High current coaxial ion beam/laser beam spectrometer

Qiang Tu
University of Nevada, Las Vegas

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High current coaxial ion beam/laser beam spectrometer

Tu, Qiang, M.S.

University of Nevada, Las Vegas, 1991
HIGH CURRENT COAXIAL ION BEAM / LASER BEAM
SPECTROMETER

by

Qiang Tu

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

Master of Science

in

Physics

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University of Nevada, Las Vegas

October, 1991
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October, 1991
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ABSTRACT

The construction and operation of a new apparatus for making spectroscopic investigations of molecular ions is described. In the new ion beam machine, the ion beam and laser beam overlap in a coaxial geometry. The machine has much higher ion current than an apparatus previously used. The laser beam induces transitions between internal states of the molecular ion. The transitions are detected by allowing the ion beam to collide with background gas and detecting the surviving ion beam current. Because the cross-section depends on the internal state of the ion, the surviving ion beam current will change when the laser frequency is resonant with the ions. In a molecular ion spectroscopic experiment, high ion current is necessary for detection by laser absorption. In addition, higher current is also desirable for collisional detection. The first measurement using the new apparatus is described: the detection of transition in CO\(^+\) using collisional detection.
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CHAPTER 1. Introduction

The study of molecular ions is very important in science and industry because of their crucial roles in the plasma processing, electron and proton transfer inside biological systems, the formation of stars, and the chemistry and physics of planetary atmospheres [1]. With the development of laser and computer technology, molecular ion spectroscopy becomes more and more important in the investigation of the structure and properties of charged molecules [2].

Due to the high chemical reactivity of charged molecules and the mutual repulsion of like charges, the main difficulty in molecular ion spectroscopy is obtaining sufficient concentrations of ions to produce a detectable interaction with electromagnetic radiation. Because of this difficulty, the molecular ion spectroscopic information previously available was limited to optical emission spectra of a variety of diatomic and a few polyatomic ions [1]. In the mid-1970s, two independent experimental breakthroughs occurred, and the new era of molecular ion spectroscopy began.

One breakthrough was carried out by Wing and his co-workers in 1975 by forming the ions into a beam and exciting it with an infrared laser beam [3] [4] [5]. By using a wide variety of ion sources, a wide variety of ions can be studied with this technique. Because the concentration of ions in such a beam is small, the effects of the infrared radiation were detected by monitoring changes induced in the ion current that resulted when ions transfer their charges through collisions with a buffer gas underwent vibrational transitions. With this technique, Wing and his co-workers observed the vibration-rotation spectrum of the simple ions HD$^+$ [3], HeH$^+$ [4], D$_3^+$ [5] and H$_2$D$^+$ [6]. In 1985, Lineberger and his co-workers obtained the first vibration-rotation spectrum of a negative ion NH$^-$ [7] [8] [9]. A more detailed study of negative ion NH$^-$ was conducted by Farley and his co-workers [10] [11] [12] [13].

Another breakthrough was carried out by Woods and his co-workers by directly
measuring rotational absorption spectra of a series of simple ions (CO$^+$, HCO$^+$, and HNN$^+$) generated in an electrical discharge [14] [15] [16]. The shortcoming of this technique is that in the plasma the ions are often outnumbered by neutral species by as much as a million to one. Hence spectra of charged molecules in discharge are often completely obscured by the much stronger absorptions of neutral molecules. Later in 1983, Saykally and his co-workers developed the technique known as "velocity modulation spectroscopy" [17] [18]. This technique is based on the fact that ions in a positive column plasma are accelerated by the axial plasma electric field to a net drift velocity of about 500 m/sec, which is superimposed on their random thermal motion. This net drift velocity causes the ions to exhibit a small Doppler shift in their spectral transitions. By rapidly reversing the polarity of the discharge, spectral transitions can be Doppler-shifted in and out of coincidence with monochromatic laser radiation. As a result, the detected laser power is modulated at the same frequency at which the polarity is switched. The electronic processing yields absorption spectra of ionic transitions. In the meantime, the much stronger absorptions of the more abundant neutral species are electronically rejected because they do not exhibit the Doppler switching effect [7] [8]. With this technique Owrutsky made the first direct observation of the vibrational absorption spectrum of the negative ion OH$^-$ in 1985 [19] [20]. In 1989, Farley and his co-workers made the first observation of the visible absorption spectrum of positive ion H$_2$O$^+$ [21]. So far, over 55 positive and negative ions have been observed with this technique.

The old ion beam machine in this lab was built by Farley, Al-Za'al and Miller at University of Oregon. With the mass-selector built inside, the machine is very good at detecting negative ions [22] [23]. The maximum negative ion current obtained in this machine is 200 nA. The maximum positive ion current of CO$^+$ obtained in this machine is 30 nA [24].

In molecular ion spectroscopic experiments higher ion beam current is always
desirable because higher ion current means there will be more ions interacting with the photons and the signal to noise ratio will be bigger. The principle in designing the new ion beam machine is to obtain a higher ion beam current. For this reason, the mass-selection is omitted in the new machine, and the equipotential tube is set short. The interaction region of ions and laser is inside the equipotential tube, where the ions move with a constant speed which is determined by the potential difference between the ion source and the equipotential tube. By modulating the potential of the short equipotential tube at high frequency, we can reduce the noise significantly. The new ion beam machine consists of only six basic parts: ion source, electrostatic lenses (extractor, focus, deflector), first quadrupole, equipotential tube, second quadrupole, and detector.

By raising the potential difference between the ion source and the extractor, we can extract a large ion current from the ion source, thus the number of ions contributing to the signal will rise significantly. In our experiment with CO\textsuperscript{+}, the potential difference between the anode of the ion source and the extractor is 4000 V, so there is a tremendous force to pull the ions out of the ion source. The maximum ion current detected by the detector (Faraday Cup) in the experiment is 1000 nA. Details about this experiment will be discussed later.

Besides the high current and high frequency modulation, another important feature about this new ion beam machine system is there is no restriction on what kind of gas we can use here. Usually, the ion pump cannot work on noble gas, and the diffusion pump does not work well on hydrogen and helium gas. But the vacuum system of this machine is pumped down by the Turbo-Molecular pump, which can work in any gaseous environment.
I. Vacuum System

In ion beam spectroscopic experiments, the first thing to be done is evacuate the system where the ions will interact with the laser beam. Evacuation is the first step in creating a new gaseous environment. After feeding the ion source with the parent gas, a large number of gas molecules will enter the chamber through the aperture on the anode. The vacuum system must satisfy the continuing requirement of removing gas as it evolves. Since the beam of ions must be handled in vacuum to decrease the loss of momentum through collisions with air molecules, a good vacuum system is an essential part of the experimental apparatus of molecular ion spectroscopy [25].

