Spectroscopy of negative molecular ions: Studies in the infrared of methide (Ch(3)-) and in the vacuum ultraviolet of No(-) and atomic and molecular oxygen (O(-) and O(2)-)

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SPECTROSCOPY OF NEGATIVE MOLECULAR IONS: STUDIES IN THE INFRARED OF METHIDE (CH₃⁻) AND IN THE VACUUM ULTRAVIOLET OF NO⁻ AND ATOMIC AND MOLECULAR OXYGEN (O⁻, AND O₂⁻)

by

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Doctor of Philosophy in Physics

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ABSTRACT

Spectroscopy of negative molecular ions: Studies in the infrared of methide (CH₃⁻) and in the vacuum ultraviolet of NO⁻ and atomic and molecular oxygen (O⁻ and O₂⁻)

by

Stephen E. Mitchell

Dr. John W. Farley, Examination Committee Chair
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The methide ion, CH₃⁻, is isoelectronic with ammonia, NH₃. Two different autodetachment lifetime have been observed. Metastable autodetaching states of methide have been observed, with an autodetachment lifetime range of 17 to 667 µs using a fast coaxial ion-laser beam apparatus. The excited states responsible for autodetachment are presumably rotationally excited states. A rovibrational transition in methide has been observed at 3206.74 cm⁻¹ using a fast coaxial ion-laser beam apparatus and sub-Doppler tuning techniques. The full-width-at-half-maximum was measured to be 22.65 MHz, which corresponds to a 7.03 ns lifetime of the vibrationally excited state. This is the first rovibrational measurement of its kind in an anion that is an oblate rotor. There are presently no theoretical calculations of the autodetachment mechanism or lifetimes of CH₃⁻. The collisional cross section was also measured for CH₃⁻ and a calibrating ion O⁻ to be 2.6 Å² and 7.2 Å² in two independent measurements, respectively. The ions are presumed to have collided with trace amounts of H₂ and H₂O.
Double photodetachment cross section measurements have also been made in NO⁻, O₂⁻, and O⁻ in the vacuum ultraviolet for the first time using a photon energy range of 18 – 100 eV. There has been much attention given to single photodetachment cross sections in atomic anions and threshold characterizations. However, there is no theory available to characterize double photodetachment cross sections for negative molecular ions. Nevertheless, the ZCC model, which is widely used in single photodetachment processes, provided reasonable results in predicting local extrema in the doubledetachment cross section, presumably at a crossover point where other channels within the inner shells opened up at higher photon energies. The observed double photodetachment may be the result of a Coster-Kronig process, but further investigation is needed for conclusive evidence of this.
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CHAPTER I

INTRODUCTION

Ions play important roles in science and industry covering a wide variety of subject areas including solar activity and earth’s aurora, chemical reactions, redox processes, electrolytic chemistry in biological systems, formation of interstellar clouds and stars, and upper atmospheric science.

The Earth’s aurora is a phenomenon that results from ion activity. The atmospheric gas molecules, mostly nitrogen and oxygen, are ionized and excited by bombarding charged particles. The sun projects these bombarding particles comprised of protons, towards the Earth but they are deflected by the Earth’s magnetic field. There is a distinct correlation between solar activity and aurora phenomena [1]. The changes in the observed intensity of aurora light correspond to changes in the ionizing stream originating from the sun.

Neutrals outnumber ions by many orders of magnitude. In some cases, by as much as $10^6$ to 1. However, ions are still critical in many reaction processes because they are so reactive and often serve as catalysts in these reactions. An additional amount of energy on the order of several eV is required for neutral-neutral reactions to occur because of a potential barrier between them. However, no such barrier exists for collisions between ions and neutral species. An ion induces a dipole moment in a neutral
thereby enabling it to react more readily. Thus, ions are very reactive, and even in low concentration they play as important a role in reactions with neutrals.

Ions play critical roles in various biological systems and diagnostics. For example, nerve activity and impulses depend on ions, and the pH level of human blood and other tissue is determined by the concentration of H$_3$O$^-$.

Ions were very important in our early universe. Shortly after the universe was born, it mainly consisted of photons, electrons, protons, and α-particles. As the universe cooled and expanded and cooled, He$^-$ followed by neutral He and H condensed out [2]. He and H$^+$ formed together to produce HeH$^+$ by radiative association and inverse rotational predissociation [3]. H$_2^+$ formed by radiative association of H and H$^+$ shortly after H appeared. HeH$^+$ formed by the reaction with He and H$_2$ formed after reactions with H shortly after H$_2^-$ appeared [4]. Hence, ions played an important role in our universe’s early evolution and formation of other stars.

It was long believed there were no molecules in the interstellar medium because photon and cosmic rays would photodissociate the molecules into atoms. However, rotational spectra of molecules were later discovered from molecular clouds. The outer portions of the clouds absorbed starlight thereby shielding the inner region and enabling molecules to form.

In the upper atmosphere, 60 km above the earth, the ions and electrons are abundant due to the photo-ionization of neutrals by the ultraviolet component of sunlight. This region, the ionosphere, affects the reflection, absorption, and propagation of radio-frequency electromagnetic waves. Formation of negative ions in this region is a key sink of free electrons, and free electrons determine the conductivity of the
atmosphere. Hence charged particles are very important for communication by radio waves [5].

With the vast improvements and developments in laser and computer technology, molecular ion spectroscopy becomes more and more important in the investigation of charged molecule’s properties and structures. However, due to the high chemical reactivity nature of ions, the main difficulty in molecular ion spectroscopy is producing sufficient concentrations of ions to produce a detectable interaction with electromagnetic radiation. Molecular ion spectroscopic information previously available was limited to optical emission spectra of a variety of diatomic and a few polyatomic ions [6]. In the mid-1970’s, two independent breakthrough experiments catapulted a new era in molecular ion spectroscopy.

One breakthrough occurred in 1976 when Wing and co-workers formed ions into a beam and excited the beam with an infrared laser beam [7] [8] [9]. A wide variety of ions can be studied with this technique. The beam of ions, which are in a range of vibrational and rotational quantum states, collide with a buffer gas. The concentrations of the ions in such a beam are low. However, the effects of the infrared radiation were detected by monitoring changes induced in the ion current that resulted from collision of ions with a buffer gas. Wing and co-workers observed the vibration-rotation spectrum of simple ions \(\text{HD}^-\) [7], \(\text{HeH}^-\) [8], \(\text{D}_3^-\) [9], \(\text{H}_2\text{D}^+\) [10], \(\text{He}^4\text{He}^-\) [11] with this technique.

In 1985, Lineberger and his co-workers obtained the first vibration-rotation spectrum of a negative ion \(\text{NH}^-\) [12] [13]. Farley and his co-workers conducted a more thorough study of the negative ion \(\text{NH}^-\) [14] [15] [16] [17] in 1986. Another breakthrough was carried out by Woods and his co-workers by the measuring
rotational absorption spectra in the microwave region of a series of simple ions (CO\(^-\), HCO\(^-\), and HN\(\text{N}^-\)) which were generated in an electrical discharge \[18\] \[19\] \[20\]. This technique was limited by the fact the ions are often outnumbered by neutral species by as much as million to one in the plasma. Hence, spectra of molecular ions in discharge are often obscured by the much stronger absorption of neutral molecules. Later in 1983, Saykally and his co-workers developed the technique of velocity modulation spectroscopy \[21\] \[22\]. In this technique, positively charged ions are accelerated in a plasma column by the plasma’s axial electric field to a net drift velocity of about 500 m/sec. The ions motion is superimposed on their random thermal motion. The ions exhibit a small Doppler shift in their spectral transitions due to this net drift velocity effect. The spectral transitions are Doppler-shifted in and out of coincidence with monochromatic laser radiation by rapidly reversing the polarity of the discharge. As a result, the detected laser power is modulated at the same frequency as the polarity of the discharge. Electronic processing yields a dispersion signal characteristic of absorption spectra of ionic transitions. In the meantime, the much stronger absorption of the more abundant neutral species are electronically rejected because they do not exhibit the Doppler modulated effect \[12\] \[13\]. With this technique, Owrustky made the first direct observation of the vibrational absorption spectrum of the negative ion OH\(^-\) \[23\] \[24\] in 1985. The H\(_2\)O\(^-\) visible emission spectrum had been observed, however it was not until 1989, Das and Farley made the first observation of the visible absorption spectrum of positive ion H\(_2\)O\(^+\) \[25\]. So far, over 55 positive and negative ions have been observed with this technique.

Electron correlation plays a larger role in negative ions than it does in positive
ions or neutrals, and negative ions are therefore good systems for studying electron correlation [26]. The autodetachment process is important because internal energy of vibration and/or rotation is converted to kinetic energy of the detaching electron, and hence autodetachment represents a violation of the Born-Oppenheimer approximation. Autodetachment lifetimes, which can vary by many orders of magnitude, are difficult to calculate because of the electron correlation and the non-Born-Oppenheimer nature of the process.
CHAPTER II

ION BEAM MACHINE

Background

The ion beam apparatus in this lab, also known as "Big Beam", used to investigate CH$_3$ and discussed in detail in this dissertation, was built by Farley, Al-Za'al and Miller [14] [15] at University of Oregon. Equipped with a velocity selector (Wien filter) and a coaxial ion beam-laser beam configuration, the apparatus is very good at detecting negative ions and high-resolution infrared negative molecular ion spectroscopy [27] [28]. A maximum negative ion current of 200 nA has been achieved, while under different conditions and settings the maximum positive ion current of 30 nA of CO$^-$ has been obtained in this machine [29]. Typically a few nA for a negative ion beam is considered a lot.

Figure 1 shows a schematic of the ion beam machine used in the experiments. A parent gas is introduced to a high-pressure discharge ion source to produce ions. Negative ions are accelerated and focused by electrostatic optics into a beam as they emerge from the anode aperture into the extraction region. The ion beam is steered through a second aperture into the Wien filter region by electrostatic deflectors. The Wien filter disperses the ions according to their mass while two Einzel ion lenses focus the mass selected ion beam onto a third aperture located at the entrance to the
Figure 1. Schematic of ion beam apparatus.
interaction region. The pumping system maintains a background pressure of $1 \times 10^{-9}$ torr, $6 \times 10^{-7}$ torr, and $2 \times 10^{-8}$ torr in the extraction, Wien filter, and interaction regions, respectively.

The ion beam is deflected through 90° in the interaction chamber. A pair of Einzel lenses and vertical deflector plates are used to steer the ion beam along the axis of an equipotential tube, which is 45 cm long. Here the ion beam overlaps the laser beam, which enters the same chamber through a calcium fluoride (CaF$_2$) window. A deflector plate steers the ion beam, emerging out of the equipotential tube, into a Faraday cup. The ion beam is detected at all apertures during the alignment process to insure a reasonable ion current at the Faraday cup. The control unit, which supplies voltages to various parts inside the machine, and the detection circuits will be discussed in the next chapter.

**Ion Source**

A hot filament discharge source is used to produce CH$_3^+$ in this work [30] [31]. Figure 2 shows a detailed cross sectional view of the source. The cathode and anode are 9 mm thick magnetic steel plates of 15.2 cm diameter. Each plate has a groove with cross section 4 mm x 4 mm, to hold an O-ring 11.7 cm in diameter. Six stainless steel bolts 7 cm long are used to hold a glass sleeve, 3 mm thick and 4.5 cm long, against the O-rings between the two plates. The anode plate is insulated from the grounded body of the machine by a Plexiglas plate, 6.5 mm thick, and the cathode plate is shielded from the bolts by Teflon sleeves. The filament is clamped at each end between a copper slab and an adjustable prong. The copper slab is supported by a high current ceramic...
Figure 2. Cross-sectional view of the ion source.
feedthrough (10 kV, 30 A). The filament assembly is mounted on a stainless steel baseplate, 1 cm thick and 7.5 cm in diameter. It attaches to the cathode plate via six bolts and an O-ring seal and can easily be detached for rapid filament replacement.

To produce a certain negative ion, a parent gas containing the constituent atoms of that ion is introduced into the ion source through Teflon tubing, of 5 mm inner diameter, attached to a quick-connect feedthrough in the cathode plate. The anode plate has a 1 mm diameter aperture at its center through which the parent gas is pumped into the extraction region. An ion gauge in the extraction region monitors the pressure, where the background pressure is typically $10^{-6}$ torr and the operating pressure is about $8 \times 10^{-6}$ torr in most cases.

The filament is heated by a DC current from a power supply, model Hewlett-Packard 6225B (10V, 20 A max.) to produce electrons by thermionic emission. A voltage difference of 50V to 300V is applied between the filament and the anode to maintain a steady discharge in the parent gas. The emission current collected by the anode is controlled by a custom designed regulating feedback circuit (see Chapter III). This assures steady discharge conditions for emission currents up to 150 milliamps. Typically, various species of negative ions are formed through collisions, from two-body or three-body reactions, within the plasma. However, the physics of the formation mechanism is not yet fully determined. It is found that the mass spectrum of negative ions extracted from the source is very sensitive to the emission current, the parent gas pressure, and the discharge voltage. Therefore, the main difficulty in producing a reasonable ion current arises in the exploration process to determine the optimum source conditions in each case. Unfortunately, ion currents of only few nanoamps can be
obtained when searching for negative ions having small electron affinities such as NO$^-$ and Fe$^+$ (0.026 eV ± 0.005 and 0.151 eV ± 0.003 respectively) [32] while currents over 100 nA of OH$^+$ can be easily obtained. However, currents of about 10 nA are considered to be a strong current for most negative ions.

The choice of the filament’s material depends mainly on the parent gas used in the source. Thoriated-iridium filaments, 0.002” x 0.027” ribbon, are the best for use with oxidizing gases such as N$_2$O with an average lifetime of about 150 hours under operation with optimum source conditions. Tungsten filaments, 15 mil in diameter, are suitable for use with hydrocarbon gases such as (CH$_3$)$_3$ Al with an average lifetime of about 50 hours.

Three stainless steel plates, of 7.5 cm diameter and 1 mm thickness are mounted on the anode plate using three bolts made of the same material but shielded from each other by glass sleeves, 1.5 cm long and 1 mm thick. The nearest plate to the anode is called the “spider plate” because it has a triangular web at its center bounded by three 1 cm diameter holes evenly spaced. Their centers lie on circle of 5 mm radius. Three stainless steel spacer rings, 3.5 mm long and 1 mm thick, are placed around the glass sleeves between the spider plate and the anode to create a field-free region in front of the aperture, which is hidden from the plasma and the filament by the web. Thus, negative ions created in the vicinity of the aperture have kinetic energies determined only by the anode voltage. The other two plates, called “plasma confining plates”, are insulated from each other and from the spider plate by glass rings, 3 mm long and 1 mm thick, placed around the glass sleeves. The middle plate has a 4 mm diameter hole at its center while the last plate has similar hole 8 mm in diameter. The plasma is confined to the volume
determined by these holes. The filament penetrates through the holes in both plates, which float at potentials determined by their relative position in the discharge region. Three permanent magnets are attached between the cathode and anode plates outside the high-pressure discharge source at about 120° from each other. They are electrically insulated from each other to prevent electrical shortage between the cathode and the anode. The magnet's purpose is to concentrate and confine emission electrons within the plasma region.

**Extraction Region**

A schematic of this region is shown in Figure 3. Negative ions emerging from the anode aperture into this region are accelerated and focused through a 1.5 mm aperture, A₁, by an ion lens. Three cylindrical lens elements and two pairs of electrostatic deflectors, all made of stainless steel, are mounted on a baseplate, 1.1 cm thick and 20.2 cm in diameter, made of the same material with a 5.2 cm diameter hole at its center. All cylindrical elements are spot-welded to stainless steel plates, 1 mm thick and 12 cm in diameter, each of which has four 5 mm holes near the edge.

The whole assembly is supported by four stainless steel bolts, 19 cm long, which are shielded from the metal parts by Teflon sleeves and fixed in position by standoff sleeves, except for two grounded plates which are used to shield the deflector pairs. The front end of the first lens element, the extractor, is cone-shaped. Its distance from the anode aperture is about 7 mm. The extractor voltage has an adjustable range of 604 to 814 V. The voltage difference between the anode and the extractor determines the initial acceleration of the ions in the relatively high-pressure region between the two
Figure 3. Cross-sectional view of the extraction region.
electrodes. The second lens element is adjustable between -1454V and 1808V, while the third lens element is externally grounded. This particular configuration of electrostatic lens focuses the ion beam through a 1.5 mm diameter aperture, $A_1$, at the exit of the extraction region. Voltages symmetric about zero volts are applied to the horizontal and vertical deflector pairs, $X_1$ and $Y_1$, to steer the ion beam through aperture $A_1$. The potential halfway between each pair of plates is automatically zero volts to minimize the acceleration or deceleration of ions as they pass through them. In principle, a well-aligned ion beam is indicative of essentially zero potential on these steering plates. A carefully designed electrometer monitors the ion current on the aperture. This circuit is described in the next chapter.

**Wien Filter Region**

A Wien filter is mounted in this region between two Einzel lenses as shown in Figure 4. Each lens consists of three stainless steel plates mounted parallel to each other separated by 4 mm. Each plate has an outer diameter of 2.4 cm and a 1.5 mm diameter hole at its center. A separate adjustable voltage is applied to each of the middle plates while the other two pairs of plates are grounded. The input lens, at the entrance to the Wien filter, is controlled at a decelerating voltage between -514V and -684V to collimate the ion beam entering the Wien filter. The output lens, located at the exit side to the Wien filter, is typically operated at an accelerating voltage between +1436 V and +1706 V to focus the mass-selected ions emerging from the filter through a 1 mm aperture, $A_2$, at the entrance to the interaction region. Electrostatic optics are similar to geometric optics in that a pair of converging lenses or a converging-diverging lens...
Figure 4. Schematic of Wien filter region.
combination may be configured to image an object at the same effective image distance. A decelerating voltage, \(-500\) V to \(-700\) V, is applied to the Wien filter output lens to achieve a similar focal length at the entrance to the interaction region. The distance between the output lens and the aperture is about 30 cm. A vertical deflector pair, \(Y_2\), mounted between the Wien filter and the output lens steers the ion beam perpendicular to the plane of dispersion.

The Wien filter is a Colutron model 600, which consists of a pair of electrostatic deflection plates and a dual-coil iron-core electromagnet. The plates are mounted between the magnet poles to produce an electric field perpendicular to the magnetic field. The filter is mounted such that both the electric and magnetic fields are perpendicular to the direction of the ion beam. The sum of both electric and magnetic forces is the Lorentz force. When both electric and magnetic forces have opposite directions and equal magnitudes, the Lorentz force \(F_L\) acting on an ion of charge \(q\) and velocity \(v\),

\[
F_L = F_c + F_m, \tag{2.1}
\]

vanishes. The magnetic force \(F_m\) is given by

\[
F_m = q\vec{v} \times \vec{B} \tag{2.2}
\]

and the electric force \(F_c\) is given by

\[
F_c = q\vec{E}. \tag{2.3}
\]
Hence $\mathbf{B}$ is the magnetic field strength, and $\mathbf{E}$ is the electric field strength. All the ions in the beam have the same potential energy $qV$, where $V$ is the anode voltage. For a nonrelativistic beam, the kinetic energy of an ion with mass $m$ and velocity $v$ is $mv^2/2$. In a grounded region, the kinetic energy is

$$\frac{mv^2}{2} = qV, \quad (2.4)$$

which can be solved for $v$ to yield

$$v = \sqrt{\frac{2qV}{m}} \quad (2.5)$$

Thus ion species of different masses have different velocities. Since the magnetic force acting on an ion is directly proportional to its velocity, the net force acting on the ion vanishes for some velocity $v_0$ given by

$$v_0 = \frac{E}{B} \quad (2.6)$$

Thus, the Wien filter is a velocity selector. Ions of velocity $v_0$ pass undeflected, while all other ions are deflected due to an imbalanced force acting on. The Wien filter is also a mass filter because the velocity of the ion depends on its mass through Equation (2.5). Setting equations (2.5) and (2.6) equal and solving for the mass $m$ yields the mass transmitted by the Wien filter,
where the mass is expressed as a function of the beam voltage, magnetic field, and electric field.

Ions emerging from the filter follow various flight trajectories for some distance before arriving at an aperture of diameter \(a\). These trajectory paths correspond to the mass dispersion at the aperture. However, there is a competing effect due to the focusing effect of the magnetic field of the filter itself, which adversely defocused the ion beam during flight. Wahlin [33], in 1964, solved this problem in the Colutron filter following a design in which a gradient on the electrostatic field is introduced by means of electrically biased guard rings stacked as shown in Figure 5(a). The guard rings are made of stainless steel shims and each guard ring is individually connected to a potentiometer which provides the right bias (see Chapter III), to compensate for the unwanted magnetic focusing effect.

Figure 5(b), showing a horizontal cross-sectional view, illustrates the mass-dispersing property. The undeflected ions, of mass \(m_o\) and velocity \(v_o\), pass through the center of an aperture of diameter \(a\). The distance between the aperture and the center of the filter is \(D\), where \(D \gg a\). A negative ion with mass \(m > m_o\) has a velocity \(< v_o\).

Therefore it is deflected to the left while another ion of mass \(m < m_o\) is deflected to the right. The net force acting on an ion of mass \(m_o + \Delta m\) in the mass filter region is \(-B \Delta v\).

Transverse momentum \(p_t\) imparted to the ion is given as
Figure 5. Vertical and horizontal cross-sectional view of the Wien filter region.
\[ p_t = -qB\Delta v \times \frac{L}{v_0} , \quad (2.8) \]

where \( p_t \) is the transverse momentum, and \( L \) is the length of the Wien filter.

The longitudinal momentum is defined as \( m_0v_0 \) and is deflected through an angle \( d\theta \) that is approximately equal to the ratio between the transverse and longitudinal momenta as follows:

\[ d\theta = -\frac{qBLdv}{m_0v_0^2} . \quad (2.9) \]

Differentiating equation (2.5) with respect to \( m \) near \( m = m_0 \) and \( v = v_0 \), we obtain

\[ dv = -\frac{v_0dm}{2m_0} . \quad (2.10) \]

and substituting equation (2.6) in equation (2.10), we get

\[ dv = -\frac{Edm}{2m_0B} . \quad (2.11) \]

Substituting equation (2.11) in equation (2.9) and replacing \( m_0v_0^2 \) by \( 2qV \), we obtain

\[ d\theta = \frac{ELdm}{4Vm_0} . \quad (2.12) \]
The maximum mass that can pass through the aperture is deflected through an angle

\[ d\theta \equiv \frac{a}{2D}. \]  \hfill (2.13)

Combining equation (2.12) and (2.13), we get the mass resolution \( m_{0}/\Delta m \) of the Wien filter

\[ \frac{m_{0}}{\Delta m} = \frac{ELD}{2aV}. \]  \hfill (2.14)

Substituting \( L = 15.2 \text{ cm}, D = 44 \text{ cm}, a = 0.1 \text{ cm}, \) and \( V = 2000 \text{ volts}, \) Equation (2.14) gives

\[ \frac{m_{0}}{\Delta m} = 1.672E, \]  \hfill (2.15)

where \( E \) is the potential gradient \( V_{d}/S \) between the electrostatic plates. \( V_{d} \) is the dispersion voltage applied to the plates and \( S \) is the distance between the plates in cm. The distance \( S \) is 1.78 cm, thus equation (2.15) is rewritten as

\[ \frac{m_{0}}{\Delta m} = 0.939V_{d}. \]  \hfill (2.16)
Thus the mass resolution is directly proportional to the dispersion voltage, which has an upper limit of 160 V. The mass resolution at a typical dispersion voltage of 100 V is 93.9. In practice, it is only about 50 due to the aberrations in the system and the spot size of the ion beam.

To estimate the maximum undeflected mass $m_0$ obtained from this system, we combine equation (2.5) and (2.6) to obtain:

$$m_0 = 2q\frac{B^2}{E^2}. \quad (2.17)$$

For an anode voltage of 2 kV, equation (2.17) yields $m_0$ in amu,

$$m_0 = 1.233\frac{B^2}{V_d^2} \text{ (amu)}, \quad (2.18)$$

where $B$ is in gauss and $V_d$ is in volts.

The electromagnet produces a maximum magnetic field of 1000 gauss. Therefore, the maximum undeflected mass with 100 V dispersion voltage is 122.3 amu.

The electromagnet is powered from a KEPCO model JQE 15-6 power supply that can be operated by remote voltage programming or as a stabilized current source. A mass scan for various ion species present in the ion beam is achieved by fixing the dispersion voltage and adjusting the magnet’s current. The current through the electromagnet is
changed smoothly between zero and 3 amps either by turning the magnet power supply’s 10-turn potentiometer manually or by programmable remote control using a simple computer program. The magnetic field strength is roughly proportional to the magnetizing current, I. Thus the undeflected mass is proportional to $I^2$ according to equation (2.17). However, it is desirable to obtain a linear mass scan where the ion current is plotted against mass. Thus, the appropriate aspect of the data acquisition system, described in Chapter IV, samples the current from the Wien filter power supply through its internal current shunt. A program written in LabView correlates the $I^2$ data to the previous assigned mass (amu) and displays and logs the X-Y data in real time to emulate a mass spectrometer. A typical mass scan will be given in Chapter III.

