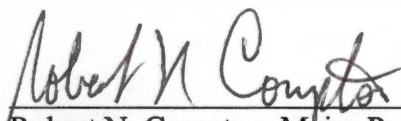
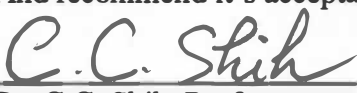


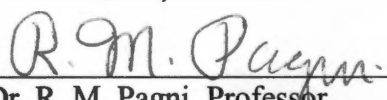
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I am submitting herewith a thesis written by Michael Straub entitled "Negative Ion Formation via Laser Desorption/Ionization of C_{60} ." I have examined the final paper copy of this thesis for the form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Physics.

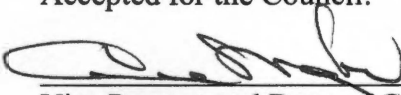

Robert N. Compton, Major Professor

We have read this thesis
And recommend it's acceptance:


Dr. C.C. Shih, Professor


Dr. R. M. Pagni, Professor

Accepted for the Council:


Vice Provost and Dean of Graduate Studies

Thesis
2002
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Negative Ion Formation via Laser Desorption/Ionization of C_{60}

A Thesis

Presented for the

Master of Science Degree

The University of Tennessee, Knoxville

Michael Straub

August 2002

Dedicated to

my wife Stacey and son Brett who have given me the strength to accomplish
anything

Abstract

The study of negative ion formation due to UV laser desorption/ablation are reported for C_{60} . Negative ion formation is studied and provides information into the major mechanisms responsible for carbon cluster anion formation. Results will be compared to known photoelectron spectroscopy data as an aid in the ion formation mechanisms. Ab initio calculations, using the Gaussian 98 package, are used to give supporting information on the structures and electron affinities of small C_n clusters $n \leq 8$. The laser desorption negative ion mass spectra are reported and explained under the conditions of the experiment. Despite the importance and widespread use of laser desorption ionization (LDI), the physical mechanisms responsible for ion formation are not well understood. This study is devoted toward a better understanding of the physics of laser desorption/ionization.

Preface

The work in this thesis is based on research carried out at the Science and Engineering Research Facility Building, the Department of Chemistry and Physics, the Compton Chemical Physics Group, University of Tennessee, Knoxville, TN. No part of this thesis has been submitted elsewhere for any other degree or qualification and it is all my own work unless referenced to the contrary in the text.

Acknowledgements

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Contents

1	Introduction	1
2	Historical Introduction of LDTOF/MS	3
3	Principles of the LDTOF	5
4	LDTOF/MS Experimental Setup	10
4.1	Mass Spectrum	11
4.2	N_2 Laser	17
4.3	Laser Desorption TOF/MS	17
4.4	Micro-Channel Plates	24
4.5	Electronics	24
5	Formation of Negative Ions	28
5.1	Photon Reactions	28
5.2	Electron Reactions	31
5.3	Collisional Mechanisms	32
6	LDTOF of C_{60}	35
7	Quantum Chemistry Techniques	45
7.1	Isomeric Structure	45
7.2	Electron Affinities	48

8	Results and Discussion	50
8.1	$1 \leq n \leq 13$	50
8.2	$14 \leq n \leq 53$	50
8.3	$54 \leq n \leq 60$	52
8.4	Conclusion	52
	References	54
	Appendix	59
	A.1. Binomial Distribution	60
	Vita	61

List of Figures

1	Wiley-McLaren TOF	6
2	Ideal Focusing Conditions	9
3	Fermi Distribution	12
4	Isotopic Abundances for Carbon	14
5	Isotopic Distribution for C_{60}	15
6	Sample Tip	16
7	Mass Spectra of Common Tip Materials	18
8	Mass Spectra of Gold Plated SS Tip	19
9	Mass Spectra of Gold Plated SS Tip Large $\frac{m}{z}$	20
10	Negative Ion Mass Spectrum Under Normal Operating Conditions . .	21
11	LDTOF Mass Spectrometer	22
12	Ionization Source	23
13	Electronics	25
14	Observed C_{60}^- Isotopic Distribution	27
15	Photon Ion Current	30
16	Electron Affinity Spectrum	33
17	C_{60}^- Mass Spectrum (High Laser Fluence)	38
18	C_{60}^- Mass Spectrum (Medium Laser Fluence)	39
19	C_{60}^- Mass Spectrum (Low Laser Fluence)	40
20	C_{60}^+ Mass Spectrum [2]	41
21	Basis Functions	46
22	Abundance of small carbon clusters	51

List of Tables

1	Electron Affinities Small Clusters	36
2	Electron Affinities Large Clusters	37
3	Quantum Chemistry Calculations of Energy and Bond Lengths	47
4	Calculated Electron Affinities	49

Chapter 1: Introduction

Since the discovery of large fullerene carbon clusters such as C_{60} , by the Smalley Group, intensive studies have been made concerning the formation of such new allotropes of carbon. Particular attention has been focused on the geometric structure of small carbon clusters and their relation to the formation of larger clusters. Laser Desorption/Ionization (LDI) has been extensively used to identify and characterize these clusters. The results of these studies are used to understand the decomposition mechanisms involved under LDI. Three major advances have aided in the study of ion formation and ionic structures 1) LDTOF/MS - Laser Desorption Time of Flight Mass Spectrometry 2) UPS - Ultraviolet Photoelectron Spectroscopy and 3) Ion Chromatography (IC). LDTOF provides qualitative information on the abundance of ions produced under laser desorption of a sample material. UPS provides accurate electron affinities (EA) of cluster species produced by various means and IC provides isomer structures of various clusters. Yang [4] have studied the UPS of negative carbon clusters for C_n^- ($n = 2$ to 29) concluding that the clusters with $n \leq 9$ are in the form of linear chains with a high binding energy. Further, the clusters with $9 \leq n \leq 29$, are largely composed of cyclic rings coexisting with linear chains. Those clusters with $n \geq 32$ are considered to be fullerenes, which dominate for $n \geq 50$.

LDTOF/MS is the experimental method discussed in this thesis. Simply, a laser is directed towards a sample material in a vacuum chamber. As the light strikes the sample, ions are produced (chapter 5). The ions are then accelerated through various electric field regions to be detected by an electron multiplier. The ions are represented as voltage pulses on an oscilloscope. If the distance between the sample and the detector is known, then the mass of the ions being detected can be determined. The LDTOF negative ion mass spectra of carbon clusters show a characteristic even/odd alternation in abundance for small $n \leq 8$, providing evidence of the open and closed shell structures. The EA for a closed shell will be less than that of an open shell for linear chains. The even clusters are more abundant for $n \leq 8$, and noting the linear isomer dominance in that range, suggests the even clusters will have an open shell.

This is consistent with empirical chemistry models. Using UV laser radiation of a solid sample, the C_n^- cluster peaks with $n > 13$ are sparse with the exception of a large C_{60}^- peak and a small contribution from C_{54}^- to C_{58}^- .

UPS can implement many different ion source configurations. As the ions are accelerated, they enter a mass selection region. A mass selected stream of ions is then photodetached by a high frequency laser. Common lasers include XeCl (308 nm, 4.02 eV, F_2 (157 nm, 7.9 eV), or ArF (193 nm, 6.42 eV). The low wavelengths are needed to photodetach the molecular anions. The kinetic energy of the free electron is then detected, which constitutes a photoelectron spectrum. In the case that the wavelength is varied, then the onset of ionization may be determined giving the binding energy of the electron (i.e. the electron affinity (EA)). More commonly, the EA is determined from the photoelectron spectrum from the equation: $EA = h\nu - KE$, where KE is the kinetic energy of the detached electron.

Ion chromatography is a very useful method for obtaining approximate structures of molecular species. Ions are produced and mass separated. A TOF is performed, in a stable gas mixture, usually a noble gas, such as He. The introduction of the gas will cause molecules of differing geometric structure to have different diffusion times. Simply, the difference in the TOF is a consequence of the isomeric structure of the species being sampled. Smaller more compact ions will diffuse faster than the larger more extended ions. Comparison of calculated diffusion times for various geometries with experiment provides structural information.

Using existing carbon cluster UPS and IC data [32], complemented with the data from the LDTOF, ion formation mechanisms may be examined. Ab initio calculations, using Density Functional Theory (DFT), are also performed in order to discuss the stability of differing carbon isomers. The calculations favor a C_n linear chain anion for $n \leq 9$ and is observed by Yang. et. al. [4] as well. A stable neutral ring structure is determined for $n = 6$ using DFT, but there is no evidence of a stable anion ring below $n = 10$. Thus low n carbon clusters are assumed to be linear in nature and this will be discussed in chapter 5.

Chapter 2: Historical Introduction of LDTOF/MS

In this chapter the origin and development of the TOF will be discussed. The original design of Wiley and McLaren [19], which employed a beam of electrons as an ionization source. The reflectron design was introduced by Mamyrin [20] and the LDTOF by Nuesser [21]. Further improvements were introduced with the MALDI (Matrix Assisted Laser Desorption/Ionization) technique, which places a sample in a material chosen carefully to produce low fragmentation of the sample. Advances in the method are characterized by the mass resolution $\frac{m}{\Delta m}$ and a complementary time resolution $\frac{\Delta t}{t}$. The mass resolution is a ratio of the mass of the detected ion to the width of the peak observed. If broad peaks are observed then the proper identification of the mass observed is uncertain. A high mass resolution provides superior peak determination.

The TOF principle was speculated since the time of J.J. Thomson due to his studies of ionized particles [14]. The TOF Mass Spectrometer was proposed by W.E. Stephens in 1946, during a talk for the American Physical Society at M.I.T. [22]. The talk proposed a mass spectrometer with time dispersion, but was not achieved until Cameron and Eggers [23] in 1948 working at the Clinton Engineering Works, with the introduction of the “Ion Velocitron”. The ion velocitron produced broad peaks, which result in a low mass resolution, largely, due to the continuous ion source.

It was not until 1955, when two major advances were proposed by 1) Katzenstein and Friedland [24] and 2) Wiley and McLaren [19]. Katzenstein and Friedland introduced a pulsed electron extraction technique coupled with a delayed ion ejection from the source [14]. The same year, Wiley and McLaren improved the mass spectrometer with the addition of two ion focusing grids to obtain a much improved mass resolution. The Wiley-McLaren mass spectrometer also employed the use of “Time Lag Focusing” (TLF), often referred to as “Delayed Pulse Extraction” (DPE) when the ionization source is LDI, which provide superior energy focusing. The first commercial TOFMS was introduced by the Bendix Corporation in 1957.

The next major development was the “reflectron” design introduced by Mamyrin

in 1971 [20]. Mamyrin noticed that the mass resolution could be greatly increased with the introduction of a longer flight tube with an ion reflection region. Keeping the overall length of the mass spectrometer to a minimum, Mamyrin designed a secondary flight tube joined to the primary tube by a electric field region. The electric field deflects the ions nearly 170° to focus on a ion detector. The reflectron region of the TOF allowed for energy compensation as well, slower ions of a given mass make a small orbit and can catch-up with the faster ions. The electric field can be adjusted to further resolve the initial energy distribution of the ions. The longer flight tube improves the mass resolution due to the initial spatial extent of the ionization region.

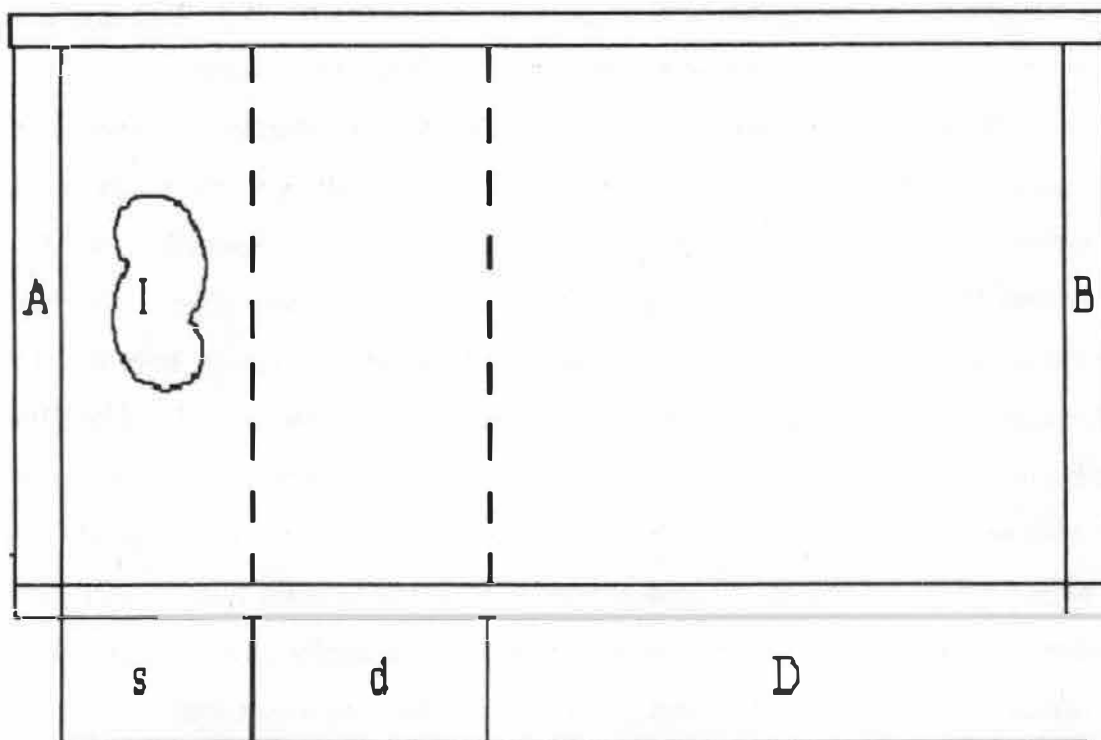
By 1979, the LDTOF Mass Spectrometer was introduced by Nuesser [21], with the mass resolution of $\frac{m}{\Delta m} > 4000$, using the reflectron design. Presently, the use of mass spectrometry has reached a very high level of resolution, with the techniques such as MALDI achieving mass detection of ions with $\frac{m}{z} > 100,000$ Da [14].

Chapter 3: Principles of the LDTOF

This chapter introduces the original Wiley-McLaren TOF design. The mathematical principles behind spatial and energy focussing are defined. The calculations show the optimization procedure for the TOF parameters. Although the original design used electron impact ionization as a ion production method, the principles discussed can be extrapolated for the use of a laser desorption ionization source.

The TOF apparatus consists of a flight tube of a known distance (D), various ion lenses/grids and an ion detection system (Fig. 1). Ions produced in the source region are formed with a spatial extent, which means, if all ions are not formed in the same place, thus there will be an initial position distribution. The ions formed also have a velocity distribution dependent upon the ion formation mechanism. Ions are then accelerated by two mesh grids with potentials of V_s and V_d , respectively. The Time Lag Focusing (TLF) technique uses a time delayed voltage pulse applied to the grids and backing plate controlled by a pulsed power supply and is a large contributor for the mass resolution. Ideally, all ions of the same charge to mass ratio should reach the detection region at the same time and position. Practically, this is unachievable, but certain modifications can be made, which limit the time dispersion.

