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Novel techniques for molecular ion spectroscopy in a discharge

Guang Lan
University of Nevada, Las Vegas

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Novel techniques for molecular ion spectroscopy in a discharge

Lan, Guang, M.S.

University of Nevada, Las Vegas, 1990
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NOVEL TECHNIQUES FOR MOLECULAR ION SPECTROSCOPY

IN A DISCHARGE

By

Guang Lan

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

Master of Science

in

Physics

Department of Physics
University of Nevada, Las Vegas
July, 1990
The thesis of Guang Lan for the degree of Master of Science in Physics is approved.

Chairman, Dr. John W. Farley

Examiner Committee Member, Dr. James C. Selser

Examiner Committee Member, Dr. David P. Shelton

Graduate College Representative, Dr. Richard Titus

Graduate Dean, Dr. Ronald W. Smith

University of Nevada, Las Vegas
Las Vegas, Nevada
July, 1990
ABSTRACT

Velocity modulation laser spectroscopy has proven to be a successful spectroscopic technique for the study of molecular ions; indeed, it has become the conventional technique. However, there are a number of limitations to velocity modulation in its conventional form. First, there is a background arising from r.f. pick-up or optical emission. Because the background is at the same frequency as the desired signals, the background is hard to eliminate. Fluctuations in the background level can make it difficult to detect signals. Second, in many experiments the dominant source of noise is the detector, and sensitive detectors are often inconveniently slow. Two new spectroscopic techniques appropriate for the study of molecular ions are described, which address these problems: (1) double modulation spectroscopy with background elimination, and (2) difference frequency spectroscopy. The first technique has been used to detect a transition in HeH⁺, the v=1-0 P(1) line at 2843.904 cm⁻¹ using a diode laser. The second technique, difference frequency spectroscopy, allows the laser and the discharge to be modulated at frequencies very different from the detecting frequency. This has been demonstrated in principle.
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I. INTRODUCTION

Molecular ions are very important in chemistry and related fields, in laboratory and terrestrial plasmas and in comet tails. The field of molecular ion spectroscopy was very poorly explored until recently, because conventional absorption spectroscopy in a discharge, which has been proven to be a very powerful method for neutral molecules, usually does not work for molecular ions. The more abundant neutral molecules will often dominate the absorption spectrum, and therefore, it is often very hard to detect ion lines in the presence of very strong neutral lines. In 1983, Gudeman and Saykally [1] developed a new molecular ion laser spectroscopic technique, "velocity modulation" laser spectroscopy. This technique is very successful for molecular ion spectroscopic studies. In this technique, the velocity of molecular ions is modulated by an a.c. discharge at frequency f. Neutral molecules have no velocity modulation, but are instead density-modulated at frequency 2f. Neutral signals can be suppressed when using lock-in detection at frequency f. Since 1983, many molecular ions have been studied by this approach, such as H$_2$O$^+$ [2], NH$_4^+$ [3], HCO$^+$ [4], HNN$^+$ [5], H$_2$CN$^+$ [6], N$_2^+$ [7], and others.

In velocity modulation laser spectroscopy, a single frequency is used to modulate the discharge. When detecting at this frequency, because the r.f. interference signal and optical emission background are at the same frequency, they give a background signal on the lock-in. Because the background level changes, it often obscures the signal. To eliminate the background, several techniques have been proposed before. Trevor J. Sears [8] frequency-modulated the diode laser and ac drove the discharge in order to eliminate the background and increase the absorption sensitivity. But as we know, frequency-modulating the laser will make the line shape very complicated [9], which is a disadvantage. Another one is so-called two-tone frequency-modulation spectroscopy
developed by Janik et al [10]. The laser was frequency—modulated at two frequencies
in this technique. Again, because of the complication of the line shapes, it is
disadvantageous. The double modulation technique which was proposed and developed
by us here is different. We both amplitude—modulated the laser, instead of using
frequency—modulation, and velocity—modulated the molecular ions, so that the
molecular ion lines still can have simple dispersion shapes like those in the
conventional velocity modulation spectroscopy. Also the background variations can be
eliminated by this technique.