The vacuum pump used in this spectrometer system is the turbo-molecular pump (Model 3102A) made by the Welch Scientific Company in 1966. This is an old version with oil lubrication. Changes were made on the structure in order to convert the oil lubrication to grease lubrication.

When the vacuum system is pumped down, the pressure may vary over several orders of magnitude. At high pressures, the mean free path of gas molecules is much smaller than the dimensions of the vacuum chamber so the gas molecules will interact with each other and behave much more like a homogeneous fluid. This is the viscous flow region. When the pressure goes lower, the mean free path of the gas molecules will become larger and larger. Finally, the mean free path will be much larger than the dimensions of the vacuum chamber, and the molecules will bounce from wall to wall. This is the molecular flow region, where the number of molecules leaving a unit of volume is proportional to the number of molecules within that volume, and this is a statistical process [25].

In general, a pump designed to work in the viscous flow region will not operate well in the molecular flow region, and vice versa. For this reason, a mechanical rotary
Figure 1. Cross-section of the oil-sealed rotary pump
pump must be used as the fore pump of the turbo-molecular pump to bring the pressure down to $1 \times 10^{-2}$ Torr before the turbo-molecular pump is turned on [26].

The oil-sealed rotary pump is shown schematically in Fig. 1 [25]. In this pump, an off-center rotor turns within a cylindrical stator. The interior of the pump is divided into two chambers by spring-loaded vanes attached to the rotor. Gas from the pump inlet enters one of these chambers and is compressed and driven through a one-way valve to the exhaust. Since the exhaust gas from the oil-sealed rotary vacuum pump contains a mist of fine droplets of oil, which is harmful to the operator's health, a filter is installed on the outlet of the rotary pump to collect those droplets.

After the pressure in the chamber is pumped down to $1 \times 10^{-2}$ torr, the turbo-molecular pump is turned on. The rotation of the rotor and the attached blades will reach 16,000 rpm within a few minutes. Fig. 2 illustrates the cross-section of the turbo the pump [26]. The molecules of air, water vapor, or other gases enter the pump from the inlet. When these molecules collide with all the interior surfaces of the inlet portion of the pump, some of them are accelerated axially toward the ends of the pump when the first disc of rotor blades strikes them. The molecules are then driven in a favorable direction by impinging upon the first disc of stator blades, which are oriented in such a way as to increase the probability of molecules being struck by the second disc of rotor blades. This process is repeated through many stages on each end of the pump and results in a high compression ratio. The faster the blades move in comparison to the speed of the free molecules, the greater the compression ratio of the pump. Thus, the compression ratio of heavy molecules, such as oil vapor, may be several orders of magnitude higher than that of the light molecules such as nitrogen and hydrogen. Since the turbo-molecular pump operates on a definite compression ratio principle, it is very important for us to keep the vacuum system away from oil or grease contamination, such as fingerprints, etc.

The fore-pressure caused by the compression of the gas is pumped by the
Figure 2. Cross-section of turbo-molecular pump
forepump connected to the outlet. The ultimate vacuum reached in the vacuum system is dependent upon the ultimate fore-vacuum, so it is very important to use an adequate pump as the forepump.

Shown in Fig.2 [26], the rotors of the turbo are supported by the refrigerated, large high speed bearings at each end of the turbo pump. In the old version Model 3102A, those bearings are lubricated by the special turbo-lubrication oil, which is more volatile than normal pump oil to prevent accidentally spattered oil from reaching the high vacuum area at the center of the pump. However, it is very easy for the inner belt to be dissolved by the lubrication oil, and this will cause the filters of the oil supply tube be blocked by the dissolved small carbon pieces. For this reason, we made some adjustments on the structure of the pump so we can use grease instead of oil to lubricate those turbo bearings.

The pumping system used, Model 3102A, includes the 3102 Turbo-molecular pump, a Welch 1397 Dul-Seal fore pump, a refrigeration system, a control panel, and a foreline manifold containing a foreline valve and a leak detection valve with coupling. The whole system is mounted on a rigid framework [26].

In order to make the upgrade conversion of Turbo Housing from oil to grease lubrication, those oil supply and drain tubes and the oil flow indicator need to be removed, and the openings will be covered with blank flanges. For the two holes right above the bearings, penetrable rubber plugs are used as the cover instead of flanges so grease can be injected to the bearing. At the time of conversion, three to four syringes full of Model 41-6331 grease are needed. For the subsequent regreasing, usually after 6-12 months service, another syringe of grease (Model 41-6331) might be needed.

Fig.3 shows the transmission part of the Model 3102A [26]. The large ball bearing is packed with red Model 41-6435 grease because there will be no more oil here for lubrication. The oil cup on the top of the transmission part is kept untouched because there will still be a need for oil to lubricate the small ball bearing of the
Figure 3. Transmission part of Model 3102A turbo pump (O-rings are numbered)
transmission. As shown in Fig.3, the three O-rings, #1, #2, #3, insulate the lubrication oil of the small ball bearing from the lubrication grease in the big ball bearing. This is the crucial part of the transmission because even a small leak in those O-rings will eventually wash out the grease in the big ball bearing. Besides, special attention must be paid to the O-rings #4 and #5, because any leak in those O-rings will cause the lubrication oil to drain out and will damage the pump. Actually, most of our time and work spent on the transmission was directed at locating and fixing the oil leaks. Usually, changing the O-ring is necessary. At other times, leaks occur because of the separation between the rubbing seal surfaces of the rotating carbon and the magnet caused by the foreign matter, or scratches across the rubbing surfaces, or noncircular gyrations and wobbling caused by installation misalignment can also cause the leakage between the rubbing seal surfaces of the rotating carbon and magnet in the magnetic seal.

Since there is no backstreaming of oil vapor in the Turbo-Molecular pump, there is no need for liquid nitrogen traps. Unlike the diffusion pump and ion pump, there is no restriction on what kinds of gas can be used in the vacuum system because any gas injected into the vacuum system will be pumped out without any damage to the vacuum system. With this advantage, this machine can study some kinds of ions which might never be made in the vacuum system evacuated by the diffusion pump or ion pump. The Turbo-Molecular pump is also free of hydrocarbon contamination because any hydrocarbons can be pumped through the pump indefinitely without damage.

After the pressure in the vacuum system is pumped down to $1 \times 10^{-2}$ Torr by the fore pump, we can turn the turbo pump on, and the pressure will reach $1 \times 10^{-4}$ Torr in 5-10 minutes, $1 \times 10^{-5}$ Torr in an hour, $1 \times 10^{-6}$ Torr in a week.