**Interaction Region**

The interaction between the ion beam and the laser beam takes place in a stainless steel vacuum chamber whose background pressure is maintained at about $10^{-8}$ torr by a 200 l/s ion pump. A schematic of the interaction region is given in Figure 6. An Einzel lens $L_1$, biased between -684V and -940V, focuses the ion beam which entered the chamber through the aperture $A_2$ through an electrostatic quadrupole [34]. The quadrupole is connected externally to the HV supply unit through a selector switch that allows operation in either a “zero-deflection” mode or a “90 degree-deflection” mode. In the zero deflection mode, the quadrupole sections are set at low voltages (near ground) such that the ion beam passes virtually undeflected through the quadrupole. A pair of vertical deflector plates, $Y_3$, adjusts the height of the ion beam so that the lens $L_1$
Figure 6. Schematic of the interaction region. L1, L2, and L3 are Einzel lens. X2 is a pair of horizontal deflector plates.
focuses it in the forward direction through a 1 mm aperture \( A_3 \) onto a collector plate \( A_4 \).

During the search process for a reasonable ion beam current, it is helpful to set the
dispersion voltage and the current through the electromagnet of the Wien filter near zero
such that ions of all masses enter the interaction region. The ion current detected by the
plate \( A_4 \) is then optimized by successive adjustments in the alignment and focusing of the
beam in the extraction, Wien filter, and interaction regions.

In the 90 degree-deflection operation mode, the attractive sections of the
quadrupole are biased between +1025V and +1436V while the repulsive sections are
biased between -940V and -1110V such that the whole combination deflects the ion
beam at essentially a right angle. Another pair of vertical deflector plates, \( Y_3 \) and \( Y_4 \), is mounted
at the exit to the quadrupole. \( Y_3 \) and \( Y_4 \) steer the ions in such a way that they move
along the axis of the chamber in a stainless steel tube with a length of 45 cm and an inner
diameter of 4 mm. If there is voltage \( V_e \) on this “equipotential tube”, the kinetic energy
of the ions will be \( q (V-V_e) \), where \( V \) is the anode voltage. Hence, the voltage \( V_e \) can be
varied allowing for continuous high-resolution Doppler tuning of the ion beam. The
kinetic energy of ions extracted from the source is typically set at 2 keV. However, it can
be raised up to 4 keV simply by applying a voltage of 2 kV to the equipotential tube.
This is done rather than floating the ion source at -4 kV in order to avoid potential
arcing, over heating of resistors in voltage dividers, and other related problems.

An electrostatic deflector \( X_2 \) deflects the ions into a Faraday cup as they emerge
from the equipotential tube. The deflector \( X_2 \) consists of two stainless steel plates, 4.7
cm x 2 cm, mounted vertically 8 mm apart. The depth of the Faraday cup is 4.8 cm and
its inner diameter is 1.8 cm. Ions enter the Faraday cup through a 3 mm wide slit shield.
The shield is at -30 V with respect to ground, which suppresses secondary electrons and discourages fast ions that might bounce off the walls of the cup. Two Einzel lenses, $L_2$ and $L_3$, are mounted on the entrance and exit ends of the equipotential tube assembly. The lens $L_2$ is biased between +193 V and +604 V to focus the ions entering the tube, while $L_3$ is biased between +1025 V and +436 V to focus the ions emerging from it through the slit into the Faraday cup.

The laser beam enters this region through a CaF$_2$ Brewster window, travels along the axis of the chamber through the quadrupole, overlapping the ion beam, and exits through a second CaF$_2$ Brewster window. The two small 1.5 mm apertures near the ends of the equipotential tube practically guarantees maximum overlap of both ion beam and laser if both are optimized for maximum ion current in the Faraday cup and laser power at exit CaF$_2$ window respectively. The ion beam current is monitored at these two apertures to aid in alignment and focusing of the ion beam to the Faraday cup.

The fast neutral molecules resulting from photodetachment, autodetachment, or collisions are not substantially affected by the electrostatic deflector, $X_2$, and strike a CaF$_2$ plate, 4.9 cm x 2.5 cm x 0.5 cm, where they eject secondary electrons. Secondary electron collection efficiency was greatly improved from 0.3% [35] to nearly 95% by modifying the original design by accelerating the electrons directly into the Vacumetrics model AEM-1000 electron multiplier (EMT) input. This was achieved by first positioning the EMT's input normal to the collision plate. Then, two fine wire mesh screens, 5 cm x 2.5 cm, were positioned between the EMT's input and the collision plate with a separation of 0.5 cm. If the voltage applied to the EMT is $V_0$, $2V_0/3$ is applied to the screen closest to the collision plate and $2V_0/3$ is applied to the other.
screen. Any secondary electrons ejected from the collision plate will be attracted right into EMT's input through this potential gradient. The Faraday cup and the electron multiplier are supported by an assembly built from a Kimball Physics eV kit components and mounted on a stainless steel baseplate, which can be detached easily from the chamber.

The electron multiplier consists of a chain of 20 dynodes biased externally from a Power Designs model 3K10B HV supply as shown in Figure 7. The material of the dynodes, typically Be-Cu alloy, has a high work function of about 10 eV. Therefore, the surface of the CaF$_2$ collision plate is biased at -400V relative to the first dynode such that each secondary electron ejected from the surface of the plate arrives at the first dynode with energy sufficient to produce two or three secondary electrons by impact. The resulting secondary electrons are then accelerated into the second dynode through a potential drop of 100V. The impact of each incident electron produces about two secondary electrons, which are in turn accelerated into the third dynode, and so on. Thus the gain of the whole chain of dynodes is $2^{20} (=10^6)$. The detection efficiency of the system is the ratio between the count rate of secondary electrons arriving at the first dynode with sufficient energy and the count rate of neutrals. Essentially, every secondary electron that enters the electron multiplier will give rise to $10^6$ counts at its output.

**Pumping System**

The pumping system is shown schematically in Figure 8. Two diffusion pumps,
Figure 7. Neutrals detection system. Fast neutrals eject secondary electrons from the surface of a CaF2 plate. The electron multiplier tube (EMT) collects and amplifies the secondary. The EMT has a load resistance of 10 MΩ.
Figure 8. Schematic of the pumping system. DP, V, IG, and T stand for diffusion pump, valve, ion gauge, and thermocouple gauge, respectively.
DPO and DPI, evacuate the extraction and Wien filter chambers, respectively. The nominal inlet port diameter of DPO is 6 inches while that of DPI is 4 inches. Both pumps use silicone oil, D.C. 704, which is electrically heated at the bottom of the pump. Oil vapor evolves upward through a tower above the boiler to an array of nozzles from which the vapor is emitted in a jet directed downward and outward toward the pump walls. The walls of each pump are water-cooled so that vapor molecule condenses on the walls. Thus, gas molecules are moved from inlet to outlet by momentum transfer from a directed stream of oil. Any oil vapor that migrates upwards enters a refrigerator-cooled trap where it condenses. A gate valve is located between the cold trap and the vacuum chamber to isolate the diffusion pump from the chamber. The forelines of DPO and DPI are copper pipes 1.5 in. and 1 in. in diameter, respectively. Both forelines are connected to a mechanical pump through a main foreline pipe, 1.5 in. in diameter. A molecular sieve trap is mounted to the main foreline in series between the mechanical pump and the diffusion pumps. It utilizes synthetic zeolite with a high surface area to trap hydrocarbons and water vapor, as well as preventing backstreaming of mechanical pump oil. The chambers are also connected to the main foreline through copper pipes similar to the corresponding foreline pipes.

To activate the system starting with all valves closed and the pumps off, the mechanical pump is turned on. When the pressure indicated by thermocouple gauge, T5, is below 200 mtorr, the foreline valves, V3 and V4 are opened. When thermocouples T3 and T4 indicate a pressure below 200 mtorr, the cooling water and the refrigerators are turned on followed by activating the diffusion pumps. The pumps require about one hour to reach operating temperature.
Before pumping on the chambers with the diffusion pumps, the pressure in the chambers must be reduced to a rough vacuum. To rough out the chambers, the diffusion pumps backing valves V3 and V4 are closed, and then the chambers roughing valves, V1 and V2, are opened. When the pressure indicated by T1 and T2 falls to about 500 mTorr, valve V5 is opened slowly. However, the outlet pressure of the diffusion pumps should stay below 500 mTorr [36]. Moreover, the roughing process is interrupted about every three minutes to pump out the forelines by closing V1 and V2, followed by allowing for the main foreline pressure indicated by T5 to reach a few milliTorr, then opening V3 and V4. If there are no vacuum leaks, the pressure indicated by T1 and T2 will stay below 100 mTorr after closing V1 and V2. Meanwhile, the pressure indicated by T3 and T4 falls below 10 mTorr after opening V3 and V4. After completing this initial rough pump procedure, the diffusion pumping can be started by opening the gate valves. Once the gate valves are opened, the pressure indicated by T1 and T2 should fall below one mTorr. The ion gauge IG1 can be turned on after about 10 minutes. Differential pumping between the ion source and the extraction chamber takes place through a 1 mm aperture in the cathode plate. The steady state pressure in the ion source under gas load conditions is estimated to be 4200 times higher than that indicated by IG1. The interaction chamber was initially baked at 250°C for 24 hours starting at a pressure of $1 \times 10^5$ Torr to get rid of water vapor adsorbed by the walls. When the pressure indicated by IG2 falls to about $1 \times 10^6$ Torr, the ion pump is turned on. The pressure in the interaction region is maintained at about $10^8$ Torr by a Perkin-Elmer model 222-0600 ion pump, with a pumping speed of 200 l/s. The ion pump operates by ionizing gas that migrate into the magnetically confined cold-cathode discharge. The ionized gases are
accelerated and buried into the cathode, thereby reducing the background pressure by two to three orders of magnitude. The pressure in the interaction region is maintained very low (about $10^{-8}$ Torr) to minimize the collisional stripping caused by the background gas.
CHAPTER III

ION BEAM ELECTRONICS

The Big Beam's power supplies are mounted on Plexiglas insulating shelves, 1.1 cm thick, inside a grounded metal cabinet. The supplies power the ion source, Wien filter, ion lenses, deflectors, and the quadrupole. Floating power supplies are powered from a 1:1 isolation transformer (1 kVA, 20 kV) placed on an insulating Plexiglas baseboard. All control knobs and switches of all supplies and electronic circuits that float at high voltages are mounted on a Plexiglas front cover, 5 mm thick, in order to protect the operator from the danger of HV electrical shocks. The use of insulating extension rods, 10 cm long, coupled to the shafts by rubber or metal couplers provides adequate insulation between the control knobs and control potentiometers.

Ion Source Supply

The ion source supply is shown schematically in Figure 9. The filament supply is a Hewlett-Packard model 6256B LV supply (10 V, 20 A). It supplies the filament with DC heating current in order to produce thermionic emission electrons. The typical heating current is 5 - 6 Amperes for thoriated-iridium filaments and 12 - 13 Amperes for 15 millimeter tungsten filaments. The effective length of the filament is about 3 cm. The discharge supply is a Heath model SP 2717A regulated HV supply (400V,
Figure 9. Ion source power supply. The filament current $I_f$ produces electrons by thermionic emission. The discharge supply creates a discharge in the source gas. The regulator samples the emission current $I_e$ and generates an output voltage $V_c$ that controls the filament supply. The anode voltage supply sets the anode voltage at $-2$ kV relative to ground.
125 mA). If the terminal potential difference of this supply is \( V \) and the emission current collected by the anode plate in milliamps is \( I_e \), then the potential difference between the anode and filament, the discharge voltage, is \( V' - R_b I_e \). \( R_b \) is the 1.8 kΩ ballast resistor, which reduces the discharge voltage as the emission current increases. The ballast resistor helps maintain a stable discharge against sudden changes in currents within the plasma. A Power Designs model 1570 HV supply (±3 kV, 40 mA) sets the anode voltage at -2 kV relative to ground, thereby establishing the ion’s potential energy. The rest of the circuit floats at the anode voltage and negligible current is drawn from this supply.

The regulator circuit shown in Figure 10 controls the temperature of the filament. It varies the filament temperature to keep to the emission current constant. The regulator utilizes an IC chip, LM324N, which consists of four op amps, and a single +5V supply to power the regulating circuit. The first stage in the regulator is a unity gain inverting amplifier whose input signal is the voltage difference across a 10 Ω sensing resistor connected in series with the discharge supply. The output voltage from this stage, \( V_1 \), is given by the equation:

\[
V_1 = -R_3 I_e, \tag{3.1}
\]

where \( I_e \) is the current through the sensing resistor in milliamps and \( R_3 \) is 0.01 kΩ. The second stage is a summing amplifier with variable gain between unity and 25. The voltage applied to the noninverting input, \( V_n \), is derived from the +5V supply using a
Figure 10. Filament regulator. The input signal is proportional to the emission current $I_e$. The output signal $V_c$ controls the filament supply as shown in Figure 9.
voltage divider such that it can be varied between zero and 2.2V. Two 10-turn potentiometers are used to control \( V_r \): the 100 k\( \Omega \) potentiometer, \( R_a \), is used for coarse control while the 2 k\( \Omega \) potentiometer, \( R_f \), allows fine control. If the feedback resistance is \( R_f \) then the gain \( \alpha \) is \(-R_f/R_4\) and the output voltage \( V_2 \) is given by

\[
V_2 = V_r + \alpha (V_1 - V_r).
\] (3.2)

The third stage is a voltage follower that isolates the load from the second stage due to its high input impedance. Thus, the output voltage from the last stage \( V_3 \) is equal to \( V_2 \). Another voltage divider is used to limit the control voltage \( V_c \) at the output of the regulator between zero and 0.2\( V_3 \).

The control signal is wired to the voltage programming circuit of the filament supply. The filament temperature regulating circuit controls the filament power supply. The filament current is given by

\[
I_f = \kappa V_c,
\] (3.3)

Where \( I_f \) is the filament current, \( V_c \) is the control voltage from the regulator circuit, and \( \kappa \) is the conductance gain factor of the filament power supply and is equal to 40 \( \Omega^{-1} \). Consequently at maximum output control limit, the filament current is given by the complete relation

\[
I_f = 8 \left[ V_c(1 + \alpha) - 0.01\alpha V_c \right].
\] (3.4)
As long as the emission current is zero, \( I_r \) is directly proportional to \( V_r \) for a fixed gain. The starting discharge voltage is usually set at about 100V in order to avoid overheating of the filament. Once emission of thermionic electrons is started, the input signal to the regulator tends to reduce \( I_r \) and a further increase in \( V_r \) is needed to compensate for that in order to maintain the same emission conditions. Then, as \( V_r \) is increased slowly, the emission current increases while the discharge voltage decreases due to the voltage drop across the ballast resistor.

The optimum source conditions to produce a reasonable ion current are usually sensitive to the emission current, discharge voltage, and gas pressure. For operation with low emission currents, the gain control is turned down in order to obtain better voltage resolution when changing \( V_r \). When operating with filaments that require small heating currents, it is necessary to turn down both the output voltage limit and the gain control on the filament temperature control unit so that a wide range of \( V_r \) is used to start emission without destroying the filament.

### Wien Filter Supply

The electrostatic deflection plates and all shims are biased using the circuit shown in Figure 11. A floating Harrison model 6207A power supply (160 V, 0.2 A) drives the circuit. The potential difference of the Harrison power supply determines the dispersion voltage \( V_d \). The ground point is connected to the wiper of a 50 k\( \Omega \) balance.
Figure 11. Wien filter supply for the electrostatic deflection plates and shims. The power supply terminal potential difference is typically 100V. The plates are biased at ±50 V while a linear potential gradient is maintained across the shims.
potentiometer. The position of the wiper is adjusted such that the terminal voltages of
the supply are +50V and -50V when $V_a$ is 100V. Each potentiometer in the circuit is a
10-turn 2 W power potentiometer. Each bias voltage is connected to a vacuum
feedthrough via a 10 kΩ resistor in order to protect circuit components against surge
currents caused by the flow of stray charge through vacuum metal parts to ground.

The output terminals are labeled with reference to Figure 5 (a). The order of
shims corresponds to their relative position with respect to the plates. The shims are
biased in a way that maintains a linear potential gradient across them. The right and left
plates are biased at -50V and +50V, respectively. The middle shim is at zero volts. The
right shims are biased at -37.5V, -25.0V, and -12.5V, respectively. Likewise, the left
shims are biased at +37.5V, +25.0V, and +12.5V, respectively.

A KEPCO power supply model JQE 15-6 powers the electromagnet. The supply is
set up to deliver a constant current in the range of 60 mA to 3 A to the electromagnet.
An external sensing resistor is placed in series between the supply and the electromagnet.
The sensing resistor consists of three 1Ω, 10W wire-wound resistors, connected in
parallel to function as a current shunt for current monitor. The output current is
adjustable from the KEPCO power supply's 10-turn potentiometer for current control. A
digital voltmeter (0 - 2V), built from Intersil model ICL 7107 evaluation kit is connected
across the sensing resistor and reads a voltage $V_s$. The square of the magnet current $I_m$,

$$I_m = \frac{V_s}{0.33Ω}.$$  (3.5)
is proportional to the mass. This establishes a reasonably linear mass scale. The mass scale is calibrated using ion species of known masses such as NO⁺ and OH⁻. Although mass readings might change slightly between scans due to the hysteresis in the magnet, the difference between readings corresponding to two specific mass peaks remains essentially the same in all scans. A typical mass scan is given in Figure 12.

**Deflectors Supply**

Each pair of deflection plates requires two voltages of equal magnitudes and opposite polarity to maintain the potential halfway between them at zero volts. This minimizes the acceleration of the ions as they pass between the plates. Therefore, all voltages on deflectors are derived from two HP6524 power supplies (±150 V, 40 mA). Under normal operation, the two HP power supply's voltages is set to 100V, and the voltage range on all deflectors never exceeds ±25V. However, it is advantageous to have a larger range when tracking the ion beam to steer it through various apertures along its path to the Faraday cup.

The deflector's supply circuit is shown in Figure 13. A resistive voltage divider network of 2W resistors drops the ±100V down to the required range. Two 10-turn potentiometers are connected in parallel with their shafts coupled together through two gear wheels 3.25 cm in diameter. The gear wheels were initially set in place near their middle position such that the voltage on each centertaps was balanced to zero volts. The voltage range of the deflectors X₁, Y₁, Y₂, Y₃, and Y₄ is ±36V. A 0.25 μF capacitor is
Figure 12. (a) The mass in amu is shown to be proportional to the square of the Wien filter supply current. (b) A typical mass spectrum of diazomethane ($\text{CH}_2\text{N}_2$) used in the infrared studies of $\text{CH}_3^-$. The massive clipped mass peak (amu = 26) is $\text{CN}^-$ and was > 10 nA. The electron affinity for $\text{CN}^-$ is ≈3.9 eV.
Figure 13. Deflectors supply circuit. Each deflector is biased from a pair of 100 kΩ 10-turn potentiometers whose shafts are coupled through a pair of gear wheels.
connected across each resistor to stabilize the voltage across it against rapid changes in voltage. Similar capacitors are also added between the centertap and both ends of each potentiometer. The current drawn by the circuit from each supply is 12 mA. Hence the total power dissipated into heat is 48 Watts. A Rotron Venturi fan is mounted on top of the box to provide adequate forced air cooling to aid in dissipating heat from all circuit components.

Decelerating Lens Supply

Figure 14 shows schematically all decelerating voltages on lens elements and the quadrupole assembly. The circuit comprises a resistive voltage divider network of various 2 W resistors and 2 W 100 kΩ potentiometers. The centertaps of the potentiometers define the respective lens element’s output voltage, which are isolated by 220 kΩ resistors. The total equivalent resistance of the chain is 588 kΩ, and hence the current drawn from the supply at −2 kV is 3.4 mA. The operating voltage ranges for various lens elements and the quadrupole were determined experimentally during an early stage of the research. The Faraday cup deflector’s repulsive plate, X₂, uses a voltage derived from the −2 kV supply rather than from the deflectors supply because it is higher than the voltage on the rest of the deflectors. Typical operating voltages from this supply are listed below.
Figure 14. Decelerating lens supply. The current drawn from the supply is 3.4 mA.
Table 1. Decelerating mode voltages

<table>
<thead>
<tr>
<th>Description</th>
<th>Voltage range</th>
<th>Typical Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wien filter input lens</td>
<td>-514 to -684 V</td>
<td>-500 V</td>
</tr>
<tr>
<td>Interaction region lens -1 (L_1)</td>
<td>-684 to -940 V</td>
<td>-725 V</td>
</tr>
<tr>
<td>Extraction element-2 (focus)</td>
<td>-1454 to -1808 V</td>
<td>-1540 V</td>
</tr>
<tr>
<td>Quadrupole repulsive sections</td>
<td>-940 to -1110 V</td>
<td>-945 V</td>
</tr>
<tr>
<td>Faraday cup deflector</td>
<td>-344 to -514 V</td>
<td>-390 V</td>
</tr>
</tbody>
</table>

Accelerating Lens Supply

Accelerating lens elements use voltages opposite in sign to the anode voltage, which is set at +2kV. The circuit is shown in Figure 15. It is similar to the decelerating lens supply described earlier except that the total equivalent resistance is 243 kΩ. Consequently, the current draw from this supply is 8.2 mA. A 0.25 \( \mu F \), 400V. capacitor is placed across each resistor. Similar capacitors are connected between the centertap of each potentiometer and its other two ends. The added capacitors filter out any rapid fluctuations present in the chain thereby stabilizing respective lens element voltages.

Typical operating voltages from this supply are listed below.

Table 2. Accelerating Mode Voltages

<table>
<thead>
<tr>
<th>Description</th>
<th>Voltage range</th>
<th>Typical Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wien filter output lens</td>
<td>1436 to 1706 V</td>
<td>+1470 V</td>
</tr>
<tr>
<td>Interaction region lens-2 (L_2)</td>
<td>193 to 604 V</td>
<td>+570 V</td>
</tr>
<tr>
<td>Interaction region lens-3 (L_3)</td>
<td>814 to 1436 V</td>
<td>+1100 V</td>
</tr>
<tr>
<td>Extraction element-1 (extractor)</td>
<td>604 to 814 V</td>
<td>+750 V</td>
</tr>
<tr>
<td>Quadrupole attractive sections</td>
<td>814 to 1436 V</td>
<td>+1050 V</td>
</tr>
<tr>
<td>Faraday cup deflector</td>
<td>193 to 604 V</td>
<td>+310 V</td>
</tr>
</tbody>
</table>

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Figure 15. Accelerating lens supply. The resistance of all potentiometers is 100 kΩ. The current drawn from the supply is 8.2 mA.
Figure 16 shows an image of the beam optics created by the Simion computer program as it would appear inside the Big Beam. The beam optics generated from Simion are dimensionally correct with the typical decelerating and accelerating voltages which simulate an ion beam focused and steered through the various regions in the apparatus.

**Ion Beam Detection**

The ion beam detection circuit comprises six electrometers built from CA3140 operational amplifiers. Each electrode that measures the ion current has a dedicated connection to the input of an electrometer. One supply at ±15V is used for all chips. A 0.1µF capacitor is connected, as close as possible to the chip, between each supply terminal of the chip to filter out sudden fluctuations in the supply voltage present at the chip's supply input. Drawing current from another chip can cause such power supply fluctuations.

One electrometer circuit is shown schematically in Figure 17. The first stage is an inverting operational amplifier that functions as a current-to-voltage converter. A 2-pole 4-position selector switch selects two equal resistors at the input and feedback loop. The ion current at the input is I flows through the feedback resistor $R_f$ because no current flows into either input of an ideal op amp. Unfortunately, there is a small nominal input bias current (10 pA typical) in CA3140 op amps. Analysis of bias current error shows that it scales with the input resistance. Therefore, using an additional resistor in the noninverting input minimizes the output error voltage. Without the
Figure 16. Image of entire electrostatic optics and ion flight path as it may appear inside the ion beam apparatus by Simion computer simulation software.
Figure 17. Electrometer circuit. The first stage is an inverting operational amplifier that functions as current-to-voltage converter. The second stage is an inverting voltage amplifier whose gain is 101 when switch S is off and unity when it is on.

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resistor to the noninverting input, the input current error is the bias current. With the resistor to the noninverting input, the error is due to the offset current (i.e. the difference in bias current between the two inputs. This value of the resistor to the noninverting input is typically chosen to be the equivalent resistance of the parallel combination involving the input and feedback resistors [37]. In this case, the largest value used is 11 MΩ. The output voltage, $V_1$, from this stage is given by

$$V_1 = -IR_f.$$ (3.6)

Hence $R_f$ determines the conversion factor of this stage in V/μA. The selector switch sets the conversion factor of this stage to 22, 2.2, 0.22, or 0.022 V/μA.

The second stage is an inverting voltage amplifier. Switch $S$ selects a unity gain in the on position and a gain of 101 in the off position. Hence, the following relations give the output voltage, $V_2$.

