Laser spectroscopy of molecular ions in an ion beam

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Laser spectroscopy of molecular ions in an ion beam

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University of Nevada, Las Vegas, 1990
LASER SPECTROSCOPY OF MOLECULAR IONS
IN AN ION BEAM

by
Jun Li

A thesis submitted in partial fulfillment
of the requirements for the degree of

Master of Science
in
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July, 1990
The thesis of Jun Li for the degree of Master of Science in Physics is approved.

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University of Nevada, Las Vegas
July, 1990
ABSTRACT

The operation of a coaxial ion beam/laser beam experimental apparatus is described, in which an ion beam is overlapped by a laser beam and the ions are Doppler–tuned into resonance. The experimental apparatus is suitable for the study of both positive and negative ions. Resonant transitions are reported in C$_2^-$ and in CO$^+$. In C$_2^-$, a two–photon resonant photodetachment experiment was performed, with detection of fast neutral C$_2$. The experiment yields a measurement of the R(10) line of the 1 – 0 band in the B – X electronic transition. In CO$^+$, the blended Q(1) and R(12) lines of the A – X electronic transition were observed using collisional detection. In both ions, the results reported here are in good agreement with previous results by other workers.
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I. INTRODUCTION

Molecular ions play important roles in chemical and physical processes in the laboratory [1], in the atmosphere [2], and in interstellar gas clouds [3]. Many molecular ions also exhibit unusual but fundamental aspects of molecular structure. The simplest molecule of all, $\text{H}_2^+$, is a molecular ion. The Schroedinger partial differential equation for its electronic motion is one of those few that can be separated into ordinary differential equations, and thus solved analytically in the Born–Oppenheimer approximation, as was first done in 1927 by Burrau [4]. After 23 years (1950), the number of known diatomic molecular ions was only 29 and none of them was a negative ion [5]. As the field of charged–molecule spectroscopy grew rapidly, more and more molecular ions were studied, until 141 cations had been put on the known list and 40 anions had been found by 1979 [6]. Since then the growth in the field of molecular ion spectroscopy has continued even more rapidly.

The most direct reason for the rapid growth is surely the many advances in spectroscopic technology. Ion traps, ion beams, jet–expansion beams, cooled discharges, and other sources especially tailored to the controlled production of molecular ions have been extensively developed. Exotic varieties of lasers and other intense coherent sources from the ultraviolet to the submillimeter parts of the electromagnetic spectrum have become routine pieces of laboratory apparatus.

In our laboratory, two very new techniques are used in the study of molecular ions. One technique is known as velocity modulated spectroscopy and was introduced by Saykally in 1983 [7]. In this technique, a discharge in a gas cell is electrically modulated so that ions move back and forth at a particular frequency. Direct absorption spectroscopy is then carried out in the plasma and phase sensitive detection is used to lock onto the absorption signal as the ions are periodically
Doppler shifted through resonance. This technique has been used to study a large number of positive and negative molecular ions such as OH\(^-\) [8][9], NH\(_2\)^- [10], N\(_2\)^+ [11], H\(_2\)O\(^+\) and HCO\(^+\) [12], and many more. The water cation, H\(_2\)O\(^+\), has been studied in emission for years, using conventional grating spectroscopy. It also has been studied in our laboratory: For the first time, the visible absorption spectrum has been observed by Das and Farley [13].

The second very new technique for studying molecular ions is the beam technique in which a mass—selected ion beam is merged coaxially with a laser beam. The well known laser photodetachment spectroscopy [14] and the high—resolution autodetachment spectroscopy can be applied here to study molecular ions. In the photodetachment technique, either the resulting neutral particles or electrons photodetached from an ion beam are monitored as a function of laser frequency. By using this technique, the infrared photodetachment cross section of NO\(^-\) has been measured by Al—Za'al et al. in our ion beam machine [15]. Such a study may provide detailed information about the near—threshold behavior of the photodetachment cross section. Also, the energy of each threshold corresponds to the energy difference between a particular state of the negative ion and a particular state of the neutral. Therefore, every level difference may be determined. These experiments are capable of better than 1 meV resolution in systems with rapidly increasing, distinct thresholds. One most notable example is in the photodetachment study of OH\(^-\) [16] in which individual rotational thresholds were resolved.