In the molecular ion beam spectroscopic experiment, the vacuum system is usually pumped down to $1 \times 10^{-5}$ Torr first. After the ion source is fed with the parent gas, the pressure inside the chamber will reach $1 \times 10^{-4}$ - $2 \times 10^{-4}$ Torr due to the
connection between the chamber and ion source. From the ideal gas law, \( PV = \frac{NK_B}{V} T \), we know that the number density of gas \( N/V = \frac{P}{K_B T} \) at \( 2 \times 10^{-4} \) Torr is about \( 6.4 \times 10^{12} \) cm\(^{-3}\).

II. Ion Beam Machine

This ion beam machine was designed to generate a high current ion beam. Fig.4 illustrates the schematic of this machine. The whole ion beam machine consists of only six parts: ion source, electrostatic lenses (extractor, focus, vertical deflector), first quadrupole equipotential tube, second quadrupole, and ion detector (grid, shield, Faraday cup). All these parts are supported by the corresponding electrical apparatus.

1. Ion Source

The ion source used is the "hot cathode, high pressure gas discharge" ion source [27], which is shown in Fig.5.

The anode and cathode are separated by a glass sleeve, and the anode is insulated from the chamber by a plastic plate. Anode and cathode are held together by six long bolts mounted on the anode plate, and teflon sleeves are used to insulate the cathode from the bolts which are attached to the anode. Inside the ion source, the two electrical feedthroughs are insulated from the cathode by two rubber and ceramic sleeves. A stainless steel shield is mounted on the cathode plate to protect the electrical feedthroughs from coating. The gas feedthrough on the cathode plate is electrically insulated from the gas tank by a teflon tube.

Fig.6 shows the electrical schematic of the supporting electrical apparatus of the ion source. After feeding the ion source with the parent gas, the filament is heated to cause emission of electrons in order to create the ions. This is achieved by connecting the filament to the transformer and putting a voltage difference of 100-200 V between the anode and cathode. The electrons are emitted by the filament and accelerated
Figure 4. Ion beam machine

- Recorder
- Electrometer
- Faraday Cup
- Quadrupole (I)
- Quadrupole (II)
- Equipotential Tube
- Laser Beam
- Ion Beam
- Vertical Deflector
- Electrostatic Lenses
- Focus
- Extractor
- Ion Source
- Brewster Window
Figure 5. Discharge ion source
towards the anode. The plasma is formed throughout the ion source due to the collision between gas molecules and electrons. The ions near the hole of the anode are extracted because of the potential difference between the ion source and outside. As shown in Fig. 6, the whole ion source is biased to +2000 V relative to the chamber wall (ground) so a lot of fast positive ions can be extracted.

2. Electrostatic Lenses

The electrostatic lenses, shown in Fig. 7, consists of three parts: extractor, focus, and vertical deflector.

The extractor is a cylinder with a diameter of 10 mm and a length of 10 mm. The voltage on the extractor is -2000 V relative to the chamber wall (ground) so the potential difference between the anode and extractor is +4000 V. With this potential difference, there is a tremendous force to draw the ions out of the ion source through the hole on the anode, thus a large ion current is obtained from the ion source. The second cylinder with diameter of 10 mm and length of 10 mm is called the focus. But actually, both the second cylinder and extractor have focusing effects. Fig. 8 shows the equipotential surfaces associated with the field produced by these two cylinders biased at different voltage $V_1$ and $V_2$. Since the voltage on the first cylinder (extractor) is fixed, the only voltage that can be adjusted to get the maximum focusing effect on ion beams is on the second cylinder. So, by convention, the second cylinder is called "focus".

The focal properties of the two-cylinder lens depend on many factors such as diameters of the cylinders, the space between them, and the ratio of the final to initial kinetic energies of the transmitted ions. Table I lists the different voltages needed on focus for different ion beam voltage. The data was obtained from Helium ions. For other kinds of gas, some slight changes may be expected.
Figure 6. Electrical schematic of ion source
Figure 7. Electrostatic lenses
<table>
<thead>
<tr>
<th>$V_{\text{beam}}$</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>300</th>
<th>370</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{\text{extra}}$</td>
<td>-100</td>
<td>-150</td>
<td>-200</td>
<td>-300</td>
<td>-370</td>
<td>-1000</td>
</tr>
<tr>
<td>$V_{\text{focus}}$</td>
<td>73</td>
<td>105</td>
<td>149</td>
<td>232</td>
<td>262</td>
<td>599</td>
</tr>
</tbody>
</table>

In the experiment on CO$^+$, the beam voltage is +2000 V, and the voltage on extractor is -2000 V. According to our experiment, the focus voltage should be about +832 V to get the maximum focal effect. Fig. 8 shows the electrical schematic of the focus. The maximum resistance of the potentiometer is 200 K, and its power rating is 8 W. All of the resistors have a 2 W power rating. With the circuit of Fig. 9, about +500 V to 1500 V output was achieved from the +2000 V input. The design principle of the circuit will be discussed in detail in the corresponding circuit of quadrupole.

The deflector consists of two parallel plates installed horizontally. Fig. 10 shows the electrical schematic of the deflector. In the experiment of CO$^+$, the potential on the top and the bottom plate of the deflector were set to +12 V and -12 V respectively to get the maximum ion current through the aperture of the equipotential tube. During the experiment, the ion source filament became thinner and thinner due to its vaporization, and the condition of the plasma in the ion source drifted around, so constant adjustments on the deflector were needed to get the maximum ion beam through. The deflector also has some focusing effects on the ion beam. After the adjustment on the deflector, adjustment on the focusing voltage was needed again to compensate for the focusing effect of the deflector.

3. First Quadrupole

Fig. 11 illustrates the quadrupole [28]. The four sections of the cylinder are insulated from ground and each other by plastic balls. The four sections are made from aluminum.
Figure 8. Equipotential surfaces of two cylindrical lenses
Figure 9. Electrical schematic of focus

DC Power Supply

$R_1''$, 220 K

$R_1'$, 200 K

$R_2''$, 220 K

To Focus

$+2000$ V

$0 \sim 200$ K

$+500$ V $\sim +1500$ V
Figure 10. Electrical schematic of deflector
Figure 11. Quadrupole beam bender
In order to bend positive ion beams by 90°, the repulsive cylinder pair is electrically connected to a common positive potential and the attractive cylinder pair is electrically connected to a common negative potential. Fig. 12 shows the equipotential surfaces associated with the field produced by the two pair of cylinders biased at positive voltage $V_+^+$ and negative voltage $V_-^-$.

Table II lists the voltages needed on the quadrupole for helium ions of different beam voltage.