With switch $S$ on, $V_2 = IR_f$ (3.7)

with switch $S$ off, $V_2 = 101 IR_f$. (3.8)

Thus, the overall currents to voltage conversion factors with switch $S$ off are 2.2, 0.022 and 0.0022 V/nA. In this mode of operation, ion currents from 10 pA to 5 μA are measurable. In the other mode of operation with switch $S$ on, larger ion currents by a factor of 100 can be measured. The bandwidth, $B$, of the electrometer is determined by the feedback $R$ and $C$ values, i.e.
\[ B = \frac{1}{2\pi RC} = 7.2 \text{Hz} \] 

(3.9)

The output voltage from each electrometer is measured by an analog panel voltmeter (0 – 15 V). This makes it possible to monitor the ion current at eight different locations in the machine simultaneously.
CHAPTER IV

DATA ACQUISITION SYSTEM

Although Big Beam has enjoyed much success [14] [15] [16] [17], major changes were incorporated to improve drastically data collection and logging by incorporating state-of-art computers, data acquisition instrumentation, and numerous custom written software applications for real-time data analysis. The data acquisition system for the Big Beam is shown as functional blocks in Figure 18. A Pentium II computer is the workstation and control center for many of the data signals to and from the Big Beam. All digital-to-analog (DAC) and analog-to-digital (ADC) voltage signals are buffered through a custom built opto-isolator circuit. The opto-isolator circuitry provides high voltage isolation and protection for the DAC and ADC cards from inadvertent high voltage arcs and shorts in the vacuum system. A schematic for 1 of the 32 opto-isolator circuits is shown in Figure 19. The input voltage is first buffered through operational amplifier U2A which is biased as a voltage follower. The output of U2A is added to the reference voltage $V_{\text{ref}}$ through the summing stage U2B. The combined current $I_T$ through diode D6 is defined as

$$I_T = \frac{V_i}{R_5} + \frac{V_{\text{ref}}}{R_4} \quad (4.1)$$
Figure 18. Block diagram of the data acquisition system and ion beam interface.
Figure 19. Schematic of the optoisolator circuit.
where \( V_i \) is the input voltage, \( R_3 \) is 2 k\( \Omega \), \( R_4 \) is 1.4 k\( \Omega \), and \( V_{\text{ref}} \) is the reference voltage defined at 3.5 VDC. The test LED is driven by this current and illuminates with intensity proportional to the current. The purpose of this LED is only for a visual verification that the circuit is functioning correctly. The same current drives the optocoupler transistor D1. The optocoupler transistor provides up to 7500 VDC isolation between the input voltage and output voltage and operates within the active region of the transistor [38]. This is critical for the overall operation of the isolation because all the bias voltages and currents should function within the linear region of the optocoupler transistor to properly map input voltage to output voltage. The collector current from D1 is summed through the second summing amplifier stage U1. The final output voltage \( V_o \) is defined as

\[
V_o = -R_2 \left( \frac{V_{\text{ref}}}{R_3} + I_c \right),
\]

(4.2)

where

\[
I_c = \left( \frac{V_c + V_{cc}}{R_1} \right) \left( \frac{\beta}{\beta + 1} \right).
\]

(4.3)

Since the transistor gain \( \beta \gg 1 \), equation (4.3) becomes

\[
I_c = \left( \frac{V_c + V_{cc}}{R_1} \right),
\]

(4.4)

where \( R_2 \) is the 5k potentiometer gain adjustment, \( R_3 \) is the 5k potentiometer offset.
adjustment, and \( V_e \) is the emitter voltage, which is operating in the linear range. Test
LED D7 is also used as a visual verification that this aspect of the circuit is functioning
correctly. The power supplies, regulators, and voltage references for the entire opto-
isolator circuit assembly are all shown in Figure 20.

A ComputerBoard model CIO-DAC16 DAC interface card is configured for 16
digital-to-analog voltage signals. Each of these DAC channels can have a separate
voltage programmable range. However, only one channel is actually used to control the
interaction region drift tube voltage. This voltage is configured for 0 – 10 VDC. This
voltage control signal, after being buffered by an opto-isolator, is directed into a voltage
translator circuit, shown in Figure 21. The input to the first stage is selected by a single-
pole-double-throw (SPDT) switch where either the computer programmable 0 – 10
VDC signal or an internal manually adjustable 0 – 10 VDC voltage is selected. The
selected voltage is then buffered by a voltage follower U3. The output from U3 is then
applied to a power booster [39] stage U4. The op amp amplifier U4 drives the transistor Q1
to produce a voltage \( V_c \) at the collector that will be 100 times greater than the input
voltage. The feedback to U4 is accomplished by sampling 1% of the collector voltage by
the resistor divider network \( R_1 \) and \( R_2 \). The voltage at \( V_{out2} \) is identical to the input
voltage and biased to be 1% of the voltage at \( V_{out1} \). \( V_{out1} \) is further defined in terms of the
input voltage by noting that

\[
V_i = V_{out2} \tag{4.5}
\]

and

\[
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Figure 20. Schematic of the optoisolator power supply circuit.
Figure 21. Schematic of the voltage translator circuit. A 0 - 10V input signal is voltage scaled to 0 - 1000 V output voltage.
\[ V_{\text{out}2} = V_{\text{out}1} \left( \frac{R_1}{R_1 + R_2} \right) , \]  

(4.6)

and finally

\[ V_{\text{out}1} = V_i \left( \frac{R_1 + R_2}{R_1} \right) \equiv 100V_i , \]  

(4.7)

where \( R_1 \) is 140 k\( \Omega \) and \( R_2 \) is 14 M\( \Omega \). The \( V_{\text{out}2} \) signal is read back by the one of the ADC channels and again is buffered by one of the available opto-isolator channels.

The following table summarizes all the ADC and DAC channels, big beam functions, and relevant LabView test programs.

Table 3. Data Acquisition functions, descriptions, and assignments

<table>
<thead>
<tr>
<th>Big Beam Function</th>
<th>Com Port</th>
<th>ADC Channels</th>
<th>DAC Channel</th>
<th>LabView Program</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collision Stripping measurements &amp; Metastable States Measurements</td>
<td>Com1</td>
<td>Faraday Cup (ch1). 0.1 V/nA Electrometer (ch3). Ion Gauge Cntrl (ch4).</td>
<td></td>
<td>Collisional Stripping Logger.vi</td>
</tr>
<tr>
<td>Photodetachment Measurements</td>
<td></td>
<td>Faraday Cup (ch1). 0.1 V/nA Electrometer (ch3). Lockin Amplifier (ch5).</td>
<td></td>
<td>Photodetachment Logger.vi</td>
</tr>
<tr>
<td>Autodetachment Measurements</td>
<td></td>
<td>Faraday Cup (ch1). 0.1V/nA Electrometer (ch3). Lockin Amplifier (ch5). 1% Voltage Translator Voltage (ch6).</td>
<td>0-10VDC Scanning Control Voltage for Voltage Translator (ch1).</td>
<td>Autodetachment Logger.vi</td>
</tr>
<tr>
<td>Mass Spectrometer</td>
<td>Stepper Motor (Com1)</td>
<td>Faraday Cup (ch1). 50% Wien Filter PS Voltage (ch2).</td>
<td></td>
<td>Mass Spectrometer.vi</td>
</tr>
</tbody>
</table>
CHAPTER V

COLOR CENTER LASER

Successful infrared spectroscopy of negative ions with the Big Beam not only depends on the ability to produce sufficient concentrations of negative ions, but also the ability of tunable infrared lasers to produce reasonable laser power over a wide tuning range. The infrared laser used in this experiment is a Burleigh FCL-20 F-center laser. It provides continuously tunable, narrow linewidth, 0.5-80 mW output power in the 2.25 to 3.33 \( \mu \text{m} \) region utilizing two separate lasing crystals. The lasing medium in a color center laser is a color-center crystal pumped by a krypton ion laser. There are defect-electron structures in the ionic crystals known as color centers and their presence imparts a strong color to the otherwise transparent perfect crystal.

Although the FCL-20 laser used in this experiment only utilized two crystals, it may be equipped with three crystals numbered 1, 2, and 3 in an order of increasing wavelength. Their main characteristics are given in Table 4 below. The rollover point of the crystal is the operation point where the maximum output power is obtained. A decrease in the output power occurs with further pump power increase beyond this rollover point. Furthermore, over pumping will cause a rapid rise in the crystal’s temperature, which may result in permanent damage to the crystals.
Table 3. FLC-20 F-Center crystal specifications

<table>
<thead>
<tr>
<th>Description</th>
<th>Crystal #1</th>
<th>Crystal #2</th>
<th>Crystal #3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>KCl:Na</td>
<td>KCl:Li</td>
<td>RbCl:Li</td>
</tr>
<tr>
<td>Color Centers</td>
<td>Fₐ (II)</td>
<td>Fₐ(II)</td>
<td>Fₐ (II)</td>
</tr>
<tr>
<td>Pump Source/ (Wavelength)</td>
<td>Ar⁺ laser/(477-530nm)</td>
<td>Ar⁺/(477-530nm)</td>
<td>Kr⁺/(647.1 nm)</td>
</tr>
<tr>
<td>Pump power at threshold</td>
<td>1W</td>
<td>250mW</td>
<td>100mW</td>
</tr>
<tr>
<td>At rollover point</td>
<td>5.5W</td>
<td>2.25W</td>
<td>900mW</td>
</tr>
<tr>
<td>Output power (multimode)</td>
<td>18mW</td>
<td>80mW</td>
<td>30mW</td>
</tr>
<tr>
<td>Tuning range (μm)</td>
<td>2.25-2.50</td>
<td>2.45-2.80</td>
<td>2.70-3.33</td>
</tr>
</tbody>
</table>

Description of Operation

The optical components of the FCL-20 F-center laser are located in two vacuum chambers as shown schematically in Figure 22. The laser cavity comprises a folding mirror M₂, an end mirror M₃, and a blazed diffraction grating M₄. The F-center crystals are placed in a cassette whose position is adjustable such that only one crystal at a time can be exposed to the pump beam in the crystal chamber. A cryopump maintains the crystal chamber’s vacuum. A liquid nitrogen dewar makes thermal contact with the crystal cassette through a copper cold finger. The temperature of the crystals is monitored using a semiconductor thermal sensor whose resistance decreases with increasing temperature as

\[
\frac{dR}{dT} = -\kappa R
\]  

(5.1)
Figure 22. Schematic of the FCL-20 F-center laser. M1, M5, and M6 are steering mirrors. M4 is the diffraction grating, M2 is a folding mirror, M3 is an end mirror, and BS is the beamsplitter. The etalon is inserted into the cavity for single mode operation.
where \( R \) is the resistance of the thermal sensor, \( T \) is the temperature of the crystal measured in Kelvin, and \( \kappa \) is a proportionality constant. By separating variables in equation (5.1) and integrating over the resistance and temperature known limits, the variable \( \kappa \) can be determined from

\[
\int_{R_i}^{R_f} \frac{dR}{R} = -\kappa \int_{T_i}^{T_f} dT
\]  

(5.2)

where \( R_i \) is 49 \( \Omega \), \( R_f \) is 64000 \( \Omega \), \( T_i \) is 77 K, and \( T_f \) is 273 K. After the integration, \( \kappa \) is determined to be 0.037. A general expression for the resistance \( R \) as a function of temperature \( T \) can be generated from solving equation (5.2) but leaving \( R_i \) and \( T_i \) as variables. The final expression for resistance \( R \) as a function of temperature \( T \) is

\[
R = 1.07 \times 10^6 e^{-0.037T}
\]  

(5.3)

where \( R \) is in Ohms and \( T \) is in Kelvin.

The steering mirror \( M_1 \) reflects the input pump laser beam through the input window of the crystal chamber. The pump beam then reflects off the beamsplitter onto the folding mirror \( M_2 \) where it is focused into the crystal. The beamsplitter is mounted at Brewster's angle \( \phi_B \) with respect to the incident pump beam in order to reflect the pump laser beam on to mirror \( M_2 \) since its polarization is normal to the plane of pump beam. The beamsplitter also passes the infrared beam having polarization in the plane of incidence with minimum attenuation. The crystal is also mounted at Brewster's angle \( \phi_B \).
in order to minimize reflection losses at its surfaces for an infrared mode polarized in the 
plane of incidence. Mollenauer and Olson [40] (1975) designed the cavity such that the 
minimum beam waist is located almost exactly at the center of curvature of mirror M3, 
and just outside the focal length of mirror M2. The weak remnant of the pump beam, 
which is not absorbed by the crystal, and the infrared beam from the crystal are reflected 
and refocused back through the crystal by M3. It is then recollimated by M2 and passes 
back through the beamsplitter. The beamsplitter splits the weak remnant of the input 
pump beam that is not absorbed by the crystal into two parts: The reflected part travels 
back towards the pump laser, and the transmitted part will be collinear with the infrared 
beam forming a useful tracer beam. The astigmatism created by rotation of the crystal to 
Brewster's angle is compensated for by the astigmatism induced by mirror M2 through 
proper adjustment of the reflection angle at its surface.

The infrared beam emerging from the beamsplitter passes through a Brewster 
angle window, which is mounted in the crystal chamber wall, into the tuning arm housing 
where it strikes the surface of the grating. An echelette reflection grating [41] mounted 
in Littrow configuration serves as both a tuning element and output coupler by using the 
first and zeroth diffraction orders of the grating as feedback and output, respectively. 
The optical surface of the grating consists of equally spaced triangular grooves. The 
angle of incidence, $\xi$, and the angle of diffraction, $\theta$, are measured from the normal to the 
plane of the grating. The optical path difference between rays from adjacent grooves 
must be an integral multiple of the wavelength, $\lambda$, to establish the condition for 
constructive interference. Therefore, the diffraction maxima satisfy the grating equation
where \( d \) is the groove spacing and \( m \) is the diffraction order \( (m = 0, \pm 1, \pm 2 \ldots) \). Angles measured to the left of the normal are counted as positive while those measured to the right are counted as negative. The zero-order diffraction \( (m = 0) \) occurs at a diffraction angle given by \( \theta = -\xi \), which means that the grating acts as a mirror. The Littrow configuration is a specific geometry in which the light of a specific wavelength diffracted from a grating, into a given diffraction order, travels back along the direction of the incident light. From equation (5.4) above, this requires \( \theta = \xi \) (the Littrow configuration).

For first-order diffraction \( (m=1) \), a Littrow-mounted grating is directed along the incident beam \( (\theta = \xi) \) thereby satisfying the condition

\[
\lambda = 2d \sin(\xi). \tag{5.5}
\]

If the beam is at normal incidence to the facets of the grooves, almost all energy is concentrated in the first order. This occurs at a particular incidence angle \( \xi \) equal to the step angle of the groove, \( \alpha \). This is called the blaze angle of the grating since the groove assembly acts like a mirror. The blaze wavelength in first-order diffraction, \( \lambda_\alpha \), is given by

\[
\lambda_\alpha = 2d \sin(\alpha). \tag{5.6}
\]
For a triangular groove having a 90° apex angle, the back facets will be normal to the beam at an angle $\beta = 90^\circ - \alpha$, and another high feedback reflectivity peak will occur at wavelength, $\lambda_p$, given by

$$\lambda_p = 2d \sin(\beta) = 2d \cos(\alpha) \quad (5.7)$$

The feedback reflectivity of the grating remains quite high between the angles $\alpha$ and $\beta$. To avoid possible defects, Loewen [42] (1977) determined $\alpha \geq 18^\circ$ and German [43] (1979) established that the effective tuning range lies between $\lambda_\alpha$ and $\lambda_p$. Combining equations (5.6) and (5.7), we get

$$d = \sqrt{\lambda_\alpha^2 + \lambda_p^2} \div 2. \quad (5.8)$$

For example, $d = 1.98 \mu m$ and $\alpha = 33.7^\circ$ for a tuning range from 2.20 to 3.30 $\mu m$. The tuning range is selected such that the big reflectivity peaks occur outside it for high power output rather than minimum threshold. The grating’s peak reflectivity with triangular grooves is $\geq 95\%$ [43] whereas holographic gratings of sinusoidal grooves have a peak reflectivity $\geq 90\%$. This makes the latter group more suitable for high-output coupling.

The laser is tuned by rotating the grating around a vertical axis using a sine-bar drive that is coupled to a mechanical wavelength readout. As the grating angle is
changed, the readout of the sine-bar mechanism changes linearly in wavelength. The grating and the output steering mirror, $M_5$, are mounted at right angles on a L-bracket assembly in order to maintain the output’s zero-order diffraction deviation. This remains fixed relative to the incident beam as the assembly is rotated about a vertical axis. Mirror $M_5$ reflects the zero-order diffraction through the output window by another steering mirror $M_6$. The output power may be optimized by an additional alignment knob, which is attached to the L-bracket assembly for an extra degree of freedom. The position of the end mirror $M_3$ can be adjusted manually while the folding mirror $M_2$ can only be translated using an electronically driven PZT, which permits cavity scans over a 300 MHz range.

The linewidth is about 1.5 GHz in multimode operation and 1 MHz in single mode operation. In single mode operation, the intracavity etalon is inserted into the tuning arm and its position is adjusted until it suppresses all but one of the laser modes. A confocal spectrum analyzer (Burleigh model FCL-975) monitors the output laser spectrum while a RC-44 electronic driver controls the analyzer. The free spectral range of the spectrum analyzer is 7.5 GHz. Both the intracavity etalon and the folding mirror are tuned by piezoelectrics controlled by two RC-45 electronic drivers to provide 1 MHz resolution over a 10 GHz range. The laser frequency jumps from one laser cavity mode to another in steps of 0.01 cm$^{-1}$ or 300 MHz when the voltage of the etalon alone is adjusted. The tuning arm chamber is evacuated to a pressure below 1 mtorr during single mode scanning. This is necessary to eliminate water vapor absorption lines and laser power losses in the air inside the cavity. In order to prevent backstreaming of pump oil into the chamber, a liquid nitrogen cold trap is used in the pumping system between the
vacuum chamber and the mechanical pump. The cold trap also helps pump out water vapor by functioning as a cryotrap.
CHAPTER VI.

DIAZOMETHANE SOURCE GAS

CH$_3^-$ is created in the hot-cathode high-pressure source described in Chapter II from the parent source gas diazomethane CH$_2$N$_2$. Diazomethane is a most common methylating reagent for carboxylic acids, enols, and heteroatoms such as nitrogen and sulfur [44]. Diazomethane is characteristic of a yellow gas at room temperature and a very noticeable musty odor. It is very toxic (OSHA pel of 2 ppm), mutagenic, and carcinogenic. It is also highly unstable and can explode if exposed to sharp nucleation sites such as sharp edges found on ground glass [45] [46] [47] or certain chemical substances such as drying agents. Diazomethane has a boiling point of -23 C, so it can easily be converted into a liquid in the lab. The melting point is just below -100 C, so it will freeze in liquid nitrogen.

Diazomethane is an ideal parent source because one of its resonant structures [48] is one step away from dissociation into CH$_2^-$ and N$_2^-$. Figure 23(a) shows the various resonant structures of diazomethane. The propensity to form molecular nitrogen from this compound makes diazomethane highly unstable. For this reason, we synthesize diazomethane in only one-gram quantities. Diazomethane is stored and utilized at dry ice temperature, which is about -70 C. Therefore, diazomethane is handled entirely in the liquid phase. State changes are avoided which may result in explosions, while the
Figure 23. (a) Five valence tautomer structures are shown, however structure 1 is the most likely to dissociate to yield a methylating reagent. (b) Diazald undergoes an internal rearrangement, a deprotonation, and dissociation to yield diazomethane.
vapor pressure is sufficient to fuel the ion source. The vapor pressure is not known at
different temperature. However, using the Clausius-Clapyron equation and the boiling
points (BP) of other gaseous substances at various pressures, an estimate may be made
for diazomethane at any temperature including dry ice temperature. First, we calculate
the latent heat from other gaseous substances given only the BP at 1 mm Hg and 760
mm Hg from the table below

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>M.W.</th>
<th>T(°C) @ 1mm [49]</th>
<th>T(°C) @ 760mm [49]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>CH₃CH₃</td>
<td>30</td>
<td>-159</td>
<td>-89</td>
</tr>
<tr>
<td>Propane</td>
<td>(CH₃)₂CH₂</td>
<td>44</td>
<td>-129</td>
<td>-42</td>
</tr>
<tr>
<td>Butane</td>
<td>(CH₃)₂CH(CH₃)</td>
<td>58</td>
<td>-101.5</td>
<td>-0.5</td>
</tr>
<tr>
<td>Pentane</td>
<td>(CH₃)₂(C₂H₅)</td>
<td>72</td>
<td>-76.6</td>
<td>36</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>(CH₃)₂(C₂H₅)</td>
<td>114</td>
<td>-45.3</td>
<td>80.7</td>
</tr>
</tbody>
</table>

From the Clausius-Clapyron equation, the latent heat for each of the substances above is
predicted from

\[ \frac{P_r}{P_i} = e^{\frac{LM}{RT_r}\left(\frac{1}{T_i} - \frac{1}{T_f}\right)} \]  

(6.1)

where \( P_r \) and \( P_i \) are the final and initial pressures, \( T_r \) and \( T_i \) are the final and initial
temperatures in Kelvin, \( M \) is the molecular weight, \( R \) is the universal gas constant, and \( L \)
is the latent heat. The latent heat \( L \) is solved as
and the calculated latent heat values for each of the substances are shown in the following table

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>M.W.</th>
<th>L (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>CH₂CH₃</td>
<td>30</td>
<td>550</td>
</tr>
<tr>
<td>Propane</td>
<td>(CH₃)₂CH₂</td>
<td>44</td>
<td>479</td>
</tr>
<tr>
<td>Butane</td>
<td>(CH₃)₂(CH₂)₂</td>
<td>58</td>
<td>440</td>
</tr>
<tr>
<td>Pentane</td>
<td>(CH₃)₂(CH₂)₃</td>
<td>72</td>
<td>412</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>(CH₃)₂(CH₂)₄</td>
<td>114</td>
<td>309</td>
</tr>
</tbody>
</table>

Knowing the molecular weight of diazomethane to be 42, the latent heat for diazomethane is linearly interpolated from this data to be about 500 kJ/kg. Therefore, at −70°C, the vapor pressure is predicted to be about 30 Torr, which is sufficient to supply the high pressure ion source.

In this work, two synthesis procedures for producing diazomethane are presented with essentially equal results in terms of producing comparable CH₃⁺ ion current. However, the second procedure discussed later in this section is simpler in procedure and glassware setup but neglects the closed vacuumline configuration, which encourages contamination due to moisture in the air.

For the first synthesis procedure, the diazomethane is produced through a one-step chemical reaction with the precursor Diazald and a strong base like potassium hydroxide, KOH. Diazald is the trade name for n-methyl n-nitroso paratoluenesulfonamide and the
empirical formula is $\text{CH}_2\text{C}_6\text{H}_5\text{SO}_2\text{N}((\text{CH}_3)\text{NO})$. This compound undergoes an internal rearrangement, a deprotonation, and a dissociation to yield the diazomethane gas. The reaction is described graphically in Figure 23(b).

Synthesis Procedure

The vacuumline to prepare is shown in Figure 24. All glassware must be free of scratches. Proper safety precautions should be taken including a blast face shield, protective clothing, and gloves. A 6 g portion of Diazald is dissolved in 20 ml of decahydronaphthalene with a magnetic stirrer and warmed to 60 C inside the three-neck flask (label B). Decalin is the trade name for decahydronaphthalene, whose empirical formula is $\text{C}_{10}\text{H}_{18}$. The water bath (label D) maintains a constant temperature of 60 C in the three-neck flask during the reaction. A heating plate with magnetic stirrer maintains the temperature of the bath (label E). A 2 g portion of KOH is dissolved in 20 ml of isopropanol and placed in the funnel above the three-neck flask (label C). The alcohol KOH mixture is dripped very slowly into the Diazald solution. An inert gas such as He or N$_2$ (label A) gently sweeps the evolving gas from the reaction through the system. The evolving gas is swept through the water-cooled jacket condenser (label F) to condense out some of the water. The majority of the gas is trapped in the coldtrap (label G) in the Stanley steel thermos (label H). The thermos contains a dry-ice isopropanol slush bath for condensing the diazomethane gas in the liquid phase and also serves as protective container in case of accidental detonation. Any gaseous diazomethane that
Figure 24. Schematic of the glassware vacuum line for diazomethane synthesis.
survives the coldtrap (label G) bubbles through an acetic acid bubbler (label I) to neutralize the hazardous gaseous diazomethane [50]. The entire reaction takes about a half-hour. Afterwards, the coldtrap (label G) thermos with the condensate may be disconnected from the vacuum line and connected to the ion source of the big-beam.

The part numbers for all the special ACE glassware is shown in Figure 25. Many of the glassware pieces had to be hand-blown together to insure adequate seals and reaction vessel integrity to guard against inadvertent chemical reactions between the highly explosive chemical and inhomogeneous glass connecting material such as teflon or tygon.

The alternative synthesis procedure suggested by Sachs [51] generates diazomethane by the precursor N-nitroso N-methylurea and a strong aqueous base. Ellison [52] described the synthesis and reaction in detail, which is shown in Figure 26. Again, glassware must be free of scratches and proper safety precaution should be taken including a blast face shield, protective clothing, and gloves.