Following electron impact, ions are produced with a mass, velocity, space and temporal distribution. The spatial distribution of the ions will cause a time differential for ions of the same mass. In an attempt to deal with the spatial distribution, Wiley and McLaren have devised an optimal approach to the problem using the TLF technique [19]. Referring to Fig. (1), there are three regions: 1) source region (s), 2) acceleration region (d) and 3) drift region (D). The length of each region is s , d and D respectively. The TOF of an ion is the sum of the TOF through each region, $T = T_s + T_d + T_D$, where T_n is the TOF through: 1) $n = s$, source region, 2) $n = d$, acceleration region and 3) $n = D$, drift region. The result obtained by Wiley and McLaren, neglecting the initial energy distribution of the ions is given by (3.1) where three is the chapter and 1 is the equation number.



This figure is a basic illustration of the original Wiley-McLaren TOF [19]. (A) and (B) are the backing plate and the ion detection system respectively. (s), (d) and (D) are the length of the source, acceleration and drift regions respectively.

Figure 1: Wiley-McLaren TOF

$$T = 1.02\sqrt{\frac{m}{2U_t}}\left(\frac{2\sqrt{k_o}d}{\sqrt{k_o}+1} + 2\sqrt{k_o}s_o + D\right) \quad (1)$$

where U_t is the velocity of the ion in the field free drift region (D), s_o is the initial position along the flight tube, E_s and E_d are the electric field strengths in the s and d regions respectively and k_o is a constant dependent upon the instrument parameters [14].

$$k_o = \frac{s_o E_s + d E_d}{s_o E_s} \quad (2)$$

It should be noted that the constant (1.02) term in the TOF equation, has been propagated over the years. Based upon a separate derivation, the term could not be reproduced and is not described in the original paper [19]. Thus, the term should be omitted until verified.

Further, optimal values can be achieved for the potential on each grid to compensate for the spatial distribution. By minimizing ΔT , i.e. $\frac{\delta \Delta T}{\delta s_o}$, optimal values for $\frac{E_s}{E_d}$, for a fixed s, d and D, are determined and the spatial distributions may be minimized. The minimization can be simplified by the use of a coordinate transformation defined below:

$$K_2 = \left(1 + \frac{2d\sigma s(E_s - E_d)}{E_s(2(E_d - E_s) + su_o^2)}\right) \quad (3)$$

$$X = \left(1 + \frac{u_o^2}{2(E_d - E_s)}\right) \quad (4)$$

$$R_2 = \frac{E_d}{E_s} \quad (5)$$

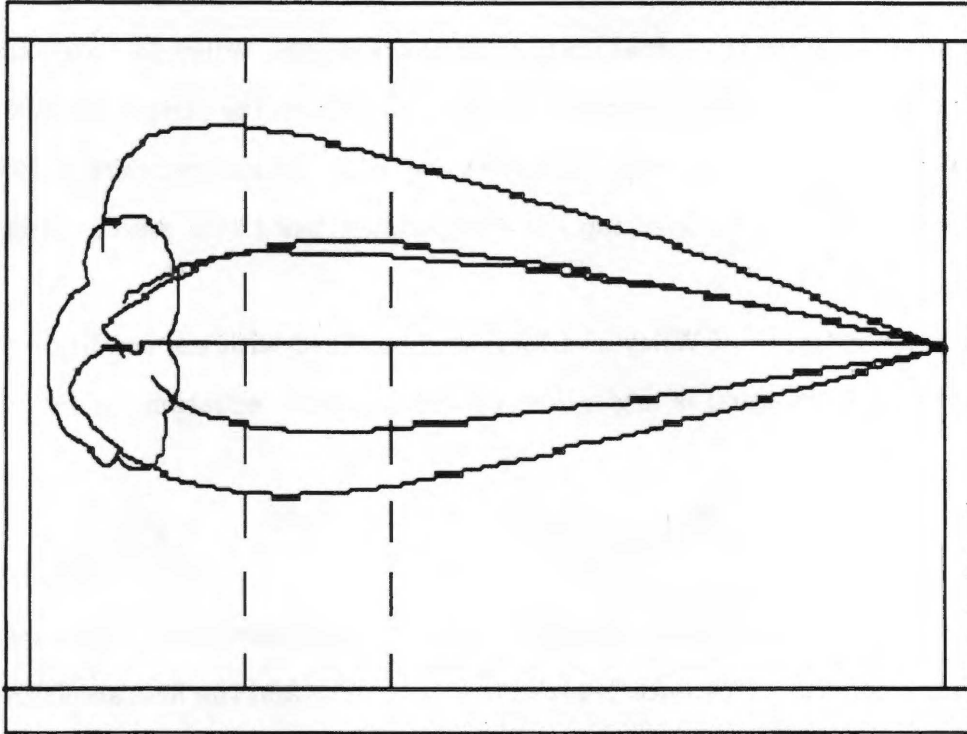
Where σ is the charge to mass ratio and u_o is the initial velocity of an ion. The two equations can now be cast in a simple form as follows:

$$2XK_2\left(\sqrt{k_2}\left(1 - \frac{1}{R_2}\right) + \frac{1}{R_2}\right) - D = 0 \quad (6)$$

$$2XK_2\left(k_2^{\frac{3}{2}}\left(1 - \frac{1}{R_2}\right) + \frac{1}{R_2}\right) - 3D = 0 \quad (7)$$

The above equations can be solved numerically for $\frac{E_a}{E_d}$ with a fixed s , d and D [13]. The solution does not depend on the absolute value for the potential in each region, only the ratio is determined, leaving the flexibility of choosing a high/low voltage.

Correction of the velocity distribution is a much more difficult problem. As the ions are formed, they leave the ionization region with a velocity distribution determined by the linear acceleration velocity modified by the initial ion velocities. Ions of the same charge to mass ratio, σ , can vary widely in initial energy. The differences arise from the competing processes involved in the formation of the ions (to be discussed in chapter 6). To compensate for the velocity distribution, the TLF method is employed. The potential on the backing plate will be pulsed with a small time delay τ with respect to the electron beam pulse. All ions with an off axis (z -axis) velocity component will travel further away from the $+z$ -axis (Fig. 2). Wiley and McLaren have determined that the addition pathlength is independent of the magnitude of the on axis velocity component when τ is properly optimized. Details of the calculation can be found in the references [19] [5].



This figure is a basic illustration of the ion trajectories under ideal conditions. All ions of the same σ will reach the detectors at the same time regardless of starting position and initial kinetic energy.

Figure 2: Ideal Focusing Conditions

Chapter 4: LDTOF/MS Experimental Setup

This chapter will use the derivations of Wiley and McLaren for electron impact ionization (EI) time-of-flight mass spectroscopy (EITOF/MS) as they pertain to a LDTOF/MS. The LDI ionization method uses a N_2 laser to desorb ions from a metal tip upon which a sample material is deposited. The approximately flat surface of the sample tip now minimizes the initial spatial distribution. The Wiley-McLaren space focusing configuration would help correct for any unevenness in the sample as well. As a result, the mass resolution is greatly enhanced over other ionization sources. It will be shown below that time lag focusing (TLF) (or sometimes DPE) greatly improve the TOF mass resolution.

Following the approach of Wiley and McLaren, modified with the condition that the initial spatial distribution is negligible, we can derive an equation for the TOF [19] [14]:

$$T = \frac{\sqrt{2m}(\sqrt{U_o + eV_{10}} \mp \sqrt{U_o})}{eV_{10}} + d \frac{\sqrt{2m}(\sqrt{U_1 + eV_{21}} + \sqrt{U_1})}{eV_{21}} + \frac{\sqrt{2m}D}{2\sqrt{U_1 + eV_{21}}} \quad (1)$$

where V_{10} is the potential difference between the first acceleration grid and the backing plate. V_{21} is the potential difference between the flight tube and the first acceleration grid. U_o is the initial energy of the ion and U_1 is the energy as the ion enters the drift region. The $\mp$ refers to the direction of the on axis ion velocity upon formation. Using the LD source, this term can be taken as positive.

Negative ion formation occurs via many pathways dependent upon the experimental method used to study the phenomenon and the molecule under investigation. Using LDTOF/MS, a sample mass is irradiated, heating the sample and producing fragment ions as well as free and 'quasi-free' electrons for attachment and dissociation of fragments [10]. Of course, collisionally induced ion formation must not be over-looked as well as other methods to be discussed later.

As mentioned above, the spatial distribution is limited due to the surface used to introduce the sample and the sample irregularity itself. A C_{60} sample is dissolved in toluene and deposited on the surface of the sample tip with a pipet then allowed

to dry. On the atomic level, all surfaces are not “smooth”, therefore, some spatial distribution should be expected, but the contribution to mass spectra resolution is much less than the EI ionization method used by Wiley and McLaren. But, there is a question as to exactly how much the surface ‘roughness’ actually effects the resolution.

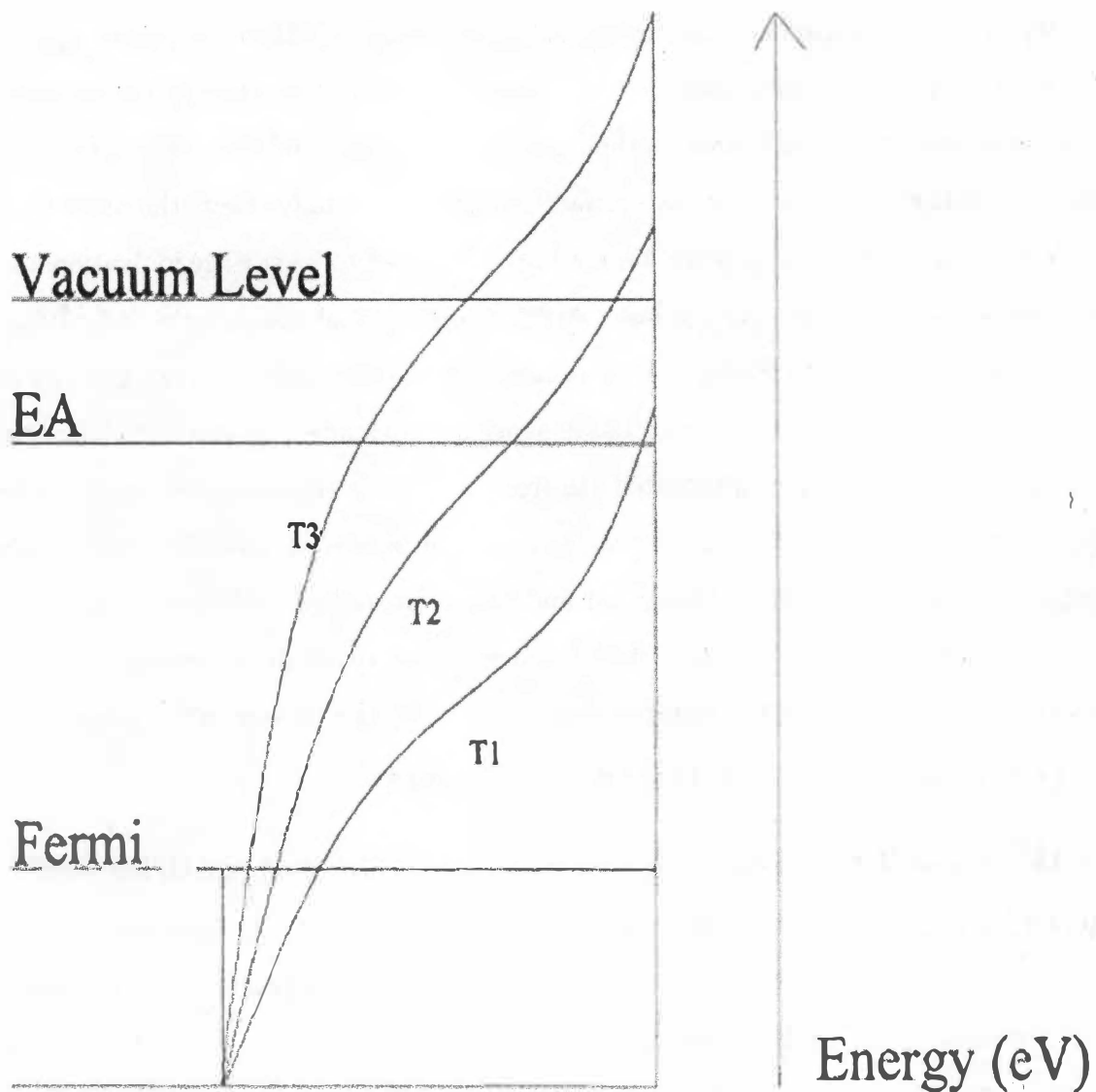
The main negative ion production method is believed to be surface ionization and electron attachment [10]. As the laser strikes the surface of the sample, the surface is heated to a temperature sufficient to produce thermionic emission. The number of electrons desorbed from the tip material depends approximately on the work function. Fig. 3, shows the commonly accepted electron thermionic emission mechanism. The electrons of the tip metal are not bound to a specific atomic site and have an energy distribution characteristic of the metal and the temperature. As the temperature increases the energy distribution allows more electrons to attain an energy closer to the that required to eject the electron from the surface (i.e. ϕ , the work function).

4.1: Mass Spectrum

The channelplates detect ions as a voltage pulse, which is amplified, and sent to an oscilloscope to be recorded as a voltage versus time data set. The data is recorded by a LeCroy 9405 oscilloscope, with a sampling rate of $1 \frac{Gs}{s}$ (Gigasample per second) and a resolution of 1 GHz, can be averaged and a distinct mass spectrum results. A mass spectrum is a plot of the ion signal abundance versus the $\frac{m}{z}$ obtained by the average time/voltage differential data from the oscilloscope. The conversion to a mass spectrum is as follows. Every ion receives the same amount of energy from the acceleration regions, independent of velocity and, therefore, the kinetic energy received is:

$$\frac{mv^2}{2} = qeE_s s + qeE_d d \quad (1)$$

where q is the charge of the ion, e is the charge of an electron, E_s and E_d are the electric field strength in the source and acceleration region, respectively, and v is the



Fermi distribution of electrons in the metal tip as a function of the temperature. The area of the graph above the vacuum level is proportional to the number of electrons thermally ejected from the surface without a sample deposited. As a sample is deposited, the EA of the surface material can lower the vacuum level. Molecules with a electron affinity EA can accept free electrons emitted from the surface as well as quasi-free electrons with potential energies down to EA.