(1) Double Modulation Technique For Background Elimination

When we modulate both the discharge and the laser beam at two different
frequencies, \( \omega_2 \) and \( \omega_1 \) respectively, the ion signals will have components at \( \omega_1 \pm \omega_2 \). But
the background coming from r.f. pick—up and emission has components only at \( \omega_2 \). If we use two lock— in amplifiers in series with the first one at \( \omega_2 \), the second one at \( \omega_1 \), then the background can be eliminated. A similar technique, called "double lock— in
detection", was developed by J. Goree in 1985 [11], but it has never been applied to
molecular ion spectroscopy before. The block diagram is shown in Fig. 1. In the first
demonstration of this technique, a HeH\(^+\) \( v=1-0 \) P(1) line was detected at 2843.904 cm\(^{-1}\). The transition was first observed by Bernath and Amano [12] in 1982.

(2) Difference Frequency Spectroscopy

Now we have shown that modulating at two frequencies is good in order to
eliminate the background. The question is what modulation frequency to use. In many
experiments the dominant source of noise is the detector, and sensitive detectors are
often inconveniently slow. If two different modulation frequencies are used, the signal
can be detected at either the sum or the difference frequency. If the frequency response
of the detector is a major problem, it will be better to detect at the difference
Fig. 1  Block diagram double modulation spectroscopy with background elimination
frequency.

If two different frequencies, $\omega_1$ and $\omega_2$, are used but $\omega_1 \approx \omega_2 >> |\omega_1 - \omega_2|$, putting them into an electronic frequency mixing circuit, a signal at frequency difference $|\omega_1 - \omega_2|$ is obtained. Using this as a reference signal for a lock-in amplifier, the background from r.f. pick-up and emission can be eliminated, because the ion signal has Fourier components at the difference frequency, $|\omega_1 - \omega_2|$, but r.f. pick-up and emission just have components at $\omega_2$. The block diagram of this technique is shown in Fig.2. This technique allows the discharge to be operated at one frequency, but detection performed at a lower frequency. Detection of the signal at low frequency is desirable because slow response detectors can be used, which are often more sensitive than fast response detectors. Experimental results were obtained with a H$_2$+O$_2$ discharge.

A great deal of work has been done on calibration of the monochromator, measurements of diode laser temperature and current tuning rates, design of the discharge tube, and building of electronic circuitry. These technical details, crucial to the success of the experiments, are included in part III, "Experimental Apparatus".
Fig. 2  Block diagram of difference frequency spectroscopy
II. THEORY

A. Conventional Velocity Modulation Spectroscopy

Fig.3 shows the basic setup of conventional velocity modulation laser spectroscopy. A laser beam passes through an a.c. discharge cell and falls on a detector. The detector measures the laser power. The output of the detector is measured by a lock-in amplifier, referenced to the discharge. A dispersion-shaped molecular ion signal is obtained.

Excited neutrals are created every half-cycle of the discharge. So there is a density modulation for neutral molecules. Because it is independent of the polarity of the electric field, the density modulation is at frequency 2f. When detecting the ion signals at frequency f, the neutral signals will be suppressed. This method is therefore a sensitive one for detecting molecular ions.

The basic idea of this technique is that in an a.c. discharge cell, the molecular ions have two contributions to the velocity. One is the thermal velocity, which is due to the random motion of molecular ions. The other is the drift velocity, which is due to the electric force on the molecular ions. The two contributions give a total velocity \( V \). The \( z \)-component of \( V \) results in a Doppler shift in the laser frequency, seen in the rest frame of the ions,

\[
\Delta v = \left( -\frac{V_z}{c} \right) v_0
\]  

(1)

where \( v_0 \) is the laser frequency in the lab frame, and \( c \) is the speed of light.

We now explain why the line shape is dispersion-shaped. First, we discuss the case where the drift velocity is small compared to the thermal velocity. The Doppler shift \( \Delta v_d \) is therefore small compared to the Doppler line width \( \Delta v_w \). Later we discuss
Fig. 3  Basic setup for conventional velocity modulation spectroscopy
the case where $\Delta v_d > \Delta v_m$.

