

**PHOTOIONIZATION DYNAMICS FOR NON-SYMMETRIC MOLECULES  
IN A HIGH INTENSITY LASER FIELD**

by

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A thesis submitted to the Faculty of the University of Delaware in partial fulfillment  
of the requirements for the degree of Bachelor of Science in Physics with Distinction.

Spring 2009

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IN A HIGH INTENSITY LASER FIELD**

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## ABSTRACT

This study addresses the question of the effect of a molecule's symmetry on its ionization. Using laser field intensities ranging from  $2 \times 10^{15}$  to  $2 \times 10^{18}$  W/cm<sup>2</sup>, different orders of charged carbon fragments, C<sup>+n</sup>, were collected for a non-symmetric molecule and for a symmetric molecule. Each fragment was collected at a fixed energy, with the only variable being the symmetry of the sample molecule. Methane (CH<sub>4</sub>) was the symmetric, non-polar molecule tested and chloromethane (CH<sub>3</sub>Cl) was used as the non-symmetric, polar molecule. C<sup>+2</sup>, C<sup>+3</sup>, and C<sup>+5</sup> ions were collected. The ions yielded for each C<sup>+n</sup> fragment for each molecule were compared to determine whether non-symmetric molecules ionize more easily or with greater difficulty than symmetric molecules.

## Chapter 1

### INTRODUCTION

#### 1.1 Light-Matter Interactions

The study of light-matter interactions in the strong field ( $10^{14}$ - $10^{15}$  W/cm<sup>2</sup>) is a growing area of interest in the field of atomic, molecular, and optical physics. It can be used to characterize the ionization mechanisms involved in the breakdown of atoms or molecules when high laser intensities are applied. The study of ionization processes through light-matter interactions has applications in fusion research, plasma physics, and atomic physics.

#### 1.2 Laser Induced Fusion

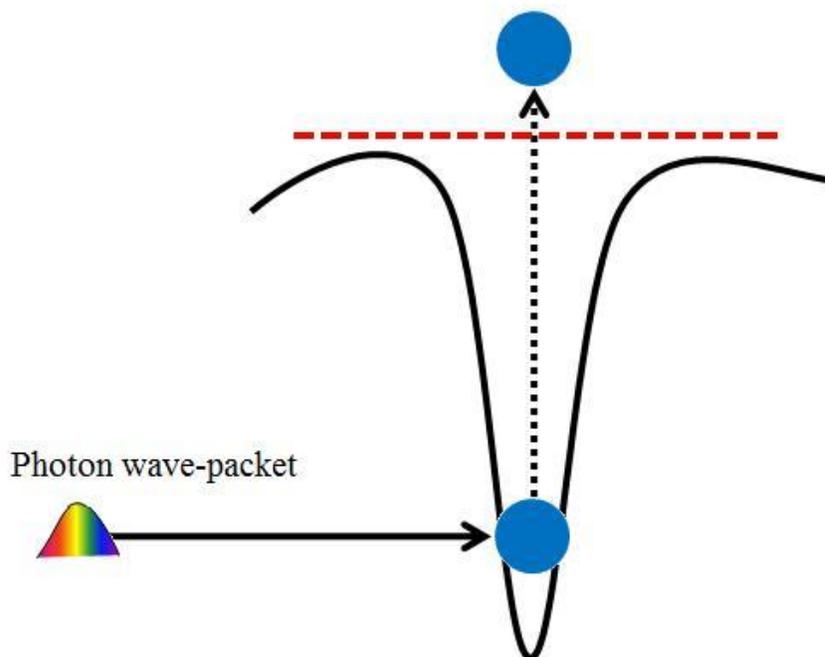
Methane cluster laser fusion is an example of one of the applications of light-matter interaction research. It uses intense lasers to create highly excited, photoionized methane clusters. To allow for the fusion reaction to take place, the hydrogen in methane (CH<sub>4</sub>) must be replaced with deuterium, hydrogen with an extra neutron in its nucleus, to give us CD<sub>4</sub>. Once ionized by the laser intensity, the free D<sup>+</sup> ions have energies of 50 keV, which is high enough to cause a D-D fusion reaction to form helium while releasing a neutron with 2.45 MeV of energy [1].

#### 1.3 Types of Ionization

In light-matter interactions, there are several key ionization processes to look at. The specific types of ionization we study are discussed below.

### 1.3.1 Resonant Excitation

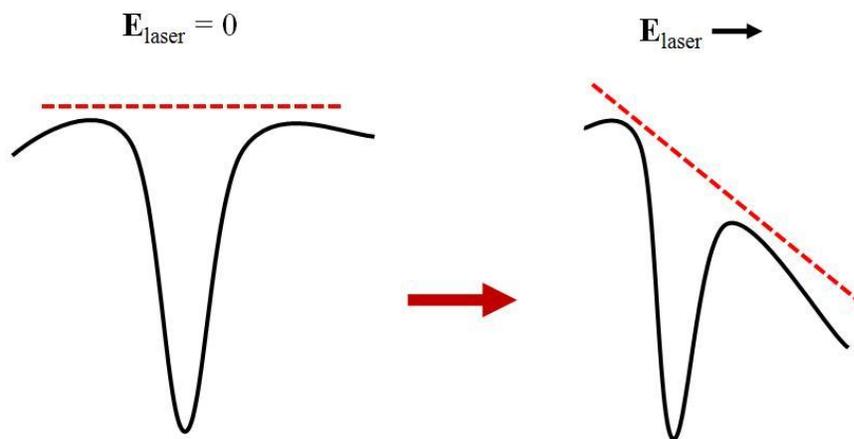
Resonant excitation occurs when an electron in the molecule is excited to a higher energy state. The excitation is achieved by the electron's absorption of the incident photon energy. In this case, the electron must be excited to a state above the potential in the continuum. Once in the continuum, the electron is free of the atom or molecule's potential and the atom or molecule is now an ion. The downside of resonant excitation is that the electron must attain a very high energy in order for ionization to take place.