Autodetachment is the non—radiative decay of a negative ion into a free electron and a neutral molecule (or atom) [17]. By using a coaxial ion beam—laser beam, if the laser is resonant with a transition to an autodetaching state of the ion, there is an increase in the laser—induced production of fast neutral particles and electrons. The value of autodetachment spectroscopy lies in the very high resolution obtainable because of kinematic velocity compression in an ion beam [18].
This technique has been very successfully used to study the hyperfine structure of NH$^-$ [19] and HNO$^-$ [20] by Farley's group at the University of Oregon.

For studying positive ions, a charge–exchange detection technique is used. The first observation of the infrared vibrational rotational spectrum of any molecular ion was performed in 1976 by Wing's group on HD$^+$ [21]. In this technique, a neutral gas is introduced as a collision gas in the interaction region where the ion beam is aligned coaxially with a laser beam. The ion beam is partially neutralized by charge–exchange processes, whose cross section depends on the internal state of the ion. When a transition in the ion is induced by the laser, the result is a change in the ion current detected due to a change in the ions surviving the collisional process. The details of this technique are described in the section on CO$^+$ in this thesis.
II. EXPERIMENTAL APPARATUS

1) Ion Beam Machine

A schematic of the ion beam machine is shown in Fig. 1. The ion beam machine consists of four major parts: (1) Ion source, (2) Extraction region, (3) Wien filter region, and the (4) Interaction region.

The pumping system maintains the whole ion beam machine under high vacuum. The extraction and the Wien filter regions are housed in two stainless steel chambers which are attached to the two diffusion pumps. The interaction region is a large cylindrical chamber pumped by a ion pump (not shown in Fig. 1). A mechanical pump is attached to both diffusion pumps as a foreline pump. Without any gas load, the background pressures in the extraction region, the Wien filter region and the interaction region are $2 \times 10^{-7}$, $1 \times 10^{-6}$ and $6 \times 10^{-8}$ Torr, respectively, measured by three ion gauges. The pressure in the ion source is not measured directly, but rather inferred from the steady state pressure in the extraction region. The parent gas is introduced to the ion source to produce ions. During operation, the gas is carefully regulated with a needle valve.

The ions are created in the ion source and subsequently accelerated and focused into an ion beam in the extraction region. When the ions pass through an aperture into the Wien filter region, they are selected by the Wien filter according to their masses. The mass-selected ions are bent $90^\circ$ by an electrostatic quadrupole and sent through a long equipotential tube which is along the axis of the interaction chamber. The laser beam enters the interaction region through a Brewster window. The overlap between the laser beam and the ion beam is precisely defined by an aperture at each end of the equipotential tube. After it leaves the equipotential tube, the ion beam is electrostatically deflected into a Faraday cup which measures the ion current. A glass plate and electron multiplier is used as a signal detector.
Figure 1. Schematic of the ion beam machine. The interaction region is pumped by a 200 L/s ion pump (not shown).
(1) Ion Source

The hot—cathode discharge ion source which is called the "Branscomb source" [22] is used to produce both negative and positive ions.

The ion source, shown in Fig. 2, consists of two 6–inch–diameter magnetically permeable steel plates separated by a glass sleeve. The back plate holds the removable filament assembly, which has two high–voltage feedthroughs, with two copper clamps for the filament. The cathode filament assembly is mounted on the back plate by six bolts, so the filament can be easily replaced without taking the rest of the ion source apart. The anode plate has a 1–mm–diameter aperture at its center. The ions are extracted and the parent gas is pumped through the hole into the extraction region. The small hole limits the pumping speed, which provides a relatively high pressure region in the ion source. The ratio of the pressure in the ion source and in the extraction region is about 4000 – 4500 : 1 [23].

Three or six permanent magnets are attached between the back plate and anode plate, with insulation, to magnetically confine the discharge electrons. The whole ion source is attached by the anode plate to the extraction region of the ion beam machine. An insulating plate and Teflon sleeve provide electrical isolation. O–rings make a vacuum seal. The parent gas is admitted through a 1/4–inch Teflon tubing connected to a feedthrough into the back plate.

Inside the ion source, there are three 1–mm–thick stainless steel plates mounted on the anode plate. The one closest to the anode plate is called the "spider plate", because it has a web at its center formed by three 1/4–inch holes drilled 120° apart on a circle of 3/16–inch radius. The "spider plate" is used for negative ions to block electrons. Three steel spacers, about 1.5 mm thick, are placed between the "spider plate" and anode plate, which creates a field–free region near the anode.
Figure 2. Ion source.
aperture. This field–free region guarantees that the kinetic energy of the ions after extraction into the extraction region is only determined by the anode voltage.