Table II. Voltages (V) on quadrupole (I) for different ion (He$^+$) beam voltage (V)

<table>
<thead>
<tr>
<th>$V_{beam}$</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>300</th>
<th>370</th>
<th>1000</th>
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<tr>
<td>$V_{rep}^+$</td>
<td>61</td>
<td>83</td>
<td>111</td>
<td>172</td>
<td>199</td>
<td>483</td>
</tr>
<tr>
<td>$V_{attr}^-$</td>
<td>-80</td>
<td>-118</td>
<td>-157</td>
<td>-233</td>
<td>-304</td>
<td>-802</td>
</tr>
</tbody>
</table>

In the experiment with CO$^+$ ions, the ion source is biased at +2000 V, so the beam voltage is +2000 V. The most effective voltage to get the ions through the equipotential tube was about +1126 V on the repulsive pair and -1436 V on the attractive pair of the quadrupole. Fig. 13 illustrates the schematic of the electrical circuit for the attractive pair of the quadrupole.

When designing an electrical circuit, the power rating of each electrical element must be taken into account. The power rating of the potentiometer here is 8 W, but the power rating of the resistor used is only 2 W. As shown in Fig. 13, the voltage input is -2000 V, in order to get the -700 V to -1700 V output to the attractive pair, the voltage put across the resistors $R''$ and $R'$ are -300 V and -700 V respectively with a voltage of -1000 V on the potentiometer. This is within its power rating. From Ohm's law, the resistances of $R'$ and $R''$ will be 140 K and 60 K ($V'/R' = V/R = V''/R''$). By connecting three 200 K resistors in parallel and two 300 K in parallel, the combined resistances $R''$ and $R'$ are 100 K and 67 K, which are close to the required resistances. The power on each resistor is only 0.45 W ($P = V^2/R$) and is far below the power rating of the
Figure 13. Electrical schematic of the attractive pair of quadrupole
resistor. All the electrical circuits in this project are designed far below the power rating.

4. Equipotential Tube

As shown in Fig. 14, the equipotential tube is a hollow cylinder held by two insulating teflon holders. The laser and ion beam are sent through and overlap each other along the axis of the tube. The tube voltage is set by a DC power supply. The kinetic energy of the ions in the tube is determined by the potential difference between the tube and the anode of the ion source. Inside the tube, there is no electric field because of the electrostatic shield, so the ions inside the tube move with constant speed. This is the region where the ions and photons interact with each other. By changing the tube voltage, we can change the speed of the ions inside the tube, thereby tuning the laser frequency in the ion rest frame to the resonant frequency of the ions because of the Doppler shift. This will be discussed in detail in the section about the observation of CO⁺.

For a longer tube, the ion beam has more overlap with the laser beam. But, a longer tube also means fewer ions will pass through the tube and reach the detector. It is desirable to take into account both sides and make a compromise to obtain the optimum effect. The tube used is 67mm long with the aperture of diameter 3 mm. In the experiment of CO⁺, about 500nA to 1μA ions passed through the tube and reached the detector (Faraday cup).

By modulating the potential of the short tube at a high frequency, the noise of the ion beam can be reduced significantly. This is another advantage of the short tube.

5. Second Quadrupole

After the ions pass through the tube, they will be bent 90° again by the second quadrupole to reach the detector (Faraday cup). The structure of the second quadrupole
Figure 14. Equipotential Tube
is the same as the first quadrupole. Table III lists the voltage needed on the second quadrupole for helium ions of different beam voltage.

Table III. Voltages (V) on quadrupole (II) for different ion (He\(^+\)) beam voltage (V)

<table>
<thead>
<tr>
<th>(V_{\text{beam}})</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>300</th>
<th>370</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>(V_{\text{rep}})</td>
<td>67</td>
<td>97</td>
<td>130</td>
<td>197</td>
<td>243</td>
<td>672</td>
</tr>
<tr>
<td>(V_{\text{attr}})</td>
<td>-37</td>
<td>-55</td>
<td>-71</td>
<td>-100</td>
<td>-128</td>
<td>-266</td>
</tr>
</tbody>
</table>

6. Detector

The detector, as shown in Fig. 15, consists of three main parts: shield, grid and Faraday cup. The ions are collected by the Faraday cup and the resultant electrical current is measured by the electrometer directly. When the fast ions hit the metal surface of the Faraday cup, the impact creates secondary electrons [25]. In the experiment with CO\(^+\) ions, the Faraday cup is used as a positive-ion collector, so the loss of secondary electrons will be looked at as additional ions by the electrometer. To prevent the escape of secondary electrons, the depth of the Faraday cup is designed bigger than its diameter, as shown in Fig. 15. The grid biased at -30 V in front of the Faraday cup is also used to prevent the escape of the secondary electrons. A grounded shield is installed to prevent the charged particle from the chamber from reaching the outside of the Faraday cup.

III. Laser

The laser used in this spectrometer system is Coherent's INNOVA 10 argon ion laser which is comprised of two major functional units: the laser head with the plasma tube and the power supply[29].

In the argon ion laser, the main contribution to the spectral linewidth is the Doppler width, which is due to the thermal motion of the absorbing or emitting
Figure 1.5. Detector
molecules in gases at low pressure.

At thermal equilibrium, the molecules of a gas follow a Maxwellian velocity distribution. At the temperature $T$, the number of molecules $n_i(v_z)dv_z$ in the level $E_i$ per unit volume with a velocity component between $v_z$ and $v_z+dv_z$ is

$$n_i(v_z)dv_z = \frac{N_i}{\sqrt{\pi}} \frac{1}{v_p} e^{-\left(\frac{v_z}{v_p}\right)^2} dv_z \quad (1)$$

where $N_i = \int n_i(v_z) dv_z$ is the density of all molecules in level $E_i$, $v_p = (2kT/m)^{1/2}$ is the most probable velocity, $m$ is the mass of a molecule, and $k$ is Boltzmann's constant.

Because of the Doppler shift, the number of molecules with absorption frequencies shifted from $\omega_0$ into the interval from $\omega$ to $\omega + d\omega$ is

$$n_i(\omega) d\omega = \frac{N_i c/\omega_0}{v_p \sqrt{\pi}} e^{-\left[\frac{(c/v_p)(\omega - \omega_0)}{\omega_0 v_p}\right]^2} d\omega \quad (2)$$

Since the emitted or absorbed radiant power $P(\omega)d\omega$ is proportional to the density $n_i(\omega)d\omega$, the intensity profile of a Doppler-broadened spectral line becomes

$$I(\omega) = I_0 \exp \left[ - \left[ \frac{c(\omega - \omega_0)}{\omega_0 v_p} \right]^2 \right] \quad (3)$$

This is a Gaussian profile with a FWHM $\delta\omega_d = |\omega_1 - \omega_2|$.

With the relation of $I(\omega_1) = I(\omega_2) = I(\omega_0)/2$, the Doppler width can be calculated as

$$\delta\omega_d = \frac{\omega_0}{c} (8kTln2/m)^{1/2} \quad (4)$$

The spacing between two adjacent longitudinal modes is $c/2L$, where $L$ is the
cavity length of the laser. The number of longitudinal mode in the laser is $\delta \omega L/(c/2L)$, and the output power is roughly spread equally on each mode.