**Figure 1. Resonant excitation.**

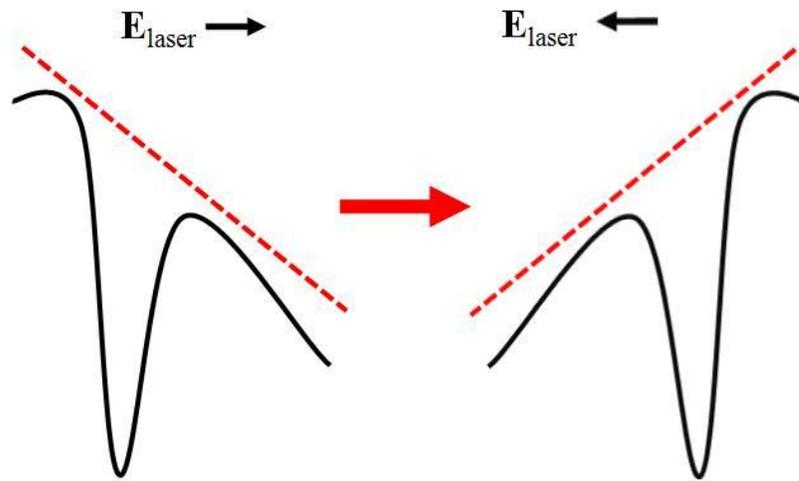
### 1.3.2 Rescattering Ionization

Rescattering ionization exploits the principles of quantum tunneling so that ionization may occur at lower energies. The goal is to help ionization occur easier and more frequently. To encourage the electron to tunnel, we make tunneling ionization by distorting the potential barrier of the atom or molecule with an applied electric field. The intrinsic electric field of the laser ( $\mathbf{E}_{\text{laser}}$ ) distorts the potential as shown in Figure 2. With a distorted potential, one of the sides of the potential well is lowered, making it easier for the electron to tunnel through because less energy is required to do so.



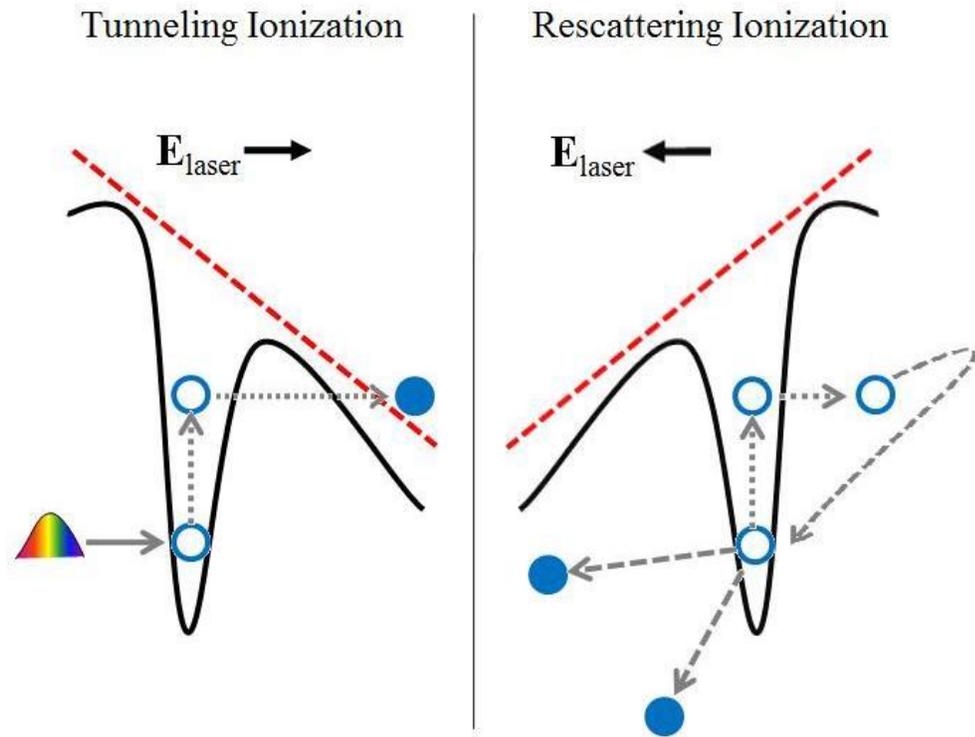
**Figure 2. Distorted potential.**

Electric fields, however, have alternating currents. Therefore, the electric field oscillates between two different directions. When this happens, the direction of the distortion changes, as well. This is demonstrated in Figure 3.



**Figure 3. Effect of the oscillating electric field.**

Figure 4 illustrates the complete process of rescattering ionization. With rescattering ionization, the excited electron tunnels through the lowered, distorted potential. When the electric field switches direction, the electron is forced back towards the parent ion. It has a charge and is affected by the electric field. The inward propelled electron then has the potential to collide with another electron that belongs to the parent ion. It is possible that the electron, if it has enough energy, will further ionize the parent ion by exciting the second electron and both will exit the parent ion's potential.