The other two plates, called plasma confining plates, have holes at their centers. The one next to the "spider plate" has a 3/16–inch–diameter hole, and the other has a 3/8–inch diameter hole. These plates confine the discharge (plasma) to the axial region near the holes. The confining plates are electrically isolated from each other and from the "spider plate" by glass spacers which slide on three glass sleeves covering mounting screws.

There are two commonly used materials for the filament: tungsten and thorium oxide–coated iridium. The choice of the filament is based mainly on the type of parent gas used in the ion source. Tungsten is good for reducing gases such as CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{2} and NH\textsubscript{3}, while thoriated iridium is best for oxidizing gases such as O\textsubscript{2}, N\textsubscript{2}O, H\textsubscript{2}O and CO\textsubscript{2}.

The anode plate is charged to the ion beam voltage which is ± 2 kV, (+2 kV for the positive ions, −2 kV for the negative ions). The filament cathode is biased with respect to the anode by a floating Heath SP–2717A (400 V, 125 mA) power supply. The discharge is initiated by heating the filament with a floating Hewlett–Packard 6256B (10 V, 20 A) power supply to produce thermionic emission electrons. The electrons accelerate toward the anode, colliding with the parent gas. Neutral fragments, secondary electrons, positive ions and negative ions are produced once electrical breakdown occurs. A regulator circuit controls the filament temperature in order to keep the discharge current constant, thus maintaining a stable discharge.

(2) Extraction Region

Figure 3 is a cross–sectional view of the extraction region. There are three cylindrical ion lens elements and two orthogonal ion beam deflectors.
Figure 3. Cross-section view of the extraction region
The first lens element is the extractor, which is cone-shaped at its front, located about 1/4 inch from the anode aperture. The extractor voltage is about 700 V with opposite polarity to the beam voltage, which extracts the ions through the anode aperture into the extraction region. The second lens element is biased in the decelerating mode to about 1600 V with respect to ground and serves to focus the ion beam. The third lens element usually is grounded externally, but it also can be supplied by a separate power supply to help the focusing.

Two ion beam deflector pairs provide two separate, orthogonal deflection fields \((X_1, Y_1)\) by two symmetrical voltages \((0 - \pm 40 \text{ V/cm})\). After passing through the lens elements, the ion beam is steered and sent through an aperture \(A_1\). The aperture is wired to an electrometer which gives the ion current \((I_1)\) on the aperture plate. All other apertures in the apparatus are also wired to electrometers. The currents are used to help align the ion beam through the machine.

(3) Wien Filter Region

After the ion beam passes through the aperture \(A_1\), it comes into the Wien filter region (Fig. 4). In this region the ions are selected by the Wien filter according to mass.

A Wien filter is also known as an \(E \times B\) filter. It consists of an uniform electric field \(E\) and an uniform magnetic field \(B\). Both fields are perpendicular to each other and to the direction of the ion beam. The forces from both fields have opposite direction and the net force is:

\[
F = F_e - F_m = qE - qvB,
\]

where \(q\) and \(v\) are the charge and the velocity of the ion.

In order for an ion to pass straight through the filter, the net force on the ion
has to be zero. Therefore,

$$E - vB = 0, \quad (3)$$

which means only ions with a velocity,

$$v = \frac{E}{B}, \quad (4)$$

can pass undeflected through the filter.

The ions coming into the Wien filter region usually have several different species. For example, using \( \text{H}_2\text{O} \) to produce negative ions, there are \( \text{O}^- \), \( \text{OH}^- \), \( \text{O}_2^- \), \( \text{OH} \cdot \text{H}_2\text{O}^- \) and \( \text{O}_3^- \) ions. All species are created in the ion source at same potential and therefore have the same kinetic energy in the Wien filter region. Ions with different masses have different velocities. The relation of the mass \( m \) and velocity \( v \) is given by

$$v = (2qV_b/m)^{1/2}, \quad (5)$$

where \( V_b \) is the beam voltage. From Eqs. (4) and (5), we have

$$m = 2qV_b(B/E)^2. \quad (6)$$

Therefore, by scanning \( E \) or \( B \), the various mass ions can be selected.

Our ion machine uses a Colutron Model 600 Wien filter. It consists of a pair of parallel deflector plates \( (\bar{E}) \) and a dual-coil iron core electromagnet \( (\bar{B}) \). Usually we keep the voltage between the plates \( (\bar{E}) \) fixed and change the magnetic field by varying the current \((0 \text{ -- 3 Amp})\) through the coils.