Figure 3: Fermi Distribution

velocity of the ion as it enters the drift region [14]. The TOF in the drift region is:

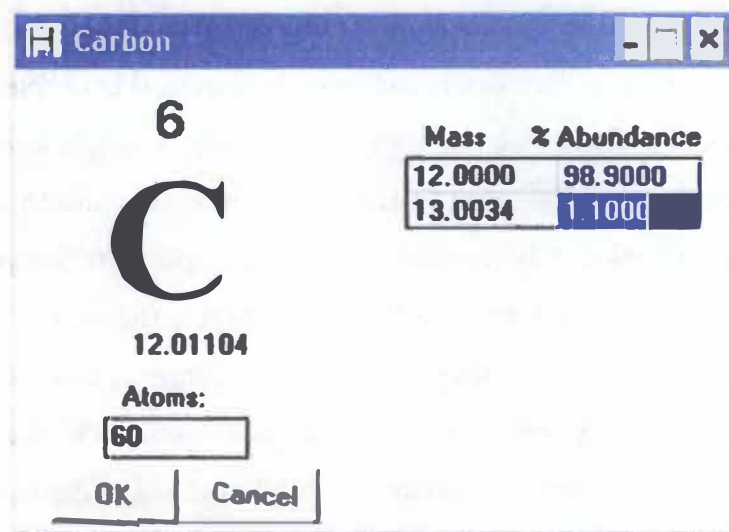
$$t \approx \sqrt{\frac{m}{2qe(E_s + E_d)}} D \quad (2)$$

Solving for $\sqrt{\frac{m}{z}}$ results in a linear dependence upon t :

$$\sqrt{2e(E_s + E_d)s} \frac{t}{D} = at + b \quad (3)$$

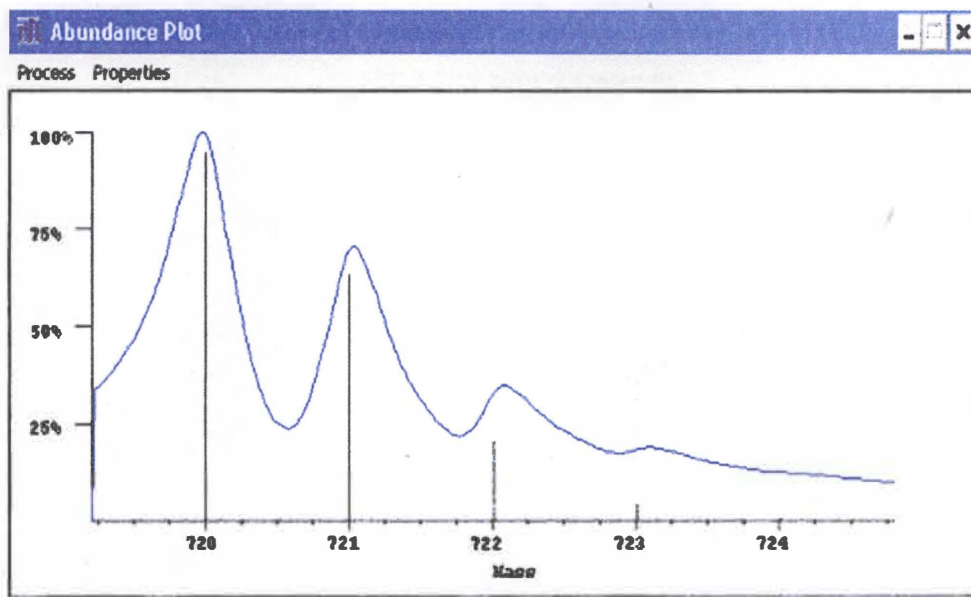
The above equation would suggest that $b = 0$, but the function for t is just an approximation and the addition of b allows for a much closer fit. Further, a and b must be determined from the knowledge of two known experimental TOF positions (i.e. peaks) in the spectrum. This can be achieved by doping the sample with a known molecular species, comparison with a known sample, or by a simple knowledge of one element in the sample. If one element in the sample is known and that element has stable isotopes then a peak can be observed and the isotopic distribution can confirm the identity. An example of such an isotopic distribution is that of C_{60}^- . There are 60 carbon atoms in C_{60} , but not all of these will be ^{12}C . According to known abundance data, found in any chemistry text, there are two stable isotopes of the carbon atom (^{12}C and ^{13}C). There are other isotopes such as ^{14}C , but the abundance is $\ll 1\%$ and not considered to contribute significantly to the mass spectrum. Therefore, the C_{60}^- ion could be composed of $^{13}C_1^{12}C_{59}$ or any other combination, dependent upon the isotopic abundance of the individual isotopes. Fig. 4, is a list of percent abundances for the carbon atom as illustrated by the Isopro package [35] and the corresponding predicted isotopic distribution (Fig. 5). The prediction is based on the binomial distribution (appendix A.1). The isotopic abundance results in a series of peaks around the central $^{12}C_{60}^-$ peak. The peaks determined to be $(^{13}C_n^{12}C_{60-n})^-$ for $n = 0$ to ≈ 4 as illustrated in Fig. (5).

A typical sample tip is shown in Fig. (6). The top of the sample tip is referred to as the tip surface and can be composed of many differing substances. The most common sample tips are composed of 1) copper, 2) stainless steel, 3) tantalum and 4) gold plated stainless steel. The laser can desorb ions from the sample tip as well as the sample, therefore, the sample tip surface chemical composition can effect the



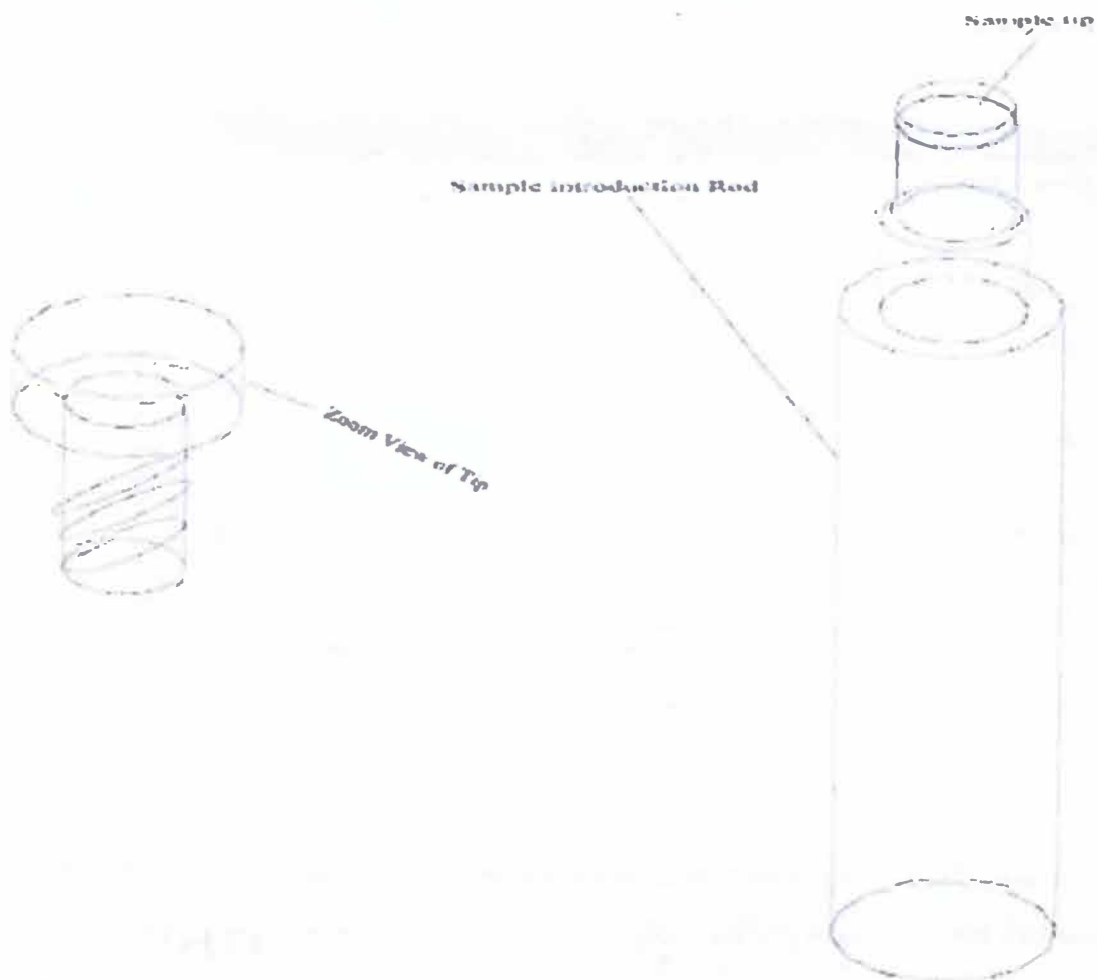
The isotopic abundances may be found in any chemistry book, but are represented here using the Isopro package [35].

Figure 4: Isotopic Abundances for Carbon



The isotopic distribution is determined by the use of a Binomial distribution and is represented by the Isopro package [35]

Figure 5: Isotopic Distribution for C_{60}



The sample tip is inserted into the TOF ionization region by a long rod with a “bullet” shaped adapter to which the flat tip is threaded.

Figure 6: Sample Tip

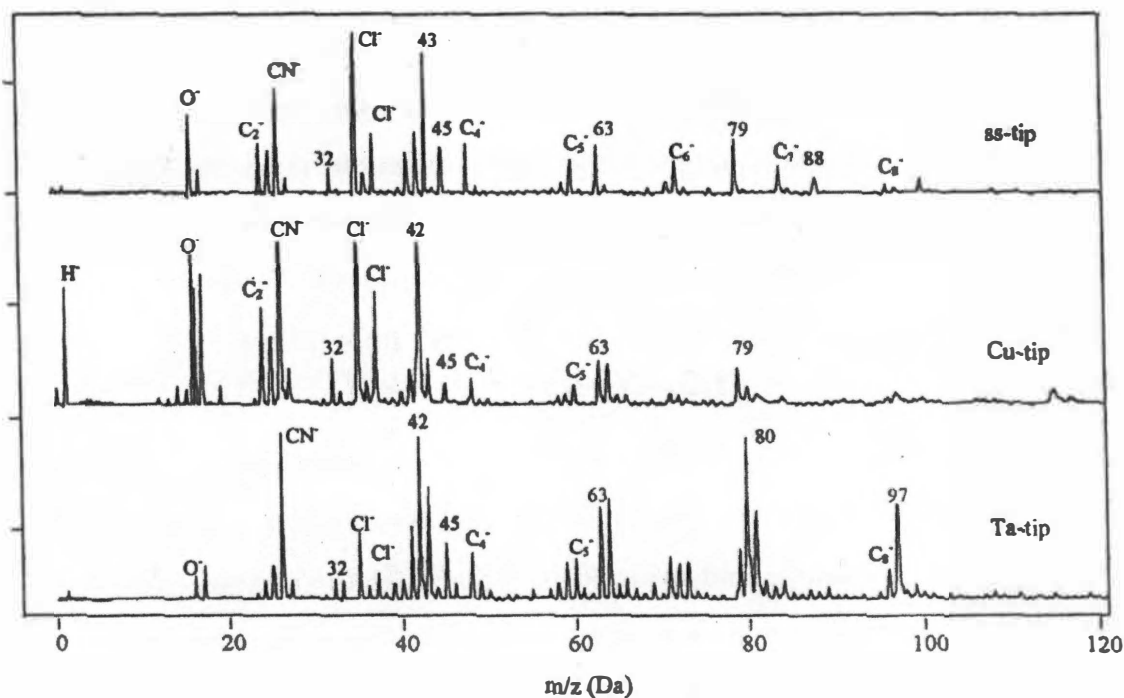
mass spectrum by introducing peaks characteristic of the sample tip surface. Surface chemistries between the sample and the surface can also occur. Compton and Tuninman [10] have reported the mass spectrum obtained for Tantalum, Stainless Steel and Copper. The results of the study are shown in Fig. (7). The mass spectrum of Gold plated SS are observed in this study and shown in Fig. (8) and (9). It should be noted that the mass spectrum obtained is a result of a much higher laser power than would be used under normal LDMS conditions. As a consequence, the spectra for the sample tip, obtained under normal operating conditions, will be much less prominent in a sample spectrum as illustrated in Fig. (10). Also, the differences in the sample tip material affect the production of ions as discussed previously. Work functions for copper and gold are provided by [33] as 4.65 and 5.1 eV, respectively.

4.2: N_2 Laser

As mentioned above, the PRL LN1000 Nitrogen Laser is used to ionize the sample material as depicted in Fig. (11). The UV (337.1 nm) laser beam is guided through a transparent circular opening and focussed in the area of the sample. The pulse width is observed to be ≈ 600 ps with a energy of $1.4 \frac{mJ}{pulse}$ and a exit area of $18 mm^2$. The laser power density can be determined to be $\approx 1.296 \times 10^7 \frac{W}{cm^2}$ or $12.29 \frac{MW}{cm^2}$. The laser should generally set to focus just beyond the sample in an attempt to keep laser power to a minimum needed to “gently” desorb the sample [10]. Also, by gently focusing the laser beam, peaks due to the sample material are kept to a minimum while ion production remains large. Further, variable beam attenuators are used to achieve a low power as well as the various lens’ and aperatures traversed by the beam.

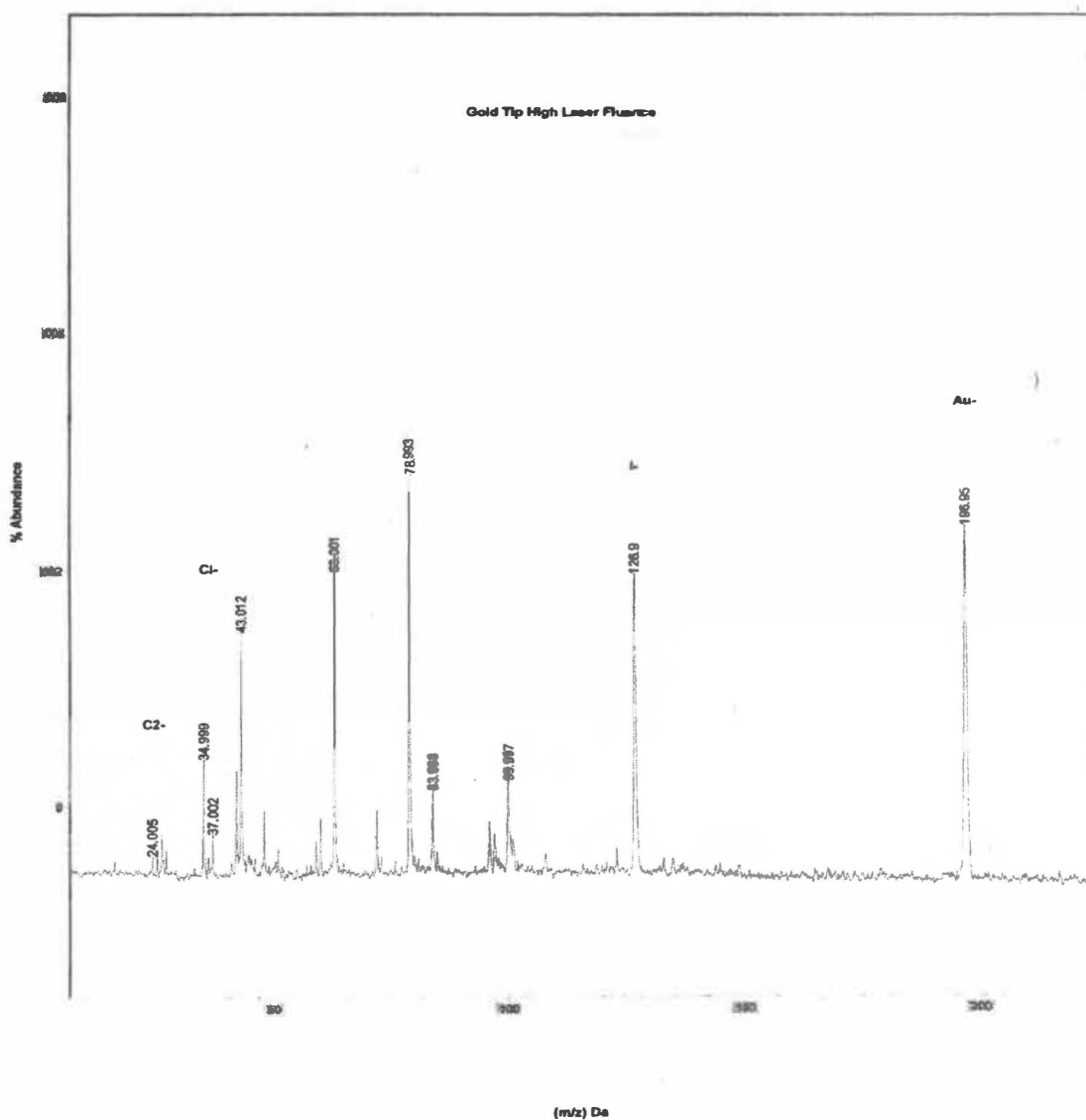
4.3: Laser Desorption TOF/MS

The Laser Desorption (LD) TOF mass spectrometer used in this study is very similar to the Wiley-McLaren design. The focussing grids have a different geometry as shown in Fig. (12) and provide superior ion focussing due to their configuration. The source and acceleration regions are 1.04 cm (s) and 4 cm (d) respectively with a 2 m drift region the backing plate operates at -1000 V for negative ions with a grounded acceleration grid. The flight tube is operated at 2000 V. As the ions enter