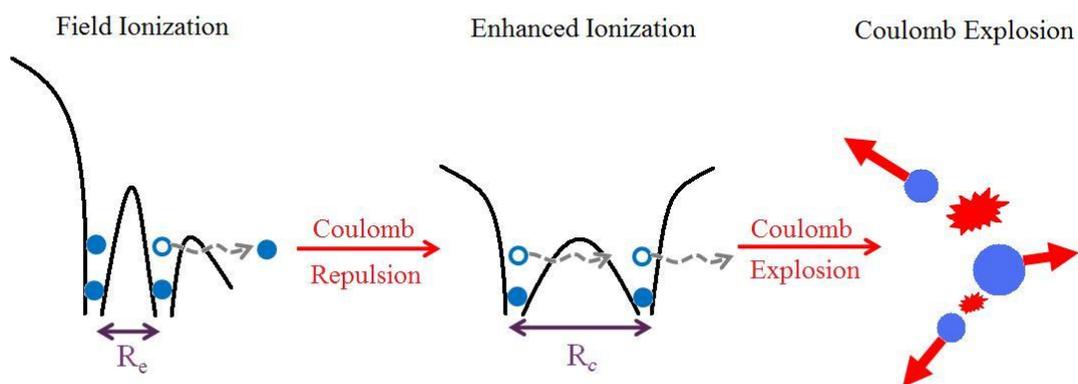
**Figure 4. Rescattering ionization.**

It must be noted that there are several possibilities with rescattering ionization. In addition to the scenario described above, it is possible for the first electron to not collide with any electrons on its way back through the parent ion. Another possibility is that the first electron will ionize the second electron, and then either the first or second electron could strike and ionize a third electron. One last possibility is that the returning electron might not have enough energy to overcome the parent ion's potential on its way back out, so it would return to its original position and no net ionization would occur.

### 1.3.3 Coulomb Explosion

The last type of ionization we study is Coulomb explosion. Coulomb explosion is the process by which the molecule explodes into highly charged fragments. The high intensity from the laser field ionizes the atom or molecule as the energy is absorbed, causing the bonds to stretch and expand until the energy becomes so great that the atom or molecule snaps and breaks apart.

This is shown in Figure 5.



**Figure 5. Coulomb explosion.**

### 1.4 Research Goals

The goal of this study is to determine whether or not the symmetry of a molecule has an effect on its ionization. The basis of this is a past experiment of our research group in which we characterized the ionization mechanisms involved in the breakdown of methane ( $\text{CH}_4$ ). Methane is a symmetric and non-polar molecule. A question that arose during the publication of this work was what would happen if we had used a non-symmetric molecule. To answer this question, we are ionizing both

methane and chloromethane ( $\text{CH}_3\text{Cl}$ ), a non-symmetric molecule. Based on the number of ions collected for each order of charged ion ( $\text{C}^{+n}$ ) when each molecule is ionized at the same energy, we will determine whether or not symmetric or non-symmetric molecule ionize with more ease.