There are two Einzel lenses and one vertical deflector \( (Y_2) \) in the Wien filter region. An Einzel lens consists of three parallel plates. The middle plate has an adjustable voltage on it while the other two are grounded. The Wien filter input
lens (WFIL), at the entrance of the Wien filter, is operated at a decelerating voltage to focus the ion beam entering the Wien filter. The Wien filter output lens (WFOL) is operated at an accelerating voltage to focus the selected ions, and the deflector (Y₂) is placed between the filter and the output lens to steer the ion beam in the vertical direction. By adjusting all the elements including the Wien filter (B field) the ion beam emerges through an aperture A₂.

(4) Interaction Region

The mass-selected ion beam intersects the laser beam in the interaction region, shown in Fig. 5. All the elements of the interaction region are contained in a large stainless steel chamber which can be maintained at $6 \times 10^{-8}$ Torr by a 200 l/s ion pump. A Brewster window is mounted at each end of the chamber which allows the laser beam to pass in and out.

The ion beam entering the interaction region passes through an Einzel lens (IL₁) and a vertical deflector (Y₃), then is bent 90° in the horizontal plane by an electrostatic quadrupole. [24]. The voltages on two diagonal pole pairs of the electrostatic quadrupole have opposite polarity. It is connected externally to a high voltage power supply unit through a selector switch that allows operation in either "0°-deflection" or "90°-deflection" modes. In 0°-mode, the ion beam can go straight through a 1-mm aperture A₃ in a collector I₃ by adjusting lens IL₁ and deflector Y₃. Maximizing the ion current on I₃ is very useful for optimizing the ion beam through the interaction region.

In 90°-mode, the ion beam is bent 90° through a second lens (IL₂) and a deflector (Y₄) into a stainless steel tube, 50 cm long and 4 mm inner diameter, which is called the "equipotential tube". There is a 1.5 mm apertures at each end of the tube. The laser beam enters the interaction region through one of the two Brewster windows. The overlap of ion and laser beams inside the tube is defined
Figure 5. The interaction region
by the apertures. The "equipotential tube" is connected to two power supplies connected in series. One provides a fixed voltage and the other gives a variable voltage. The variable voltage is controlled by a microcomputer which scans the voltage over a range of 300 V using a digital-to-analog converter. The variable voltage on the potential tube changes the speed of the ions when they enter the tube. This technique is called the Doppler tuning technique. If the voltage on the tube is $V_t$ ($V_t = V_f + V_v$, both fixed and variable) and the beam voltage is $V_b$, the kinetic energy of the ion is $q(V_b - V_t)$. The Doppler shifted frequency $\nu_{\text{ion}}$ of the laser beam seen by ions in the equipotential tube is related to the fixed laboratory frame laser frequency $\nu_{\text{lab}}$ by

$$\nu_{\text{ion}} = \nu_{\text{lab}} \left(1 \pm \beta\right),$$

where

$$\beta = \left[\frac{2q(V_b - V_t)}{M c^2}\right]^{1/2},$$

in which $M$ and $q$ are the mass and charge of the ion, $\beta$ is $v/c$. For our experiment, the $\beta$ is in a range of $10^{-4}$. The +/- sign is for anti-parallel and parallel laser and ion beam momentum vectors.

After the ions come out the potential tube, they pass through a final lens (IL3) and a horizontal deflector (X). The lens focuses the ions and the deflector bends them in horizontal direction in order that they pass through a grounded slit into a Faraday cup. The Faraday cup is 4.8 cm deep, 1.8 cm diameter and with a 3 mm slit cover so that the ions will not bounce out of the cup. The final ion current is measured by an electrometer which is connected to the Faraday cup. All the lenses and deflectors in the ion beam machine are used to maximize the ion current in the Faraday cup.

Different detection techniques are used for different experiments. They are
discussed in the experimental part of this paper.

2) Argon Ion Laser

A Coherent Innova-10 argon ion laser is used for both C\textsubscript{2}– and CO\textsuperscript{+} experiments. The operating range of this laser is 333.6 – 528.7 nm. All–line output power is 10 Watts.