The output of the INNOVA 10 is 10 W when the laser runs in multiline operation. With the installation of Mdl 434 prism, the laser could run in different single lines. The multimode output of a single line 457.9 nm is 300 mW. The exact temperature inside the tube of the argon ion laser we used is not known. According to one authority [30], the temperature inside the Argon ion laser tube could be as high as 3000 K, which means the Doppler linewidth could be as wide as 4.0 GHz. The typical Doppler linewidth of argon ion laser is 3.5 GHz [30]. The cavity length of our argon ion laser with the Mdl 434 prism is 1800 mm. The spacing between two adjacent longitudinal modes is 80 MHz. The number of modes (include those run in the wing area) is about 100. The power on each longitudinal mode is about 3.0 mW.
CHAPTER 3. $\text{CO}^+$ Resonance Experiment

I. Theory

1. The Born-Oppenheimer Principle

The Born-Oppenheimer principle, based on the concept of separability between electronic and nuclear motions, vastly simplifies the assignment of different spectral features to different types of molecular motion. Without it, electronic and nuclear motions would be scrambled in complicated molecular Hamiltonians, and extensive numerical calculations would be necessary to extract even the most qualitative features of vibrational and rotational structure\[31\].

The non-relativistic Hamiltonian for a diatomic molecule with $m$ electrons is

$$
H = \sum_{n=1}^{2} \frac{-\hbar^2}{2m_n} \nabla_n^2 + \sum_{i=1}^{m} \frac{-\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{4\pi\varepsilon_0} \sum_{i<j}^{m} \frac{e^2}{|r_i - r_j|}
$$

$$
- \frac{1}{4\pi\varepsilon_0} \sum_{i=1}^{m} \sum_{n=1}^{2} \frac{Z_ne^2}{|r_i - R_n|} + \frac{1}{4\pi\varepsilon_0} \frac{Z_aZ_be^2}{|R_a - R_b|} + H_{so}
$$

where the contributing terms include the nuclear kinetic energy, the electronic kinetic energy, the electron-electron repulsion, the electron-nuclear attraction, the nuclear-nuclear repulsion, and the spin-orbit coupling.

The Schrödinger equation for the diatomic is

$$
H(r,R) \mid \Psi(r,R) \rangle = E \mid \Psi(r,R) \rangle
$$

where $r$ and $R$ represent the sets of electronic and nuclear coordinates, respectively.

By subtracting the nuclear kinetic energy and spin-orbit operator, the electronic Hamiltonian $H_{el}$ may be defined as follows
It is possible to find eigenfunctions of $H_{\text{el}}$ for fixed $R$, such that

$$H_{\text{el}}(r,R) \mid \Psi_k(r;R) \rangle = \mathcal{E}_k(R) \mid \Psi_k(r;R) \rangle$$

The resulting electronic states $\mid \Psi(r,R) \rangle$ depends parametrically on $R$ in the choice of fixed nuclear positions influences the electronic states. The $\mathcal{E}_k(R)$ are the diatomic potential energy curves, i.e., the electronic energies of the various states $k$ as functions of the internuclear separation $R$.

The solutions $\mid \Psi(r,R) \rangle$ to the full diatomic Hamiltonian can be achieved by expanding the form

$$\mid \Psi(r,R) \rangle = \sum_k a_k \mid \Psi_k(r;R) \rangle \mid \chi_k(R) \rangle$$

where the $\mid \chi_k(R) \rangle$ are the diatomic nuclear (vibrational-rotational) wave functions in electronic state $k$, and $a_k$ are expansion coefficients.

With the substitution of $\mid \Psi(r,R) \rangle$ into the diatomic Schrodinger equation and neglect of the terms of $\langle \Psi_k \mid V_r \mid \Psi_k \rangle$ (i.e., the electronic states $\mid \Psi_k \rangle$ do not normally oscillate violently with internuclear separation $R$), we obtain

$$\left[ -\frac{\hbar^2}{2\mu_n} \nabla_R^2 + U_{kk}(R) - E \right] \mid \Psi_k(R) \rangle = 0$$

where $U_{kk}(R) = \langle \Psi_k \mid H_{\text{el}} + H_{\text{so}} \mid \Psi_k \rangle$

$$= \mathcal{E}_k(R) + \langle \Psi_k \mid H_{\text{so}} \mid \Psi_k \rangle$$

when the spin-orbit coupling is small, $U_{kk}(R) = \mathcal{E}_k(R)$, and $\mu_n$ is the reduced mass of the nuclei. The equation becomes a Schrodinger equation for nuclear motion (vibration and rotation) in the potential $U_{kk}(R)$ specified by the potential energy curve $\mathcal{E}_k(R)$ of electronic state $k$. This eigenvalue equation then leads to the diatomic rotational and vibrational states in molecular spectroscopy.
2. Diatomic Rotational Energy Levels

For the rotational motion of an idealized rigid diatomic rotor, the R is considered fixed at \( R_0 \). By setting the constant \( U_{kk}(R) = U_{kk}(R_0) = 0 \), the Schrödinger equation of the diatomic becomes

\[
- \frac{\hbar^2}{2\mu_n} \left[ \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) - \frac{J^2}{\hbar^2 R^2} \right] |\chi_{\text{rot}}\rangle
\]

\[
= \frac{J^2}{2\mu_n R_0^2} |\chi_{\text{rot}}(\theta,\phi)\rangle = E_{\text{rot}} |\chi_{\text{rot}}(\theta,\phi)\rangle
\]

where \( J = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \).

Hence the rigid rotor Hamiltonian is

\[
H_{\text{rot}} = \frac{J^2}{2\mu_n R_0^2} = \frac{J^2}{2I}
\]

where \( I \) is the rotational moment of inertia, \( I = \mu_n R_0^2 \).

The eigenfunctions of \( H_{\text{rot}} \) are the spherical harmonics

\[
|\chi_{\text{rot}}(\theta,\phi)\rangle = Y_{JM}(\theta,\phi)
\]

\( J = 0, 1, 2, ... \)

\( M = J, J-1, ..., -J+1, -J \)

The eigenvalues are

\[
E_{\text{rot}}(\text{cm}^{-1}) = B J (J+1)
\]

where \( B \) (the rotational constant in cm\(^{-1}\)) is

\[
B = \hbar^2 / 2\hbar c I = \hbar / 8\pi^2 c I
\]

3. Diatomic Vibrational Energy Levels
The Schrödinger equation for nuclear motion in the Born-Oppenheimer approximation is

\[ \left[ \frac{U_k(R)}{2\mu_n} - \frac{\hbar^2}{2\mu_n} \left( \frac{1}{R^2} \frac{\partial}{\partial R} \left[ R^2 \frac{\partial}{\partial R} \right] - \frac{J^2}{\hbar^2 R^2} \right) \right] |\chi_k(R)> = E |\chi_k(R)> \]  

where \( |\chi_k(R)> \) is the wave function for nuclear motion in electronic state \( k \).