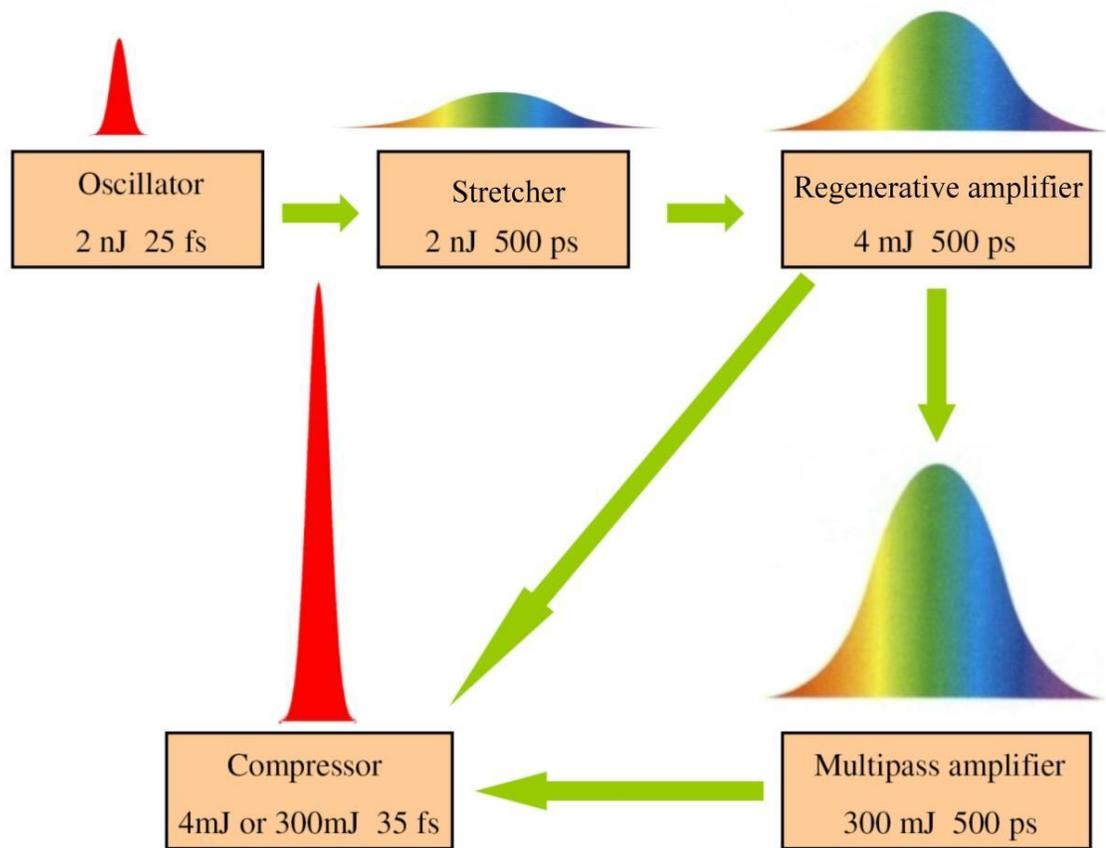
## **Chapter 2**

### **EXPERIMENTAL METHODS**

#### **2.1 Laser System**

A Ti:Sapphire, terawatt laser with chirped pulse amplification (CPA) was used to conduct this study. This system has been described in the thesis of Anthony DiChiara in great detail [2]. The major components of this laser will be discussed here.

The CPA scheme includes an oscillator, optical stretcher, regenerative amplifier, multipass amplifier, and optical compressor, as shown in Figure 6.



**Figure 6. Chirped pulse amplification (CPA) system scheme [3]**

The oscillator mode locks the pulse and then sends the pulse into the optical stretcher. Here, the pulse width is stretched using two antiparallel gratings. The input pulse width from the oscillator is 25 fs long and has an energy of 3 nJ. This pulse has a repetition rate of 77 MHz. After going through the optical stretcher, the pulse width is 500 ps [2].

The pulse then enters the regenerative amplifier. The regen includes two Ti:Sapphire crystals and a Pockels cell. The purpose of the regen is to select pulses at the desired repetition rate, as well as amplify the pulse. Our terawatt system is capable of selecting 10 Hz or 1 kHz pulses. The 10 Hz system was used for the entirety of this

study. The 10 Hz pulses can be amplified to energies of 5 mJ. If the 1 kHz system had been needed, the pulses would have been amplified to 8 mJ [2]

The multipass amplifier consists of a Ti:Sapphire crystal lasing medium with an anti-reflective (AR) coating ( $\text{MgF}_2$ ). The crystal rod has a 15 mm diameter and is 21 mm in length. A water cooling system is used to prevent thermal lensing in the crystal. The Ti:Sapphire crystal is simultaneously pumped at 10 W from both sides with a Quanta Ray Nd:YAG laser from Spectra Physics. This multipass amplifier has a five pass, bow-tie configuration. With each pass, the beam excites the atoms of the crystal, adding more photons to the pulse. Once amplified by the multipass, the pulse energy reaches 250 mJ [2].

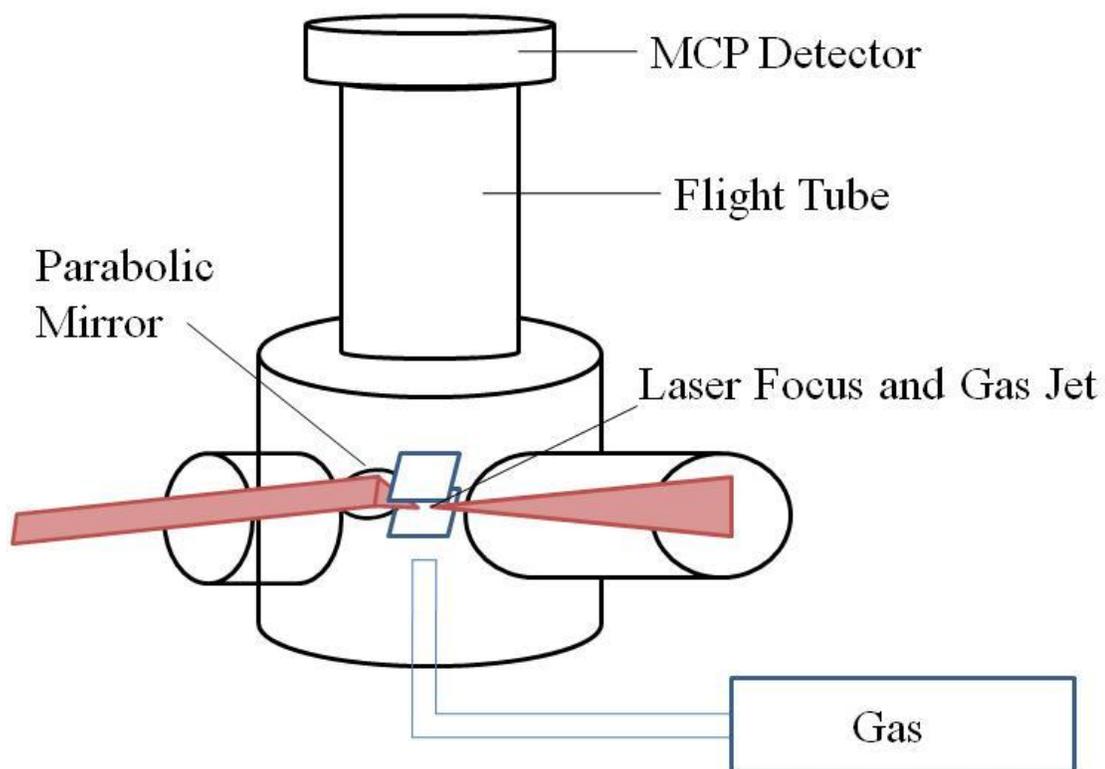
The pulse is then sent into the optical compressor to fix any spatial mode distortions. It is made up of two parallel gratings and a retro-reflector. The compressor compresses the pulse down to a pulse width as short as 30 fs [2].