By using a Model 434 Wavelength Selector, the laser can be operated at each individual single line. For our experiments, 488.0 nm and 457.9 nm lines are used. The maximum specified output power of these two lines are 3.5 W and 700 mW, respectively. In multimode laser operation, the linewidth of the lasing medium is nominally 10 GHz and the mode spacing is 150 MHz. There are over 60 possible cavity modes within the gain curve of the lasing medium.
III. OBSERVATION OF RESONANT 
TWO-PHOTON PHOTODETACHMENT OF C$_2^{-}$

1) Apparatus and Procedure

The experimental apparatus in this work consists of an ion beam machine, an argon ion laser and a neutral signal detection system. A schematic of the apparatus is shown in Fig. 6. The ion beam machine is described in Chapter II. A more detailed description of the ion beam machine and its electronics is given by Al-Za' al [25] and by Miller [17]. The neutral signal detection system consists of an electron multiplier, home-made electrometer, an EG&G Model 5209 lock-in amplifier and a strip-chart recorder.

In the interaction region the ion beam intersects the laser beam. When the laser photodetaches the ions into neutral molecules and free electrons, the fast neutral molecules are not deflected into the Faraday cup. They go straight through deflector (X) and collide with a glass plate. The Faraday cup, glass plate and electron multiplier are supported by a stainless steel mount with insulation, shown in Fig. 3. The glass plate is charged to a potential of -2000 V. When the neutral molecules strike the glass plate, they eject secondary electrons. The first dynode in the electron multiplier is biased at -1600 V. The secondary electrons are accelerated toward the first dynode (Fig. 7). The electron signal cascades up the dynode chain to the ground where it is coupled out of the chamber and converted to a voltage by the electrometer. The gain of the whole 20-stage electron multiplier is about 10$^6$. The voltage signal is sent to the lock-in amplifier and recorded by the chart recorder.

The optimum ion source conditions to produce 1–1.5 nA of C$_2^{-}$ ions in the Faraday cup are listed below in Table I.
Figure 6. Block diagram of the apparatus used for the C$_2^-$ experiment.
Figure 7. Electron multiplier. The glass plate is charge at -2000 V. Secondary electrons ejected from the fast neutrals are accelerated toward the first dynode. The total number of dynodes is 20.

Table I. Ion source conditions for the production of C$_2^-$ ions

<table>
<thead>
<tr>
<th>Source gas</th>
<th>Acetylene (C$_2$H$_2$) + Carbon monoxide (CO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filament material</td>
<td>Tungsten</td>
</tr>
<tr>
<td>Beam voltage</td>
<td>-2000 V</td>
</tr>
<tr>
<td>Discharge voltage</td>
<td>135 – 150 V</td>
</tr>
<tr>
<td>Filament supply voltage</td>
<td>4 – 6 V</td>
</tr>
<tr>
<td>Filament current</td>
<td>~ 12 A</td>
</tr>
<tr>
<td>Emission current</td>
<td>10 – 15 mA</td>
</tr>
</tbody>
</table>

To produce ions from C$_2$H$_2$ and CO is not difficult, but to produce C$_2^-$ ions is very difficult. The ion source conditions and the C$_2$H$_2$ – CO mixture ratio are very important for getting C$_2^-$ ions. Figure 8 shows the mass spectrum of the anions.
Gas pressure: $\text{C}_2\text{H}_2 + \text{CO} = (2.5 + 1) \times 10^{-5}$ Torr,
Discharge voltage: 240 V,
Filament supply: 5 V, 12 A,
Emission current: 15 mA,
Dispersion voltage: 100 V.

Figure 8. Mass spectrum (1) of ions produced from $\text{C}_2\text{H}_2 + \text{CO}$. 
measured from the Faraday cup. There is an apparently clean and sharp peak around mass 24 amu with a peak current of 300 pA. The low mass ions \( \text{CH}_n^- \) \((n = 0 - 3)\) can be photodetached by 606.3 nm laser beam from a ring-dye laser and can serve as a reference signal to set the phase of the lock-in amplifier. The spectrum of \( \text{C}_2^- \) in the 600 nm range has been studied in great detail by Lineberger's group [26], but there is no resonance to be found from the mass peak near 24 amu, shown in Fig. 8.