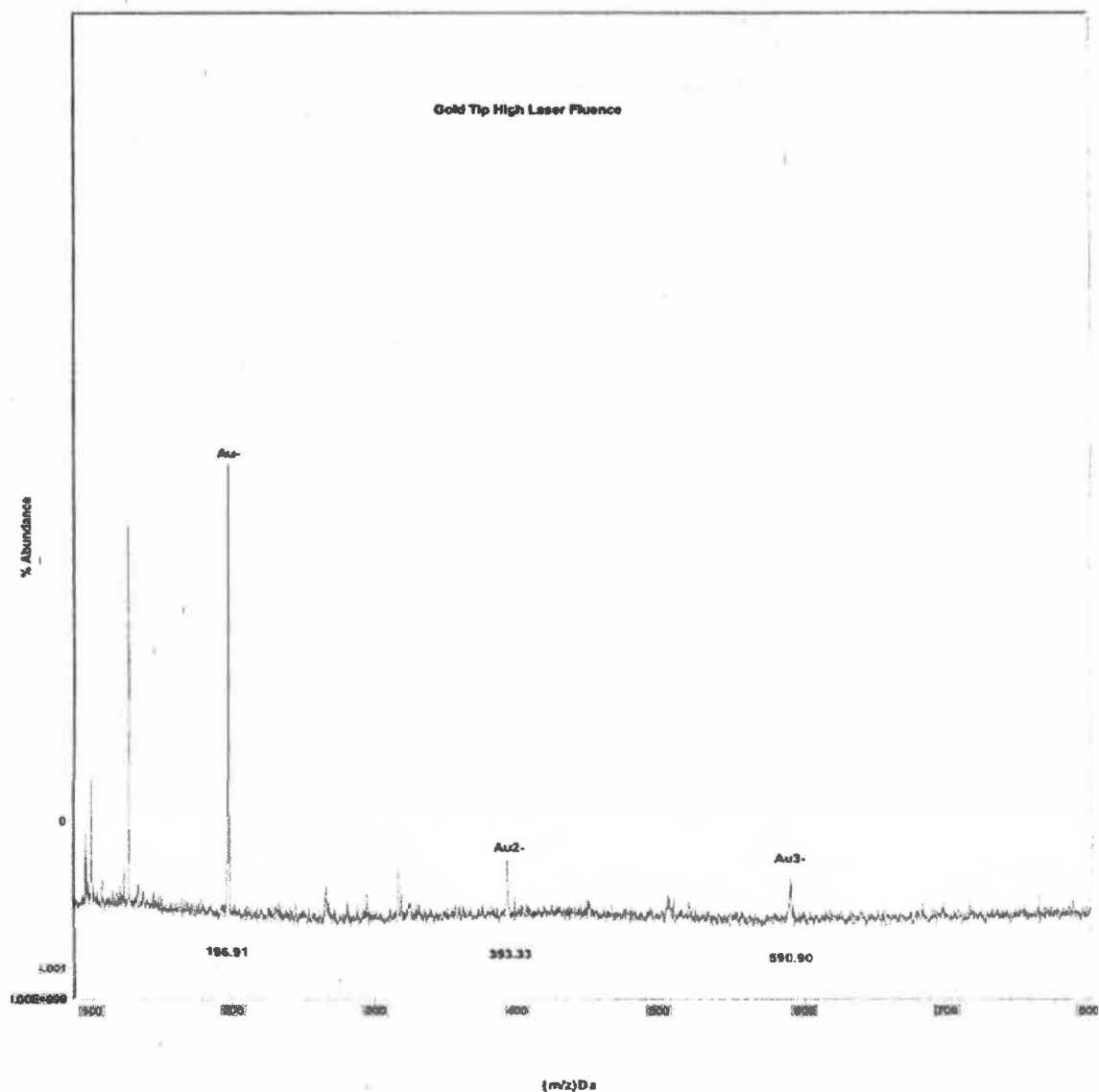
Mass spectra obtained by Tuinman and Compton et. al. [10]. The mass spectra illustrates the contribution of impurities and chemicals used in the processing of the tip material. Some peaks include, both isotopes of Cl^- at 35 and 37 Da, small carbon clusters, peaks from 41 - 43 Da and a peak at 79 Da.

Figure 7: Mass Spectra of Common Tip Materials



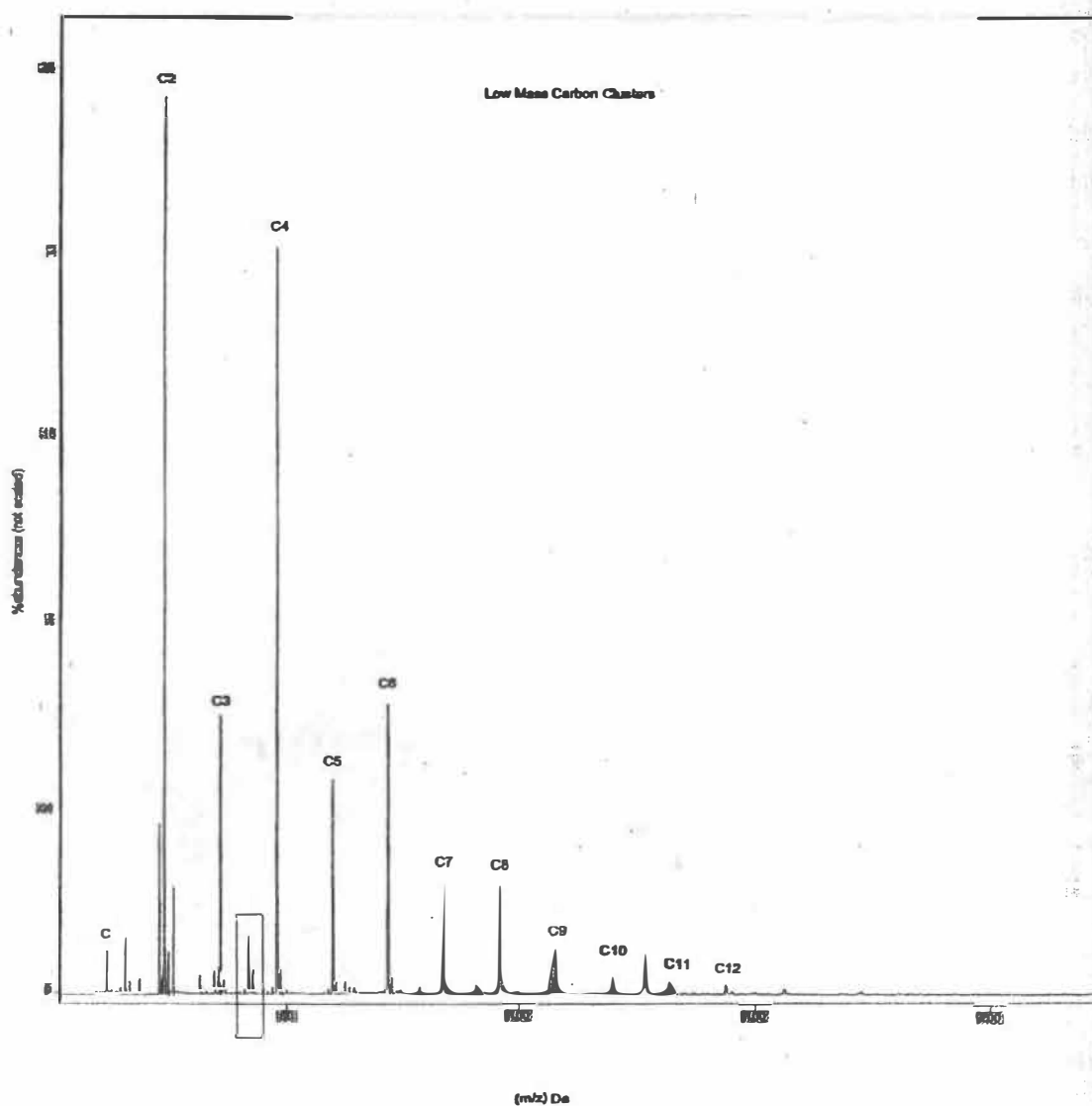
The mass spectrum provides evidence of Au^- , I^- , $^{35}Cl^-$ as well as some peaks characteristic of all tips studied by Tuinman et. al.[10]. Peaks at 79, 42, 43 and the Cl^- show a close correlation.

Figure 8: Mass Spectra of Gold Plated SS Tip



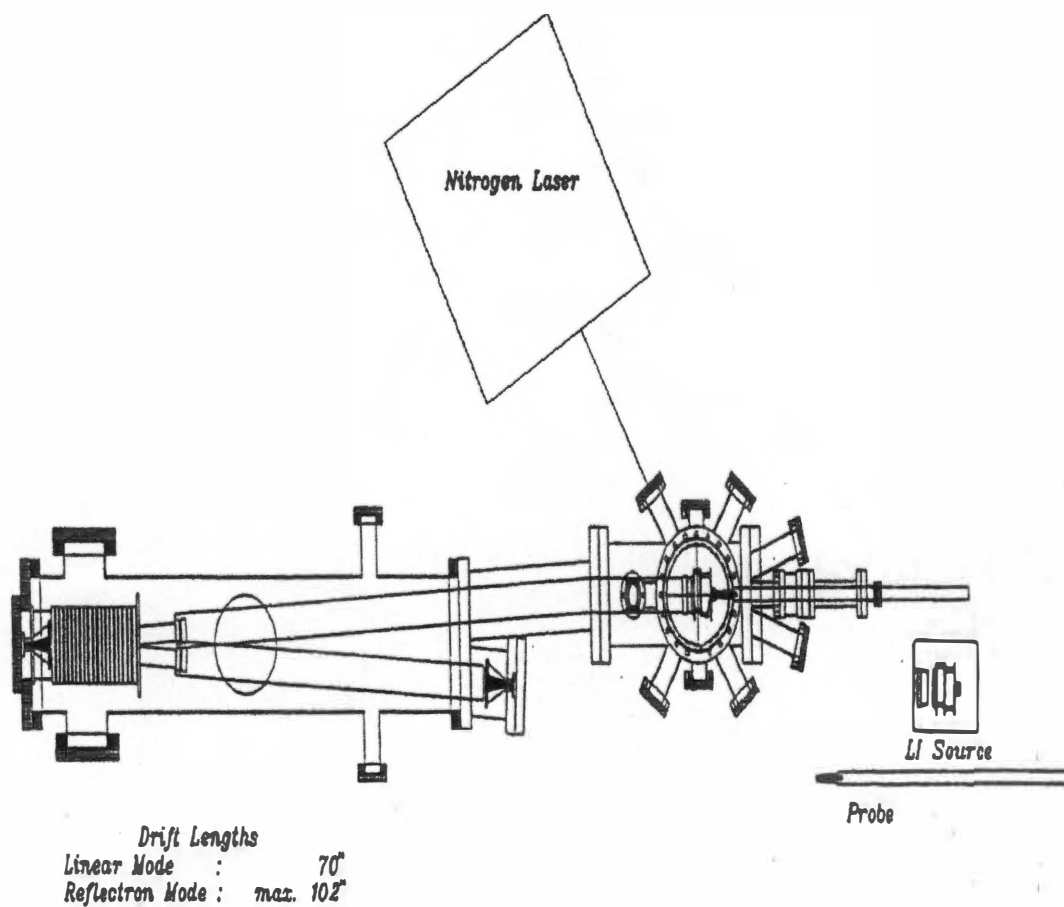
The mass spectrum is a continuation of fig. (9) and provides evidence of Au^- , Au_2^- , Au_3^- , showing the stability of anionic gold clusters.

Figure 9: Mass Spectra of Gold Plated SS Tip Large $\frac{m}{z}$



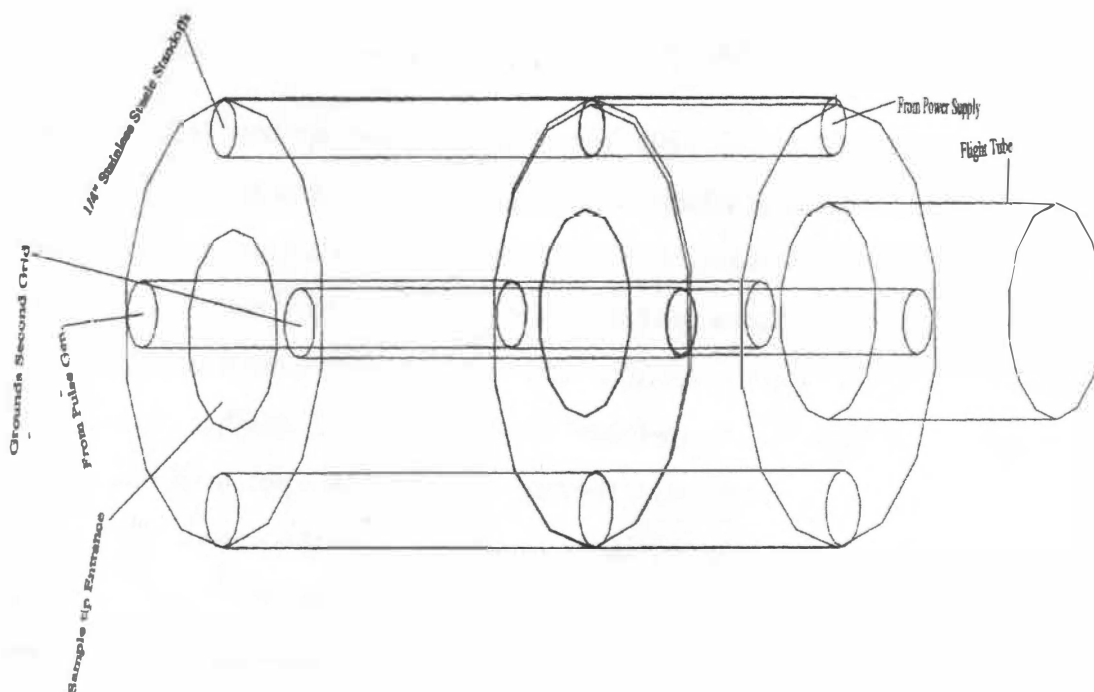
The mass spectrum of C_{60}^- up to $\frac{m}{z} \approx 280$. The mass peaks from $\frac{m}{z} = 41$ to 43 (boxed region) are observed and considered to be provided by the sample tip. A comparison with fig. (7) shows the degree to which the sample tip peaks contribute to the mass spectrum.