## **2.2 Ultra-High Vacuum Chamber**

The laser field is focused into an ultra-high vacuum (UHV) chamber. A detailed description of the UHV setup is available in Enam Chowdhury's dissertation [4], however we will highlight the main aspects here.

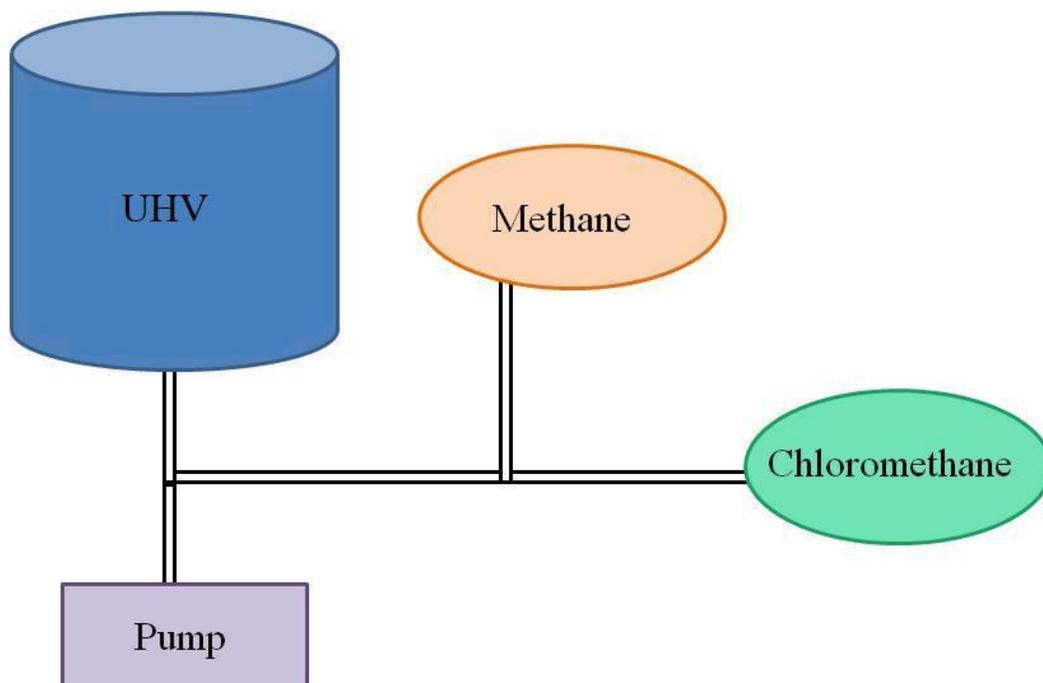
The UHV setup can be seen in Figure 7. Once directed inside the chamber, the laser beam is tightly focused using a  $45^\circ$  parabolic mirror that is gold-coated and three inches in diameter [4]. An effusive gas jet of molecules intersects with the laser focus. This is the point of ionization. The use of the parabolic mirror to focus the beam allows us to optimize the positioning of the mirror from outside the chamber to ensure that the maximum amount of ion counts are being detected. The

position of the mirror at which the most ions are collected during optimization is the position necessary for the laser focus to intersect with the sample gas.



**Figure 7. Ultra-high vacuum (UHV) chamber diagram.**

The gas jet apparatus is outlined in Figure 8. A four-way regulator was used so that both methane and chloromethane gas could be connected to the chamber at the same time. The third arm goes to the chamber, and the fourth to a roughing pump. When it was time to switch gases, it was only necessary to close the valve of the current gas, pump the excess gas out, and then open the new gas' valve, as opposed to having to disconnect everything.



**Figure 8. Gas jet apparatus.**

### 2.3 Ion Spectrometer

Time of flight (TOF) mass spectrometry is used to collect the ionized fragments. A flight tube of fixed length is located above the laser focus and gas jet. The detector, which will be discussed in the next section, is fastened to the top of the flight tube. In order to propel the positively charged ions toward the detector, a positive voltage is applied to metal plates at the point of ionization and a negative voltage is applied to the detector plates. The amount of time that an ion takes to travel to the detector is its TOF. The TOF for a particular ion is dependent on its charge to mass ratio. Energy can be equal to both

$$E = \frac{1}{2}mv^2, \quad 2.1$$

and

$$E = qV. \quad 2.2$$

By setting these equations equal to each other, replacing the velocity with  $v = x/t$ , moving the constants  $x$  and  $V$  to one side and setting the constants for one ion equal to that of a second ion, we obtain

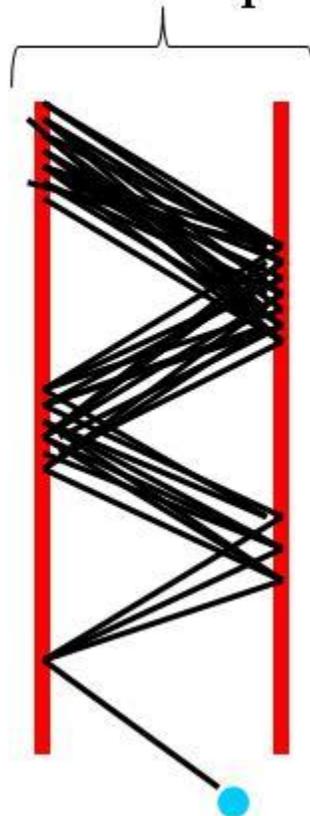
$$(\tau_1/\tau_2)^2 = \frac{m_1/q_1}{m_2/q_2}. \quad 2.3$$

This allows for the calculation of the TOF for an ion when we know the TOF of another. Usually, it is very easy to pick out the ionized water ( $\text{H}_2\text{O}^+$ ) peak from the water vapor in the chamber. This is used as our standard, and we can calculate the expected TOF for any ion based on the water peak, and the desired ion's charge and mass.