We examined the mass peak near 24 amu and found that most of the ions are not \( \text{C}_2^- \). Figure 9 shows a mass spectrum of the ions which has a different \( \text{C}_2\text{H}_2^- \) - CO ratio and different source conditions. Comparing with Figure 8, there are two shoulders coming out at both sides of the peak, which tells that this whole peak is not a single mass peak. It has three different ion components, and the mass difference between them is 1 amu. These three ion peaks are \( \text{C}_2^- \), \( \text{C}_2\text{H}^- \) and \( \text{C}_2\text{H}_2^- \). After working with the ion source more carefully, a mass spectrum with a better resolution was obtained, as shown in Fig. 10. By changing the dispersion voltage (E field), the \( \text{C}_2^- \) ion peak can be separated from the \( \text{C}_2\text{H}^- \) ion peak (Fig. 11). After these adjustments a good single mass \( \text{C}_2^- \) ion beam is sent through the ion beam machine into the Faraday cup.

The 488 nm line argon laser beam is sent through the interaction region and chopped at about 800 Hz. The power is 700 mW at the output of the laser. Since the argon laser beam travels more than 4.5 m to the ion beam machine, two lenses \((f = 100 \text{ cm})\), located about 10 cm and 200 cm from the interaction region, are used for focusing the laser beam through the equipotential tube. The transmission of the laser beam is 66 percent.

The fixed voltage on the potential tube is 1000 V and the variable voltage scanning range is 0 - 300 V. The computer scans the 300 V by 300 steps at 1 second per step. The output from the lock-in is sent to the strip-chart recorder on
Gas pressure: $\text{C}_2\text{H}_2 + \text{CO} = (1.6 + 1.8) \times 10^{-5}$ Torr,
Discharge voltage: 200 V,
Filament supply: 5 V, 12 A,
Emission current: 15 mA.

Figure 9. Mass spectrum (2) of ions produced from $\text{C}_2\text{H}_2 + \text{CO}$. 
Gas pressure: \( \text{C}_2\text{H}_2 + \text{CO} = (1.8 + 1.8) \times 10^{-5} \) Torr,
Discharge voltage: 145 V,
Filament supply: 5 V, 12 A,
Emission current: 15 mA.

Figure 10. Mass spectrum (3) of ions produced from \( \text{C}_2\text{H}_2 + \text{CO} \).
Gas Pressure: \( \text{C}_2\text{H}_2 + \text{CO} = (2.8 + 2.4) \times 10^{-5} \text{ Torr}, \)
Discharge voltage: 135 V,
Filament supply: 4 V, 10 A,
Emission current: 7 mA,
Dispersion voltage: 150 V.

Figure 11. Mass spectrum (4) of ions produced from \( \text{C}_2\text{H}_2 + \text{CO}. \)
which voltage markers are recorded during the scan.

2) Experimental Result

Figure 12 shows the experimental result. The laser wavenumber ($v_{\text{lab}}$) is 20486.65 cm$^{-1}$ in the fixed laboratory frame in vacuum [27]. The ion beam voltage tuning range is 3000 – 3300 V. The center of the resonance is located at 3171.4 V, shown in Fig. 13. In the case that the laser beam and the ion beam are parallel, Eq.(7) is expressed by

$$v_{\text{ion}} = v_{\text{lab}} (1 - \beta).$$

(9)

For $C_2^-$, $M = 24$ amu, and 1 amu = 931.4 MeV. From Eq.(8), the tuning range of the kinetic energy of the ions of 3000 – 3300 V corresponds to $\beta = 5.18 \times 10^{-4}$ to $5.43 \times 10^{-4}$. Substituting $\beta$ into Eq. (9), we have the Doppler tuning range of the laser wavenumber in the ion frame is 20476.04 to 20475.53 cm$^{-1}$, with the transition centered at 20475.74 cm$^{-1}$ (Fig. 12). The smooth curve is drawn to aid the eye and the center the transition is determined by measuring the top position of the smooth curve.

3) Discussion and Conclusions

This experiment has demonstrated resonant two–photon photodetachment, shown in Fig. 13. Since $C_2$ has an electron affinity $3.37 < EA < 3.40$ eV [28], single photodetachment is energetically impossible for photon energies less than 28000 cm$^{-1}$. The photon energy of the argon laser 488 nm line is well below the single photon photodetachment threshold. The two photon photodetachment process is: one laser photon excites the $C_2^-$ ion from the ground electronic state, and a second laser photon photodetaches the excited state $C_2^-$ ion, producing neutral $C_2$ and a free electron.
Figure 12. Experimental result for $C_2^+$. Argon laser 488 nm line, R(10) transition in the $(1 - 0)$ band. The center of the transition is 20475.74 cm$^{-1}$, FWHM $\pm$ 6.4 GHz.
The excited electronic states lying about 2 eV above the ground state have been studied by Herzberg and Lagerquist of a spectrum of diatomic carbon in their flash discharge apparatus [29]. Our measured value of the frequency of the R(10) line by this two photon photodetachment technique is in good agreement with their previous work. The R(10) transition in the 1 – 0 band of the B – X system is shown in Table II.