Figure 10: Negative Ion Mass Spectrum Under Normal Operating Conditions



The experimental setup of the LDTOF. The N_2 laser irradiates the ionization region through a circular opening on the side.

Figure 11: LDTOF Mass Spectrometer



The ionization region of the LDTOF/MS. The acceleration grids are circular electrodes as opposed to a wire mesh.

Figure 12: Ionization Source

the drift region they are guided by two sets of deflection plates. The plates are parallel to the flight axis and focus the ions onto the channelplates for detection. The plates can be controlled separately in a range from 0.00 to 10.00 V above the flight tube potential. Optimal values for the voltage on the deflectors are obtained by monitoring the ion signal on the oscilloscope. The potential is set to obtain the largest signal in the region of interest.

4.4: Micro-Channel Plates

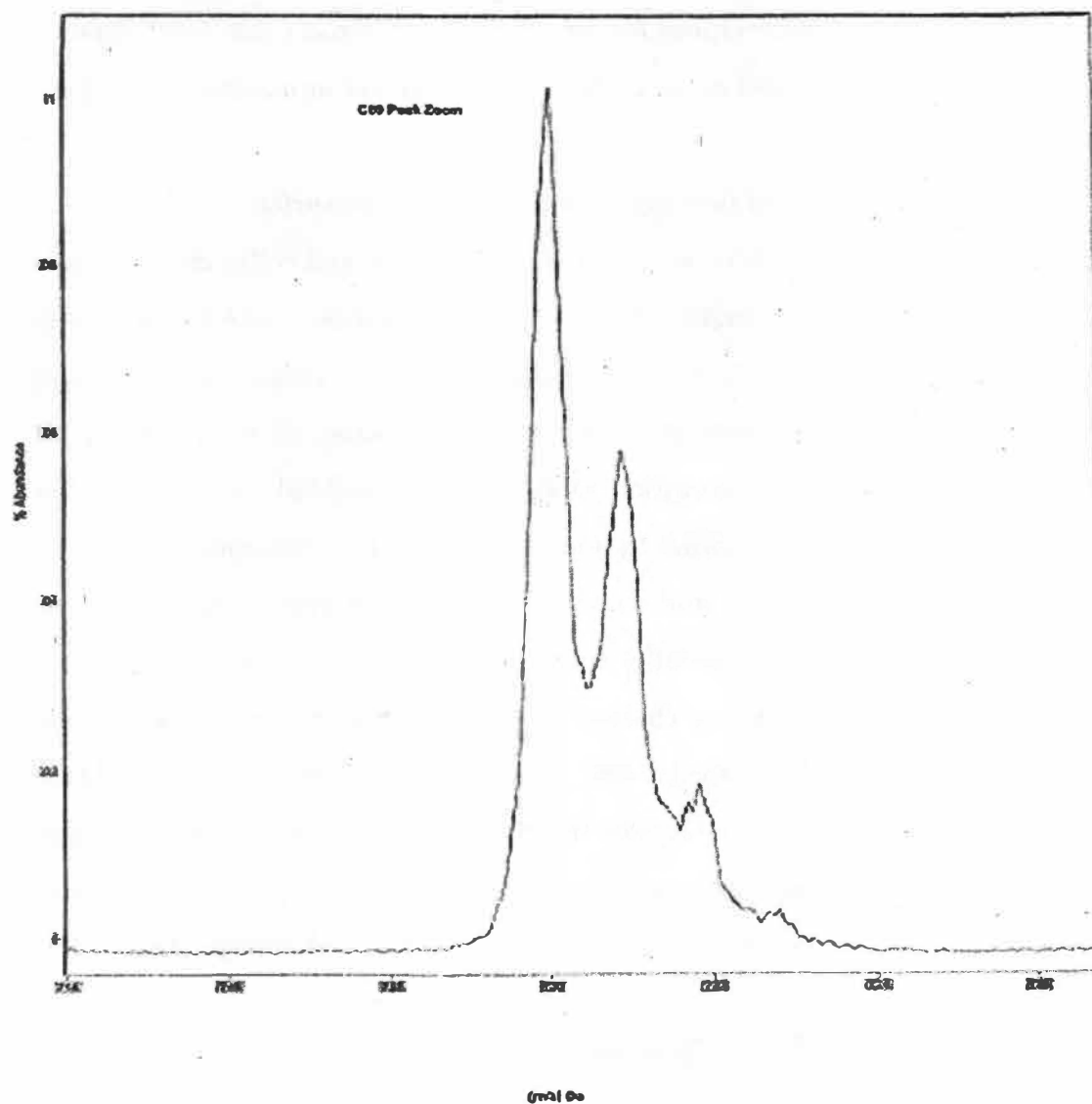
The Comstock Model CP-625C/50F Micro Channelplates are used to detect ions. Channelplates are composed of a large number of microtubes of $\approx 8 - 25\mu m$ in diameter. As an ion strikes the entrance of a tube, it will desorb electrons from the inner walls of the tube. The electrons ejected at the point of impact will strike another point in the tube and eject more electrons, as the process continues a geometric progression of electrons leave the channelplates caused by a small number of ions. The electrons are allowed to travel through the tubes by a positive potential bias (1000 V) at the back of the channelplates relative to the front. In this thesis, the front of the first plate is set to the potential of the drift tube while the front plate is set to 2125 V. The difference being 125 V is enough to prevent electrons from moving back into the drift region. The backing plate is at ground potential providing a difference of 2000 V from front to back. Behind the back plate is a collector plate, which collects the electrons ejected from the channelplates. As the pulses are collected the data is sent to the oscilloscope for processing at 2500 Mhz. The data collection is limited by the resolution of the oscilloscope (1GHz).

4.5: Electronics

Fig. (13), gives a general diagram of the electronics composing the experimental apparatus. The Comstock Model TFP-101 Power Supply supplies voltage to the flight tube, X/Y deflectors, the front channelplate and to the secondary ion lens (when applicable), which can supply up to $\pm 5kV$ and is a large contributor for the mass spectra resolution due to the particular stability of the output voltage. The

pulsed voltages are produced by the DEI GRX-3.0K-H pulser, offering rise and fall times of $< 45ns$. The backing plate is pulsed with -1000 V for negative ions as determined by the Wiley-McLaren procedure for secondary spatial focusing. The pulse extraction time delay (τ) has been optimized to $\approx 100ns$, under experimental conditions, resulting in an optimized mass resolution. The delayed pulse extraction (DPE) allows for energy compensation in the TOF. Ions with greater kinetic energy move further into the acceleration region. Upon application of the backing plate pulse, the faster ions will receive less energy from the acceleration field allowing the initially slower ions to catch up at the detector. A magnified C_{60}^- peak is shown in Fig. (14), which clearly shows the isotopic distribution and a large mass resolution (≈ 1400).

As the laser fires, a photodiode detects the beam and triggers a SRS Model DG535 Digital Delay/Pulse Generator. The output of the DG535 (used as a delay) triggers the LeCroy 9405 Digital Oscilloscope and the DEI pulser with a time difference of $\approx 100ns$. The output of the DEI Pulser provides the proper pulse waveform to the acceleration regions with a delay time controlled by the DG535. As ions are formed by the laser, the acceleration regions are pulsed to provide the energy focusing described above. The ions enter the drift region through a set of parallel plates (X/Y Deflectors), which further focuses the ions onto the channelplates. The X/Y deflector voltage is controlled by the Comstock power supply. As the ions are detected by the channelplates, the signal is sent to the oscilloscope for mass analysis.



The full width half maximum of the peak at 720 Da results in a value of $\frac{1}{2}$ Da. Thus, the mass resolution can be obtained as ≈ 1400 .

Figure 14: Observed C_{60}^- Isotopic Distribution

Chapter 5: Formation of Negative Ions

This chapter will discuss various mechanisms which can lead to negative ion formation. Only those processes assumed responsible for anion production are discussed. Known and experimental data are used as an explanation of the ion formation mechanisms for the case of C_{60} .

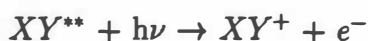
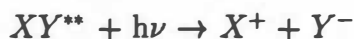
Due to the large amount of heat generated on the sample surface by the focused laser, fragmentation, electron attachment, surface ionization and collisional processes can occur. As the N_2 laser strikes the surface of the sample, photons of energy $\approx 3.68\text{eV}$ bombard both the C_{60} target and the surface. If a single photon collides with a C_{60} molecule in the ground state, the energy will access an electronically allowed excited state. Since the ionization energy of C_{60} is $\approx 7.6\text{eV}$, a single photon cannot ionize a C_{60} molecule. In order to produce negative ions, the energy deposited must cause thermionic emission from the surface. The ion process is assumed to be thermal and multiphotonic, initially, and can involve either photon reactions or collisional reactions as a secondary channel. The laser light excites the conduction electrons, locally heating the metal producing free and “quasi-free” electrons. These electrons can attach to surface molecules to produce negative ions. The light also interacts with the C_{60} molecules through photon and collisional processes. We also observe C_{60}^+ ions from the surface. These ions are also a result of multiphoton excitation leading to ionization.

5.1: Photon Reactions

- | | |
|---|-------------------------|
| a. $XY^{**} + h\nu \rightarrow X^+ + Y^-$ | Polar Photodissociation |
| b. $XY^- + h\nu \rightarrow X + Y^-$ | Photodissociation |
| c. $XY^- + h\nu \rightarrow X^- + Y$ | |
| d. $XY + nh\nu \rightarrow X^+ + Y^-$ | |
| e. $XY + nh\nu \rightarrow XY^+ + e^-$ | Multiphoton Ionization |
| f. $XY + nh\nu \rightarrow X + Y$ | |
| g. $XY + nh\nu \rightarrow XY^{**}$ | Multiphoton Excitation |

where (**) represents an excited state of the molecule.

Polar Photodissociation (channel a) is the only direct single photon mediated pathway to negative ion formation. Morrison studied this mechanism by bombarding a target with photons of varying energy and detecting product ions. The experiments involved using high energy photons from a discharge in a hydrogen filled tube and a 60° magnetic sector mass analyzer. The photon ion current is recorded over a set of incident wavelengths from the discharge tube. Using this method, there are two competing channels 1) polar photodissociation and 2) photoelectron detachment as represented below:



Where, in this case, both X and Y represent iodine atoms. Therefore, when the product is mass selected a peak representing the single cation would prove the existence of the photodissociation channel, while, a peak representing the molecular iodine cation would prove the photoelectron dissociation channel. Fig. (15), provides evidence for such a peak, just below the electron detachment limit [25].

Multi-photon processes may exhibit a large contribution to anion formation as well. Channel (e), thermionic emission, is possibly the most abundant process. Concerning gas phase samples, studies by Wurtz and Lykke [2] have observed that direct multi photon ionization (MPI) occurs by the absorption of 2 to 3 photons. However, under relatively long pulse length ($\geq 10^{-9}s$), laser excitation then ionization occurs through the absorption of many (≥ 20) photons followed by “thermionic emission”. As the number of photons per molecule increases, fragmentation and delayed ionization becomes the predominant pathways for C_{60} . Since the conversion from electronic to rovibrational excitation within the molecule is much faster than the absorption rate for ≈ 10 to 20 photons, ionization seems to be negligible. This suggests that channels d and e represent the major competing processes in the gas phase. In the solid phase, molecules can undergo MPI with the absorption of ≈ 20 photons and delayed ionization of C_{60} is not seen in the LDI to produce C_{60}^+ [10]. The fact that the mass resolution of the products formed is high implies that the ions are produced

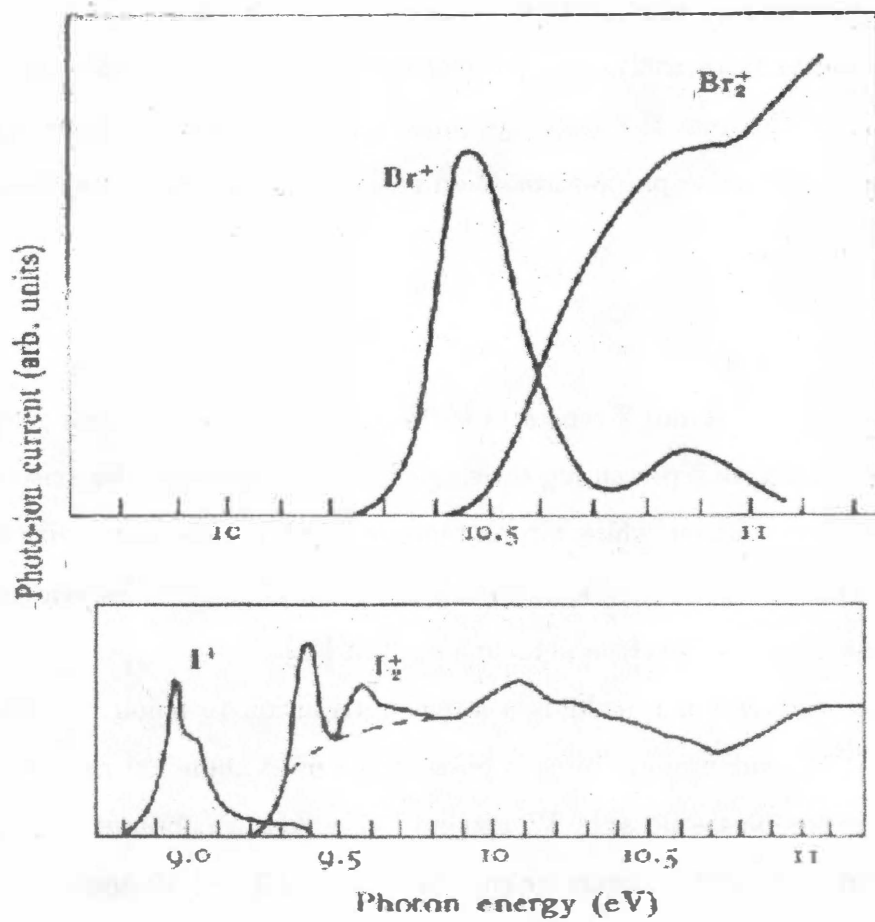


Illustration of photon initiated ion-pair formation as measured by Morrison [25]. The photon ion current obtained by varying the wavelength. The cations of Br and Cl shown must be accompanied by an anion of Br and Cl, respectively.

Figure 15: Photon Ion Current

very close to the surface. Delayed ionization is always observed as a “trailing edge” of a particular peak, due to the time differential between the ion and the electron ejected. Studies have shown no evidence of a “trailing edge”, and therefore, delayed ionization is not to be considered a large contributor to the mass spectrum. Thus, we invoke the formation of negative ions by electron molecule surface interactions, Rydberg charge exchange, multiphoton absorption and fragmentation. It is believed the small anionic carbon clusters are produced by multiphoton absorption. Thus, dissociation of C_{60}^- into $C_{n=1to10}^-$ appears to dominate electron loss.