## 2.4 Detection System

The detector at the end of the flight tube is made up of micro-channel plates (MCPs). An MCP is a thin, charged, circular disk with millions of  $10 \mu\text{m}$  holes called channels. As stated earlier, the MCPs have a negative voltage applied to them. This accelerates the positively charged ions to fly up the flight tube to the detector. The fact that the MCPs have a negative charge also means that the channel walls are home to a number of extra electrons. The channels amplify the signal of an ion through a cascade process, shown in Figure 9. An ion that is being detected enters one of the channels and collides with the electrons on one of the channel walls, releasing some electrons. Those electrons, in turn, each collide with another portion of the channel wall and release an even greater number of electrons. This process continues until enough charge has built up for the computer to register that an ion has been detected. The cascade process is fixed: a certain amount of charge, or number of electrons, corresponds to one ion.

Charge detected and  
sent to computer



**Figure 9. MCP cascade process.**

The computer recognizes the time elapsed since the initial laser pulse that ionized that particular ion and the time the ion was detected. This is the ion's TOF and the computer adds one ion "count" at that particular TOF on the data collection screen. Figure 10 is an example of the detection spectra.

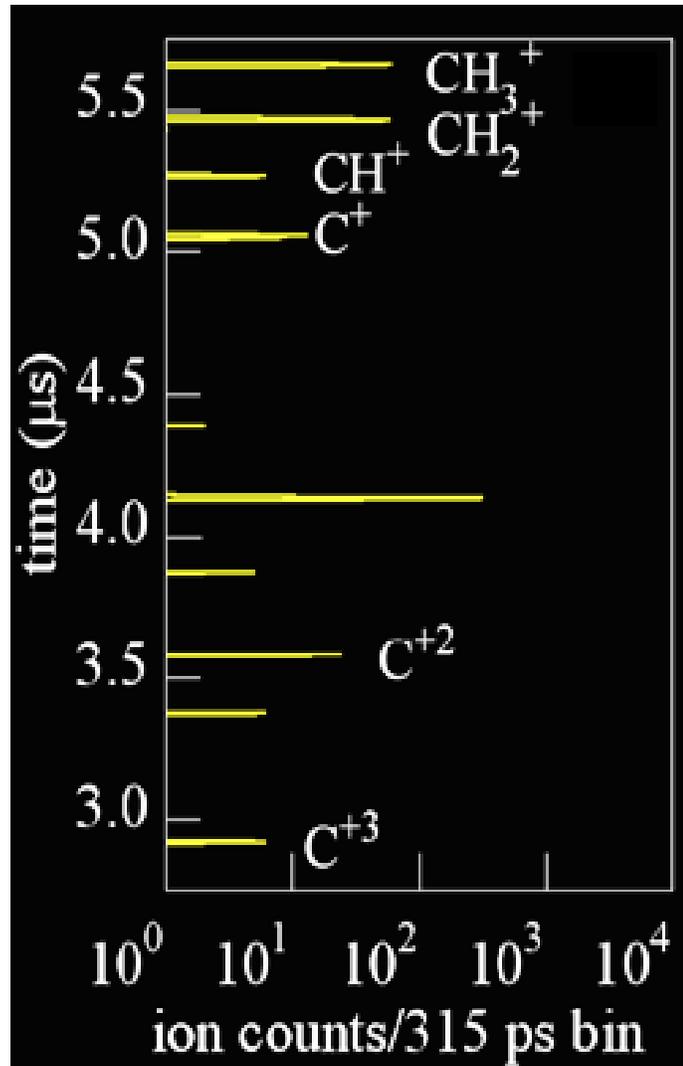


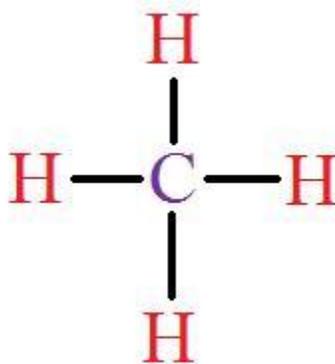
Figure 10. TOF signal example.

## Chapter 3

### METHANE

#### 3.1 Background

A previous study of our research group investigated the ionization mechanisms of methane ( $\text{CH}_4$ ).  $\text{CH}_4$  is a symmetric, non-polar molecule, illustrated by Figure 11. To avoid problems with mass degeneracies, we used  $\text{CH}_4$  with a carbon-13 isotope instead of the more common carbon-12. In particular, this was done to distinguish the  $\text{C}^{+4}$  data peak from that of an ionized trace contaminant that has a very similar TOF to that of  $\text{C}^{+4}$ .



**Figure 11. Atomic structure of methane.**

### 3.2 Experimental Procedure

CH<sub>4</sub> was ionized at decreasing energies to obtain ionization curves for each carbon fragment. Each data point was normalized with respect to the number of laser pulses applied to the sample and the pressure inside the chamber so that the units of each point are in ions per shot•Torr.