An Erlenmeyer flask containing a mixture of 50 ml of 50% aqueous KOH and 30 ml of decalin was placed in an ice-bath. After the mixture reached equilibrium at 0°C, 8 g of N-nitroso N-methylurea was added to the cold mixture and stirred with a stirring bar in the ice-bath until all of the solid N-nitroso N-methylurea dissolved and the solution turned a canary yellow color. The Erlenmeyer flask containing the resulting mixture was removed from the ice-bath and placed in a dry ice-alcohol bath. After the mixture reached equilibrium at about −70°C, the mixture separated out into two noticeable layers; the top layer being the desired diazomethane and decalin product and the bottom layer of water and other biproducts. The top layer is then decanted from the
Figure 25. Special glassware from ACE Glass Inc.
Figure 26. Schematic of methylurea reaction to yield diazomethane. Similar to the Diazald reaction, methylurea undergoes an internal rearrangement, deprotonation, and dissociation to yield diazomethane.
suspension by pipette and placed in an ampule, which was then connected to the ion source of the big-beam.

Because the entire synthesis procedure takes place outside an enclosed vacuum line, additional time and care must be taken to evacuate the ampule of atmosphere after it is connected to the high-pressure ion source.
CHAPTER VII.

INFRARED STUDIES OF CH₃⁻

Background

The methide ion, CH₃⁻, is a good system for studying electron correlation effects. The energy due to the correlation effect is the difference between the Hartree-Fock predicted energy for the complete system and the exact energy of the same system. The Hartree-Fock treatment approximates the correlation effect by assuming uncorrelated motion of each electron relative to the average position of the remaining electrons [53]. Methide is unusual in a few ways: Methide is isoelectronic to ammonia, NH₃, and is expected to exhibit a fluctuational structure; i.e., an inversion motion analogous to the well-known 23 GHz tunnelling motion in ammonia. Methide is the simplest fluctuational anion. In addition, methide is the simplest oblate rotor anion; i.e. its two largest rotational constants are equal. Prolate or nearly prolate rotor molecules are much more common than oblate rotors because of carbon chains. Methide has been the subject of many theoretical studies, but is poorly explored experimentally, because of the experimental difficulty is producing the ion.

Ever since the first observation of the methyl radical CH₃ [54] [55], numerous experimental techniques have been employed to study this radical. In contrast, Lineberger and coworkers [56] accomplished the only experimental study of the...
molecular anion CH$_3^-$ in 1978. In his work utilizing the photoelectron spectroscopy technique, the adiabatic electron affinity of the radical was determined to be 0.08 ± 0.03 eV for the radical and geometry to be near planar with a barrier height of no more than 150 cm$^{-1}$.

Autodetachment in negative molecular ions is similar to autoionization in neutral molecules. The simplest physical model for autodetachment is a three-level system in which the initial and intermediate levels are connected by a radiative transition, and the intermediate level can undergo irreversible decay to a third level. The internal excitation mode in this process could be electronic, vibrational, or rotational. Simons [57] discussed the nature of the coupling between nuclear motions and the electronic degrees of freedom. Analogous couplings, which give rise to vibration-induced ionization of molecular Rydberg states, have been analyzed by Duzy and Berry [58].

Simon derived a set of propensity rules for vibrational-rotational autodetachment. These rules are: (1) the anion and neutral potential energy surfaces approach or intersect one another in regions where both vibrational-rotational wavefunctions are nonvanishing and the electronic force operator is large; (2) the change in slope in going from one potential curve to the other is small; (3) the kinetic energy of the detached electron is small and corresponds to a de Broglie wavelength of the order of the radial size of the anion's highest occupied molecular orbital (HOMO). Acharya et al. [59] performed ab initio calculations of vibrationally-induced autodetachment rates of LiH$^-$ and OH$^-$. Their results show the time required to "shake" an electron off LiH$^-$ is 0.1 - 1.0 ns whereas OH$^-$ requires 1-10 μs. They also believed that the ejection rates of all molecular negative anions that had been experimentally studied up to 1984 lie between 0.1 ns and 10 μs.
Fano [60] (1961) examined the general problem of bound states embedded in continua. The photodetachment cross section can be written as

\[ \sigma = \sigma_b + \sigma_a \frac{(\varepsilon + q)^2}{(\varepsilon^2 + 1)} \]  

(7.1)

where

\[ \varepsilon = \frac{(E - E_r)}{\frac{1}{2} \Gamma} \]  

(7.2)

\( E \) is the energy of the detached electron, \( \Gamma \) is the width of the resonance peak at full-width half-maximum (FWHM). The system \( \sigma_a \) denotes the partial cross for angular momentum \( L \) in the absence of resonance, where \( \sigma_b \) is the nonresonant background contribution. The line profile index \( q \) describes the asymmetry of the resonance. At resonance \( \varepsilon = 0 \) and \( \sigma = \sigma_b + \sigma_a q^2 \).

Therefore, \( q^2 \) gives an estimate of the ratio of autodetachment to direct photodetachment. The Fano line shape reduces to a symmetric Lorentz profile for large \( q \) values and to a dispersion shape for \( q = 0 \). Interference between direct transition and the transition via the discrete state into the continuum leads to an asymmetry in the line shape. However, this picture is complicated in vibrational-rotational spectra due to the interference effects from nearby rotational channels.
Previous Work on CH₃⁻

Ellison, Engelking, and Lineberger [56] performed the only other experimental study of CH₃⁻ using the photoelectron spectroscopy technique. In the gas phase, they produced a weak mass selected beam of CH₃⁻ from ketene. While crossing an argon laser operating at 488nm (2.54eV) with the ion beam, the ejected electrons were energy-analyzed and counted. The adiabatic electron affinity of the radical CH₃ was obtained, vibrational energy levels in the neutral were obtained, and the geometry of the radical was further confirmed to be planar.

There have been many theoretical studies on CH₃⁻ involving predictions of the anions energy surfaces and geometry [61] [62] [63] including predictions on the electron correlation effects on inversion potential barrier [64] [65]. Apart from the early prediction by Dreissler et al. [64] that CH₃⁻ would exist, nearly all the earlier predictions agree that CH₃⁻ is unstable against autodetachment. In most calculations, the electronic energy of the stable planar radical is lower than the corresponding energy for the equilibrium anion. Ortiz [66] concluded studies and predictions on the vertical ionization and adiabatic energies of CH₃⁻ and CH₃ respectively to be in good agreement with experimental measurements. Spirko and coworkers [67] performed a full dimensional potential energy surface calculation, which predicts a photoelectron spectrum and adiabatic electron affinity based on the previous PES experimental results by Lineberger et al.

In spite of these theoretical studies, there have been no theoretical predictions of the frequency dependence of the photodetachment cross section.
Apparatus

The present work employs an updated version of an experimental apparatus previously used [14] [15] [16] [17] [68] for laser detachment and autodetachment studies of NH\(^+\), HNO\(^-\) and Al\(^-\). The coaxial ion-laser beam apparatus used in this experiment is described in Chapter V.

Negative ions are produced in a high-pressure (0.02-0.04 torr) hot-cathode discharge through pure diazomethane, CH\(_2\)N\(_2\) and trace amounts of water vapor in the high-pressure source. The diazomethane is produced by decomposition of Diazald with base, trapped in a dry ice/isopropanol bath, and introduced through a needle valve into the ion source. The complete procedure for synthesizing diazomethane is described in Chapter VI. The negative ions are electrostatically extracted through a 1-mm diameter hole in the anode of the ion source, formed into a 2-keV beam, and mass-selected by a Wien filter. The mass-selected beam is deflected at right angles by an electrostatic quadrupole [34], and directed into a tube (500 mm long by 4 mm inside diameter), whose voltage can be varied. After the tube, the ions are electrostatically deflected into a Faraday cup, where the current is recorded. The ion source is floated at -2 kV, and the tube can be varied from +1 kV to -1 kV, resulting in ion kinetic energies in the tube of 1 - 4 keV. The ability to vary the tube voltage is necessary for Doppler tuning the ions kinetic energy. Although the anode voltage of -2kV defines the ion's basic kinetic energy, the ions must be Doppler tuned through fixed laser frequencies during autodetachment studies of CH\(_3\)\. Two power supplies connected in series set the voltage on the equipotential tube relative to ground enable the ions modulation in kinetic energy. Therefore, the tube voltage, V\(_t\), consists of two parts: A fixed part, V\(_0\), and a variable
part for scanning, \( V_s \), which can be varied though a dynamic range up to 500V. The kinetic energy of ions inside the equipotential tube is \((2000 + V_i + V_e) \text{ eV}\).

Neutrals can be produced during the trajectory of the ions through the tube, by collisions of the ions with the background gas or with apertures at either end of the tube, or by autodetachment of the ions during flight. The neutrals produced by either collisions with background gas or by autodetachment have nearly the same energy as the parent anions. This is because collisions at large impact parameter and small energy transfer are more probable than head-on collisions, and because in autodetachment the outgoing electron carries off a few eV or less of energy. The fast (keV) neutrals produced during the flight through the tube are not electrostatically deflected, but instead continue undeflected, and collide with a collision plate consisting of CaF\(_2\) with a thin metal film coating. The fast neutrals eject secondary electrons, which are detected by an electron multiplier. The current output of the electron multiplier in turn is converted to a voltage by a fast (3 kHz bandwidth) homemade electrometer, with effective resistance of \(10^8 \Omega\) and hence 0.1 V/nA current to voltage conversion factor. The laser beam is chopped mechanically at about 1 kHz. To discriminate against neutrals resulting from collisional stripping by the background gas in the interaction region, a lock-in amplifier (EG&G model 5408A) was used for phase-sensitive synchronous detection, with a time constant typically set at 3 seconds. The entire apparatus is controlled by a Pentium-class computer, which runs applications written with LabView software suite. The data acquisition system is described in Chapter IV of this manuscript. Optimum source conditions to produce 5-10 pA (measured at the Faraday cup) of CH\(_3^+\) are similar to those listed in Table 7.
Table 6. Optimum ion source conditions to produce CH$_3^-$

<table>
<thead>
<tr>
<th>Source gas</th>
<th>Diazomethane (CH$_2$N$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filament</td>
<td>thoriated-iridium ribbon</td>
</tr>
<tr>
<td>Filament current</td>
<td>5 - 6 A</td>
</tr>
<tr>
<td>Filament supply voltage</td>
<td>4 V</td>
</tr>
<tr>
<td>Emission current</td>
<td>2.5 mA</td>
</tr>
<tr>
<td>Discharge voltage</td>
<td>50V</td>
</tr>
<tr>
<td>Pressure in the extraction region</td>
<td>3.6x10$^{-6}$ Torr</td>
</tr>
<tr>
<td>Estimated ion-source pressure</td>
<td>15 mTorr</td>
</tr>
</tbody>
</table>

The data acquisition system, described in Chapter IV, is used to control and
datalog all aspects of the experiment. All voltages proportional to the neutral signal, ion
current, interaction pressure, and laser power are measured and stored in computer
memory by the data acquisition system. At the fixed laser frequency, the system samples
the data inputs at user defined time duration and intervals, typically every 2 seconds for
20 seconds. The relative cross section was computed using Equation (7.3). A value for
the cross section was calculated every 2 seconds, and a simple LabView program
returned the average values of all quantities in real time.

**Photodetachment Cross Section Measurement**

The probability for photodetachment per ion is given by

$$\xi = \frac{I_n}{I_i}$$  \hspace{2cm} (7.3)

and

$$\frac{I_n}{I_i} = \left( \frac{P}{E} \right) \left( \frac{\sigma}{A} \right) \left( \frac{d}{v} \right)$$  \hspace{2cm} (7.4)
where $\nu$ is the fraction of ions that are photodetached in the big beam apparatus, $I_n$ and $I_i$ are the neutral and ion currents, respectively. $P$ is the laser power. $E$ is the photon energy, $\sigma$ is the photodetachment cross section, $A$ is the cross sectional area of the ion beam, $d$ is the length of the interaction region, and $v$ is the ion velocity from equation 2.1. The photodetachment cross section is given by

$$\sigma = A \left( \frac{v}{d} \right) \left( \frac{E}{P} \right) \left( \frac{I_n}{I_i} \right)$$

Equations (7.3) through (7.5) assumes 100% neutral current detection, however, this is not the case. The efficiency is characterized as detecting secondary electrons as a result of collisions of neutral with the collision plate and amplifying the secondary electron current through the EMT. To obtain a reliable efficiency $\varepsilon$, a measurement is first carried out on another ion (calibrating ion) whose cross section is known absolutely. From this measurement, a reliable detection efficiency is obtained and may be used to make accurate photodetachment cross section measurements of other ions. The calibrating ion is $O$ because the photodetachment cross section is known absolutely [69] in the photon energy range and because it is already present in the ion beam. We find the efficiency $\varepsilon$ by noting

$$\varepsilon = \frac{I_{nd}}{I_n}$$
where \( I_{\text{nd}} \) is the neutral current detected and \( I_n \) is the neutral current from equation (7.4).

The current from the anode of the electron multiplier tube (EMT) \( I_{\text{emt}} \) is

\[
I_{\text{emt}} = \alpha I_{\text{nd}}, \tag{7.7}
\]

where the gain of the EMT is a function of the voltage applied to the cathode (see Figure 27). The EMT current is fed to a 100 mV/nA electrometer with resistance of 100 M\( \Omega \), whose output is then measured by a lockin amplifier (model EG&G model 5204A) for phase sensitive detection. The lockin amplifier signal \( V_1 \) is defined as

\[
V_1 = R_e I_{\text{emt}}, \tag{7.8}
\]

where \( R_e \) is the electrometers resistance of 100 M\( \Omega \). From equations (7.6) through (7.8) the efficiency \( \varepsilon \) is shown to be

\[
\varepsilon = \left( \frac{V_1}{\alpha I_n R_e} \right). \tag{7.9}
\]

After substituting the definition of \( I_n \) from equation (7.4), the efficiency \( \varepsilon \) is defined completely in terms of observed quantities.
Figure 27. The gain versus applied voltage for the EMT model AF 120. The gain is expressed in logarithmic coordinates and the voltage is in Cartesian coordinates.
\[ \varepsilon = \left( \frac{V_1}{\alpha I_i R_e} \right) \left( \frac{E \sqrt{2}}{0.26P} \right) \left( \frac{A}{\sigma} \right) \left( \frac{v}{d} \right), \]  

(7.10)

where \( V_1 \) is the lockin amplifier signal, \( I_i \) is now in nA and \( P \) is multiplied by 0.26 to account for losses at the first CaF\(_2\) window and the beam waste at the equipotential tube aperture. The beam waste at the equipotential tube aperture is discussed in the subsequent procedure section. The power \( P \) is also divided by \( \sqrt{2} \) because the lockin voltage \( V_1 \) is the rms value of the chopped laser beam. Assuming complete overlap between the ion and laser beams, the detection efficiency \( \varepsilon \) is determined from equation (7.10) and the table of experimental conditions listed in Table 8 below.

Table 7. Typical ion beam data values.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Data value</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_1 )</td>
<td>0.89V</td>
<td>t=3 sec. lockin amplifier time constant</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>4x10^4</td>
<td></td>
</tr>
<tr>
<td>( I_i )</td>
<td>0.35x10^-9A</td>
<td>1500V (EMT applied voltage)</td>
</tr>
<tr>
<td>( E )</td>
<td>3.04x10^-19J</td>
<td>Photon energy at 647 and 676nm</td>
</tr>
<tr>
<td>( P )</td>
<td>1.14W</td>
<td>Before interaction region and chopper</td>
</tr>
<tr>
<td>( A )</td>
<td>1.8x10^9m^2</td>
<td></td>
</tr>
<tr>
<td>( d )</td>
<td>0.45m</td>
<td></td>
</tr>
<tr>
<td>( v )</td>
<td>1.5x10^3ms^-1</td>
<td>2000V beam voltage for O^-</td>
</tr>
<tr>
<td>( \sigma(O^-) )</td>
<td>6x10^-22m^2</td>
<td>Branscomb et. al. [69]</td>
</tr>
</tbody>
</table>

The detection efficiency \( \varepsilon \) is about 95% and is assumed to be the same for all ions. For completeness, the photodetachment cross-section for any ion in this apparatus at beam energy of 2 keV is defined as

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\[
\sigma = \left[ 5.44 \frac{A_v}{d \xi} \right] \left[ \frac{V_i}{\alpha l R_c} \frac{\sqrt{m_o}}{\sqrt{m}} \left( \frac{1}{E} \right) \right] \tag{7.11}
\]

which is numerically is
\[
= 3.55 \times 10^{-33} \left[ \frac{V_i}{\alpha l} \left( \frac{\sqrt{m_o}}{\sqrt{m}} \right) \left( \frac{1}{P \lambda} \right) \right] \tag{7.12}
\]

where \(m_o\) is the mass for \(O^-\) in amu, \(V_i\) is the signal of the lockin amplifier in volts, \(l\) is the ion current in the Faraday cup in Amperes, \(P\) is the laser power before the chopper and interaction input window, \(\lambda\) is the wavelength of the laser, \(m\) is the mass of the mass selected ion, \(\alpha\) is the EMT gain at a particular applied voltage, and \(E\) is replaced by \(hc/\lambda\), and \(hc\) is absorbed into the constant \(3.55 \times 10^{-33}\) in equation (7.12).

**Background and Noise Calculation**

A collision between a negative ion and the background gas in the interaction region detaches an electron from the ion, which results in a fast neutral and a free electron. The neutral is fast because it continues after collision with essentially the same momentum as the ion. The probability of collisional detachment, or “collisional stripping”, per ion is given by

\[
\varphi_c = \frac{l_n^c}{l_i} = \sigma_c \rho d \tag{7.13}
\]
where the ratio of $I_n^*$ to $I_i$ is the fraction of ions that are collisionally detached and $I_n^*$ and $I_i$ are the collisional-detachment neutral current and ion current, respectively. The cross section $\sigma_c$ is the collisional detachment cross section, $\rho$ is the number density of the background gas, and $d$ is the interaction length. The collisional stripping rate $R_c$ is given by

$$ R_c = \varepsilon \sigma_c \frac{I_i}{e} $$  \hspace{1cm} (7.14)

or

$$ R_c = \varepsilon \sigma_c \rho d \frac{I_i}{e} $$  \hspace{1cm} (7.15)

where $\varepsilon$ is the detection efficiency, $I_i$ is the ion current, and $e$ is the electron charge. The detected neutral current $I_{nd}$ is equal to $eR_c$ and the EMT current $I_{emt}$ is given as

$$ I_{emt} = \alpha I_{nd} $$  \hspace{1cm} (7.16)

or

$$ I_{emt} = \alpha e R_c $$  \hspace{1cm} (7.17)

where $\alpha$ is the gain of the EMT at a particular applied voltage. The EMT current $I_{emt}$ is fed into an electrometer with internal resistance $R_e = 100 \, \text{M}\Omega$ (0.1 V/nA). The voltage signal $V_e$ from the electrometer is given as
By combining equations (7.15) through (7.18), the cross section $\sigma_c$ can be expressed by

$$\sigma_c = \frac{kT}{133.3p} \left[ \frac{V_e}{\alpha \varepsilon d_i R_e} \right]$$

(7.19)

or

$$\sigma_c = 6.49 \times 10^{-31} \left[ \frac{V_e}{\alpha p l_i} \right]$$

(7.20)

where $p$ is replaced by $p/kT$ to emphasize the pressure dependence and will later be used to determine lifetime measurements. $p$ is the background pressure in the interaction region in Torr and is typically $2 \times 10^{-8}$ Torr during normal operating conditions. The factor 133.3 is the conversion factor from Torr to Pascal.

The collisional stripping signal due to 1 nA of O$^-$ is 4 V measured at the 0.1 V/nA electrometer output. For a 95% detection efficiency, pressure of $2 \times 10^{-8}$ Torr, and a gain of $2 \times 10^6$, we obtain a collisional cross section $\sigma_c$ of about $6.5 \times 10^{-20}$ m$^2$ or 6.5 Å$^2$ which is typical for most collisional cross sections. For reference, other collisional cross sections reported are 3.8 Å$^2$ and 3.4 Å$^2$ for Br$^-$ and I$^-$ respectively at the same kinetic energies [70] [71].

Photodetachment study of CH$_3^-$

The low electron affinity of CH$_3$ makes CH$_3^-$ an ideal candidate for...
photodetachment by photons in the tuning range of the FCL-20 F-center laser. The laser beam is chopped mechanically at 1 kHz, and the photodetachment signal is detected with phase sensitive detection. The relative photodetachment cross section is measured as a function of the laser frequency. The infrared photodetachment cross section of CH$_3^-$ was measured at photon energy of 15455.45 and in the range 3862.49-3610.10 cm$^{-1}$. The experimental results are compared with theoretical calculations based on a simple physical model, the “zero-core contribution” model, which was developed by Stehman and Woo [72] in 1979 and successfully applied to the visible spectra of some atomic and molecular negative ions.

**Procedure**

An electrometer and a digital voltmeter continuously monitors the ion current collected by the Faraday cup. Special optics consisting of gold-plated mirrors steer the laser path through the interaction region in order to maximize the laser power through it. The power-meter, Scientech model 36-2002, is coupled to the CaF$_2$ vacuum window through a Plexiglas tube, which is purged with dry nitrogen in order to eliminate any absorption effects due to atmospheric water vapor. Depending on the laser wavelength, the peak laser power ranges between 4 and 30 mW, of which 66% survives the input CaF$_2$ window and 39% survives the apertures of the interaction region. The 39% value is calculated by the theory of a Gaussian TEM$_{00}$ beam in a homogeneous medium [73]. A Gaussian beam propagating in the z-direction, with r being perpendicular to the z axis, has an optical electric field $E$ given by
\[ E(r, z) = E_0 \left( \frac{\omega_0}{\omega(z)} e^{-\frac{r^2}{\omega^2(z)}} \right) \] (7.21)

where \( \omega(z) \) is the beam waist parameter and is defined as

\[ \omega^2(z) = \omega_0^2 \left( 1 + \frac{z^2}{z_0^2} \right). \] (7.22)

The beam waist parameter \( \omega \) has minimum value \( \omega_0 \), and \( z_0 \) is the Rayleigh length defined as

\[ z_0 = \frac{n\pi\omega_0^2}{\lambda}, \] (7.23)

where \( \lambda \) is the wavelength of the Gaussian beam and \( n \) is the index of refraction. The intensity \( I \) is proportional to \( E^2 \) and given as

\[ I(r, z) = I_0 \left( \frac{\omega_0}{\omega(z)} \right)^2 e^{-2\frac{r^2}{\omega^2(z)}}. \] (7.24)

The power through an aperture of diameter \( D \) is
or

\[ P = \int_0^{D/2} I(r, z) 2\pi r dr \] (7.25)

or

\[ P = I_0 \omega_0 \frac{2}{\pi} \left( \frac{\pi}{2} \right) e^{-s'} ds' \] (7.26)

where \( S' \) is a substitute variable for \( 2r^2/\omega^2(z) \) and \( S \) is given as

\[ s = \frac{D^2}{2\omega^2(z)} \] (7.27)

where \( D \) is the diameter of the aperture. The resulting integral is

\[ P = I_0 \omega_0 \frac{2}{\pi} \left( \frac{\pi}{2} \right) \left[ 1 - e^{-\frac{D^2}{2\omega^2(z)}} \right] \] (7.28)

or

\[ P = P_0 \left[ 1 - e^{-\frac{D^2}{2\omega^2(z)}} \right]. \] (7.29)

For \( \lambda = 3 \, \mu m \) (typical FCL wavelength), \( z = 225 \, mm \) (this is half the interaction region length), \( D = 1.25 \, mm \) (diameter the aperture), \( \omega(z) = \sqrt{2} \omega_0 \) at the aperture, The ration of
P/P₀ is approximately 0.39 or 39%. The laser frequency is measured by a wavemeter, Burleigh model WA-20IR, which can read either the wavelength (nm) or the frequency (cm⁻¹).

A source of systematic error was variation in the geometrical overlap between the ion beam and the laser beam. Such variation arose from two sources: (1) Changes in alignment of the laser beam as the laser frequency is changed; such changes are appreciable when the laser frequency changes by more than 200 cm⁻¹. (2) Slow drift in the direction of the ion beam due to the charging nature of the beam and electrostatic optics.

To minimize these effects, the laser beam is realigned in the ion beam apparatus to maximize the transmitted laser power at each laser frequency. This keeps the geometrical overlap roughly constant. The ion current is readjusted to maximize the current in the Faraday cup for each laser frequency. However, because the realignment procedure never reproduces exactly the same overlap, the result is a piecewise-continuous spectrum with discontinuities over the 100 cm⁻¹ spectral range. The discontinuities are removed with a smoothing procedure: Each scan has 20 cm⁻¹ overlap with the adjacent scan. All points of a single scan are multiplied by a common factor in order to produce agreement at the overlap points. This smoothing process makes small (few percent) adjustments in the data, which are equally likely to be increases as decreases. Thus it is not a source of systematic error but is a source of random error. The minor fluctuations in the ion current I do not contribute to systematic error because the cross section in equation (7.12) is a ratio of cross section σ to ion current I.

The possibility of another source of systematic error was examined. If there
were a systematic variation of the laser-beam divergence with laser frequency, then the laser power transmitted by the interaction region would not be a constant fraction of the laser power interacting with the ions. This possibility was investigated by measuring the fraction of the laser power transmitted by the interaction region. It was found that this fraction was constant over the laser frequency range within ±3.8% (rms) with no systematic increase or decrease.