By making the substitution \( |\chi_k(R)> = S_k(R) Y_{JM}(\theta,\phi)/R \), the Schrödinger equation for vibrational motion with eigenstates \( S_k(R) \) becomes

\[ \frac{d^2}{dR^2} S_k(R) + \frac{2\mu_n}{\hbar^2} \left[ E - U_{kk}(R) - \frac{J(J+1)}{2\mu_n R^2} \right] S_k(R) = 0 \]  

where \( S_k(R) \) represent vibrational wave functions in electronic state \( k \) under the effective vibrational potential \( U_{vib}(R) = U_{kk}(R) + J(J+1)/2\mu_n R^2 \).

The \( U_{kk}(R) \) is the electronic potential energy curve \( \varepsilon_k(R) \), corrected by the expectation of the spin-orbit coupling Hamiltonian. It can be expanded in a Taylor series about the equilibrium separation \( R = R_e \)

\[ U_{kk}(R) = U_{kk}(R_e) + \left( \frac{dU_{kk}}{dR} \right)_{R_e} (R - R_e) + \frac{1}{2} \left( \frac{d^2U_{kk}}{dR^2} \right)_{R_e} (R - R_e)^2 + ... \]  

The \( U_{kk}(R_e) \) can be set to zero and \( dU_{kk}/dR \) vanishes at the local minimum \( R = R_e \), thus
U_{kk}(R) \equiv \frac{1}{2} K (R - R_e)^2 \quad (15)

where \( K = \left( \frac{d^2 U_{kk}}{dR^2} \right)_{R_e} \) is the spring constant.

For pure vibrational motion \((J = 0)\), the Schrödinger equation of the diatomic becomes

\[
\left[ -\frac{\hbar^2}{2\mu_n} \frac{d^2}{dR^2} + \frac{1}{2} K (R - R_e)^2 \right] S_k(R) = E \ S_k(R) \quad (16)
\]

Its eigenfunctions and eigenvalues are

\[
S_k(R) = N_v \ e^{-x^2/2} H_v(x) = |v> \quad (17)
\]
\[
E_{vib} = \hbar \ \omega (v + 1/2) \quad (18)
\]
\[ v = 0, 1, 2, ... \]

where \( x = (R - R_e) \sqrt{\mu_n/\hbar} \), \( \omega = \sqrt{K/\mu_n} \), and the \( H_v \) are the Hermite polynomials in \( x \).


An ion of mass \( M \) and charge of \( q \) is created in the ion source at electrostatic potential \( V_s \), having initial kinetic energy \( T_s \). In the interaction region, the ion has potential energy and kinetic energy given by \( qV \) and \( T \). The total energy \( E \) is conserved in the electrostatic acceleration process, and therefore

\[
T_s + qV_s = T + qV \quad (1)
\]

We neglect the small probability of collision between ions and background gas (buffer
gas) during the extraction. Such collisions might produce a small asymmetry to the resonances. \( V_s \) is the voltage applied to the anode of the ion source, with a small correction arising from space-charge and similar effects within the ion source, and the width \( \Delta V_s \) is determined by the variation of the potential over the effective source volume. \( T_s \) and \( \Delta T_s \) are determined by the production mechanism for the ion. \( V \) is the voltage on the equipotential tube.

The kinetic energy \( T \) is given by special relativity as

\[
T = \left[ (1 - \beta^2)^{-\frac{1}{2}} - 1 \right] \frac{1}{2} \text{Mc}^2
\]  

where \( \beta = v/c \). The ion beam overlaps the laser at an angle \( \theta \), defined so that \( \theta = 0(\pi) \) corresponds to parallel (antiparallel) beams. The laser frequency \( v \) is Doppler shifted to \( v' \) in the ion frame. The two frequencies are related by

\[
v' = v \left( 1 - \beta \cos \theta \right) \left( 1 - \beta^2 \right)^{\frac{1}{2}}
\]

In order to obtain \( v' \) as a function of \( V \), we rearrange Eq.(2) to express \( \beta \) as

\[
\beta = \frac{1}{(2\eta + \eta^2)^{\frac{1}{2}} / (1 + \eta)}
\]

where the small ratio \( \eta \) is \( T/\text{Mc}^2 \).

From Eq.(1), \( \eta \) can also be expressed as

\[
\eta = [T_s + q (V_s - V)]/ \text{Mc}^2
\]
Insertion of Eq.(3) in Eq.(2) yields

$$v' = v \left[ 1 + \eta - \left(2\eta + \eta^2\right)^{\frac{1}{2}} \cos \theta \right]$$

(6)

The Doppler shift thus can be expressed as a function of $V$

$$\Delta \nu(V) = \nu - v'$$

$$= v \left[ \eta - \left(2\eta + \eta^2\right)^{\frac{1}{2}} \cos \theta \right]$$

(7)

where $\eta = \frac{T_s + q(V_s - V)}{M c^2}$.

As the voltage of the ion beam is scanned, the ions are Doppler tuned through resonance. The conversion between frequency and voltage, the differential Doppler shift, is given by

$$\frac{d\nu'}{dV} = -(q\nu/Mc^2)[1 - \left(2\eta + \eta^2\right)^{\frac{1}{2}} (1 + \eta) \cos \theta]$$

(8)

For $\beta \ll 1$, the useful approximation can be made as

$$v' = v \left[ 1 - \left(2(T_s + qV_s - qV) / Mc^2\right)^{\frac{1}{2}} \cos \theta \right]$$

(9)

and

$$\frac{d\nu'}{dV} = q\nu \left[2Mc^2(T_s + qV_s - qV)\right]^{\frac{1}{2}} \cos \theta$$

(10)

In our experiment on $\text{CO}^+$, the numerical values of the relevant quantities are $q(V_s - V) = 2.6 \text{ KeV}$, $T_s \approx 0$, $\cos \theta = -1$, $M = 28 \text{ amu}$, $\nu = 21830.96 \text{ cm}^{-1}$, yielding $\beta = 4.47 \times 10^{-4}$, $\eta = 9.94 \times 10^{-1}$, $\Delta \nu = 9.93 \text{ cm}^{-1}$, $\frac{d\nu'}{dV} = 2.1 \times 10^{-4} \text{ cm}^{-1}/V$ ($6.3 \text{ MHz/V}$).
II. Observation of electronic absorption spectra of CO$^+$

1. Experimental Procedure

Fig. 16 illustrates the schematic of the experiment on CO$^+$. By feeding the ion source with high purity carbon monoxide gas, about 500 nA to 1000 nA CO$^+$ ion currents are detected by the Faraday cup. A homemade electrometer is connected to the Faraday cup so the current signal is converted to a voltage signal. The electrometer has two outputs, one of which goes to the voltmeter and another goes to the lock-in amplifier. The ion beam current is monitored by the voltmeter. The signal is amplified by the lock-in amplifier and sent to the chart record. The argon laser used is the Coherent Innova-10 with the output of 300 mW at 457.9 nm. The laser beam is mechanically chopped at 1000 Hz before being sent through the rear Brewster window. The chopper sets the reference frequency to the lock-in amplifier. Two convex lenses ($f_1 = 500$ mm, $f_2 = 100$ mm) are used to focus the laser through the aperture of the equipotential tube. The laser power inside the equipotential tube is about 230 mW due to the energy losses caused by the lenses, mirrors, and windows.

