molecule has been widely studied there exists many details still to be determined such as the method of fragmentation and the fragmentation pathways and also whether photoionization or photodis-
sociation occurs first. Because photons of different energies produce different stabilities of fragments, scans of the fragment intensity versus wavelength were obtained over this region. This is shown in Figure 4-2. The multiphoton ionization spectra obtained yielded similar results as expected to those reported by Gedanken, et. al in 1982.\textsuperscript{5} Figure 1-1 is an energy diagram of methyl iodide that shows the required number of photons to ionize methyl iodide and the different excited states. The spectra show that as photon energies are lowered fewer ions are produced and that the fragments are likely created from the ionized parent ion instead of fragmentation occurring prior to ionization.

**4.2 Water Cluster Precursor for Vibrational Spectroscopy**

Water is one of the most abundant compounds that exists in nature. The binding of an excess electron has serious biological and physiological implications. The method of
transport and binding has been known for over four decades and is still not fully understood.\textsuperscript{44-46} These are the reasons that cluster interactions with water and the binding of an excess electron are one of the chosen areas of study. After the completion of the methyl iodide project the logical direction was to proceed towards the creation of water clusters followed by the interaction of water clusters with the system of study. At this point the ionization source was switched to the electron gun. This allowed a harder ionization source for studying water cluster interactions. The electron gun is described in more detail in Chapter 3. The first step in progressing to the final goal was the creation of water clusters binding a proton. The spectra also shows the extremely stable protonated water cluster H\textperiodcentered(H_2O)_n^+ where \(n=21\).\textsuperscript{47} The spectra of water clusters H\textperiodcentered(H_2O)_n^+ where \(n=7\text{-}32\) is shown in Figure 4-3. After this was performed, the next step involved obtain-

![Figure 4-3 - Spectra of water cluster fragments of H\textperiodcentered(H_2O)_n^+ where \(n=7\text{-}32\).](image)

28
ing the anion clusters binding an excess electron. This was more difficult due to the lower relative stabilities compared to the cation clusters. The identification of the clusters were also plagued by a few instrumental issues such as vacuum leaks that are still trying to be completely resolved. This has led to slower progress in this region. However, some of the heavy water clusters\textsuperscript{48-49} have been obtained while progressing to the end goal. Figure 4-4 shows the heavy water clusters binding an excess electron obtained during the course of the last few months. These heavy water clusters were first studied in 2004.\textsuperscript{48-49} Many of the other fragments such as \((\text{H}_2\text{O})_n^-\) where \(n=2,3,6,7,11-21\) have been obtained,\textsuperscript{50-52} but due to lack of stability in the mass spectrometer these clusters have not been spectroscopically studied. There is still much more work that needs to be accomplished prior to being able to perform vibrational spectroscopy of the systems of interest.

![Figure 4-4](image)

**Figure 4-4** - Spectra of the water cluster \((\text{H}_2\text{O})_n^-\) where \(n=15-55\).
4.3 Conclusion

Experimental physical chemistry is a broad area of research that constantly requires the development of novel approaches and methods to study systems of interest. Even though much progress has been made toward the creation of a reflectron time of flight mass spectrometer for the performance of spectroscopic studies of mass selected clusters, it will never be complete. The largest aspect in the field involves the modification of current instrumentation, or the creation of a new instruments to perform specific experiments.

4.4 References


(47) Shin, W.; Hammer, N. I.; Diken, E. G.; Johnson, M. A.; Walters, R. S.; Jaeger,