In conclusion, the uncertainty in an individual data point arises from the inability to keep the geometrical overlap between ion beam and laser beam exactly constant as the laser frequency changes.

Photodetachment Results

The experimental results are shown in Figure 28 for the photon energy ranges measured in this experiment.

Theory

The $v'' = 0$ state of CH$_3^-$ is bound by 80 meV relative to $v' = 0$ of CH$_3$. All vibrationally excited states of CH$_3^-$ can autodetach. In principle, there are two routes to photodetachment: direct detachment and resonant detachment. The direct detachment is represented by the following equation, in which vibrationally excited states of the ion do not play a role:

$$\text{CH}_3^-(v''=0) + h\nu \rightarrow \text{CH}_3(v') + e^-.$$  \hspace{1cm} (7.30)
Figure 28. Photodetachment cross section of CH$_3^-$ in the 0.44–0.48 eV photon energy range. The average cross section in this range is $7.89 \pm 1.02 \times 10^{-22}$ m$^2$. 
In contrast, the resonant photodetachment process is represented by a bound-bound transition in the ion,

$$\text{CH}_3^+ (v'' = 0) + h\nu \rightarrow \text{CH}_3 (v' > 0)$$  \hspace{1cm} (7.31)

followed by autodetachment,

$$\text{CH}_3 (v'' > 0) \rightarrow \text{CH}_3 (v') + e^-.$$  \hspace{1cm} (7.32)

These two different processes can give rise to the same final state. Therefore, in order to calculate the cross section theoretically one should add the amplitudes, rather than the probabilities. The resonant contribution is expected to be centered at the photon energy corresponding to the transition energy in the ion, with a width given by the autodetachment lifetime of the excited state in the absence of strong interference effects between the resonant and nonresonant contribution.

The photodetachment cross section $Q$ for direct detachment is given by the following expression [74], derived from Fermi's golden rule:

$$Q = \left( \frac{32\pi^4 m^2 e^2 \nu^4}{3\hbar c^3} \right) |\bar{M}|^2,$$  \hspace{1cm} (7.33)

where $\bar{M}$ is the electric dipole matrix element, given by
\[ \tilde{M} = \langle f, k | i, h\nu \rangle. \] (7.34)

In this expression, \( m \) is the electron mass, \( v \) is the final velocity of the departing electron, and \( \nu \) is the laser frequency. The final state \( | f, k> \) is characterized by the neutral in state \( f \) and the detached electron having momentum \( \hbar k \). The cross section decreases to zero at threshold because the phase space available to the departing electron vanishes. Below threshold there is no final state available. Far enough above threshold, the cross section decreases because the wave function of the free electron oscillates more rapidly than the wave function of the initial state, yielding cancellation in the integral for \( \tilde{M} \). Roughly speaking, the maximum in the cross section occurs where the DeBroglie wavelength of the free electron matches that of the bound electron. That means that the photon energy at maximum cross section should be approximately twice the electron affinity.

Following the born-Oppenheimer approximation, the matrix element \( \tilde{M} \) can be written as a product of electronic and vibrational matrix elements

\[ \tilde{M} = (\tilde{V}, \tilde{v}) \langle f_e, k | i_e, h\nu \rangle \tilde{v}_i \] (7.35)

The inner electronic factor depends on the photon energy. Below threshold no final state exists. In the Franck-Condon approximation, the vibrational factor \( < v_f | v_i > \) does not depend on the photon energy. Therefore, the problem can be simplified by assuming that the Franck-Condon principle applies. This assumption uncouples the vibrational motion.
from the electronic transition. Therefore

$\tilde{M} = \langle v_f | v_i \rangle (f_e, k | \tilde{r}| i_e, h_u).$  \hspace{1cm} (7.36)

and the square of the matrix element is

$|\tilde{M}|^2 = |\langle v_f | v_i \rangle|^2 |\langle f_e, k | \tilde{r}| i_e, h_u \rangle|^2. \hspace{1cm} (7.37)$

The vibrational factors $|\langle v_f | v_i \rangle|^2$ are the Franck-Condon factors.

Siegel et al [75] assumed that the electronic part of the matrix element was constant with varying photon energy in their photodetachment study of NO$. Therefore the observed peak intensities were proportional to the Franck-Condon factors. On that assumption, they derived values for the vibrational frequency and equilibrium internuclear distance by adjusting the molecular constants so that the calculated Franck-Condon factors match the experimental resonance intensities. Kraemer and Spirko [67] calculated Franck-Condon factors based on the PES study at 488 nm on CH$_3^-$ by Ellison et al [56]. The calculated Franck-Condon factors were normalized to the 0-0 transition and are listed in Table 9.

<table>
<thead>
<tr>
<th>Source</th>
<th>0-0</th>
<th>1-0</th>
<th>2-0</th>
<th>3-0</th>
<th>4-0</th>
<th>5-0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spirko et al. [67]</td>
<td>1.0</td>
<td>1.60</td>
<td>1.73</td>
<td>1.62</td>
<td>1.07</td>
<td>0.78</td>
</tr>
</tbody>
</table>
In order to calculate the electronic dipole matrix element, we have to know the effective electronic affinity of the transitions CH$_3$ (v',J') $\leftrightarrow$ CH$_3$ (v",J") , averaged over the initial rotational states of the ion. The corrected Franck-Condon factor for each transition is the relative vibrational intensity calculated by Spirko et al. divided by the calculated electronic cross section. In order to compare with experiment, we must sum over the final states. Our experiment is insensitive to the final state of the CH$_3$, because we assume that all fast neutrals with the same kinetic energy will have the same detection efficiency. The total infrared photodetachment cross section is calculated by summing the partial cross sections weighted by the Franck-Condon factors.

The ZCC Model

Stehman and Woo [72] developed a simple physical model and semiempirical formulae for the shape of the photodetachment cross section of negative atomic ions. Their “zero-core-contribution” model (ZCC) is based on the following simplifying assumptions: (1) the wave functions of both the initial and final states can be approximately factored into the wave function of the neutral atomic core of radius $r_0$ and the wave function of the “extra electron” of angular momentum $l$, (2) the wave function of the atomic core is unchanged during the photodetachment process, and (3) the relevant electric dipole matrix element can be calculated by neglecting the contribution from the atomic core.

These assumptions simplify the calculation by reducing the calculation of the matrix element to a one-electron problem. This model needs three parameters: The electron affinity, the core radius $r_0$, and the angular momentum of the orbital of the
photodetaching electron. The ZCC model then yields an explicit analytical expression for the absolute photodetachment cross section as a function of photon energy.

The model fits the experimental cross sections quite well for H⁻, C⁻, O⁻, and the alkali metal anions; and (somewhat less well) I⁻. The model applies for several eV above threshold, not just near threshold. Stehman and Woo [76] applied this model to O₂⁻ and S₂⁻. It was also applied to OH⁻, SH⁻, NO₂⁻ and SeH⁻ by Clodius et al [77] [78], and to transition metal anions by Stehman et al [79] in 1985.

According to the ZCC model, the shape of the cross section depends on whether the detached electrons come from a s orbital or a p orbital. In the case of CH₃⁻, which is isoelectronic to neutral NH₃, detachment is from a p orbital from the carbon atom. For the photodetachment of an electron from a p orbital, the cross-section is

$$
\sigma = \frac{8\pi e^2}{9hc} \frac{m\omega}{h} \left( R_{sp}^2 + 2R_{dp}^2 \right),
$$

where $h\ k$ is the momentum of the departing electron and $\omega$ is the photon energy. The radial integral, $R_{sp}$ and $R_{dp}$ are given by

$$
R_{sp} = \frac{Ne^{-\gamma}}{\gamma k(\gamma^2 + k^2)} \left[ \left( \frac{3\gamma^2 k + k^3}{\gamma^2 + k^2} + \gamma kr \right) \cos(kr) + \frac{2\gamma^3}{\gamma^2 + k^2} + \gamma^2 r \right] \sin(kr)
$$

and
where $N^2 = \frac{2\gamma e^{2\gamma}}{1 + \frac{2}{r\gamma}}$.  

The variable $\gamma$ is given by $\gamma = \sqrt{\frac{2mE}{\hbar^2}}$, and $E$ is the electron affinity.

The ZCC Calculation

The core radius $r_o$ for atomic negative ions is taken to be

$$r_o = 1.3 \, r_{\text{RMS}}.$$  \hfill (7.42)

where $r_{\text{RMS}}$ is the root-mean-square radius of the outermost occupied orbital in the neutral atom taken from the Hartree-Fock calculation compiled by Lu et al [80].

Stehman and Woo [72] used the factor of 1.3 for all ions because it yielded the best overall agreement of the calculated cross sections with experimental results. However, this choice implies a potential energy region large enough to overlap almost all of the charge distribution of the neutral atoms for radii equal to 0.77 and 0.53 Å for C and H, respectively.

The question is how to obtain an effective core radius, $r_e$, for CH$_3$. We have
done two sets of ZCC calculations for a p orbital electron as a function of photon energy for three values of \( r_0 = 1, 2, \) and \( 3 \) Å. Stehman and Woo recommends two different scaling factors, 0.3 and 0.6, for an anion having either four or five outer-shell p electrons respectively to be multiplied to the total cross section. Therefore, two different sets of calculations are performed to ascertain the difference between the two scaling factors. Calculated photodetachment cross section values, \( \sigma \), as a function of various core radii are correlated and compared graphically with the measured cross section. The ZCC cross section values calculated with the 0.6 scaling factor at various core radii are shown in Figure 29(a), while Figure 29(b) indicates the extrapolated core radius to be \( 0.73 \pm 0.034 \) Å. This value indicates an unrealistic low \( r_{\text{RMS}} \) of \( 0.56 \pm 0.026 \) Å compared to the radius of \( 0.77 \) Å for \( C^- \) because from equation (7.42), the \( r_{\text{RMS}} \) is the outermost occupied orbital in the neutral and is \( r_0/1.3 \). However, the ZCC cross section values calculated with the 0.3 scaling factor at various core radii are shown in Figure 30(a), indicates an extrapolated core radius to be \( 1.068 \pm 0.037 \) Å. Thus, this value indicates a believable \( r_{\text{RMS}} \) of \( 0.82 \pm 0.028 \) Å.

Using a core radius of \( 1.068 \) Å, scaling factor of 0.3 multiplied to the calculated total cross section, and measured cross sections for two photon energy ranges, other comparisons are shown in the table below.

<table>
<thead>
<tr>
<th>Photon Energy (eV)</th>
<th>( \sigma ) Measured (Å(^2))</th>
<th>( \sigma ) Calculated (Å(^2))</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.046</td>
<td>0.079 ± 0.0042</td>
<td>0.081</td>
<td>Agreement within uncertainty</td>
</tr>
<tr>
<td>1.94</td>
<td>0.0038 ± 0.0011</td>
<td>0.048</td>
<td>Order disagreement</td>
</tr>
</tbody>
</table>

Table 9. Photodetachment \( \sigma \) measurement and calculation comparison for \( \text{CH}_3^+ \).

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Figure 29. (a) ZCC calculation for a p electron detachment for three different radii in the same infrared and visible photon energy range. (b) Correlation between the three ZCC predictions at three different radii made in (a) enables prediction of core radius in neutral. In this case, the predicted core radius corresponds to an unrealistic rms radius that is 37% less than C\(^-\) radius which is 0.77 Å.
Figure 30. (a) ZCC calculation for a p electron detachment for three different radii in the same infrared and visible photon energy range with the 0.3 scaling factor recommended by Stehman et al. (b) Correlation between the three ZCC predictions at three different radii made in (a) enables prediction of core radius in neutral. In this case, the predicted core radius corresponds to a realistic rms radius that is 6% greater than C$^+$ radius which is 0.77 Å.
Photodetachment conclusion

The absolute photodetachment cross section of CH₃⁻ has been measured and analyzed in the range 15455.45, and 3862.49-3610.10 cm⁻¹. The agreement between the ZCC model and experiment is encouraging considering the theory assumes no coupling between the electronic and vibrational wavefunctions and the scaling factor choices recommended by Stehman and Woo are limited regarding the number of p electrons in the outer most orbit of the neutral.

Rovibrational line spectrum prediction

In preparation for investigating the rotational-vibrational infrared spectrum of CH₃⁻, a calculation of the anticipated rovibrational spectrum was performed. From this calculation, one can gain an appreciation of the spectrum, location of dense portions of the spectrum, and probable strong lines. The methide ion, CH₃⁻, is polyatomic and has a symmetric top symmetry very similar to the well-studied neutral ammonia (NH₃). A great deal of insight can be gained from treating these symmetric rotors as rigid rotors in a classical mechanical sense. By ignoring high order effects such as centrifugal distortion terms, and anharmonicity correction terms, valuable information can still obtained without sacrificing the integrity of the spectrum characteristics. The question at hand is how many energy levels or rovibrational transitions will be populated in CH₃⁻ below the autodetachment limit? Moreover, what is the general expected shape and profile of the infrared spectrum? By constructing the rotational Hamiltonian for a symmetric rotor, such questions can be answered by using spectroscopic constants data, such as the major
and minor rotational constants, and obeying particular selection rules.

The electron affinity of CH$_3$ has already been measured at 0.08 ± 0.03 eV (643 ± 241 cm$^{-1}$) by Ellison, Engelking and Lineberger [56] and is taken to be the autodetachment limit for CH$_3$. The rigid-rotor energy levels are described in many physics text books including Townes and Schawlow's Microwave Spectroscopy [81] text and is shown as

$$E(J,K) = BJ(J+1)+(C-B)K^2$$

(7.43)

where B is the principal rotational constant about its principal axis, C is the minor rotational constant, J represents the total angular momentum quantum number, and K is the projection of J along the symmetry axis. The rotational constants B and C are defined as

$$B = \frac{\hbar}{8\pi l_B^2}$$

(7.44)

and

$$C = \frac{\hbar}{8\pi l_C^2}$$

(7.45)

where $l_B$ is the moment of inertia about the B principal axis and $l_C$ is the moment of inertia about the C principal axis. Each of the respective moments of inertia are given by
\[ I_B = m_1 l_{12}^2 (1 - \cos \theta) + m_1 m_2 l_{12}^2 \left( \frac{1 + 2 \cos \theta}{3m_1 + m_2} \right) \]  

(7.46)

and

\[ I_C = 2m_1 l_{12}^2 (1 - \cos \theta), \]  

(7.47)

where \( l_{12} \) is the bond length between H and C, \( m_1 \) is the mass of H, \( m_2 \) is the mass of C, and \( \theta \) is the H-C-H bond angle. By comparing \( \text{CH}_3^- \) to \( \text{NH}_3 \) in terms of the bond angles and bond lengths, the corresponding rotational constants of \( \text{CH}_3^- \) can be found. From the following table, spectroscopic constants for both \( \text{NH}_3 \) and \( \text{CH}_3^- \) are listed along with their references:

<table>
<thead>
<tr>
<th>Species</th>
<th>B (cm(^{-1}))</th>
<th>( l_{12} ) (Å)</th>
<th>( \theta ) (degrees)</th>
<th>( \hbar \omega ) (cm(^{-1}))</th>
<th>( \nu_1 ) transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NH}_3 )</td>
<td>9.93</td>
<td>1.104</td>
<td>106.47</td>
<td>3336</td>
<td></td>
</tr>
<tr>
<td>( \text{NH}_3 ) references</td>
<td>(a)</td>
<td>(a)</td>
<td>(a)</td>
<td>(b)</td>
<td></td>
</tr>
<tr>
<td>( \text{CH}_3^- )</td>
<td>8.39</td>
<td>1.1082</td>
<td>108.3</td>
<td>2608</td>
<td></td>
</tr>
<tr>
<td>( \text{CH}_3^- ) references</td>
<td>See below</td>
<td>(c)</td>
<td>(c)</td>
<td>(c)</td>
<td></td>
</tr>
</tbody>
</table>

where (a) Townes and Schawlow [81], Table 3-1, p53. (b) Guelachvili et al [82] (c) Kathy Robins ab initio calculation [83].

The calculated moments of inertia about the B axis for \( \text{NH}_3 \) and \( \text{CH}_3^- \) from the given table values are 1.686 and 1.979 amu-Å\(^2\) respectively. Consequently, the B rotational constant for \( \text{CH}_3^- \) is expected to be 8.39 cm\(^{-1}\). From the same Table, \( l_c \) is 3.227 amu-Å\(^2\) and C rotational constant for \( \text{CH}_3^- \) is predicted to be 5.15 cm\(^{-1}\).

For \( \text{CH}_3^- \), the rotational constant B is larger than the C constant, and the quantity
C-B is therefore predicted to be -3.24 cm\(^{-1}\). The negative number is an indication that the symmetric rotor is an oblate top, which resembles a pancake. There are a finite number of J and K state combinations below the autodetachment limit. The maximum value of J, for K = 0, is determined to be 8 from solving the resulting quadratic equation in equation (7.43) after substituting all the corresponding values. The energy level J=9 and K=0 will be above the autodetachment threshold, and may or may not autodetach before the ions reach the laser interaction region. In addition, since energy decreases with increasing K (note the second term in equation 1 is negative), there will be a few additional levels below the autodetachment threshold such as J=9, K=7, 8, and 9, and J=10, K=10. For an \(^1\)R transition, in which both J and K are increasing, the transition frequency is given by

\[
\nu = \nu_0 + 2B(J + 1) + (C - B)(2K + 1) \tag{7.48}
\]

This expression is determined first by equation (7.43) with the addition of the vibrational energy term, \(E(v)\), and second, taking the energy difference after incrementing \(v, J, \) and \(K\). The subband origin occurs when \(K = 0\). Therefore, the spacing between adjacent subband origins is \(2B\), or 16.78 cm\(^{-1}\). The subband origin does not occur at the strongest line in the subband.

For \(K = J\), the spacing between the strongest line in one subband and the strongest line in the next subband is spaced by \(2C\), 10.3 cm\(^{-1}\). Under this particular condition, J is changing, but \(K = J\). The transition within a given subband (for fixed J and varying K) will be spaced by \(2(C-B)\) or 6.48 cm\(^{-1}\). With increasing \(K\), the transition frequency
decreases. The width of a given subband is $2|C - B|$ or 6.48 cm$^{-1}$. Therefore, the width of a subband can be as much as 51.84 cm$^{-1}$ for $J = 8$, or as little as 6.48 cm$^{-1}$ for $J = 1$. At higher $J$, the subbands are wide enough to overlap into the next subsequent subband(s).

This characteristic is indicated in the following table, which shows calculated wavenumbers for $J$ and $K$ transitions in the $^3R$ branch with respect to a band origin of 2608 cm$^{-1}$. Each boldface $J$ transition wavenumber within a column represents a transition frequency which appears in the adjacent $J$ subband.

### Table 11. Calculated $J$ and $K$ transition frequencies in the $^3R$ branch for CH$_3^+$.  

<table>
<thead>
<tr>
<th>$K$</th>
<th>$J$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>2621.54</td>
<td>2638.32</td>
<td>2655.1</td>
<td>2671.88</td>
<td>2688.66</td>
<td>2705.44</td>
<td>2722.22</td>
<td>2739</td>
<td>2755.78</td>
<td>2772.56</td>
</tr>
<tr>
<td>1</td>
<td>2631.84</td>
<td>2648.62</td>
<td>2665.4</td>
<td>2682.18</td>
<td>2698.96</td>
<td>2715.74</td>
<td>2732.52</td>
<td>2749.3</td>
<td>2766.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2642.14</td>
<td>2658.92</td>
<td>2675.7</td>
<td>2692.48</td>
<td>2709.26</td>
<td>2726.04</td>
<td>2742.82</td>
<td>2759.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2652.44</td>
<td>2669.22</td>
<td>2686</td>
<td>2702.78</td>
<td>2719.56</td>
<td>2736.34</td>
<td>2753.12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2662.74</td>
<td>2679.52</td>
<td>2696.3</td>
<td>2713.08</td>
<td>2729.86</td>
<td>2746.64</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2673.04</td>
<td>2689.82</td>
<td>2706.6</td>
<td>2723.39</td>
<td>2740.16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2683.34</td>
<td>2700.12</td>
<td>2716.9</td>
<td>2733.68</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2693.64</td>
<td>2710.42</td>
<td>2727.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2703.94</td>
<td>2720.72</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2714.24</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For $J = 8$, the subband spacing from the band origin $\nu_0$ is thus 16B or 134.24 cm$^{-1}$ to the blue. The maximum population as a function of $J$ ($J = K$) will be $J_{\text{max}} = (kT/2B)^{1/2}$. Thus, assuming $kT = 400$ cm$^{-1}$ ($T = 600$ K), the $J_{\text{max}} = 5$. The $J = 5$, $K = 5$ line will be separated from the band origin by $5 \times 10.2 = 51$. cm$^{-1}$. Whether or not we can see the infrared spectrum depends on the value of the band origin. Presumably, there will also be an approximately equal interval to the red side $^3P$ bands, but these lines may not be accessible to our laser.
Another important question to be answered is how many lines can be anticipated?

As \( J \) increases from 0 to 8, \( K \) increases from 0 to each \( J \) transition, thus, totaling 1 transitions for every value of \( J \) as shown in the table below.

<table>
<thead>
<tr>
<th>( J )</th>
<th>( K )</th>
<th># states</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>0, 1</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>0, 1, 2</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>0, 1, 2, 3</td>
<td>4</td>
</tr>
</tbody>
</table>

The total number of states is given as

\[
N = \sum_{i=1}^{J+1} i = \frac{(i+1)(i+2)}{2}.
\] (7.49)

Therefore, for \( J = 8 \), there will be 45 initial states, each of which has an \( \text{^1}R \) line. That means 45 lines in a region of 134.24 cm\(^{-1}\), or about 134.24/45 \( \approx 3 \) cm\(^{-1}\) between lines (on the average). There will be one additional band for a total of two bands: The \( \nu_1 \) and \( \nu_2 \) bands, so there will be twice that many lines. There exist inversion doubling of several wavenumbers. This should double the number of lines as well. So the grand total is 45 x 4 = 190 lines in a 134.24 cm\(^{-1}\) range or 1.4 lines/cm\(^{-1}\) or 0.7 cm\(^{-1}\) between lines on the average. Figure 31 shows the predicted \( \text{R} \) branch infrared rovibrational. Each of the individual \( J \) transitions, with decreasing \( K \), are separated out in staggered formation for clarity.
Figure 31. Computer program to simulate the rovibrational transition “sticks” plot of CH₃. The computer program was written in VisualBASIC and source code is listed in the appendix.
An interactive computer program was developed out of the desire to visualize any symmetric rotor infrared "sticks" spectrum rapidly with any user input of different spectroscopic constants. Essentially, all the aforementioned formalization was coded in a VisualBASIC program that allows one to input information such as the autodetachment limit threshold energy, B and C rotational constants, temperature, and centrifugal distortion and anharmonicity correction terms.

**Autodetachment Procedure**

Again, the infrared laser is chopped at 1 kHz, and the resulting neutral signal is detected by phase sensitive detection. The anode voltage is fixed at -2 kV while the voltage on the equipotential tube consists of two parts: An offset voltage fixed at about +800V and a scan voltage ranging from about 100 to 500V. The laser frequency is fixed while the Doppler shift in the ion frame changes at a rate of about 10 MHz/Volt over a range of about 5 GHz during each scan.

The laser is used in single mode operation as described in Chapter V. with continuous pumping on the tuning arm chamber. For this experiment, crystal #3 is utilized and is pumped with 800 mW of Kr laser (all red lines). The laser frequency is measured in cm⁻¹ with a resolution 0.01 cm⁻¹ by a Burleigh WA-20IR wavemeter.
The Doppler shifts at the ion beam energy were added to laser frequencies in the ionic rest frame in order to predict the laser frequencies for the line in the lab frame. The laser frequency is kept fixed while the voltage on the equipotential tube, $V_\text{e}$, is varied through 500V. Fast scans through 500 V at a rate of 2.5 V/sec were used to find a potential line resonance. Once a resonance peak is observed, scanning is repeated in at a slower rate (1 V/sec) in order to obtain better resolution and a better estimate of the line position and the necessary scan range. For typical scanning rates, scanning at a rate of 0.25 V/sec through narrow lines and 1 V/sec for broad lines is sufficient for most applications.

Another source of systematic error, other than those already discussed earlier in this chapter, is the variation in the geometrical overlap between the ion beam and the laser beam caused by changes in the focusing and alignment of the ion beam due to systematic changes in $V_\text{e}$. The first effect is minimized by optimizing the alignment and focusing of the ion beam at an equipotential-tube voltage that lies near the middle of the scan.