![Diagram of photodetachment process]

**Figure 13.** Resonant two–photon photodetachment in C$_2^-$: The first photon excites a B – X transition and the second photon photodetaches the B state.

**Table II.** Experimental measurements of the R(10) line in the B – X (1 – 0) band of C$_2^-$

<table>
<thead>
<tr>
<th></th>
<th>value (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>this work</td>
<td>20475.74 ± 0.05</td>
</tr>
<tr>
<td>previous work</td>
<td>20475.77 ± 0.01</td>
</tr>
<tr>
<td>difference</td>
<td>0.03 ± 0.05</td>
</tr>
</tbody>
</table>
The transition in Fig. 12 shows the broad linewidth of FWHM = 6.4 GHz, because the argon laser operates multimode. The uncertainty of the line comes from how to locate the center of the transition. To get single-mode operation of the laser, an etalon would have to be inserted in the laser cavity.

A ring–dye laser pumped by argon ion laser was used by Mead et al [30] to study C\textsuperscript{2–} ion in the 600 nm range, in which transitions were induced from highly vibrationally excited state (v \geq 6). In our laboratory, no transitions of the C\textsuperscript{2–} ion were observed in the ring–dye laser range. Our ion source must therefore be producing vibrationally cold ions.
IV. OBSERVATION OF AN ELECTRONIC ABSORPTION SIGNAL IN CO$^+$

1) Apparatus and Procedure

The experimental apparatus for studying the positive ion CO$^+$ is almost the same as for C$_2^-$ . The "spider" plate is removed from the ion source to produce positive ions. A different signal detection technique is used here for the CO$^+$ experiment. The Faraday cup is directly used as a signal detector and the electron multiplier is removed from the interaction chamber.

Air, as a collision gas, is introduced into the interaction region at about $1 \times 10^{-4}$ Torr and charge-exchange reactions result in attenuation of the CO$^+$ ion beam by 50 percent. The Faraday cup is directly connected to the electrometer, as shown in Fig. 14. The D.C. component of the output from the electrometer is measured by a digital multimeter, whose signal is used to maximize the ion current in the Faraday cup. By using the Doppler tuning technique, the ions are brought into resonance with the laser beam and the electronic excitation of the ions results in a change in the charge-exchange cross section. The change of the charge-exchange cross section causes a change in the intensity of the CO$^+$ ion beam in the Faraday cup, which is measured by the lock-in amplifier and recorded by the strip-chart recorder.

The ion source conditions for producing 20 – 30 nA of CO$^+$ ions in the Faraday cup are listed in Table III.

Because high purity carbon monoxide gas (99.99%) and low gas pressure are used to produce CO$^+$ ions, no other ion peaks appear shown in the mass spectrum (Fig. 15). Air, as a background gas, is carefully regulated with a needle valve into the interaction region and strips the beam current of CO$^+$ in the Faraday cup by 50 percent.
Figure 14. Block diagram of the apparatus used for the CO\(^+\) experiment.
Figure 15. Mass spectrum of CO\(^+\) ion.

Table III. The ion source conditions for the production of CO\(^+\) ions

<table>
<thead>
<tr>
<th>Source gas</th>
<th>Carbon monoxide (CO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filament material</td>
<td>Tungsten</td>
</tr>
<tr>
<td>Beam voltage</td>
<td>2100 V</td>
</tr>
<tr>
<td>Discharge voltage</td>
<td>100 V</td>
</tr>
<tr>
<td>Filament current</td>
<td>10 - 12 A</td>
</tr>
<tr>
<td>Filament supply voltage</td>
<td>4 - 6 V</td>
</tr>
<tr>
<td>Emission current</td>
<td>10 mA</td>
</tr>
<tr>
<td>Extraction region pressure</td>
<td>2 - 4 \times 10^{-6} \text{ Torr}</td>
</tr>
<tr>
<td>Estimated ion source pressure</td>
<td>9 - 18 mTorr</td>
</tr>
</tbody>
</table>
The 457.935 nm (air) argon laser line is used, with 700 mW output power. The laser beam is sent through the "back" Brewster window into the interaction region. Configuration of counter-propagating laser beams is used here to shift the laser frequency to the range of the ion resonance (Fig. 14). Once again, two lenses are used to focus the laser through the equipotential tube. The transmission is about 70 percent. The laser is mechanically chopped at about 1000 Hz.