With the help of a computer, the voltage on the equipotential tube scans from -800 V to -400 V. The scanning parameters are 400 points and 3 seconds per point. Since the voltage of the anode is +2000 V, the tuning range of kinetic energy of the ion beam is from 2800 V to 2400 V.

2. Results

Tuning the voltage on the tube causes the change of the speed of ions inside the tube. The Doppler shifted frequency $\nu'$ of the laser beam seen by ions in the equipotential tube is:

$$\nu' = \nu \left[ 1 + \eta - (2\eta + \eta^2)^{-\frac{1}{2}} \cos \theta \right],$$
Figure 16. Block Diagram of the CO$^+$ Experiment
where ν is the laser frequency in the fixed laboratory frame, cosθ is -1 corresponding to the antiparallel beam, and the η can be expressed as

\[ \eta = \frac{T_s + q(V_s - V)}{Mc^2}. \]

The experimental result, Fig.17, shows that resonance occurs when the potential difference the ions experience is between 2564 V and 2655 V. Details about the observed signal will be discussed later. Table IV shows the important information about the ion beam in this experiment.

Table IV. Ion beam parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resonant beam voltage (V)</td>
<td>2564.0 - 2655.0</td>
</tr>
<tr>
<td>Ion current (nA)</td>
<td>500.0</td>
</tr>
<tr>
<td>Length of ion beam (cm) L</td>
<td>6.7</td>
</tr>
<tr>
<td>Ion beam cross-section (cm²) A</td>
<td>1.8 x 10⁻²</td>
</tr>
<tr>
<td>Volume of ion beam (cm³) LA</td>
<td>1.2 x 10⁻¹</td>
</tr>
<tr>
<td>Ion density (ions/cm³)</td>
<td>1.3 x 10⁷</td>
</tr>
<tr>
<td>Ion velocity (cm/s)</td>
<td>1.3 x 10⁷</td>
</tr>
<tr>
<td>ratio β</td>
<td>4.5 x 10⁻⁴</td>
</tr>
<tr>
<td>ratio η</td>
<td>9.9 x 10⁻⁸</td>
</tr>
<tr>
<td>Number of ions in beam (ions) n</td>
<td>1.6 x 10⁶</td>
</tr>
<tr>
<td>Pressure of background gas (Torr)</td>
<td>2.0 x 10⁻⁴</td>
</tr>
<tr>
<td>Density of background gas (molecules/cm³)</td>
<td>6.4 x 10¹²</td>
</tr>
</tbody>
</table>

The laser wavenumber in this experiment is 21830.96 cm⁻¹ in the laboratory frame. The mass of CO⁺ is 28 amu, which equals 28 x 1.66 x 10⁻²⁷ kg = 4.65 x 10⁻²⁶ kg. Since the resonant potential difference between the anode and the tube is from 2564 V
to 2629 V, it is very easy to show that the resonant frequency of the laser beam seen by CO\(^+\) ions ranges from 21840.63 cm\(^{-1}\) to 21840.75 cm\(^{-1}\).

3. Signal Analyses

The previous work done by Carrington and Sarre shows that this is about the voltage range where the ions excited from the \(X^2\Sigma^+ (v''=0)\) to the \(A^2\Pi(v'=1)\) electronic states \([32]\ [33]\). The radiative lifetime of CO\(^+\) in A state is 3.4 x 10\(^{-6}\) s. Thus the Einstein coefficient is

\[
B_{10} = \frac{c^3}{8\pi\hbar^2} A_{10} = \frac{c^3}{8\pi\hbar^2} \frac{1}{\tau_1} = 5.9 \times 10^{18} \text{ (m}^3/\text{joule.s}^2) \]

\[
B_{01} = B_{10} = 5.9 \times 10^{18} \text{ (m}^3/\text{joule.s}^2) \]

The laser power in the interaction region is 230 mW. The cross-section of the laser beam is 1.8 x 10\(^{-1}\) cm\(^2\), thus the laser intensity is 12.8 W/cm\(^2\). The energy density in the laser beam is

\[
\rho(v) = \frac{I}{c\delta v} = 1.2 \times 10^{-13} \text{ (joule.s/m}^3) \]

where \(I\) is the laser intensity in the interaction region, and \(\delta v\) (3.5 GHz) is the FWHM linewidth of the laser.

The probability of laser-induced transition of ions from the X state to the A state is

\[
P_1 = \frac{dP_{01}}{dt} = B_{01} \rho(v) \delta t = 33.3\% \]

where \(\delta t\) is the time the ions fly through the interaction region.

Before the laser interacts with the ions, almost all the ions are in the ground
Figure 18. Population distribution of CO among different rotational states
vibrational state, but they are spread in different rotational states. Fig. 18 shows that about 5% of the ions are in the J = 11 rotational state when the rotational temperature is in the range of 300 K - 1200 K, and it is almost independent of the temperature of the plasma in the ion source. Due to the collision between the ions and the background gas molecules, the ion flux at the Faraday cup can be expressed as

$$N_{\text{cup}} = N_0 \exp(-d\sigma_x L)$$

where $N_0$ is the ion flux with zero background gas, $d$ is the density of the background gas, $\sigma_x$ is the collisional cross-section between CO$^+$ ions in the X-state and the background gas molecules, and $L$ is the length of the interaction region.

After the laser is turned on, some of the ions in the X-state will be excited to the A-state. Since the lifetime of the A-state ($3.8 \times 10^{-6}$ s) is longer than the time during which the ions interact with the laser ($5 \times 10^{-7}$ s), the flux of ions in the X-state and the A-state can be expressed as

$$N_A = N_0 P$$
$$N_X = N_0 (1 - P)$$
$$P = P_1 f$$

where $P_1$ is the transition probability from the X-state to the A-state, and $f$ is the population fraction of ions in a specific rotational state of the X-state.