**Doppler Tuning**

Almost all the interaction length between ions and photons takes place along the axis of an equipotential tube. Therefore, Doppler tuning of the ion beam is achieved by scanning the voltage on the tube rather than the anode voltage. When an ion beam with velocity $u$ interacts with a laser beam, the effective frequency in the ionic rest frame, $\nu$, is given by
\[ u = u' \left(1 - \frac{u \cos \theta}{c} \right) \frac{1}{\sqrt{1 - \left(\frac{u}{c}\right)^2}} \]  \hspace{1cm} (7.50)

where \( u' \) is the laser frequency measured in the lab frame, and \( \theta \) is the angle between the directions of the two beams in the lab frame [84]. The kinetic energy of ions, \( T \), inside the equipotential tube is given by

\[ T = q(V_a - V_e). \]  \hspace{1cm} (7.51)

where \( V_a \) is the anode voltage and \( V_e \) is the voltage on the equipotential tube. To express the velocity in terms of \( T \), the following relation is used

\[ E = mc^2 \left(1 - \frac{1}{\sqrt{1 - \left(\frac{u}{c}\right)^2}} \right) \]  \hspace{1cm} (7.52)

and

\[ E = T + mc^2, \]  \hspace{1cm} (7.53)

where \( m \) is the ionic rest mass and \( E \) is the total energy of the ion. Combining equations
(7.52) and (7.53), the following is obtained

\[
\frac{u}{c} = \sqrt{\frac{2T}{mc^2}} \sqrt{1 + \frac{T}{2mc^2}} \left(1 + \frac{T}{2mc^2}\right)^{-1}
\]

\[7.54\]

\[
= \sqrt{\frac{2T}{mc^2}} \left(1 + \frac{T}{2mc^2}\right)
\]

\[7.55\]

\[
= \sqrt{\frac{2T}{mc^2}} \left(1 - \frac{3}{4} \frac{T}{mc^2} + \ldots\right).
\]

\[7.56\]

For CH\(_3^+\) ions: \(m=15\) amu. Using \(1\) amu=931.5 MeV and assuming, typically, \(T=3\) keV, we obtain

\[
\frac{T}{mc^2} = 2.15 \times 10^{-7}
\]

\[7.57\]

Therefore the nonrelativistic approximation is accurate to \(1.6 \times 10^{-7}\), i.e.,

\[
\frac{u}{c} = \frac{\sqrt{2T}}{mc^2}.
\]

\[7.58\]

For parallel beams \(\cos \theta = 1\). An approximate form of equation (7.50) can be obtained by expanding the denominator. Such an expansion yields
From equation (7.58),

\[ \left( \frac{u}{c} \right)^2 = 4.3 \times 10^{-7} \]  

(7.60)

Therefore

\[ u = u \left( 1 - \frac{u}{c} \right) \]  

(7.61)

is a useful approximation accurate to about \(2.15 \times 10^{-7}\). For a laser frequency of \(3100 \text{ cm}^{-1}\), the error due to this approximation is only \(0.00066 \text{ cm}^{-1}\) \((20 \text{ MHz})\), which is well below the accuracy of the apparatus in the measurement of absolute line positions.

The Doppler shift, \(\Delta u\), is defined by

\[ \Delta u = u - u' \]  

(7.62)

Using equation (7.61), the Doppler shift becomes

\[ \Delta u = -u \frac{u}{c} \]  

(7.63)

or
\[ \Delta \omega = -u \sqrt{\frac{2T}{mc^2}}. \] (7.64)

For \( u' = 3100 \text{ cm}^{-1} \) and \( T = 3 \text{ keV} \), equation (7.64) yields 2.033 cm\(^{-1}\) as the value for the Doppler shift. The rate of change of the Doppler shift with beam energy is easily obtainable by differentiating both sides of equation (7.64),

\[ \frac{d(\Delta \omega)}{dT} = -\frac{u'}{\sqrt{2Tmc^2}} \] (7.65)

or

\[ \frac{d(\Delta \omega)}{dT} = -\frac{\Delta \omega}{2T}. \] (7.66)

Substituting \( T = 3 \text{ keV} \) and \( \Delta \omega = 2.033 \text{ cm}^{-1} \), we get 0.00034 cm\(^{-1}\)/eV as the value for the change in the Doppler shift per eV change in the ion beam energy. Inspection of equation (7.60) shows that higher and higher resolution is obtained by increasing the ion beam energy, which demonstrates the idea of using fast ion beams in high-resolution measurements.

**Resolution**

The basic limiting factors to the resolution of this experiment are the velocity spread, divergence of the ion beam, and the linewidth of the laser. The color-center laser (model FCL-20) has a linewidth less than 1 MHz \((3.3 \times 10^{-5} \text{ cm}^{-1})\). Therefore, the laser
itself allows for very high resolution ($\leq 1$ MHz) if it were the only limiting factor in the resolution. If the divergence of the ion beam is $\Delta \phi$, the Doppler broadening due to this effect is obtained from equation (7.50) by substituting $\theta = 0$ then $\theta = \Delta \phi$. For a nonrelativistic ion beam,

$$\Delta u_{\text{div}} = u \left( \frac{u}{c} \right) \left( 1 - \cos \left( \frac{\Delta \phi}{2} \right) \right).$$

(7.67)

Normally $\Delta \phi$ is $< 20$ mrad; consequently

$$\cos \left( \frac{\Delta \phi}{2} \right) \approx 1 - \frac{1}{8} (\Delta \phi)^2$$

(7.68)

$$\therefore \Delta u_{\text{div}} = \frac{1}{8} u \left( \frac{u}{c} \right) (\Delta \phi)^2.$$  

(7.69)

Assuming an interaction length of 45 cm and 1.5-mm apertures, we find $\Delta \phi = 1.67$ mrad. Substituting typical numbers ($u = 3100 \text{ cm}^{-1}$, $u/c = 6.55 \times 10^{-4}$), one obtains $\Delta u_{\text{div}} = 7.1 \times 10^{-7} \text{ cm}^{-1}$, which is negligible.

The Doppler broadening due to the velocity spread in the ion beam, $\Delta u$, is obtained from equation (7.50) by differentiating $v$ with respect to $u$ and replacing the differentials by infinitesimal differences. With $\theta = 0$ (perfectly overlapping parallel beams), one obtains
Differentiating equation (7.58) with respect to $T$, one obtains

\[
\Delta u = \left( \frac{\Delta u}{c} \right). \quad (7.70)
\]

Substituting equation (7.71) into equation (7.70), we obtain

\[
\Delta u_{VS} = \frac{\Delta T}{\sqrt{2mT}}. \quad (7.72)
\]

where the subscript $VS$ indicates velocity spread. The frequency spread due to a given ion-beam energy spread, $\Delta T$, can be reduced by increasing the kinetic energy of the ion beam. The initial energy spread of the ions extracted from the ion source, which is directly proportional to the velocity spread $\Delta u$, is related to the physical size of the region of extracted ions and the electric field in that region. Inhomogeneous broadening effects caused by inelastic collisions with the source gas in the region between the anode and the extractor worsens the broadening effect. The energy spread $\Delta T$ due to the initial velocity spread $\Delta u$ is given by
\[ \Delta T = \frac{1}{2} m (\Delta u_i)^2. \] (7.73)

The energy spread is unchanged as the ions are accelerated to a final kinetic energy \( T \).

The relation between the final velocity spread \( \Delta u \) and the initial velocity spread \( \Delta u_i \) can be obtained by combining equations (7.71) and (7.73). The result is

\[ \Delta u = \frac{1}{2} \sqrt{\frac{\Delta T}{T}} \Delta u_i. \] (7.74)

This relation demonstrates the concept of velocity compression as the ions are accelerated to higher kinetic energies [85]. The real energy spread of ions extracted from a hot discharge has not been measured quantitatively, but it can be estimated from the lineshape analysis of the observed resonance in the ions to range from a fraction of a meV to a few eV. Previous studies on \( \text{C}_2^- \) using a hot discharge source indicate that the velocity spread is greatly reduced by reducing the ion-source pressure [86]. In this experiment, the energy spread is expected to be small because the operating source pressure is about 30 mtorr. The linewidth sets an upper bound on the energy spread since the observed lineshape is a convolution of the "real" resonance, the laser linewidth, and the shape of the velocity distribution of the ion beam.

**Autodetachment result**

A single vibrational-rotational transition of \( \text{CH}_3^- \) has been obtained at a photon energy of 3206.74 cm\(^{-1}\), using a coaxial ion-laser beam apparatus. The line consist of a
strong autodetachment resonance from the rotational levels of CH$_3^-$ (v=1). Transitions from CH$_3^-$ (v"=0) to CH$_3$ (v'=1) were excited with photons from the FCL-20. The highly resolved line was obtained through scanning the Doppler shift of the ion beam and fitted to a Lorentzian for further analysis. The CH$_3^-$ transition is shown in Figure 32.

**Metastable autodetaching states of CH$_3^-$**

Metastable states in CH$_3^-$ were also observed unexpectedly and described in this section. The collision stripping signal of CH$_3^-$, as a function of pressure, had a stripping signal which was not proportional to the background pressure. This observation is indicative of long-lived metastable (vibrationally or rotationally) excited states in the anion. Results from other species, which do not exhibit this behavior, are compared and lifetime limits are imposed based on changing the ion's flight time through the system.

**Metastable states procedure**

During the investigation of metastable states discussed in this section, a mass-selected beam of CH$_3^-$ was produced, and the ion current in the Faraday cup was recorded, along with the fast neutral signal. The fast neutral can arise from collisions with background gas, from collisions with apertures, or from autodetachment. In order to distinguish the pressure-dependent component of the neutral signal from the pressure-independent component, the vacuum pump evacuating the interaction region was turned off, and the background pressure was allowed to rise from its normal operating pressure of 3 - 4x10$^{-8}$ torr. The ion current, background pressure, and neutral signal were recorded simultaneously. This procedure was performed both for CH$_3^-$ and
Figure 32. Observed rovibational transition in CH$_3^+$ with SNR $\approx$ 25:1. The bottom graph shows a Lorentzian fit through the data points which revealed a width (FWHM) of 22.65 MHz.
for a well-understood reference ion, O', for comparison. Typical source conditions for this experiment are listed in Table 14 below.

Table 13. Ion beam source conditions and parameters for CH₃⁻:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>ion source voltage</td>
<td>-2 kV</td>
<td></td>
</tr>
<tr>
<td>tube voltage</td>
<td>0 to +1 kV</td>
<td></td>
</tr>
<tr>
<td>O⁻ ion current</td>
<td>35 pA</td>
<td>typical</td>
</tr>
<tr>
<td>CH₃⁻ ion current</td>
<td>1 - 5 pA</td>
<td>typical</td>
</tr>
<tr>
<td>CH₃⁻ neutrals</td>
<td>1 - 2x10⁴ particles/second</td>
<td></td>
</tr>
<tr>
<td>CH₃⁻ neutrals/CH₃⁻ ions</td>
<td>0.3%</td>
<td></td>
</tr>
<tr>
<td>flight time of CH₃⁻ in tube</td>
<td>4.4 µs</td>
<td></td>
</tr>
<tr>
<td>effective electrometer resistance R</td>
<td>0.1 V/nA</td>
<td></td>
</tr>
<tr>
<td>electron multiplier gain G</td>
<td>3 - 10x10⁶</td>
<td>depends on applied voltage</td>
</tr>
<tr>
<td>Flight time from ion source to interaction region</td>
<td>7 µs</td>
<td></td>
</tr>
</tbody>
</table>

Results

Figure 33(b) shows the ratio of the fast neutral signal to the mass-selected O⁻ ion current, as a function of background pressure. The slope of the curve yields the collisional cross section. The curve goes almost exactly through the origin, indicating that the ion collisions with apertures are very unimportant. The behavior of O⁻ is therefore understood.

In contrast, the behavior of CH₃⁻ is anomalous. At the low pressures (3 - 4 x 10⁻⁸ Torr) of normal operation, the neutral signal is nearly independent of pressure. At higher pressure (10⁻⁶ Torr), the neutral signal increases measurably with pressure, as shown in Figure 33(a). Figure 33(a) also indicates a neutral signal that is not
Figure 33. (a) Shows the collisional stripping signal for CH$_3^-$ as a function of background pressure. There is a large pressure-independent offset, which is attributed to autodetachment. (b) The stripping signal for O$^\cdot$ goes through zero thereby verifying the pressure dependence.
proportional to the pressure; there is a large pressure-independent offset, which is attributed to autodetachment. At typical operating pressure of $3 - 4 \times 10^4$ torr, about 93% of the neutral signal are due to autodetachment. The signal cannot be due to scattering of the ion beam on the apertures of the tube, because that would also affect the other ions as well. Figure 33(b) shows that such a “beam-scraping” artifact is minimal for $\text{O}^-$, although of course it can be deliberately introduced by misfocussing the ion beam.

**Analysis**

Collisional cross sections for $\text{O}^-$ and for $\text{CH}_3^-$ can be extracted from the slopes of Figures. 33(b) and 33(a) respectively. The collisional cross section $\sigma_c$ is given in equation (7.20) and is shown here again for reference

$$\sigma_c = 6.49 \times 10^{-31} \left[ \frac{V_n}{\alpha p I} \right],$$  

(7.75)

where $V_n$ is the neutral signal measured from the 0.1 V/nA electrometer, $\alpha$ is the gain of the EMT, $p$ is the background pressure in the interaction region in Torrs, and $I$ is the ion current in Amperes.

The collisional cross section $\sigma_c$ depends on the nature of the background gas, which is presumed to be water. Our pressure reading is the uncorrected Bayard-Alpert ion gauge reading. A typical cross section for the collisional stripping process is in the range $10^{-20} - 10^{-19}$ m$^2$, or $1 - 10$ (Å)$^2$. In our apparatus, the gain $\alpha$ of the electron multiplier is about $0.3 - 1.0 \times 10^3$, depending on the voltage applied to the electron.

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multiplier, and the efficiency $\varepsilon$ is 0.95. The efficiency $\varepsilon$ was measured in a separate experiment using a Kr$^-$ ion laser at 647 nm and has already been described in Chapter VII. The visible photodetachment cross section of O$^-$ was measured absolutely by Branscomb et al [69].

The collisional stripping cross section of O$^-$ can be extracted from the slope of Figure 33(b). The solid line has a slope of a signal rise $V_s/I$ is 0.0031 V/pA for a pressure increase of $1 \times 10^4$ Torr (corresponding to a density increase of $3.2 \times 10^{14}$ m$^{-3}$). In this measurement, the electron multiplier gain $\alpha$ was $3 \times 10^6$. From Equation (7.20), the resulting collisional cross section $\sigma$ is 7.2 (Å)$^2$.

The collisional stripping cross section of CH$_3$ can be extracted from the slope of Figure 33(a), in which the data were taken to higher pressure in order to obtain the cross section. The electron multiplier gain $\alpha$ for this experiment was $1 \times 10^7$. A calculation yields a value of 2.6 (Å)$^2$. Both values are physically plausible. It should be noted that neither cross section has been corrected for a source of systematic error, the ion-gauge sensitivity of the unknown background gas, which is presumed to be water.

**Autodetachment lifetime estimates**

Our apparatus is not well designed for precise measurement of autodetachment lifetimes of metastable ions. However, some rough experimental limits can be placed on the lifetime, using two methods: First, the ratio of the neutrals detected to the ions in the Faraday cup is utilized to set an upper bound for the lifetime. Second, a rough lower bound on the lifetime was made by establishing limits on the decay of the methide ions during the flight through the apparatus.
First, the neutrals are measured relative to the ions. If the lifetime were too long, there would be no autodetachment-based neutrals at all. When the ion source is floated at -2kV, and the tube in the interaction region at +1kV, the ion kinetic energy is 3 keV. The resulting ion flight time through the 0.5 meter tube is 4.4 μs. The number of fast neutrals detected was 0.3% of the number of CH₃⁺ ions in the Faraday cup.

Assume that the methide beam emerges from the ion source with intensity I₀, having a stable fraction fₛ and an autodetaching fraction fₐ (hence fₛ + fₐ = 1), having (for simplicity) a single autodetachment decay time τ. Under these simplifying assumptions, after time flight t the ion current will be given by

\[ I(t) = I₀ \left[ fₛ + fₐ e^{-t/τ} \right] \]  

(7.76)

and the number of neutrals produced in a short time Δt will be

\[ -Δt \left( \frac{dl}{dt} \right) = \left( \frac{Δt}{τ} \right) I₀ fₐ e^{-t/τ} \]  

(7.77)

Dividing Equations (7.77) by (7.76) yields the ratio of the fast neutrals to ions,

\[ \frac{\text{neutrals}}{\text{ions}} = \left( \frac{Δt}{τ} \right) \left[ \frac{fₐ}{fₛ + fₐ e^{-t/τ}} \right] e^{-t/τ} \]  

(7.78)

We cannot proceed further without knowledge of the fractions fₛ and fₐ. An
upper bound on the lifetime can be obtained by assuming the extreme limit that \( f_0 = 0 \) and \( f_b = 1 \), so the entire beam is assumed to be metastable. Then Equation (7.78) yields simply \( \Delta t/\tau \). Since the ratio is observed experimentally to be 0.3%, with \( \Delta t = 4.4 \mu s \), this yields \( \tau = 667 \mu s \). This is an upper limit (probably unrealistic) on \( \tau \).

The second approach yields a lower bound on the autodetachment lifetime. If the autodetachment lifetime is very short compared with several microseconds, most of the ions will decay between the ion source and the interaction tube. In that case, altering the ion flight time would have a large effect on the fraction of \( \text{CH}_3^- \) ions that survives to reach the Faraday cup. Altering the ion flight time by varying the potential on the tube would then vary the \( \text{CH}_3^- \) ion current: longer flight times would correspond to a smaller \( \text{CH}_3^- \) ion current in the Faraday cup. Of course, varying the tube potential will have another effect, a focusing effect on the ion beam, which will also affect the ion current in the Faraday cup. In order to compensate for this important systematic effect, the ratio of the \( \text{CH}_3^- \) current to the \( \text{O}^- \) current is studied at two different flight times. By taking the ratio of the methide to \( \text{O}^- \) ions we hope to compensate for the focussing effects, which affect both autodetaching and non-autodetaching ions.

When the ion flight time was varied from 11.26 to 12.13 \( \mu s \), a difference of 0.87 \( \mu s \), the ratio of the \( \text{CH}_3^- \) current to the \( \text{O}^- \) current did not change, within the limits of our measurement, estimated to be approximately 4 - 5\%. This sets a lower bound on the lifetime. Assuming the applicability of Equation (7.78), and for simplicity assuming that the entire beam is autodetaching \( (f = 0, f_b = 1) \), a 5\% decay in 0.87 \( \mu s \) corresponds to a lifetime of \( 0.87/0.05 = 17 \mu s \). This is not a rigorous lower bound on the lifetime, because undoubtedly the \( \text{CH}_3^- \) ion beam contains some stable states that are stable against...
autodetachment.

Finally, for completeness it should be noted that present experiment approach is completely insensitive to autodetaching states with lifetimes much less than the 7 µs flight time between the ion source and the interaction region. Such states, produced in the ion source, will decay before the ions reach the interaction region.

State of theory

There have been a number of theoretical studies of CH₃⁻, which yield calculated values of the geometry, electron affinity, and vibrational frequencies (including the crucial inversion vibration). There are studies by Driessler et al. [64], Surratt and Goddard [63], Marynick and Dixon [61], Dykstra et al. [65], Lee and Schaefer [87], Ortiz [66], Kraemer et al [67], and unpublished work by Adamowicz [88] and Robins [89]. Simons and co-workers [57] [90] [91] [92], based on an approach by Berry [93], were able to formulate propensity rules [94] for vibration-rotation-induced autodetachment of diatomic anions, and thus they were able to explain the experimental measurement of autodetachment rates in NH⁻ by Neumark et al [12]. An extension of autodetachment propensity rules to polyatomics would be extremely valuable.

Comparison with previous studies

In the one and only previous experimental study on CH₃⁻ by Ellison et al. [56], they did not detect the metastable states reported here. One prosaic possible explanation is a lack of sufficient signal strength. Another more obvious reason is that their interaction region length is about 0.1 mm, which translates to about a 0.9 ns interaction time, and they do not detect fast neutrals in their PES experiments. More intriguingly,
the autodetaching states may be populated from an ion source employing diazomethane (used in the present work) but not ketene (used by Ellison, Engelking and Lineberger).

In principle, the long lifetime arising from autodetachment arises because of large geometry change between ion and neutral. The ion is expected on theoretical grounds to be pyramidal (give symmetry group), because it is isoelectronic with neutral ammonia, NH$_3$, which has been heavily studied; while neutral CH$_3$ is nearly planar. Some Franck-Condon factors have been calculated by Kraemer et al. [67] for methide and methyl radical. They calculated the Franck-Condon factors relevant to the photodetaching transitions observed in the experiment by Ellison, Engelking and Lineberger; i.e., from the stable $v'' = 0$ and $v_z'' = 1$ of the ion to various higher-energy $v'$ values of the neutral. In the present experiment, the relevant Franck-Condon factors are from higher energy states of the ion (above the autodetachment limit) to lower-energy states of the neutral.

Although there is no published theoretical study of the autodetachment process in CH$_3^-$, it is plausible to believe that small Franck-Condon factors can give rise to autodetachment lifetimes in the 10 microsecond range, based on two examples in the literature: OH$^-$ and CO$_2^-$.

Bae, Cosby and Peterson [95] found metastable autodetaching states of OH$^-$, with lifetimes exceeding 10 $\mu$s. The OH$^-$ beam was produced by passing a H$_2$O$^-$ beam through a Cs vapor target. Their data was consistent with vibrational autodetachment from vibrationally excited states (with $v'' > 4$) of the ground electronic state. Earlier, Dooverspike, Champion, and Lam [96] found metastable states of OD$^-$, having lifetimes of 10 $\mu$s, in collisions of O$^-$ and D.

Similarly, CO$_2^-$ is long-lived, even though the electron affinity is negative; i.e., the
ion is unstable with respect to autodetachment to neutral CO\textsubscript{2}. Cooper and Compton [97] produced beams of CO\textsuperscript{2−} from electron bombardment of succinic anhydride (C\textsubscript{4}H\textsubscript{4}O\textsubscript{3}), maleic anhydride (C\textsubscript{4}H\textsubscript{6}O\textsubscript{3}), and 1,2-Cyclo-butane dicarboxylic anhydride (C\textsubscript{6}H\textsubscript{6}O\textsubscript{3}), producing metastable autodetaching CO\textsuperscript{2−} with lifetimes of 26 ± 5, 60 ± 5, and 46 ± 5 μs. Metastable CO\textsuperscript{2−} ions were also produced from glutaric anhydride (C\textsubscript{5}H\textsubscript{6}O\textsubscript{3}), although no lifetime was stated. The ion is bent, while the neutral is linear. The small Franck-Condon factors inhibit autodetachment and result in a metastable anion. In addition, metastable, internally excited states of other polyatomic ions (e.g., SF\textsubscript{6}−), produced by electron impact, were reviewed by Christophorou [98].

Metastable states conclusion

Metastable autodetaching states of methide, CH\textsubscript{3}−, have been observed, with an autodetachment lifetime in the range of 17 to 667 μs. The autodetaching states are unknown, but could be a vibrationally excited state, because since the electron affinity is low (0.080 eV = 643 cm\textsuperscript{-1}), one vibrational quantum of the \textit{v}_1, \textit{v}_2, or \textit{v}_4 vibrational mode has sufficient internal energy to produce autodetachment of the low electron affinity ion. Alternatively, the autodetaching states could be rotationally excited states of the ground vibrational state, with \textit{J} values greater than 8 (see Chapter 7; Rovibrational line spectrum prediction). The long lifetime may arise from small Franck-Condon overlap between the initial pyramidal ion and the final planar neutral. There are presently no theoretical calculations of the autodetachment mechanism or lifetimes. Experimentally it may be possible to distinguish between the alternatives, by performing a laser-excited experiment from a stable to an autodetaching state. In this work, metastable autodetaching states of
$\text{CH}_3^-$ are reported for the first time. Rough limits are placed on the autodetachment lifetime. These states were not predicted by any theoretical calculation beforehand. We hope that this work stimulates theoretical attention to this problem.
CHAPTER VIII

VACUUM ULTRAVIOLET STUDIES OF NO\(^{-}\), O\(_2\)^{-} AND O\(^{-}\)

Introduction

The source of intense VUV photon energy from the 1.9 GeV synchrotron was utilized to explore the double photodetachment process in negative molecular ions NO\(^{-}\), O\(_2\)^{-}, and one negative atomic species, O\(^{-}\). This chapter discusses the experimental apparatus, experiment, and the cross sections in a photon energy range of 20-100 eV and makes comparisons to simple theoretical models. Currently, there is no theoretical calculation on the observed nature of this cross section in this energy range in these negative molecular ions.

ALS

The Advanced Light Source (ALS), a division of Lawrence Berkeley National Laboratory, is a national user facility that generates intense light for scientific and technological research. Constructed in 1993, the facility has the world's brightest source of ultraviolet and soft x-ray beams in addition to being the world's first third-generation synchrotron light source in its energy range. Scientists studying materials such as atoms and molecules use x-rays to determine the electronic and
internal energy structure. The ALS produces light in the x-ray region of the electromagnetic spectrum that is a billion times brighter than the sun. Figure 34 illustrates typical brightness from familiar sources for comparative purposes. This extraordinary tool offers unprecedented opportunities for state-of-the-art research in materials science, biology, chemistry, physics, and the environmental sciences. Ongoing research topics include the electronic structure of matter, semiconductors, crystallography, polymers, ozone, photochemistry, and optics testing. ALS research includes studies of HIV [99]. For Earth and environmental sciences, studies in photodissociation of the ozone layer have been feasible. In physical chemistry, a recent important discovery made by the Lindle group at the ALS was the unexpected breakdown in the dipole approximation at sufficiently low photon energies [100].