The experiment was run using linear polarized (LP) light and circular polarized (CP) light separately. By conducting this experiment using LP and then CP light, it was noticed that there are differences in the carbon ion yields. Certain ionization mechanisms are not characteristic of CP light. Rescattering ionization is not possible with CP light due to the CP light's manner of radiating outward. It is not likely that an electron would be able to return into the parent ion. Comparison of the ion yields for the LP and CP light can determine whether or not rescattering ionization created each of the charged carbon fragments.

### 3.3 Results

The data from this experiment is shown in Figure 12. Looking at the C<sup>+2</sup> and C<sup>+3</sup> curves, we see that their LP and CP ion yields match up at all intensities. From this, we can conclude that rescattering ionization had nothing to do with the formation of C<sup>+2</sup> and C<sup>+3</sup>. All of the ionization can be attributed to Coulomb explosion. The LP and CP data curves for C<sup>+5</sup> do not overlap at all. Therefore, only rescattering ionization was responsible for the formation of C<sup>+5</sup>. Inspection of the C<sup>+4</sup> ion yields reveals that the LP and CP data matched up for a portion of the curve, but at the bottom, they deviate from each other. This can be interpreted as both Coulomb explosion and rescattering ionization being the ionization mechanisms that formed

$C^{+4}$ . All of these results, as well as further information about this study can be found in the *Physical Review Letters* publication of this work [5].

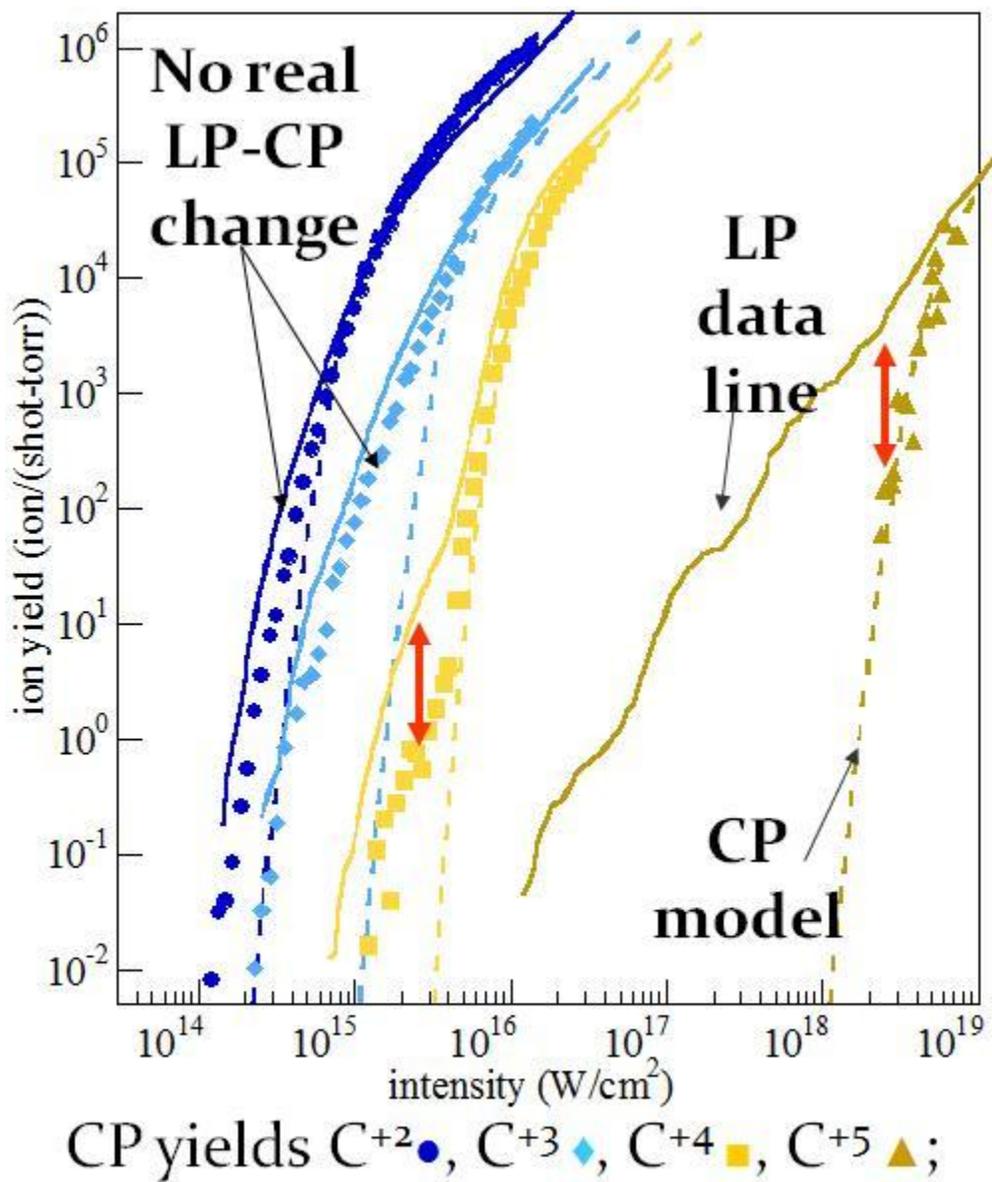


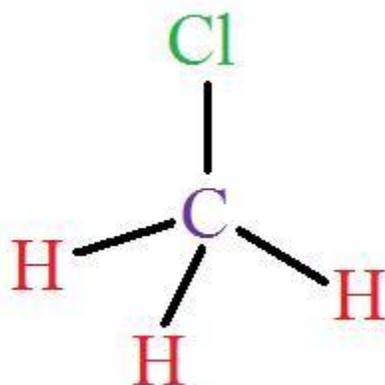
Figure 12. LP and CP data comparison for methane [5].