On the potential tube, the fixed voltage is set at −700 V, which gives a total energy of the ion of 2800 V. The variable voltage is always on the positive side and reduces the energy of the CO⁺ ions. The scanning range is 0 – 400 V and scanning parameters are 400 steps and 3 seconds per step. The same recording technique is used as in the C₂⁻ work, described above.

2) Experiment Result

The experimental result is shown in Fig. 16. The laser wavenumber is 21830.96 cm⁻¹ (vacuum) in the fixed laboratory frame. The voltage tuning range of the ion beam is 2400 – 2800 V. Since an anti-parallel laser beam/ion beam arrangement is used, Eq.(7) is

\[ v_{\text{ion}} = v_{\text{lab}} (1 + \beta). \]  

For CO⁺, M = 28 amu, and 1 amu = 931.4 MeV. By using Eq.(8), the voltage tuning range 2400 – 2800 V gives a range of β from 4.29 \times 10^{-4} to 4.66 \times 10^{-4}. Substituting β into Eq.(10), the Doppler tuning range of the laser seen by the ions is 21840.33 to 21841.08 cm⁻¹. The center of the resonance occurs at 21840.74 cm⁻¹, as shown in Fig. 16.

3) Discussion and Conclusions

The CO⁺ transition line shown in Fig. 16 has a linewidth of about 8.5 GHz.
Figure 16. Experimental result for CO$^+$. Argon laser 457.9 nm line, Rotational absorption line in the (1 – 0) Band. The center of the transition is 21840.74 cm$^{-1}$, FWHM ≈ 8.5 GHz.
The broad linewidth comes from the multimode operation of the argon laser. During the scan, the voltage on the equipotential tube changes the focusing of the ion beam, which changes the ion current in the Faraday cup and gives a sloping background in the result of CO⁺, as shown in Fig. 16.

Rotational lines in the A — X electronic absorption system of CO⁺ have been observed by Carrington and Sarre in their ion beam apparatus [31]. For their experiment, an electron impact ionization source was used to produce 10 µA of CO⁺ ions, and an argon laser with an etalon gave 400 mW output power at the single mode 457.9 nm line. They observed two rotational lines in the (1 — 0) band, Q(1) and R(12). Our experimental result is compared with their previous work in Table IV.

Table IV. Experimental measurements of the blended of Q(1) and R(12) lines in the A – X transition of CO⁺

<table>
<thead>
<tr>
<th>value (cm⁻¹)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>this work</td>
<td>21840.74 ± 0.05</td>
</tr>
<tr>
<td>previous work [31]</td>
<td></td>
</tr>
<tr>
<td>Q(1)</td>
<td>21840.79 ± 0.01</td>
</tr>
<tr>
<td>R(12)</td>
<td>21840.90 ± 0.01</td>
</tr>
</tbody>
</table>

The line spacing between Q(1) and R(12) in Table IV is about 3.3 GHz, and the intensity ratio of these two lines is 3 : 2. Our result shows (Fig. 16) that the center of the transition, from the smooth curve, is located at 21840.74 cm⁻¹ which is closer to the stronger Q(1) line. Two individual lines can not be resolved in Fig 16. The argon laser, in our experiment, runs in multimode operation, with a nominal linewidth of about 10 GHz. So it is impossible to resolve the two individual lines.
The experimental technique for studying positive ions, like CO$^+$, in the ion beam machine requires high ion beam intensity. In this experiment, the CO$^+$ ion current in the Faraday cup is 10 times stronger than C$_2^-$ ion current. So far, 30 nA ion beam current is the maximum which can be obtained in the our ion beam machine. There is a major limitation on the sensitivity of this charge-exchange detection technique, because it depends upon detecting a small change in a large ion beam flux, which therefore gives a larger noise. The noise in Fig. 16 is due to noise in the ion beam. In the earlier unpublished work in Farley's group, the ion beam noise near a frequency of 1 kHz was determined to be within a factor of two of the shut noise limit. The experimental result of CO$^+$ has demonstrated that it is possible to perform a resonance in a positive ion in our ion beam machine. Improvements are possible by using more intense ion source or by performing mass selection on the ion beam after interaction with the laser beam. A new apparatus based on the latter principle is under construction.
REFERENCES