**ALS theory of operation**

Figure 35 illustrates the principal components of the beam. The linear accelerator, or linac, is the electromagnetic catapult that accelerates electrons from rest to relativistic velocity in a distance of only 4 meters. The linac includes an electron gun and a buncher. The electron gun assembly generates the electrons and initiates acceleration. The electrons start out in a 1 cm² sample of barium aluminate, at the cathode of the electron gun, which has a negative electrical bias relative to the anode. Barium aluminate is a thermionic material whose electrons boil off when heated above the work function of the material near the surface of the cathode, thereby creating the negative charge of the cathode. A gate consisting of a copper grid is pulsed with a high
Figure 34. A brightness comparison of familiar items to the ALS insertion devices such as undulators and bending magnets. Undulators produce light that is a billion times brighter than the sun.
Figure 35. Illustration of ALS principal components and location.
positive voltage at 500 MHz, which causes electrons to accelerate from the cathode
toward the grid in bunches every 2 ns. The electron gun functions much like a triode
tube: the electrons are attracted to the gate and the electrons travel through the gate to
the anode. The anode, which is a shaped like a toroid, also has electromagnetic windings
around it to create a magnetic field that confines the electrons along the direction of
propagation through the hole into the next part of the accelerator, the buncher.

The purpose of the buncher is to pack the pulsing electrons into bunches and
accelerate them as they come out of the electron gun. Powerful microwave radiation
from the klystron drives the buncher to accelerate the electron bunches in the way that
ocean waves accelerate surfers on surfboards. A detailed description of klystrons is given
later in this section. Figure 36 illustrates this effect, which shows the power of the
microwave radiation in the buncher. The electrons receive more energy from the
microwave radiation, which produces more acceleration, depending on their position
relative to the crest of the wave. The linac itself is just an extension of the buncher. It
receives additional RF power to continue accelerating the electrons and it compacts them
into tighter bunches. Electrons enter the linac from the buncher at a velocity of 0.6 c. As
the electrons leave the linac, they are traveling very close to the speed of light. In spite of
this accomplishment, a linac, in general, is not an efficient way to accelerate a particle to
relativistic speeds. By comparing the ratios of the linear and centripetal forces exerted by
the accelerated particles, the enormity of the difference can be realized. The relativistic
momentum of a particle is given as
Figure 36. (a) Schematic of the Linac. (b) Illustration of the buncher effect.
\[ \ddot{p} = \gamma m \ddot{v} \] (8.1)

but if \( \ddot{v} \) changes only in direction, as in circular motion, the force exerted on the particle is

\[ \vec{F}_\perp = \frac{d}{dt} (\gamma m \ddot{v}) \] (8.2)

which is

\[ \vec{F}_\perp = \gamma m \frac{d\ddot{v}}{dt} \] (8.3)

or

\[ \vec{F}_\perp = \gamma m \ddot{a}_\perp . \] (8.4)

If \( \ddot{v} \) changes only in magnitude, as in linear motion, the force exerted by the particle is

\[ \vec{F}_\parallel = \frac{d}{dt} (\gamma m \ddot{v}) \] (8.5)

which is

\[ \vec{F}_\parallel = \gamma^3 m \frac{d\ddot{v}}{dt} \left( \frac{1}{\gamma^3 + \beta^2} \right) \] (8.6)

where the bracket term in equation (8.6) is equal to 1 in the limit of \( \beta \) approaching either 0 or 1. Therefore, equation (8.6) can be rewritten as
If both accelerations are the same, \( |\vec{a}_\perp| = |\vec{a}_\parallel| \), then \( F_\parallel / F_\perp = \gamma^2 \). In the limit of \( \beta \) approaching 1, the force exerted on a relativistic particle moving in a straight line is extremely large compared to the force on a particle moving in a circle with the same magnitude of acceleration. In other words, a linear accelerator would require a tremendous amount of energy to propel a particle at relativistic speeds over an extremely large distance. Therefore, a linac long enough to accelerate electrons to the energy needed by the ALS would not fit inside the building. Instead, a circular booster synchrotron is used to give electrons an additional "boost" from an accelerating chamber (RF cavity) each time they go around. In less than one second inside the booster, the electrons make \( 1.3 \times 10^6 \) revolutions (and travel 98,000 kilometers), reach 99.999994% of the speed of light, attain their target energy of 1.5 GeV, and are ready to be transported to the storage ring.

Once the electrons reach their target energy in the booster synchrotron, an injection system transfers them from the booster to the storage ring where they circulate for hours. The electrons travel in an aluminum vacuum chamber with fewer atoms per unit volume than outer space (the pressure is about one trillionth that of the atmosphere), so there are essentially no collisions to slow them down. The storage ring is roughly circular with 12 arc-shaped sections (approximately 10 meters long) joined by 12 straight sections (approximately 6 meters long). Hundreds of precision electromagnets focus and
bend the electron beam as it circles the storage ring more than a million times a second. Electrons curving through the ring's 12 arc sections at relativistic speeds emit a narrow cone-shape beam of photons, like the headlights of a car rounding a bend at night. Jackson [101] explains this phenomenon by choosing a coordinate system such that instantaneously \( \dot{\beta} \) is in the \( z \) direction, \( \dot{\beta} \) is in the \( x \) direction, and customary polar angles \( \theta, \varphi \) defining the direction of observation, the differential radiative power per solid angle is given by

\[
\frac{dP}{d\Omega} = \frac{e^2}{4\pi c^3} \frac{|\dot{v}|^2}{(1 - \beta \cos \theta)^3} \left[ 1 - \frac{\sin^2 \theta \cos^2 \varphi}{\gamma^2(1 - \beta \cos \theta)^2} \right].
\] (8.8)

In the limit as \( \beta \) approaches 1, the angular distribution is tipped forward more and more toward the \( z \) axis and increase in magnitude because \( d\Omega \) decreases. The angle \( \theta_{\text{max}} \) for which the intensity is maximum can be found by setting \( dP/d\Omega = 0 \). The angle \( \theta_{\text{max}} \) is

\[
\theta_{\text{max}} \approx \frac{1}{2\gamma}.
\] (8.9)

Between the curved sections of the storage ring are straight sections where insertion devices called undulators and wigglers modulate the electrons trajectory in a sinusoidal path to form a narrow beam of light 100 million times brighter than conventional x-ray sources. Undulators contain over one hundred permanent magnetic poles lined up in rows above and below the electron beam. The magnets force the
electrons into a sinusoidal path, so that the light from all the poles interferes constructively. This provides the brightest coherent light possible. Although they are about 4.5 meters long and weigh about 40,000 pounds, the undulators are built with extreme precision. Many of the design tolerances are approximately 50 μm. Wigglers are similar to undulators but have fewer magnetic poles and the magnetic field is stronger than those in undulators. The stronger magnetic fields cause a larger deviation in the electrons trajectory compared to the emission cone of radiation, which results in no coherence between the radiation emitted from each pole. The difference in spectrum between an undulator and a wiggler is as follows.

Insertion devices, such as undulators and wigglers, are characterized by the magnetic period length λ₀ and the magnetic field strength which can be described by the dimensionless wiggler parameter

$$K = \frac{e\lambda_0 B_0}{2\pi mc} \quad (8.10)$$

where e is the electron charge, m is the mass, B₀ is the amplitude of the periodic magnetic field on axis, and c is the speed of light. The periodicity of the magnet structure leads to a corresponding periodicity in the emitted electromagnetic radiation. For small K a dipole radiation pattern is obtained which when transformed to the lab frame of reference produces the first undulator maximum. As the K value is increased, the radiation patterns become more complex and significant intensity is generated in higher-order harmonics. For a symmetric device, only odd harmonics n are obtained on axis at wavelengths given by
\[ \lambda_n = \frac{\lambda_0}{2\gamma^2 n} \left( 1 + \frac{K^2}{2} \right), \quad n = 1, 3, 5, \ldots \tag{8.11} \]

or corresponding photon energies

\[ E_n = n \frac{hc}{\lambda_0} \left( \frac{2\gamma^2}{1 + \frac{K^2}{2}} \right), \quad n = 1, 3, 5, \ldots \tag{8.12} \]

where \( h \) is Planck's constant, \( \gamma \) is the relativistic correction factor, and \( n \) is the harmonic order number. The width of the undulator maximum is proportional to \( 1/nN \), where \( N \) is the number of periods, and the position of the maximum can be changed by altering \( K \) through variation of the gap between the poles of the permanent magnets. For a well-collimated electron beam, the increase in spectral brightness is proportional to \( N^2 \). The maximum deflection angle of the electron trajectory is given by \( K/\gamma \) and the angular opening of the radiation cone is \( \equiv \gamma^4 \). Thus, undulators are classified as devices with \( K \leq 1 \) and wigglers with \( K > 1 \). The total radiated power is proportional to \( K^2 \), so wigglers are high-power broadband devices, whereas undulators provide a quasimonochromatic beam in a very small solid angle. As the electrons travel in their circular orbit in the storage ring and through various insertion devices, they emit synchrotron light in the ultraviolet and x-ray range of the spectrum. Beamline optics steers and focuses a thin beam of light from the storage ring down meters of vacuum pipe to the experiment stations. Scientists are able to select photons energies with monochromators in situ with
the beam lines.

The radio frequency (RF) system supplies power to the ALS components in the form of microwaves. Microwaves are radio waves whose wavelengths extends just outside of 1 mm to 1 m range. However, most parts of the RF system supply microwave radiation with wavelength of about 0.6 m (500 MHz). Microwave power synchronizes the electron’s kinetic energy, maintaining their trajectory around inside the ALS storage ring at nearly the speed of light. The electrons release energy in the form of synchrotron radiation as x rays and ultraviolet light. The ALS’s RF power supplies replenish the electron’s kinetic energy after they release energy as synchrotron radiation. The basic components of the RF system include klystrons (a very powerful type of microwave amplifier), waveguides, and RF cavities.

The RF cavities receive RF energy from a klystron and transfer it to electrons as they pass through the cavities on their way around the booster synchrotron and storage rings. RF radiation interacts with electrons, supplying energy to increase or maintain their speed. In the storage ring, two RF cavities replenish energy to the electrons (approximately 100 MeV per revolution around the storage ring) which they lose after emitting synchrotron light.

The RF cavity is configured to transfer maximum power at 500 MHz, which is the frequency at which the electron bunches pass. The cavity is made out of very pure copper so that the current induced by the radiation will be spread evenly over its interior. Cooling coils wrapped around the cavities prevent them from overheating and possibly melting. The microwaves in the cavity are synchronized to the crest in which each bunch of electrons enters the cavity (every 2 ns), so that the bunch is accelerated by a wave that
is approaching peak amplitude. This synchronization takes into account the time it takes
the control signal to reach the controls for the klystron, the time it takes the microwave
radiation to reach the RF cavity, and the relativistic mass of the electrons in the storage
ring.

**ALS IPB endstation**

The ALS ion-photon-beam (IPB) endstation is designed for photoion
spectroscopy, photoionization cross-section measurements, and excitation spectra of
multiply charged positive and singly charged negative ions. The high brightness and low
emittance that characterize the ALS make it an ideal facility for the study of photon-ion
interactions. A common objective of the experiments to be conducted at the IPB is to
gain a deeper understanding of the complex multielectron interactions that govern
inelastic processes occurring in ionized plasmas, which constitute more than 99.99% of
the known mass in the universe. The IPB endstation, which is designated as beamline
10.0.1 in Figure 37, has been designed for absolute measurements, which are important
for benchmarking theoretical calculations of x-ray opacities. These are critical to the
modeling of astrophysical, fusion, pulse-power, and x-ray laser plasmas. Systematic
studies along isoelectronic and isonuclear sequences of ions will permit a fine-tuning of
their electronic structures and therefore provide a sensitive probe of the electron-electron
interaction. The following table indicates the IPB endstation specification:
Figure 37. General layout of ALS and various endstations that are operational and underconstruction as of May 2001.
Table 14. ALS IPB 10.0.1 endstation specifications.

<table>
<thead>
<tr>
<th>Description</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photon Energy Range</td>
<td>17-340eV</td>
</tr>
<tr>
<td>Photon Flux</td>
<td>( \leq 10^{12} ) photon flux at ( E/\Delta E = 10,000 ) could be more for lower ( E/\Delta E )</td>
</tr>
<tr>
<td>Spectral Resolution</td>
<td>( E/\Delta E &lt; 10,000 ) (selectable by slit width)</td>
</tr>
<tr>
<td>Spot Size</td>
<td>1.5 (h) X 1.5(v) mm</td>
</tr>
</tbody>
</table>

Typically, the IPB endstation is configured either for a Colutron ion gun apparatus (CIGA), electron cyclotron resonance (ECR) source, or a Source of Negative Ion by Cesium Sputtering (SNICS) source. However, the IPB endstation was reconfigured for retrofitting our hot-cathode high-pressure source for negative ion studies in the gas phase for the first time. Our high-pressure source was re-engineered to adapt to the ion-photon beam line. Much of the beam apparatus was very similar to the Big Beam.

**IPB general operation**

The IPB endstation is based on the technique of photo-ion spectroscopy, and is illustrated schematically in Figure 38. A well-focused and collimated beam of ions of typical energy 6 keV and diameter 2 mm is merged electrostatically with the photon beam from the ALS 10-cm period undulator on beamline 10.0. Positive photo-ions produced in an electrically insulated cylindrical interaction region of length 29.4 cm (typically biased at + 2 kV for positive ions) are magnetically analyzed upward at 45°,
Figure 38. Illustration of IPB endstation components and descriptions.
deflected 90° by spherical analyzer and counted as a function of photon energy. The
two-dimensional spatial intensity distributions of the ion photon beams are measured
along the merged path by two rotating wire beam profile monitors located upstream and
downstream of the central interaction region. In the center of the interaction region, a
translating-slit scanner moves into the beams from above in a vertical motion. This
scanner has two narrow slits oriented at ±45° from the horizontal, to measure the spatial
beam intensity distribution along two orthogonal axes with a single translational motion.
A microspherical-plate detector registers secondary electrons produced by impact of the
photo-ions onto a negatively biased stainless-steel plate (typically at ~400V). The photo-
ion detection system may be absolutely calibrated using a high-sensitivity current meter.
The photo energy and spectral resolution are selected by a precision grating
spectrometer. The gap of the 10 cm period undulator is continuously varied during scans
of the photon energy to optimize the photon beam intensity at each selected energy. The
photon beam is chopped at a frequency of 1 Hz by a stepping-motor-controlled
mechanical shutter to subtract the background in the photo-ion channel due to stripping
collisions of primary ions with residual gas. The absolute photon beam intensity is
measured by a calibrated and biased silicon protodiode.

Ultra-High Vacuum System

To reduce background in the photo-ion channel due to collisions with residual gas,
the merged-beams technique typically operates at a vacuum in the 10^-10 Torr range. This
is accomplished by a 1,000 ℓ/s turbomolecular pump located near the ion beam entrance
into the endstation, a 2,000 ℓ/s cryopump located in the beam merging cross, and two
500 ℓ/s mag-ion pumps located at the center of the interaction region and just
downstream of the demerging magnet. A small mag-ion pump is installed on the ion
detector chamber to provide additional pumping, but is normally turned off during data
taking to reduce the background counts in the product ion detector. The particular
combination of vacuum pumps has been designed to minimize the loading of the vacuum
system by gases from the ion source and by the ion beam itself for the variety of gases
and ion species anticipated during the experiments. Oil-free scroll backing pumps are
used for the turbomolecular pumps on the ion source and endstation to ensure the
integrity of the ultra-high vacuum system, and to meet ALS standards for hydrocarbon
contamination in the beamlines. The turbomolecular pump and cryopump have air-
actuated gate valves to isolate them from the vacuum system. Switches located on a
panel on the endstation control these valves. These two pumps are valved and turned off
to minimize wear during periods when the endstation is idle, and to prevent possible
venting of the vacuum system to the atmosphere during power interruptions. Turning off
the cryopump during idle periods also allows it to be purged of accumulated gases off-
line using a portable pumping station. During such idle periods, the endstation vacuum is
maintained close to the base vacuum by the three mag-ion pumps. The vacuum in the
endstation may be monitored by the meters on the ion pumps, and by two nude
ionization gauges (labeled UHV-1 and UHV-2) controlled by the multigauge unit on the
endstation. After any exposure to atmosphere, the endstation must be baked to 100 °C for
several days to reach base vacuum.
Ion Beam Analysis and Transport

The analyzing magnet serves as the mass spectrometer by deflecting a collimated ion beam emerging from the ion source depending on its charge-to-mass ratio. The ion beam is deflected through $60^\circ$ and has radius of curvature of 60 cm. The required magnetic field for a given ion beam may be estimated from the following empirical formula

$$B = 57 \frac{\sqrt{mE}}{q}$$

(8.13)

Where $m$ is the ion mass in amu, $E$ is the ion beam energy in keV, and $q$ is its charge state (an integer), and $B$ is the magnetic field in Gauss.

The direction and position of the ion beam trajectory may be adjusted by two sets of vertical and horizontal steering plates, labeled H1, H2 and V2. The ion beam axis may be offset horizontally by setting H1 and H2 to equal values but opposite polarities using the reversing switches located just above the modular Bertan power supplies. Similarly, the ion beam axis may be offset vertically by setting V1 and V2 to equal values but opposite polarities. The order of the polarities determines the direction of offset. The ion beam encounters the plates with label 1 before label 2. Unequal values on V1 and V2 will give a combined beam offset and deflection.

Three cylindrical Einzel lenses focus the ion beam. Einzel lens 1 is located just upstream of the steering plates. Einzel lenses 2 and 3 are located just upstream and
downstream of the central interaction region, respectively. They are operated as deceleration lenses (i.e. with the same polarity as the ion beam charge). Lenses 1 and 2 are critical to the transport and overlap of the ion beam with the photon beam. Lens 3 serves as a diagnostic to guarantee complete collection of photo-ions, and is usually turned off during data collection (V=0). Typically, for a 6 keV positive ion beam. Einzel lens 1 has a voltage of +2.5kV and Einzel lens 2 has a voltage of +4.5kV.

For beam tuning purposes, removable Faraday cups are located behind the spherical merger on the ion beam axis emerging from the main analyzer magnet (Cup2), and behind the demerger magnet (Cup3). A third fixed Faraday cup is located behind the spherical deflector that is just upstream of the photo-ion detector (Cup3 or detector cup). These cups are used to tune the ion beam sequentially through the endstation.

The ion beam is merged onto the photo beam axis by spherical deflectors to which positive and negative voltages are applied. The outer plate must have the same polarity as the ion beam charge. The trajectory of the ion beam in the interaction region may be shifted horizontally by making these voltages slightly asymmetric. The sum of the absolute values of the two voltages (approximately 28% of the ion beam accelerating voltage) determines the angle of the trajectory. The angle should be 90° for an optimal overlap with the photon beam.

NEC rotating-wire beam profile monitors installed just upstream and just downstream of the central interaction region permit real-time monitoring of the horizontal (x) and vertical (y) profiles of the ion and photon beams on an oscilloscope. These are controlled by rack-mounted modules located on the end-station. A multiplexer and switching box permits the signals of either monitor to be directed a digital storage
oscilloscope. To prevent wear and tear of the motor-driven devices, as well as spurious background, these devices should be turned off during photoionization measurements, or whenever their output is not being monitored. A computer-controlled translating slit scanner is also located at the center of the interaction region. The scanner moves into the beams from above in a vertical motion. The scanner has two narrow slits oriented at 45° from the horizontal, to measure spatial beam intensity distributions along two orthogonal axes with a single translational motion.

The central interaction region consists of an electrically isolated cylindrical tube with one apertures on each end to control fringing electric fields. The effective length is 29.4 cm. The tube is constructed of wire mesh to ensure good vacuum within the tube. It permits energy labeling of photo ions produced within the tube, and accurate absolute cross section measurements to be determined because the interaction length of the beams and their spatial overlap are well defined. A decelerating voltage on the tube of about 1/3 of the ion accelerating voltage has been observed to improve the signal-to-background ratio for positive ions because the stripping cross section on residual gas decreases rapidly with decreasing energy. For example, a 6 keV X⁺ ion beam decelerated by +2 kV on the tube will interact with the photon beam within the tube at kinetic energy of 4 keV and the X²⁺ photo-ions will be charge analyzed downstream at 8 keV. For double-photoionization of negative ions, accelerating or decelerating voltage will have opposite and double the effect on the lab energies of photo-ions downstream of the tube (because of the change in the sign of the charge). For example, a 6 keV X⁻ beam decelerated by −2 kV on the tube will interact with the photon beam in that region at 4 keV, but X⁻ photo-ions produced within the tube will be charge-analyzed downstream at 2 keV.
Because of the large effect on the final kinetic energy of the photo-ions, and probable
defocusing, less deceleration and/or use of Einzel lens 3 to re-focus the photo-ions may
be optimal for experiments with negative ions.

A dipole magnet deflects the ion beam vertically, thereby demerging the beams.
The photo-ions are deflected upwards by $45^\circ$ and then $90^\circ$ in the transverse direction by
spherical electrostatic deflector shown in Figure 39. This allows the photo-ions to be
swept across the detector in two orthogonal directions to guarantee their complete
collection. Voltages $+V$ and $-V$ are applied to the outer and inner spherical surfaces,
respectively. The demerger/analyzing magnetic field $B$ and magnitude of the spherical
deflector voltage $V$ are given approximately by

$$B = 135 \frac{\sqrt{mE}}{q}$$

and

$$V = 140 \frac{E}{q}$$

where $m$ is the ion mass in amu, $E$ is the energy of the photo-ions in keV, $q$ is their
charge state (an integer), and $B$ is magnetic field in Gauss. The positive parent ions are
deflected less by the magnet and collected in a large Faraday cup, which has a hole
through which the photo-ions pass. Negative parent ions are collected in a separate
Faraday cup located below the magnet. The ability to simultaneously collect the negative
parent beam in this cup determines the maximum decelerating (or
Figure 39. Cross section illustration the demerging magnet, Faraday cups, and MCPs. Note that cations are deflected upwards while anions are deflected downwards.
accelerating) voltage that is possible in the interaction region.

The ion detector consists of a stainless steel plate to which a potential in the range -150 to -450 Volts is applied. Secondary electrons from the plate are accelerated to a microsphere-plate detector, to which the maximum applied voltage is +3,500 V. This voltage should be applied slowly while observing the pulses from the amplifier on an oscilloscope. The discriminator should be set to the minimum value to eliminate most of the spurious noise counts when the ion beam is absent (typically 0.3 V). The pulse transmission through the electronics will then be about 0.7. The detector response has been observed to be linear up to count rates of 100 kHz.

An absolutely calibrated and biased Si photodiode is installed on a linear motion feedthrough at the end of the endstation closest to the walkway. For initial alignment or troubleshooting, the photodetector can be moved off the photo beam axis to allow the photons to strike a phosphor deposited on a vacuum window at the end of the beamline. The photodetector should be repositioned such that it is centered on the photon beam (as judged by monitoring the output current). The absolute sensitivity of the photodiode as a function of photon energy was measured by Bozek [102] and is given by

\[ \varepsilon = 0.258E_{\gamma} - 1.49 \, \text{(electrons/photon)} \tag{8.16} \]

where \( E \) is the photon energy in eV.

A computer-controlled mechanical beam flag is installed in the photon beamline just upstream of the endstation. This has been used to block the photon beam, and also to chop the photon beam at a frequency of approximately 1 Hz in order to subtract
background due to collisional stripping of ions by residual gas. A higher speed photon beam chopper is currently under development.

**Interfacing the Ion Source to the IPB Endstation**

The high-pressure source described in Chapter II was affixed to the IPB endstation. A custom flange was machined to mate properly to both our high-pressure source and the IPB Einzel lens assembly. The IPB Einzel lens assembly is housed inside a special NEC flange chamber (part number 2JD020410). The Einzel lens extractor cone extends out past the NEC flange by 1". The NEC flange is a special 8" OD flange with a raised surface with dimensions 6 27/32" OD and 6 3/16" ID. Thus, the custom mating flange was machined with a 6 1/2" nominal diameter recessed 1/8" deep, width 3/32" O-ring groove to seal with the NEC raised surface side. Figure 40 shows an exploded view of our Branscomb source, Plexiglas insulator flange, custom mating flange, and the NEC Einzel lens assembly.

The power supplies that bias the high-pressure source are nearly configured the same as in Figure 9 from Chapter III. However, the main difference is that everything is referenced from the outside chamber of the Einzel lens and is understood to be at ground potential. Moreover, the Power Designs Model 1570 3 kV supply power is not used because the IPB's 10 kV power source is used instead, and is biased relative to the same chassis ground. As in Figure 9, all remaining sources and regulators are floated relative to the IPB endstation power supplies. For protection from inadvertent electrical
Figure 40. Exploded diagram of high-pressure ion source and the ALS IPB enstation adaptation.
shock from potentials present in the power supply chassis and floating potential reference, the power supplies for the high-pressure source were installed in fail-safe interlocked protective cage rack. Whenever the door is opened to service the high-pressure source, all power present in the cage is immediately turned off.