5.2: Electron Reactions

a. $XY + e^- \rightarrow XY^-$	Unimolecular Attachment
b. $XY + e^- \rightarrow XY^- + h\nu$	Radiative Attachment
c. $XY + e^- \rightarrow X^+ + Y^- + e^-$	Ion Pair Process
d. $(XY^-)^{**} + e^- \rightarrow X + Y^-$	Dissociation
d. $XY + e^- \rightarrow X^- + Y$	Dissociative Attachment
e. $(XY^-)^{**} \rightarrow e^- + XY$	Autodetachment

Numerous electron capture processes to carbon clusters have been identified and studied resulting in an obviously different mechanism between small and large clusters, due presumably to differences in the numbers of quantum states available to dissipate energy. Massey gives plausible reasons for the existence of only one electronic state, the ground state, for most negative ions [16]. C_2 is one of the few small molecules which is known to possess a bound anionic excited state. In general, excited anions may spontaneously detach an electron. The detachment produces a photon of energy E_{ds} , where s represents the energy released upon electron detachment from a state s.

The emission spectrum of the radiative electron capture process (b) will exhibit a continuous energy spectrum up to a limit, where the energy of the electron is equal to the EA. The wavelength of the emitted photon is determined by

$$\lambda = \frac{hc}{E_e + EA}$$

31

Where E_e is the energy of the electron before detachment and the long wavelength cut-off is

$$\lambda_{max} = \frac{hc}{E_a}$$

The radiative cross section for attachment is small except for certain cases where slow electrons are attached. A slow electron stays in the vicinity of the atom or molecule for a long enough period of time for photon emission to occur.

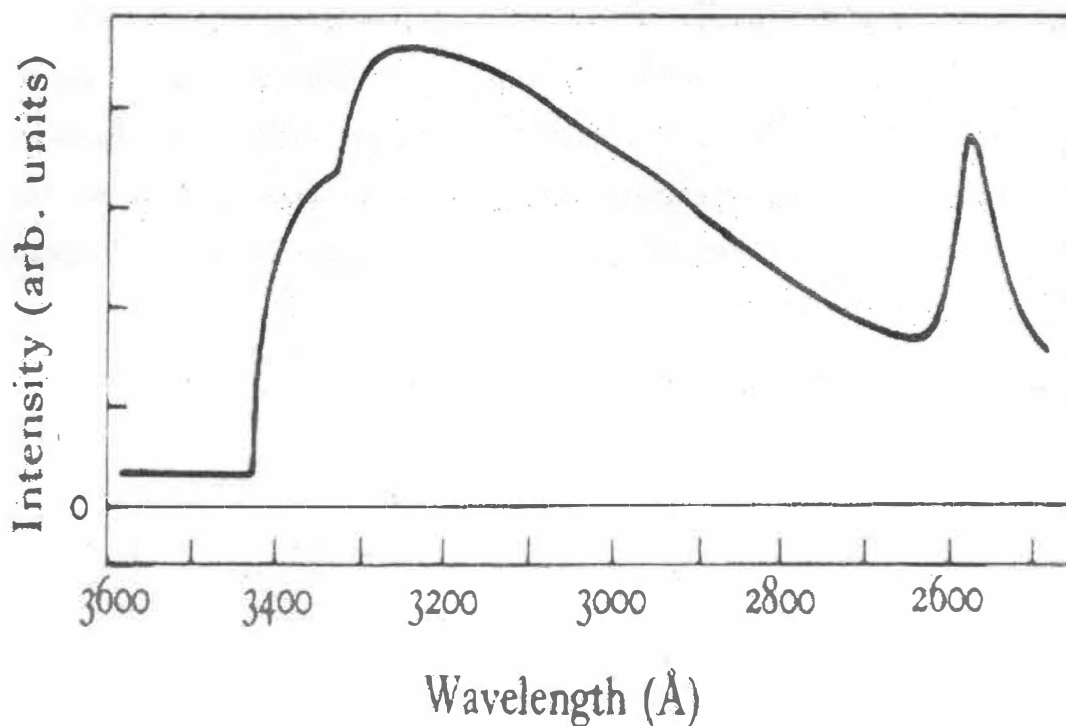
Extensive studies have shown the existence of the limit on the long wavelength limit λ as shown in Fig. (16), [26] [9]. The graph shows the wavelength observed from a heated anionic sample of chlorine gas Cl^- . The most notable features include two peaks at 3428 and 3326.5 Angstroms, respectively, which correspond to the fine structure split energy of the chlorine atom. Therefore, electrons may attach to differing electronic states. The dynamics of electron capture are largely dependent upon the state to which the electron attaches. A electron will, obviously, attach differently into a s-state than into a p-state due to the Pauli Exclusion Principle and symmetry differences in the states involved. This gives rise to a very different wavelength dependence for the radiative attachment cross section.

For the case of dissociative attachment, the energy of the electron must be resonantly absorbed by the molecule XY. Studies have shown the cross section for electron attachment to be $Q_a^t \approx 10^{-15}$ to 10^{-20} cm^2 [16].

5.3: Collisional Mechanisms

- | | |
|---|--------------------------------|
| a. $X^{**} + YZ \rightarrow X^- + YZ^+$ | Collisional Polar Dissociation |
| b. $X^{**} + YZ \rightarrow X^+ + YZ + e^-$ | Collisional Detachment |
| c. $X^{**} + YZ \rightarrow X^+ + YZ^-$ | Electron Transfer |

Although, electron attachment is believed to be the main mechanism for negative ion formation in LDMS, collisional reactions are assumed to contribute to the mass spectra obtained by LDTOF, primarily in the form of Rydberg Charge Exchange (i.e. $X^{**} + YZ \leftrightarrow X^+ + YZ^-$). The laser liberates excited ions from the surface, which subsequently collide with other ions. Carmen and Compton [7] have determined



The electron affinity spectrum as measured by Muck [26]. The two peaks represent the detachment of an electron from two Cl states. In this case, the peaks correspond to the fine structure states of Cl.

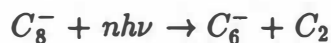
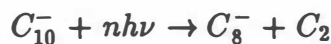
Figure 16: Electron Affinity Spectrum

this mechanism to be substantial for highly excited Rydberg atom charge exchange (RET). The highly excited X atom/molecule collides with another atom/molecule and the excited atom/molecule will transfer an electron and settle into a stable negative ion state. This can only happen when $IE_X - E_{state-X} + EA_{YZ}$ is a minimal value. As YZ accepts the electron it will give up an amount of energy equal to EA_{YZ} . The energy needed to ionize X minus the energy of the excited state is equal to the amount of energy which needs to be supplied by YZ. Due to many different combinations of ions, this process is very probable. It is known that positive ions are also produced in the LDMS at the laser power employed for negative ions studies. Thus, we can expect that many highly excited atoms and molecules are present leading to collisional negative ion production.

Chapter 6: LDTOF of C_{60}

This chapter will discuss the mechanisms of negative ion formation as they pertain to laser desorption of C_{60} . Table 1 and 2, are given for quick reference on the following pages.

Figures (17,18,19,20), show the experimental negative ion mass spectrum of C_{60} dissolved in toluene and allowed to dry on a sample tip of stainless steel (SS). C_2^- is shown to be the most abundant product anion, although this experiment used a high laser fluence. At low laser powers a single C_{60}^- peak can be achieved, which is expected from the above discussion on the number of photons absorbed [10]. At high laser fluence the fragmentation will occur more readily due to multi photon absorption. Photo-dissociation of secondary ions is also possible down to C^- and C_2^- as represented below:



etc...

Other experimental observations [2] show the propensity of C_{60}^+ fragmentation by the ejection of a small neutral cluster in favor of a positive fullerene. The difference in the observed spectra between cation and anion production can be postulated as due to the EA of the smaller linear chains being larger than the fullerenes. In other words, as a excited positive C_{60} cluster fragments, the stability of the positive fullerene will dominate the spectrum. As a excited negative C_{60} cluster fragments the preferred pathway seems to favor the ejection of a negative small cluster fragment due to the larger electron affinity for the small clusters. Autodetachment is presumably in competition with the channel above and an observed deficiency in the mass spectrum (C_n^- , $n = 14$ to 54) with the exception of a few stable molecular structures (Chapter 8).

The mass spectrum for C_n^- , $n \leq 7$, shows the characteristic even/odd alternating abundance. This alternation can be explained by the corresponding alternation in

Table 1: Electron Affinities Small Clusters

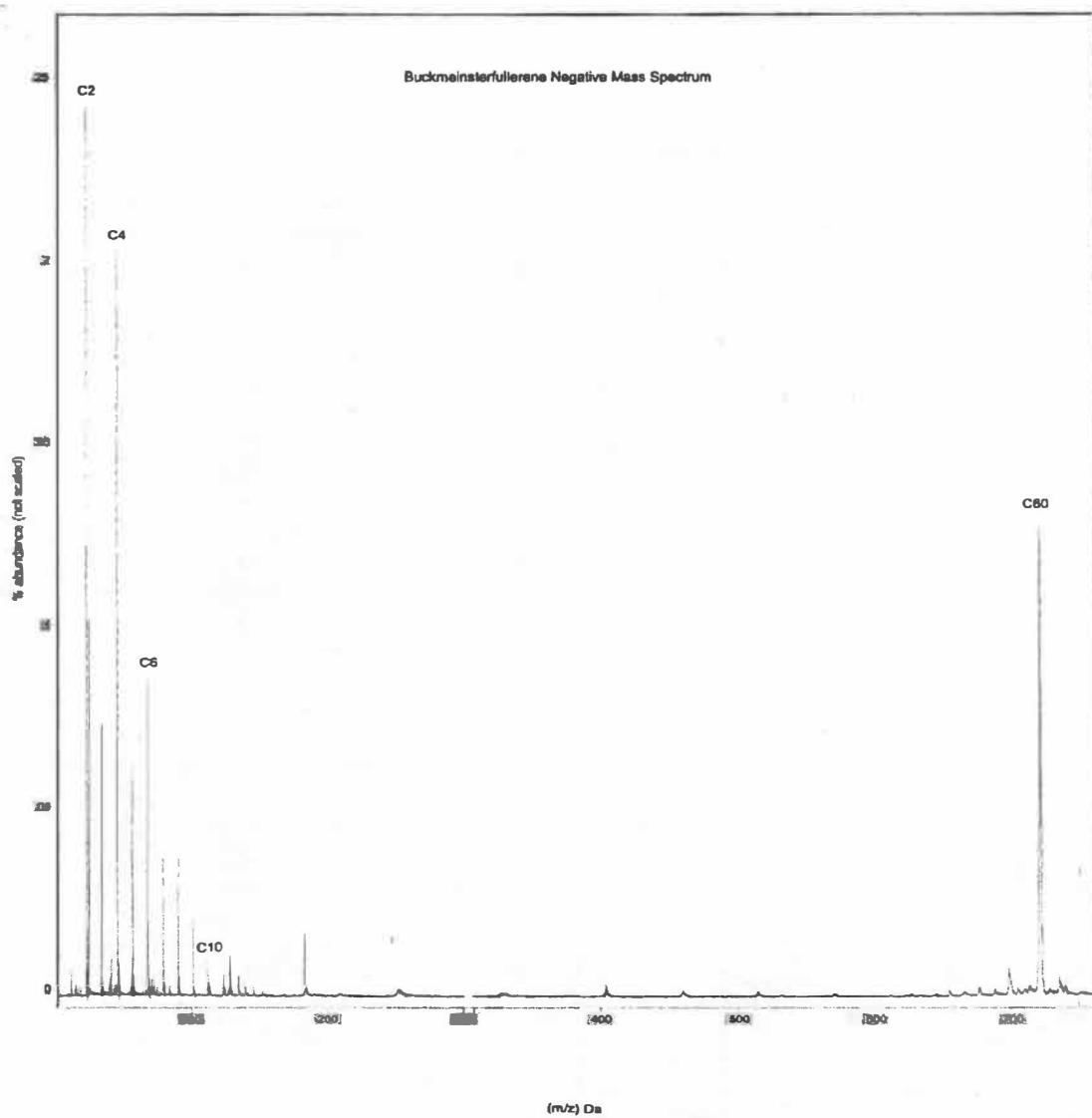
Linear Chain C_n	EA (eV)	Ring C_n	EA (eV)	Fullerene C_n	EA (eV)
2	3.30	10	2.30	30	na
3	1.95	11	2.85	31	na
4	3.70	12	2.55	32	na
5	2.80	13	3.60	33	na
6	4.10	14	2.50	34	na
7	3.10	15	3.20	35	na
8	4.42	16	2.50	36	na
9	3.70	17	3.60	37	na
10	—	18	2.75	38	na
11	—	19	3.52	39	na
12	—	20	2.70	40	na
13	—	21	3.70	41	na
14	—	22	2.90	42	na
15	—	23	3.65	43	na

The UPS electron affinities of small carbon clusters isomers as measured by Yang et. al. [4]

Table 2: Electron Affinities Large Clusters

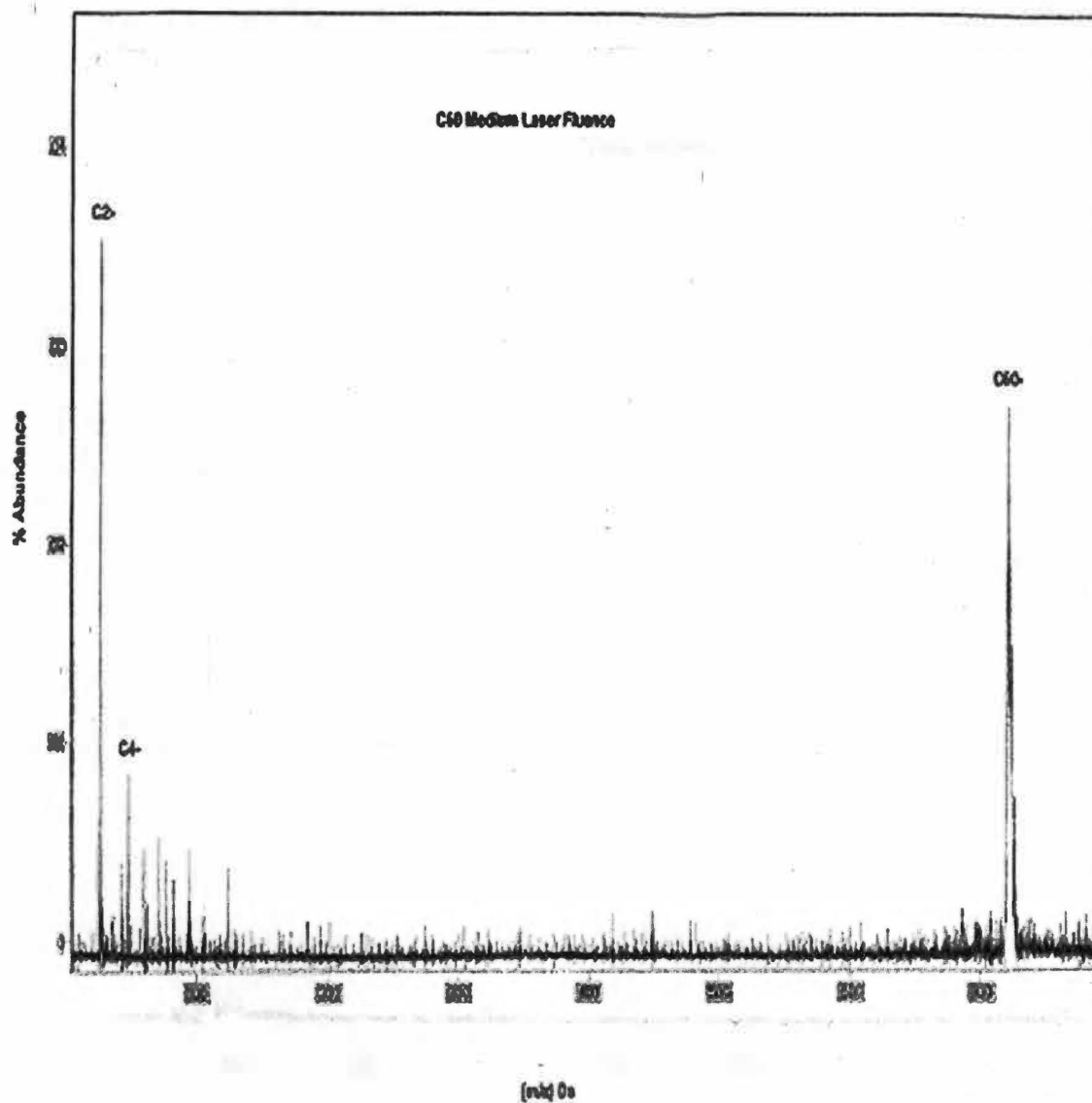
Linear Chain C_n	EA (eV)	Ring C_n	EA (eV)	Fullerene C_n	EA (eV)
16	—	24	2.90	44	na
17	—	25	3.85	45	na
18	—	26	2.95	46	na
19	—	27	3.70	47	na
20	—	28	3.00	48	na
21	—	29	3.85	49	na
22	—	—	—	50	na
23	—	—	—	51	na
24	—	—	—	52	na
25	—	—	—	53	na
26	—	—	—	54	na
27	—	—	—	55	na
28	—	—	—	56	na
29	—	—	—	57	na
30	—	—	—	58	na
31	—	—	—	59	3.3
32	—	—	—	60	2.67

The UPS electron affinities of large carbon clusters isomers as measured by Yang et. al. [4].