## Chapter 4

### CHLOROMETHANE

#### 4.1 Background

Chloromethane ( $\text{CH}_3\text{Cl}$ ) is a non-symmetric, polar molecule, shown in Figure 13. In order to study the effects of the symmetry of a molecule on its ionization patterns  $\text{CH}_3\text{Cl}$  is a perfect candidate for our test molecule. Since it essentially has methane in it, it is extremely easy to compare the ionization of the two structures.



**Figure 13.** Atomic structure of chloromethane.

## 4.2 Experimental Procedure

To determine whether or not CH<sub>3</sub>Cl ionizes more easily or more difficultly than CH<sub>4</sub>, the ionized C<sup>+n</sup> fragments were counted at a fixed intensity. A significant difference in the ion yields of one molecule compared to the other would indicate that the molecule with less ions was harder to ionize.

Again, the data was normalized with respect to the number of laser pulses applied to the sample and the pressure inside the chamber so that the units of each point are in ions per shot•Torr. For both CH<sub>4</sub> and CH<sub>3</sub>Cl, carbon-12 was used, so C<sup>+4</sup> data has been omitted.

## 4.3 Methane and Chloromethane Results

Table 1 shows the C<sup>+2</sup> ion yields from both CH<sub>4</sub> and CH<sub>3</sub>Cl when ionized at a laser intensity of  $2 \times 10^{15}$  W/cm<sup>2</sup>. We see that CH<sub>4</sub> yields two orders of magnitude more C<sup>+2</sup> ions than CH<sub>3</sub>Cl does.

**Table 1. C<sup>+2</sup> ion yields for methane and chloromethane**

Molecule	Intensity (W/cm <sup>2</sup> )	Ion Yield (ions/(shot•Torr))
CH <sub>4</sub>	$2 \times 10^{15}$	$1.49 \times 10^5$
CH <sub>3</sub> Cl	$2 \times 10^{15}$	$4.83 \times 10^3$

Table 2 shows the number of C<sup>+3</sup> fragments formed by the ionization of CH<sub>4</sub> and CH<sub>3</sub>Cl. This ionization was performed at an intensity of  $5 \times 10^{15}$  W/cm<sup>2</sup>. Again, CH<sub>4</sub> yielded more ions than CH<sub>3</sub>Cl did, but with a difference of one order of magnitude. One order of magnitude, however, is still a substantial difference.

**Table 2. C<sup>+3</sup> ion yields for methane and chloromethane.**

<b>Molecule</b>	<b>Intensity (W/cm<sup>2</sup>)</b>	<b>Ion Yield (ions/(shots•Torr))</b>
CH <sub>4</sub>	5 x 10 <sup>5</sup>	1.12 x 10 <sup>5</sup>
CH <sub>3</sub> Cl	5 x 10 <sup>5</sup>	2.57 x 10 <sup>4</sup>

Table 3 shows the amount of C<sup>+5</sup> ions that formed from ionizing CH<sub>4</sub> and CH<sub>3</sub>Cl at an intensity of 2x10<sup>18</sup> W/cm<sup>2</sup>. CH<sub>4</sub> produced five times the amount of C<sup>+5</sup> fragments than CH<sub>3</sub>Cl. This is slightly less than an order of magnitude, but still a significant disparity.

**Table 3. C<sup>+5</sup> ion yields for methane and chloromethane.**

<b>Molecule</b>	<b>Intensity (W/cm<sup>2</sup>)</b>	<b>Ion Yield (ions/(shots•Torr))</b>
CH <sub>4</sub>	2 x 10 <sup>18</sup>	6.8 x 10 <sup>3</sup>
CH <sub>3</sub> Cl	2 x 10 <sup>18</sup>	1.47 x 10 <sup>3</sup>

## Chapter 5

### CONCLUSION

#### 5.1 Effect of Symmetry on Ionization

This study successfully determined that symmetry and the substitution of a chlorine atom for a hydrogen atom on  $\text{CH}_4$  does have an effect on the ionization of a molecule. We found that chloromethane yielded significantly less ions for  $\text{C}^{+2}$ ,  $\text{C}^{+3}$ , and  $\text{C}^{+5}$  than were formed from methane. As chloromethane is non-symmetric and polar and methane is symmetric and non-polar, we can conclude that non-symmetric, polar molecules require more energy to ionize and are, therefore more difficult to ionize than symmetric, non-polar molecules.

#### 5.2 Future Work

In order to continue the study of the effect of a molecule's symmetry on its ionization patterns, the original methane experiment in which the ionization processes were determined for each charged carbon fragment should be repeated using chloromethane. This would characterize the ionization mechanisms involved in the formation of each individual charged carbon fragment for chloromethane. It would then be possible to compare the results of this characterization to that of the methane study discussed in Chapter 3. We would then be able to tell whether or not symmetry affects the ionization mechanisms involved in the breakdown of molecules, or if the ionization processes are the same and it is only the energy that the ionization occurs at is different. Other future work pertaining to this study includes performing this

experiment with dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), trichloromethane ( $\text{CHCl}_3$ ) which is more commonly known as chloroform, to further verify the effects of the symmetry.

Finally, the experiment should be repeated with carbon tetrachloride ( $\text{CCl}_4$ ), a symmetric molecule, in order to determine whether or not the addition of the chloride is affecting the ionization as well as the symmetry.

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