A tank of nitrous oxide (N$_2$O) was used for the parent gas for the entirety of the experiment and was introduced to the high-pressure source through the usual high-pressure precision leak super valve and teflon tubing. The optimum ion beam source conditions were similar to that indicated in Table 7 except for a few minor differences.

The following table shows typical values during the experiment

<table>
<thead>
<tr>
<th>Table 15. Optimum ion source conditions at IPB</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Source gas</strong></td>
</tr>
<tr>
<td>Nitrous Oxide (N$_2$O)</td>
</tr>
<tr>
<td><strong>Filament</strong></td>
</tr>
<tr>
<td>thoriated-iridium ribbon</td>
</tr>
<tr>
<td><strong>Filament current</strong></td>
</tr>
<tr>
<td>5-6 A</td>
</tr>
<tr>
<td><strong>Filament supply voltage</strong></td>
</tr>
<tr>
<td>4 V</td>
</tr>
<tr>
<td><strong>Emission current</strong></td>
</tr>
<tr>
<td>4 mA</td>
</tr>
<tr>
<td><strong>Discharge voltage</strong></td>
</tr>
<tr>
<td>80V</td>
</tr>
<tr>
<td><strong>Pressure in the IPB extraction region</strong></td>
</tr>
<tr>
<td>2 x10$^{-2}$ torr</td>
</tr>
<tr>
<td><strong>Estimated ion-source pressure</strong></td>
</tr>
<tr>
<td>15 mtorr</td>
</tr>
<tr>
<td><strong>IPB beam voltage</strong></td>
</tr>
<tr>
<td>5 kV</td>
</tr>
<tr>
<td><strong>Ion current (e. g. O$_2$)</strong></td>
</tr>
<tr>
<td>10 nA (Faraday cup 1)</td>
</tr>
</tbody>
</table>

**Signal to Noise Prediction**

The signal to noise criteria is an important benchmark for this particular experiment in measuring double photodetachment cross sections. As in the Big Beam apparatus and its experiments, the signal to noise (SNR) is highly dependent on the
source conditions. A conservative estimate of the SNR is made here to gauge the experiment success in terms of its SNR.

If we can measure the ion current in the IPB endstation we can predict the number of ions in the machine per unit time by

$$N = \frac{I}{e}.$$ (8.17)

Here, $N$ is the number of ions per unit time, $I$ is the ion current, and $e$ is the electron charge.

The IPB photon flux is specified at about $10^{12}$ photons per second at 0.01% bandwidth. For a larger bandwidth, the photon flux is expected to be larger, perhaps by as much as a factor of 10 better. The probability of detachment $\psi$ is given as

$$\psi = \sigma \left( \frac{\Phi}{A} \right) \left( \frac{L}{v} \right)$$ (8.18)

where $\sigma$ is the photodetachment cross section (typically around $10^{-17}$ cm$^2$ for single detachment processes in the visible but probably smaller for higher photon energy), $\Phi$ is the photon flux, and $A$ is the area of the ion beam, $L$ is the interaction length of about 30 cm, and $v$ is the velocity of the ions. The velocity $v$ can be defined further in terms of the beam voltage by

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where \( e \) is the electron charge, \( V \) is the beam voltage, and \( M \) is ion mass. For example, for an ion current of 1.25 nA of \( \text{O}_2^+ \) and a beam voltage of 4 kV, the velocity is \( 1.55 \times 10^7 \) cm/s, and the number of ions in the machine at any instance is about 15,120.

Our predicted signal count rates is the same as the total detachment rate \( S \). where

\[
S = \varphi N
\]  

(8.20)

or

\[
S = \sigma \left( \frac{\Phi}{A} \right) \left( \frac{L}{e} \right) \left( \frac{1}{v} \right)
\]  

(8.21)

Therefore, if \( A = 0.0225 \) cm\(^2\), \( \Phi = 10^{13} \) photons per second, \( \sigma = 10^{17} \) cm\(^2\), the predicted count rate is about 90 counts per second. Moreover, the signal to noise ratio (SNR) is shown as

\[
\text{SNR} \propto \sqrt{S \sqrt{\tau}}
\]  

(8.22)

where \( \tau \) is the integration time. Thus, the predicted SNR is about 9.5. Some typical photo-induced count rates observed in the experiment were about \( 1.5 \times 10^4 \) and total count rates were about \( 2 \times 10^6 \) for an integration time of 10 seconds. These measure values corresponds to a SNR of about 10.6, which is in good agreement with the
Double photodetachment theory

The ALS IPB endstation was used to study double photodetachment cross sections in molecular anions in gas phase for the first time in the vacuum ultraviolet (VUV). A single photon is responsible for removing two electrons as shown as

\[ XY^- + h\nu \rightarrow XY^+ + e^- \]  \hspace{0.5cm} (double photodetachment)

unlike single photodetachment process discussed in Chapter VII,

\[ XY^- + h\nu \rightarrow XY + e^- \]  \hspace{0.5cm} (single photodetachment)

Note that in the double photodetachment process not only does the anion undergo a charge state change of two but also the final cation maybe left in some excited state.

The VUV photon energy in not sufficient enough to remove a K-shell electron from any of the species studied in this experiment. The binding energy for a K-shell electron in oxygen and nitrogen is 543.1 and 409.9 eV respectively [103]. These values aren’t expected to change much in their anion configurations because the binding energy of the outer most electron is a small perturbation on the order of a eV compared to binding energies of the inner shell electron. However, the probability of removing a L-shell electron is high with photon energies in the VUV thereby leaving a vacancy in the L shell. An electron from within the L-shell with slightly higher energy immediately fills the
vacancy, however, the energy released from the deexcited L-shell electron is enough to eject yet another electron most likely from the same L shell. This whole process is best described by the radiationless Auger process [104], which was first discovered by Pierre Auger in 1923 in a x-ray cloud-bubble chamber and heavily investigated in many publications [105] [106] [107] [108] [109]. Wentzel formulated the quantum-mechanical theory of radiationless transitions in 1927. From perturbation theory, the nonrelativistic matrix element for a direct Auger transition is

\[
D = \int \int \psi^*_{n\gamma\gamma'}(1)\psi^*_{l\lambda\lambda'}(2) \left| \frac{e^2}{r_{12}} \right| \psi_{nlj}(1)\psi_{n'l'j'}(2) d\tau_1 d\tau_2 \tag{8.23}
\]

whereas the exchange Auger process is given as

\[
E = \int \int \psi^*_{n\gamma\gamma'}(2)\psi^*_{l\lambda\lambda'}(1) \left| \frac{e^2}{r_{12}} \right| \psi_{nlj}(1)\psi_{n'l'j'}(2) d\tau_1 d\tau_2 \tag{8.24}
\]

In either case, the quantum numbers \( n, l, \) and \( j \) characterize electrons that are identified schematically in Figure 41. Note that in the physically indistinguishable exchange process, described by matrix element \( E \), the roles of electrons \( nlj \) and \( n'l'j' \) are interchanged.

The Auger-electron energy is
Figure 41. Graphical representation of two possible non-radiative Auger process.
The subscripts pertain to the states indicated in Figure 41. The absolute values of both $E_{n'r'}$ and $E_{n'}$ are neutral-atom binding energies, $E_{n'r'}$ is the binding energy of the $n't$ electron in the presence of an $n\ell$ vacancy.

However, in the VUV photon energy range, one of the two final vacancies could be in a different subshell of the same principle quantum number of the initial vacancy or both vacancies will have the same principle quantum number as the initial vacancy. These two separate cases designate a special class of Auger processes: Coster-Kronig and a super-Coster-Kronig transitions. This subclass of Auger transitions are characteristic of a vacancy "bubbling up" among subshells of the same shell. For example, $X_u-X_{\mu}X_{\xi}$ where $X_u$ is the initial inner shell vacancy, $X_{\mu}$ is the electron which undergoes a radiationless transition to fill the initial vacancy, and $X_{\xi}$ is the final ejected electron. Nomenclature for various vacancies are listed in the following table.

Table 16. Nomenclature for Auger transitions and vacancy states.

<table>
<thead>
<tr>
<th>n</th>
<th>s_{1/2}</th>
<th>p_{1/2}</th>
<th>p_{3/2}</th>
<th>d_{3/2}</th>
<th>d_{5/2}</th>
<th>f_{5/2}</th>
<th>f_{7/2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>L_{-1}</td>
<td>L_{-2}</td>
<td>L_{-3}</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>M_{1}</td>
<td>M_{2}</td>
<td>M_{3}</td>
<td>M_{4}</td>
<td>M_{5}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>N_{1}</td>
<td>N_{2}</td>
<td>N_{3}</td>
<td>N_{4}</td>
<td>N_{5}</td>
<td>N_{6}</td>
<td>N_{7}</td>
</tr>
</tbody>
</table>

Coster-Kronig transitions are exceptionally fast because cancellation is minimized by the wave function of the ejected electron and the other factors in the matrix element in equation (8.23) and (8.24) and the overlap of the bound state wave functions can be...
large owing to their similarities.

Procedure

After the ion beam is successfully aligned through the machine, a scan of the mass spectrum is first performed for proper mass assignment. Figure 42 shows the anion mass spectrum produced in the IPB with the given source conditions cited previously in table 16. The particular negative molecular ion species of interest created from N₂O in this experiment are NO⁻ (30 amu), O₂⁻ (32 amu), and O⁻ (16 amu). The only negative atomic species included in this experiment for comparative studies was O⁻.

The mass assignment for a 5 kV beam voltage are indicated in the following table.

Table 17. Assignment of mass spectrum in IPB.

<table>
<thead>
<tr>
<th>Species</th>
<th>Mass (amu)</th>
<th>Analyzing magnetic field (Gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O⁻</td>
<td>16</td>
<td>817.4</td>
</tr>
<tr>
<td>OH⁻</td>
<td>17</td>
<td>842.6</td>
</tr>
<tr>
<td>CN⁻</td>
<td>26</td>
<td>1042</td>
</tr>
<tr>
<td>NO⁻</td>
<td>30</td>
<td>1119</td>
</tr>
<tr>
<td>O₂⁻</td>
<td>32</td>
<td>1156</td>
</tr>
<tr>
<td>³⁵Cl⁻</td>
<td>35</td>
<td>1209</td>
</tr>
<tr>
<td>³⁷Cl⁻</td>
<td>37</td>
<td>1243</td>
</tr>
<tr>
<td>N₃⁻</td>
<td>42</td>
<td>1324</td>
</tr>
</tbody>
</table>

The ion beam was tuned for a particular ion species and source conditions were optimized for the double photodetachment aspect of the experiment. For each of the ion...
Figure 42. NO₂ negative ion mass spectrum produced at ALS-IPB endstation.
species, a slow scan covering only a fraction of the photon energy range, typically 20 –
30 eV, was performed. During each of these scan segments, a high precision grating and
monochromator tunes for a photon energy at a spectral resolution of 0.5 eV. At this
resolution, overall spectral range was optimized for time sake at the expense of high-
resolution. Singly charged cations resulting from the double photodetachment process in
the interaction tube are collected in terms of signal count rates and the accumulated
statistics per photon energy is acquired. For each of the photon energy points, several
cumulative scans were acquired and stored in computer memory. Data such as photon
energy, absolute counts, cation counts with laser on and off, primary ion beam absolute
count with laser on and off, and photon flux on and off are all stored for further data
manipulation. The relative cross section is then computed as

\[ \sigma_r = \frac{C_s}{C_i \Phi} \]  \hspace{1cm} (8.26)

where \( \sigma_r \) is the relative cross section, \( C_s \) is the signal count, \( C_i \) is the primary ion count,
and \( \Phi \) is the photon flux in counts.

Results

Each scan segment is piece-wise connected to construct the overall cross section
as a function of the photon energy, \( h \kappa \), for each ion specie in this study. The
conservation of energy equation,
\[ h \omega = E + \frac{h^2 k^2}{2m}, \]  

(8.27)

relates the photon energy, \( h \omega \), to the electron affinity, \( E \), and the kinetic energy of the free electron, \( \frac{h^2 k^2}{2m} \). Figure 43 shows cross sections of all three ions as a function of the photon energy in the range 18 – 100 eV. The cross sections are consistent with typical cross section behavior because at photon energies well above threshold, cross sections decrease with photon energy.

The threshold energy for production of a cation in the ground state is represented as

\[ E_{\text{threshold}} = E(XY^+ \rightarrow XY)_{\text{electron affinity}} + E(XY \rightarrow XY^+)_{\text{1st LP}}, \]  

(8.28)

where \( E_{\text{threshold}} \) is the threshold and is the sum of two processes (detachment and ionization) which occur nearly simultaneously because Auger transition rates can be very high. Auger rates can be several orders of magnitude higher than the radiative rate, and thus essentially determine the lifetime.

The threshold energies are listed below in Table 18 for each of the ions in this experiment. The cations are left in the ground state.
Table 18. Threshold energies for ion species.

<table>
<thead>
<tr>
<th>Ion Species</th>
<th>Electron Affinity (eV) [110]</th>
<th>$1^{st}$ Ionization Potential (eV) [111]</th>
<th>Threshold Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$^-$</td>
<td>0.026</td>
<td>9.264</td>
<td>9.29</td>
</tr>
<tr>
<td>O$_2^+$</td>
<td>0.451</td>
<td>12.071</td>
<td>12.522</td>
</tr>
<tr>
<td>O$^+$</td>
<td>1.461</td>
<td>13.618</td>
<td>15.079</td>
</tr>
</tbody>
</table>

If the cation is left in an excited state, equation (8.28) will include a third term which represents the energy difference between the ground state of the cation and an excited state of the cation. In this case, the threshold energy is indicative of a resonant process. However no resonance was observed in these experiments.

In Figures 44 and 45, the log of the cross section is plotted as a function of the log of the photon energy for each ion species. Each cross section was investigated for any power law dependency, $\sigma \propto E^n$ or $\log(\sigma) \propto -n \log(E)$. At energies near threshold, Wigner [112] derived an expression for the single photodetachment behavior of the cross section,

$$\sigma \propto E^{f+1/2}$$  \hspace{1cm} (8.29)

or

$$\sigma \propto k^{2f+1}$$  \hspace{1cm} (8.30)

where $f$ is the angular momentum of the outgoing electron and $E$ is the photon energy, which is related to the momentum $k$ of the ejected electron through equation (8.27). The Wigner law is really the first term of a power law expansion in terms of the electron’s momentum. At higher photon energies and corresponding increasing momentum, the higher order terms in the expansion exponents $n$, which contribute to
Figure 44. Double detachment cross section $\sigma$ versus photon energy $E_\gamma$ plots for $O_2^-$ and $NO^-$. 

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Figure 45. double detachment cross section $\sigma$ versus photon energy $E_\gamma$ plots for O$^-$. 

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the fall-off behavior of the cross section, become significant.

Investigation revealed widely varying exponents $n$ over certain photon energy ranges after performing a linear regression on each of the graphs of $\log(\sigma)$ vs $\log(E)$. The following table shows the resulting power law dependence for each of the ion species.

<table>
<thead>
<tr>
<th>Species</th>
<th>$E^a$ (18 \leq E \leq 30 \text{ eV})</th>
<th>$E^m$ (30 \leq E \leq 100 \text{ eV})</th>
<th>Ratio $n/m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$^-$</td>
<td>$E^{-8.55 \pm 0.53}$</td>
<td>$E^{-3.74 \pm 0.11}$</td>
<td>2.29 $\pm$ 0.31</td>
</tr>
<tr>
<td>O$_2^-$</td>
<td>$E^{-11.92 \pm 1.53}$</td>
<td>$E^{-3.76 \pm 0.20}$</td>
<td>3.17 $\pm$ 1.29</td>
</tr>
<tr>
<td>O$^-$</td>
<td>$E^{-10.36 \pm 0.95}$</td>
<td>$E^{-3.07 \pm 0.093}$</td>
<td>3.37 $\pm$ 1.04</td>
</tr>
</tbody>
</table>

A possible explanation for the apparent slope changes in the cross section is that at higher photon energy, the innermost electrons are probed deeper into the core thereby opening other available channels of detachment. This is demonstrated in a calculation by Yeh and Lindau [113] [114] of the photoionization cross section, shown in Figure 46. In this calculation, a one-electron central-field frozen-core model was used with first-order perturbation theory. No single model accurately predicts the photoionization process of all orbitals for all elements from the VUV to 1.5 keV. The complexity of the physics of different atomic orbitals makes it impossible for any single rule to describe all of them. The accuracy of Yey and Lindau's model is discussed in detail by Cooper and Manson [115] [116] [117]. Note in Figure 46, the cross section falls off for detachment of the 2p electron above the ionization threshold of about 30 and 25 eV for both oxygen and nitrogen respectively. At approximately 42 and 35 eV, the 2s channel...
Figure 46. Yeh and Lindau calculated photoionization cross section for a 2s, 2p, and 1s electron in nitrogen and oxygen.

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is at a maximum giving rise to the other photoionization cross section for oxygen and nitrogen respectively. Moreover, the ratio of the 2p slope to the 2s slope is approximately 2, which agrees with the observed results, as indicated in Table 19. In contrast, the total calculated cross section (the weighted sum of the 2s and 2p cross sections) in the photon energy range of 20 – 100 eV yielded a slope of 2.26 and 1.66 for oxygen and nitrogen respectively.

We now address the ZCC model, which by definition is not a particularly well suited model for the complex double photodetachment process. The ZCC model makes several simplifications such as neglecting the long-range effects of the potential outside some finite range. The model is also based on one free electron (not two electrons) departing from a neutral atom or molecule whose potential is localized to some specified core radius. For double photodetachment systems, there are two electrons departing from a resultant positive charged atom or molecule. Nevertheless, if we abandon the Auger scenario and assume the first ejected electron leaves the neutral in an excited state, the excited neutral can relax and eject a second electron. With this motivation, the limitations of the ZCC model were ignored and a calculation revealed interesting results in spite of its inherent shortcomings.

In each calculation, the threshold energy given in Table 18 was used for each ion. The channels available for double photodetachment for these species studied are assumed to be 2p and 2s electrons. A weighted sum of the cross sections for the 2s and 2p channels was calculated, weighted by the total number of 2p and 2s electrons. Table 20 lists the weighting factors used in the ZCC calculations.
Table 20. Weighting factors for 2p and 2s electrons in experiment.

<table>
<thead>
<tr>
<th>specie</th>
<th>configuration</th>
<th>2p orbital weight</th>
<th>2s orbital weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>O⁺</td>
<td>atomic configuration: 1s² 2s² 2p³</td>
<td>5/7</td>
<td>2/7</td>
</tr>
<tr>
<td>O₂⁻</td>
<td>Molecular configuration: (1σ_u)²(2σ_u)²(2σ dü)²(1π dü)²(3σ dü)²(1π_u)²</td>
<td>2/3</td>
<td>1/3</td>
</tr>
<tr>
<td>NO⁺</td>
<td>Molecular configuration: (1σ_u)²(2σ_u)²(2σ dü)²(1π dü)²(3σ dü)²(1π_u)²</td>
<td>9/13</td>
<td>4/13</td>
</tr>
</tbody>
</table>

(1) SCF-LCAO-MO notation.

The question also arose of the effective core radius \( r_e \) for NO and \( O_2 \). Stehman and Woo [72] determined the effective core radius \( r_e \) of \( O \) and \( N \) to be 0.96 and 1.11 Å respectively. The effective core radius \( r_e \) for NO and \( O_2 \) was naively determined by

\[
R(N) + R(O) - \frac{1}{2} R_e(NO)
\]  

(8.31)

and

\[
2R(O) - \frac{1}{2} R_e(O_2)
\]  

(8.32)

respectively, where \( R_e \) is the equilibrium internuclear separation and \( R \) is the given effective core radius. For \( R_e \) of 1.15 and 1.217 Å for NO and \( O_2 \) respectively [49], equation (8.31) and (8.32) yield an effective core radius of 1.495 and 1.311 Å for NO and \( O_2 \) respectively.

Two sets of calculations were performed one for each of the ejected s and p electrons in each of the ions. The total cross section \( \sigma \) was determined by summing the calculated cross sections \( \sigma_s \) and \( \sigma_p \) for the ejected s and p electron respectively. Figures
47 and 48 show the results of the ZCC calculation for $O_2^-$, NO$^-$, and O'. $\log(\sigma)$ is plotted against $\log(E)$. Two of the three graphs, for NO$^-$ and $O_2^-$, reveal a local minima similar to the minima found in all three experimental plots shown in Figures 44 and 45. Presumably, this inflection point occurs at the crossover point where the 2s channel opens up. According to the ZCC calculation, the 2s channel peaks at about 60 and 45 eV for nitrogen and oxygen respectively, which is within about 10\% of the value found by Yeh and Lindau (shown in Figure 46). However, the positions of the predicted inflection points are more than 25\% in disagreement with observed measurements.

The effective neutral core radius of each species was then adjusted to yield reasonable predictions for the observed inflection points. Table 20 shows a summary of the experimental results compared to the ZCC calculations.

Table 21. Double photodetachment $\sigma$ comparison to ZCC calculations.

<table>
<thead>
<tr>
<th></th>
<th>$O^-$ meas.</th>
<th>$O^-$ calc.</th>
<th>$O_2^-$ meas.</th>
<th>$O_2^-$ calc.</th>
<th>NO$^-$ meas.</th>
<th>NO$^-$ calc</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^{st}$ minima</td>
<td>30.20</td>
<td>43.65</td>
<td>29.51</td>
<td>39.80</td>
<td>27.94</td>
<td>36.31</td>
</tr>
<tr>
<td>(eV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Error (%)</td>
<td>30.81</td>
<td>25.80</td>
<td>23.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2^{nd}$ maxima</td>
<td>39.80</td>
<td>61.66</td>
<td>33.88</td>
<td>54.95</td>
<td>34.99</td>
<td>51.28</td>
</tr>
<tr>
<td>(eV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Error (%)</td>
<td>35.45</td>
<td>38.34</td>
<td>31.77</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_o$ (Å)</td>
<td>1.35</td>
<td>1.4</td>
<td>1.27</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In Figure 44 and 45, a subtle inflection peaks around 39.80, 33.88, and 34.99 eV for $O^-$, $O_2^-$, and NO$^-$ respectively which agree to within few eV of the predicted binding energies of the L-shell electron for nitrogen and oxygen [103].
Figure 47. ZCC calculation for double photodetachment of \( \log(\sigma) \) versus \( \log(E_{\gamma}) \) plots for \( O_2^- \) and \( NO^- \) in VUV.
Figure 48. ZCC calculation for double photodetachment of $\log(\sigma)$ versus $\log(E_r)$ plots for $O^-$ in VUV.
Conclusions

The unexpected variations in the observed double photodetachment cross section with two distinct minima were eclipsed by the equally surprising ZCC prediction of them. Other than that aspect of the ZCC calculation and agreement with experimental data, still other parts of the calculation are in error. For example, the departing electrons leave behind a positive charged ion whose potential now has long range effects. The departing electrons are not so “free” at least outside the designated core radius \( r_c \). Secondly, the designated core radii for each ion may be indicative of the radius to the intermediate neutral but does not suggest what the radius is for the final cation. After the partial success of the ZCC predictions with experimental data, it is not surprising that the cross section could not successfully be fitted to a power law due to the variations in the cross section over a large photon energy range.

Another remarkable observation is that all three observed cross section appear to be similar. This indicates that the double detachment process is of an atomic origin, from 2p and 2s orbitals.
CHAPTER IX

CONCLUSIONS

The high resolution of the coaxial ion-laser beam apparatus combined with the long lifetimes of the autodetaching states allowed us to observe a transition of CH$_3^-$ The Doppler tuning technique offers higher resolution ability to observe such a transition. The photodetachment cross section was measured in two ranges: a few tenths of an eV above threshold and in the visible. The experimental results were in good agreement with the ZCC model. However the level of theory should be advanced to investigate other appropriate scaling factors. Metastable autodetaching states of CH$_3^-$ have been observed with an autodetachment lifetime of 17 to hundreds of 667 $\mu$s. The excited state responsible for autodetachment is probably rotationally excited states. There are presently no theoretical calculations of the autodetachment mechanism or lifetimes. A collisional cross section was also measured for CH$_3^-$ and O$-$ to be 2.6 Å$^2$ and 7.2 Å$^2$ respectively.

The rovibrational sticks plot program that was developed for anticipating and visualizing the infrared spectrum for CH$_3^-$ can be improved to incorporate models beyond the rigid rotor approximation. Other features could also be included to import and display real spectral data and to manually or automatically adjust the predicted spectrum to match the real data.
Double photodetachment cross section measurements have been made in NO', O_2', and O' in the VUV for the first time. This is the first measurement of any negative molecular ion in the gas phase in the VUV. There has been much attention given to single detachment cross sections in atomic anions and threshold behavior. However, there is no theoretical understanding of double photodetachment cross sections for negative molecular ions and much less well beyond threshold. The ZCC model surprising prediction of the variations and minima in the cross section should certainly inspire further theoretical investigation of this complicated process. All these cross sections decreased with photon energy and were broadly similar. The continuum process dominated. The double detachment process in interpreted as detachment from an atomic 2s or 2p orbital: the molecular features are not evident.
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