The ion flux in the Faraday cup becomes

$$N'_{\text{cup}} = N_X \exp(-d\sigma_x L) + N_A \exp(-d\sigma_A L)$$
$$= N_X (1 - d\sigma_x L) + N_A (1 - d\sigma_A L)$$
$$= N_0 - N_0d\sigma_x L + N_0PdL(\sigma_x - \sigma_a)$$

The resonance can be observed through the change of the ion flux in the Faraday cup before and after the laser interacts with the ions. The signal observed can be expressed as

$$\text{Signal} = N'_{\text{cup}} - N_{\text{cup}}$$
$$= N_0 - N_0d\sigma_x L + N_0PdL(\sigma_x - \sigma_a) - N_0 \exp(-d\sigma_x L)$$
The collisional cross-section between the ions in the X-state and the background gas molecules can be obtained by considering the ion flux in the Faraday cup without the resonance induced by laser. Since the ion flux in Faraday cup can be obtained by measuring the ion current in the cup, the ion flux with and without the background gas is calculated as $3.1 \times 10^{12}$ and $3.8 \times 10^{12}$ ions/s, respectively. Since the ion flux in the Faraday cup with the background gas can be expressed as

$$N_{\text{cup}} = N_0 \exp(-d\sigma_x L)$$

the collisional cross-section between the ions in the X-state and background gas molecules can be calculated as follows

$$\frac{N_{\text{cup}}}{N_0} = \exp(-d\sigma_x L) = \frac{3.1}{3.8}$$

$$\sigma_x = \frac{1}{dL} \ln(3.8/3.1)$$

$$= 4.7 \times 10^{-15} \text{ (cm}^2)$$

Since we don't know the collisional cross-section between the ions in the A-state and the background gas, a reasonable assumption can be made here. We assume that $\sigma_a = \sigma_x (1 + 0.07\%)$, then the difference between these two collisional cross-sections is -0.07% $\sigma_x$; thus the signal is

$$\text{Signal} = N_0 PdL(\sigma_x - \sigma_a)$$

$$= -0.07\% N_0 PdL \sigma_x$$

$$= -8.82 \times 10^6 \text{ (ions/s)}$$

The shot noise is

$$\text{Noise} = \sqrt{N_{\text{cup}}} = 1.8 \times 10^6 \text{ (ions/s)}$$
The signal to noise ratio is

\[ R = \frac{\text{Signal}}{\text{Noise}} = 4.9 \]

This result matches the observed signal to noise ratio shown in Fig.17.

Table V shows all the parameters related to the calculation of the signal to noise ratio.

Table V. Parameters for calculation of signal/noise ratio

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion flux at zero background pressure (ions/s)</td>
<td>(3.8 \times 10^{12})</td>
</tr>
<tr>
<td>Ion flux at operating background pressure (ions/s)</td>
<td>(3.1 \times 10^{12})</td>
</tr>
<tr>
<td>Shot noise in ion beam (ions/s)</td>
<td>(1.8 \times 10^6)</td>
</tr>
<tr>
<td>Laser power (mW)</td>
<td>(2.3 \times 10^2)</td>
</tr>
<tr>
<td>Probability of laser-induced transition for ions (X-A)</td>
<td>33.3%</td>
</tr>
<tr>
<td>Fraction of ions in a single rotational state (J=10-12)</td>
<td>5%</td>
</tr>
<tr>
<td>Signal (ions/s)</td>
<td>(8.8 \times 10^6)</td>
</tr>
<tr>
<td>Signal/Noise</td>
<td>4.9</td>
</tr>
</tbody>
</table>

In the previous experiment done by Carrington and Sarre, \(H_2\) was used as the buffer gas. By monitoring the \(HCO^+\) mass peak, two rotational lines in the \(A^2\Pi(v'=1) \rightarrow X^2\Sigma^+(v''=0)\) electronic absorption system of \(CO^+\) were observed, and the resonance voltages were 2647 V for the \(R_{12}(10.5)\) line and 2590 V for the \(Q_{11}(11.5)\) line. The laser frequency was 21831 cm\(^{-1}\) [33]. If the linewidth of the laser is 3.5 GHz, the signal observed should be approximately the one shown in Fig.19. There are some discrepancies between this theoretical prediction and the real signal we observed. There is no sign of any \(R_{12}(10.5)\) resonance in our result. There are several factors
Figure 19. Theoretical prediction of CO⁺ resonance signal.
which might have contributed to the discrepancies. First, the ion source used in Carrington's experiment was the "electron impact" ion source, which might have populated the ions in different energy levels from the "high-pressure discharge" ion source which we used in our experiment. Second, the buffer gas used in Carrington's experiment was H₂ gas, and the kinetic energy of the ions in the collisional area was only 2 eV. In our experiment, the kinetic energy of ions was more than 2000 eV, and we used CO gas as the buffer gas. The collisional cross-section between the internal state of the CO⁺ ions and the CO molecules might be different from the collisional cross-section between the CO⁺ ions and H₂ molecules, and this could cause the collisional detection technique to fail to detect certain resonance lines. Finally, there is also a probability that the sensitivity of this experimental is not high enough to detect the weak resonance lines such as R₁₂(10.5). If we were to use a single mode laser in a future experiment, we could find out if there is any R₁₂(10.5) resonance in this experiment. Since this experiment was basically designed to test the newly built ion beam spectrometer, the observed resonance of Q₁(11.5) of CO⁺ is considered good enough to show that the new ion beam machine works well.
CHAPTER 4. Conclusion

So far, the maximum ion current obtained in this new ion beam machine is 1000 nA. Because there is no mass selector built inside, this machine is desirable for studying positive ions with the collisional detection technique. The observation of CO⁺ resonance shows that this project is successful.

In the experiment with CO⁺, the argon ion laser ran in multimode, and the power on each mode was about 2.3 mW. Because the wavelength of the laser is not tunable, we could change only the speed of ions to tune the laser frequency seen by ions to the resonance frequency by tuning the voltage on the equipotential tube. In the future, a tunable, single mode output ring laser will be used to investigate certain molecular ions, and the equipotential tube will be voltage modulated at high frequency. The signal to noise ratio is expected to be raised significantly after these improvements of the spectrometer system are made:

1. So far, we obtained only a 10% ion current through the equipotential tube. By improving the focusing apparatus, we believe we can also raise the ion beam current in the interaction region significantly.

2. In the future, an optical cavity will be built inside the chamber so the laser beam can bounce inside the cavity many times and the number of interactions with the ions can also be raised many times. An increase by a factor of 100-200 is to be expected by the building of optical cavity inside the ion beam machine.

3. By floating the inner part of the ion beam machine to high voltage and keeping the ion source and the detector at low potential, we can perform collisional detection at low collisional energy. With this technique and the help of a mass spectrometer, we can understand precisely what kind of ions are obtained and detected by this spectrometer system.

4. It is also possible to implement laser absorption detection by detecting the
attenuation of the laser beam caused by the resonance absorption of ion beam. In this case, the equipotential tube needs to be voltage modulated at high frequency, and this can also be done in the new ion beam machine.
REFERENCES