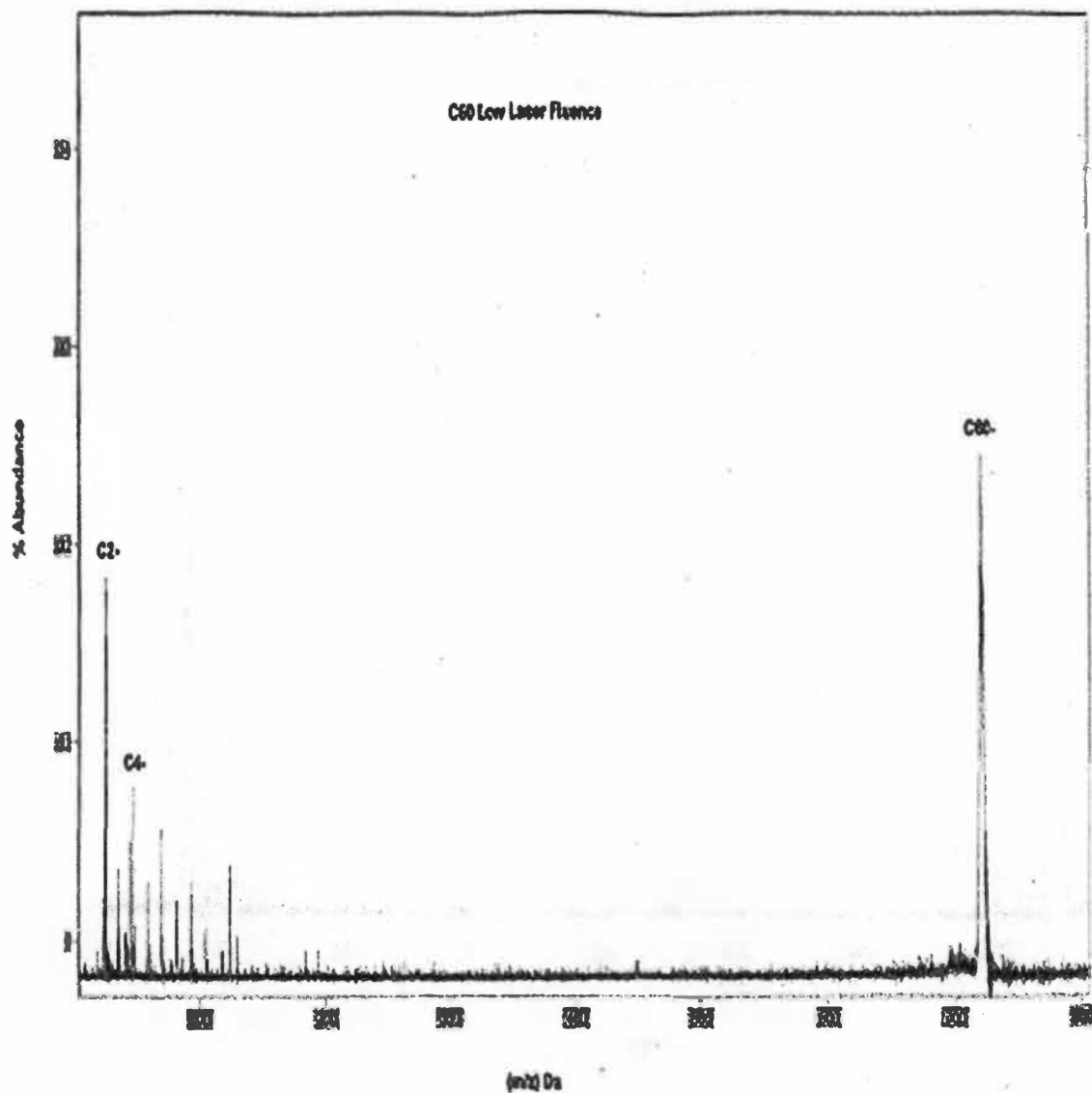
Low mass carbon clusters are prevalent as well as a strong C_{60}^- and evidence of C_n^- ($54 \leq n \leq 60$).

Figure 17: C_{60}^- Mass Spectrum (High Laser Fluence)



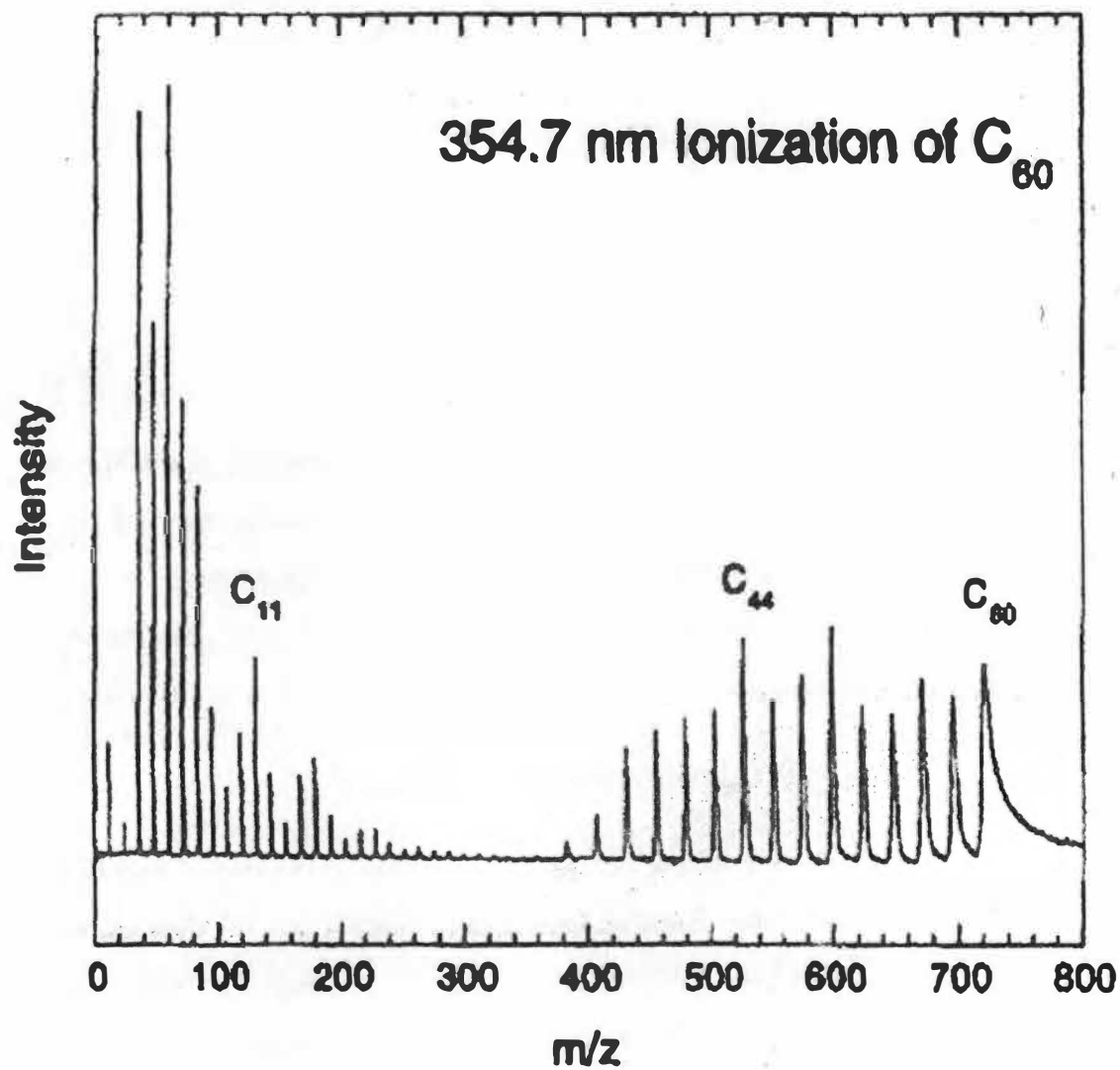
Low mass carbon clusters are prevalent as well as a strong C_{60}^- and evidence of C_n^- ($54 \leq n \leq 60$) has diminished completely. Although the small mass peaks only extend to C_8^- and the abundance has lowered, as expected.

Figure 18: C_{60}^- Mass Spectrum (Medium Laser Fluence)



Low mass carbon clusters are present, but the abundance has greatly decreased for C_2^- , in particular, providing evidence of a favorable C_2^- ejection.

Figure 19: C_{60}^- Mass Spectrum (Low Laser Fluence)

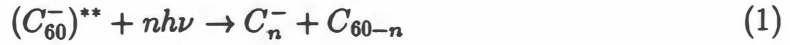


The low mass carbon clusters possess an odd/even alternation. High mass even positive carbon clusters are produced in abundance.

Figure 20: C_{60}^+ Mass Spectrum [2]

electron affinities observed by [4] [32] [39]. This would further suggest electron attachment and subsequent multiphoton absorption/fragmentation to be a large contributor for the formation of these small anions. As C_{60} captures an electron and undergoes multiphoton absorption, the excited state is typically a dissociative state [16].

The following procedure depicts some probable fragmentation pathways available caused by multiphoton absorption.



Due to the sparse peak coverage in the range C_n^- ($n > 13$) and the small contribution for $54 \leq n \leq 60$, (6.2) seems to be a very small contributor. Due to the relatively high ionization potential of ($C_{60} = 7.6$ eV), (6.3) will be a much higher energy process and ions are less likely, but not ruled out. In terms of energy, (6.3) is represented by the following approximate equation. The IE (ionization energy) of C_{58} is 7.07 eV.

$$E_{n\delta} = D(C_{n\delta}) + EA(C_{60-n}) + IE(C_{60-n}) \quad (4)$$

where $E_{n\delta}$ is the activation energy of the process as a function of the state δ and IE is the ionization energy of the cluster. Further, $D(C_{n\delta})$ and $EA(C_n)$ are the dissociation energy of a C_n from a C_{60} and the EA of the fragment C_n , respectively. In the case that $n = 2$, observations by Wurz [2] approximate a C_2 ejection from C_{60} , in the ground state, as 5.6 eV. The EA of C_2 was determined to be 3.3 eV by Yang [4]. The energy required for (6.3) is determined to be approximately $E_{n0} = 12.67$ eV. As for the channel (6.2) a similar calculation can be expected to be much less and tend to favor the fragment with a larger EA. Thus, the EA of the fragment will tend to lower the activation energy and (6.1) would seem to be the dominant pathway. Yang [4] give evidence of a competitive ring structure around $n = 9$. The abundance should switch to favor anions of the form C_{4n+1}^- ($n = 2$ to 13). The reason being, the “magic numbers” for rings are $4k + 2$, where k is the number of π electrons. When k is

replaced by n , for carbon clusters, the magic numbers apply. The “magic numbers” are assumed to be closed shell and a low electron affinity compared with open shell structures. On further observation, the C_9^- peak is larger in abundance than C_{10}^- peak, giving possible evidence of a linear to ring conversion. Although Deluca [11] have suggested linear structures to be the most probable up to C_{13}^- . The observations made in this study, find the small cluster peaks do indeed terminate at C_{13}^- suggesting most small cluster anions observed to be linear.

Other possible pathways can be postulated such as the ejection of C_n molecules ($n > 2$) from C_{60} and other fragments followed by an electron attachment to the fragment. M. Foltin [27] has observed that sequential C_2 evaporation is the dominant pathway for C_{60}^+ and on the scale of 10^{-5} s. The time scale used in this study is known to be much less than 10^{-5} s and can be used to prove the above mechanism is unlikely. Further, the mass spectrum consistently shows a large C_4^- peak, meaning that C_4^- is being produced by some mechanism. One possibility would be the attachment of two C_2 fragments and a subsequent electron attachment. No current studies have considered this mechanism. Another possibility would be a C_4 evaporation from a C_n^+ cluster and subsequent electron attachment. Although, C_{2n}^- up to $n = 14$ can be liberated [30] [4], successive C_2 evaporations are considered to be the most energetically favored processes, due to the very high energies involved in C_{2n} ($n > 1$) evaporation [27]. Nevertheless, the time scale involved in the processes of this paragraph seem to disfavor these mechanisms.

Another interesting feature of the observed mass spectra is the lack of peaks in the $14 \leq n \leq 53$ range. As evidenced by B. Baguenard [18], anionic rings, in general, have a lower electron photodetachment energy than linear conformations. Anionic rings are believed to coexist with linear chains as low as C_{10}^- and increase in abundance as the number of carbon atoms increases [18] [2] [4] [11]. It seems most probable that ring isomers readily photodetach an electron leading to the detection of only linear isomers as anions. In this study the laser, at 337.1 nm (3.68 eV), will photodetach electrons from most anionic rings formed by the sample. Although dissociation is a

plausible pathway as well. It would then seem reasonable that there would be an absence of peaks in this range.

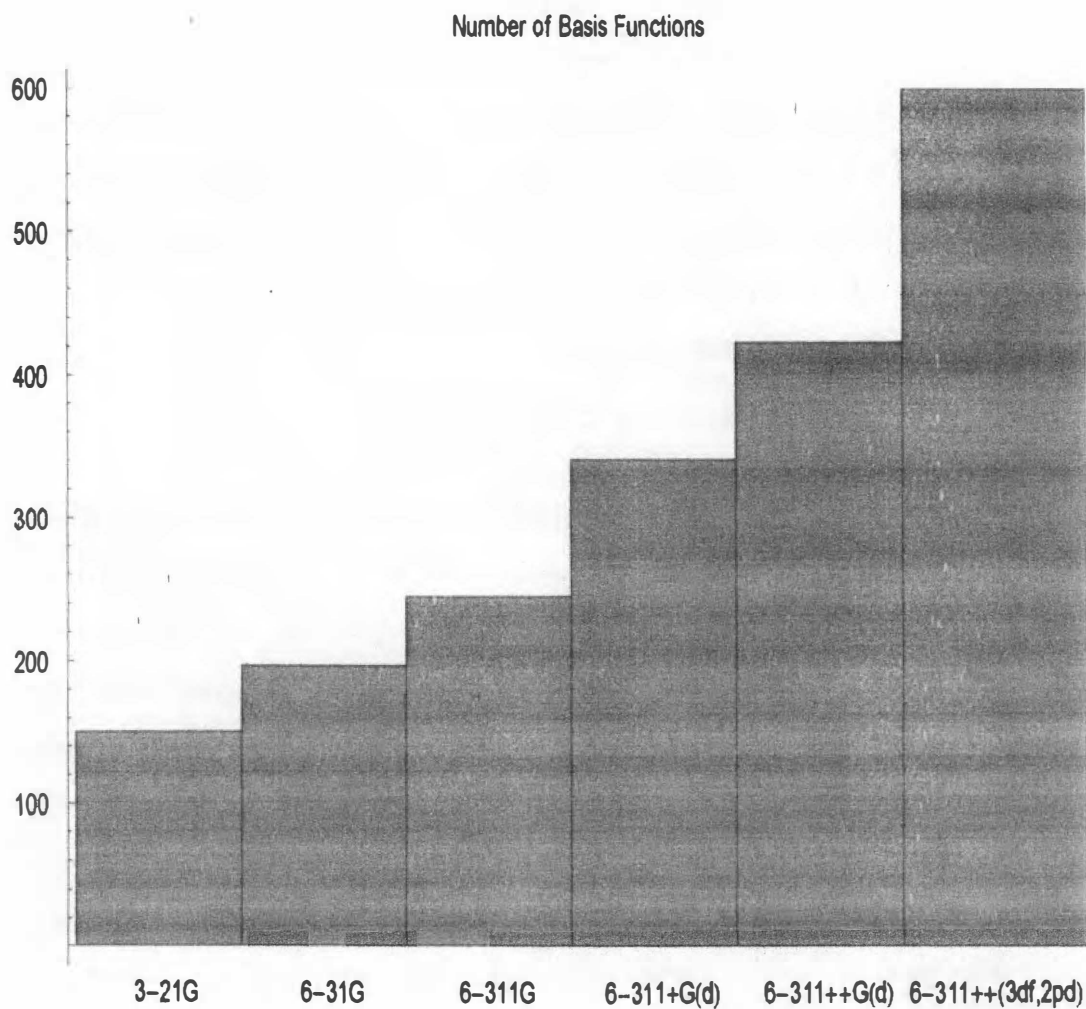
The question then becomes, why such a large C_{60}^- yield? Experimental results by A. Bekkerman [3], using a C_{60}^- beam scattered off a NiC target, show a large production of C_{60}^- anions at ≈ 52 eV incident energy. Therefore C_{60} is particularly stable compared to any C_n species with n comparable with 60. The results show a large fragmentation channel determined to be from multiphoton absorption. The explanation of the large C_{60}^- peak can be seen as caused by surface ionization. The molecules closest to the tip surface will accept electrons from the "Fermi sea" of the tip and are ejected before fragmentation can occur. Compton and Tuinman et. al. [10] give evidence of this process by noting at low laser fluence a single C_{60}^- peak can be achieved. Thus it seems that surface ionization accounts for the C_{60}^- peak and is the most probable mechanism for this peak, but radiative electron attachment must not be discounted [9].

Chapter 7: Quantum Chemistry Techniques

This chapter will discuss calculations performed using the Gaussian 98 Quantum Chemistry package [34] as they pertain to carbon clusters of small n . Electron affinities of stable isomers will be studied using high level calculations. Geometry optimization will be determined at the B3LYP Density Functional Theory (DFT) level of theory [37]. The DFT method is used for the superior electron correlation considerations, which give more accurate results for bond lengths. Energy calculations will be determined at the QCISD(T) level of theory, which consistently provide accurate energies for most small molecular systems [38].

7.1: Isometric Structures

Carbon ring as small as C_6 have been postulated to exist and confirmed in this study using quantum chemistry calculations. Ab initio calculations using DFT converge to a stable C_6 ring structure in the singlet ground state with the best estimate for the bond length being 1.3 Angstroms. The bond length are all the same value and it is assumed that the structure is the ethylenic configuration. The charge density for the configuration is equal for all atoms furthering the double bonded structure. Although, no evidence of a stable anionic carbon ring clusters smaller than C_{10}^- were obtained using the methods above. Fig. (21), represents the number of basis function for the particular basis set used in these calculations. This study will use a very large basis set labeled 6-311++(3df,2pd). The label assigns 6 slater orbitals composed of 3 primitive gaussian functions with 2 diffuse functions on the center of each bond, with the addition of 3d, 1f, 2p, 1d polarization functions. The methods used to determine the interatomic radii use a variational method. This method will give energy results which are always larger than the actual values and will slowly converge to a minimum. As the energy increases the radius is seen to decrease, therefore the data with the largest value are the best estimate at 1.3012 Angstroms for C_6 (Table 3).



The number of basis functions as a function of the particular method employed by the Gaussian 98 quantum chemistry package [34][38].

Figure 21: Basis Functions

Table 3: Quantum Chemistry Calculations of Energy and Bond Lengths

C_n^p	p	Avg. Bond Length (Angstroms)	Energy (Hartrees)
C_2	0	1.2471	75.7815346
C_2	-1	1.2578	75.8991947
C_3	0	1.2868	113.8339231
C_3	-1	1.3006	113.9041128
C_4	0	1.3056	151.7599725
C_4	-1	1.3356477	151.8910384
C_5	0	1.28	189.837943
C_5	-1	1.2997695137	189.9380996
C_6	0	1.3012	228.3131075
C_6	-1	1.326025285	228.4642574
C_7	0	1.27153	265.841222
C_7	-1	1.2835666666	265.874157

All bond lengths use a linear model with B3LYP/6-311++G(3df,2p) Density Functional Theory. All energies used the optimized geometry from the DFT method and a further QCISD(T) calculation was performed.

7.2: Electron Affinities

The EA may also be determined by the difference in energy between the C_n and C_n^- clusters. The results are provided in table (4) with experimental UPS data to illustrate the accuracy of the method. The quantum chemistry results show very good agreement with the UPS data of Yang [4] [39], with a maximum difference being .13 eV. As the method is accurate, stability calculations at all levels of theory confirm a C_{13}^- linear cluster and do not provide for a stable C_{14}^- , which are consistent with the observations of the previous chapter. Also, there are no stable anions smaller than C_{10}^- using quantum chemistry calculations.

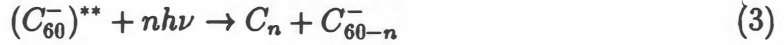
Table 4: Calculated Electron Affinities

C_n	$En_0(\text{Hartrees})$	$En_-(\text{Hartrees})$	$\Delta E = EA(\text{eV})$	expt [4]	diff. (eV)
2	75.7815346	75.8991947	3.20	3.30	.1
3	113.8339231	113.9041128	1.92	1.95	.03
4	151.7599725	151.8910384	3.57	3.70	.13
5	189.9380996	189.9406720	2.73	2.80	.07
6	228.3131075	228.4642574	4.11	4.10	.01
7	265.841222	265.727410	3.09	3.10	.01

The electron affinities using the QCISD(T) method to determine the energy difference between neutral and anion.

Chapter 8: Results and Discussion

The negative ion mass spectrum of a solid C_{60} consistently results in three distinct regions of interest 1) $1 \leq n \leq 13$, 2) $14 \leq n \leq 53$ and 3) $54 \leq n \leq 60$. A model mechanism for the formation of anionic carbon clusters seems to be surface ionization and multiphoton absorption to dissociative states.

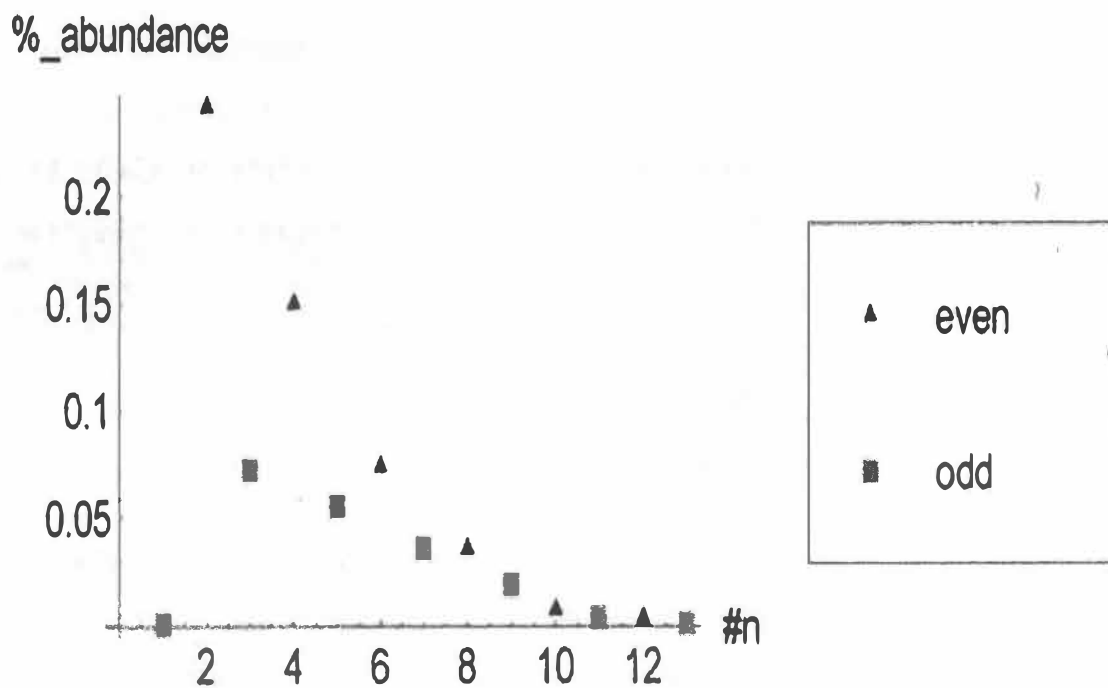


8.1: $1 \leq n \leq 13$

Carbon clusters, in this range, increase with laser fluence favoring a C_2^- ejection. Further, evidence shows fragmentation to occur by means of a C_n^- , $n \leq 13$. Due to the discussion on isomer structure (chapter 6), these peaks are most probably linear and result from (8.2). As n increases it becomes more difficult to eject the fragment and the peak abundance decreases rapidly as n increases. Fig. (22), shows a graph of the abundance (arbitrary units) versus the number of carbon atoms. It should be noted that around $n = 8$ the ion production of both even and odd fragments converge and rapidly approach zero. Thus, clusters with $n \leq 8$ are favored and more abundant for even clusters. An alternating even/odd abundance supports (8.2) as the formation mechanism, due to the correspondence between EA on the even/odd clusters. Clusters in this range are, therefore, largely produced by (8.1).

8.2: $14 \leq n \leq 53$

The lack of clusters in this range can be explained by the fact that carbon rings readily photodetach [18] and would be less likely to be detected. The results of this study indicate that these anions are either not formed or that they detach before



The abundance of even/odd small negative clusters. Even clusters are much larger up to ≈ 8 , where the two plots converge and approach zero near C_{13}^- .

Figure 22: Abundance of small carbon clusters

detection. Observations by Gotts [6] show a full mass spectrum of peaks in this range and are attributed to the He gas relaxing the hot negative clusters. Thus, the energy released upon ejection of a negative cluster in this range excites ring isomers past their dissociation limit leaving linear chains.

8.3: $54 \leq n \leq 60$

A small contribution to the mass spectra are the observance of peaks from C_{54} to C_{58} . This suggests a minor competing process as described by (8.3). The peaks are only observed at high laser fluence and absent at low fluence. Further, there is a distinctive even/odd abundance for these large anions, providing further evidence of (8.3) and (8.2). C_{60}^- has been discussed and can be predominantly formed by surface ionization. Rydberg charge exchange is also a possible pathway which cannot be distinguished using the methods employed in this study [9].

8.4: Conclusion

The spectrum observed under the conditions of this experiment are most probably surface ionization and multiphoton absorption to a dissociative state. The evidence suggests small n clusters are mostly linear and the absence of peaks in the mid range is explained as the ring isomer is less stable to multiphoton absorption to a detached electron state than a chain. Further, when the fluence reaches a limit to produce small fragments C_2^- is favored with larger even clusters as high as C_{12}^- . Although the small odd clusters are less favored, they do contribute significantly to the mass spectrum. It would seem that C_{60}^- fragments by sequential C_2^- ejections at low fluence, similar to a “unzipping” of the carbon cage as a function of energy. When the fluence is high, observed peaks as large as C_{13}^- provide evidence of large C_{60} fragmentation. Observations by Gotts et. al. [6] have shown negative ions in this range using a He gas to cool the clusters. Thus, it seems reasonable to assume that the larger negative clusters fragment before detection with the exception of the most stable structures. Gotts et. al. [6] provides a maximum in abundance for C_{15}^- , C_{18}^- , C_{22}^- , C_{24}^- , C_{30}^- and the progression of even clusters from C_{30}^- to C_{60}^- . Further, due to the even large mass

carbon cation abundance, a probable pathway would seem to be (8.4). This pathway would strongly favor even n negative clusters, due to the lack of large odd positive clusters [2].

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Appendix

A.1 Binomial Distribution

The probability of k isotopic substitutions to occur on a n atom cluster is shown below [36]:

$$p_{n,k} = \binom{n}{k} x^k (1-x)^{n-k} \quad (1)$$

Where the variant x represents the abundance of the isotope in the cluster of n atoms.

The first term can be written explicitly as given below:

$$\binom{n}{k} = \frac{n!}{(n-k)!k!} \quad (2)$$

The average mean and standard deviation have been determined for this distribution and are given below:

$$\langle k \rangle = nx \quad (3)$$

$$\delta k = \sqrt{nx(1-x)} \quad (4)$$

Where δk and $\langle k \rangle$ are the standard deviation and average mean, respectively. As n increases, the width of the distribution increases, allowing a larger isotopic contribution. Further, the peak in the distribution shifts to larger k values as n increases.

Vita

Michael Cronin Straub was born in Mobile, AL on March 11, 1972. He was raised in Mobile, AL and went to grade school at St. Pius X elementary school. He attended McGill-Toolen high school in 1986 graduating in May 1990. After a five year hiatus from school, he worked as an AC repairman and painter, while getting married and fathering a son. He then went to school at the University of South Alabama, Mobile, AL, graduating in May 2000, with a B.S. majoring in Physics with a minor in Mathematics.

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