First, let's choose the frame of reference of the molecular ions. Assume that the laser frequency in the laboratory frame is fixed. The laser frequency in the ion frame will be alternately blue shifted and red shifted during the discharge cycle. As shown in Fig.4, the molecular ion absorption line is Doppler–broadened. We fix the laser frequency at the point c. In the first half cycle, the laser frequency is blue shifted, and in the second half cycle, the laser frequency is red shifted. We can see from Fig.4(a) that when the laser frequency in the ion frame increases, the absorption signal from the detector also increases. When the frequency decreases, the output decreases. That means they are in phase. The detector output is the input of the lock–in amplifier. The lock–in output is positive at point c, which corresponds to the point c' in Fig.4(b). Now if we fix the laser frequency at point e, the signal from the detector is out of phase with the modulation signal. We have a negative signal from the lock–in amplifier. The corresponding point is e' in Fig.4(b). If we fix the laser frequency right at the center of the molecular ion line, because of the symmetry of the line shape, the signal from the output of the detector is the same in both halves of the cycle. The lock–in amplifier output will be zero, shown at point d'.

Therefore if we now scan the laser frequency through the whole line shown in Fig.4(a), we will get a dispersion–shaped molecular ion line shown in Fig.4(b).

The discussion so far is for $\Delta v_d < \Delta v_m$. The case $\Delta v_d > \Delta v_m$ is shown in Fig.5(a)–5(b). If $\Delta v_d > \Delta v_m$, the line shape is still dispersion–shaped, but the peaks are well separated.

B. Difference Frequency Spectroscopy

Velocity modulation laser spectroscopy is a technique for obtaining high resolution spectra of charged molecules present in electrical discharge plasma. In
Fig. 4  Velocity modulation line shape: the ions are alternatively red-shift and blue shift, leading to a dispersion-shaped signal.
Fig. 5  When $\Delta v_d > \Delta v_m$, the two peaks of the dispersion-shaped lined get splitted.
previous work by Saykally, Oka and others, the discharge has been modulated but the laser has not been amplitude-modulated. When there are some instabilities in the a.c. discharge, significant background from r.f. interference and emissions will be picked up by the lock-in amplifier, since they are all oscillate at frequency $f$. It is very hard to get rid of this background by using modulation at only one frequency. Fluctuations in the background can obscure the signal. To solve this problem, two modulation frequencies are used to modulate both the discharge and the laser beam. Molecular ion signals have components at the sum or difference frequency. But background from r.f. pick-up and emissions has only one frequency. When detecting at the sum or difference frequency of the two modulations, the noise level can be greatly reduced. This is the idea for the double frequency techniques.

If two modulations are sine waves, the laser intensity incident upon the discharge cell is

$$I(t) = I_0(1 + m_1 \cos \omega_1 t) / (1 + m_1)$$

(2)

where $m_1$ is the modulation index of the laser beam, and $I_0$ is the laser beam intensity before the modulator. The absorption by the molecular ions in the discharge cell is

$$A(t) = A_0(1 + m_2 \cos \omega_2 t) / (1 + m_2)$$

(3)

So the transmission is, assuming there are no reflection or other losses

$$T(t) = 1 - A(t)$$

$$= 1 - A_0(1 + m_2 \cos \omega_2 t) / (1 + m_2)$$

(4)

where $A_0$ is the absorption factor for molecular ions, and $m_2$ is the modulation index of
the absorption. For the velocity modulation spectroscopy, the laser intensity upon the
detector which can be amplified by the lock-in is

\[
P(t) = \frac{I(t)T(t)}{1 + \frac{1}{m_1}(1 + \frac{1}{m_2})} = \frac{I_0(1 + m_1 \cos \omega_1 t)}{(1 + m_1)(1 + m_2)} \frac{A^*_0(1 + m_2 \cos \omega_2 t)}{(1 + m_2)}
\]

\[
= \frac{I_0}{1 + m_1(1 + \frac{1}{m_2})} \frac{m_1 I_0 \cos \omega_1 t}{1 + m_1}
\]

\[
= \frac{m_1 I_0 A^*_0 \cos \omega_1 t}{1 + m_1(1 + \frac{1}{m_2})} - \frac{m_2 I_0 A^*_0 \cos \omega_2 t}{(1 + m_1)(1 + m_2)}
\]

\[
- \frac{m_1 m_2 I_0 A^*_0 \cos (\omega_1 + \omega_2) t}{2(1 + m_1)(1 + m_2)}
\]

\[
- \frac{m_1 m_2 I_0 A^*_0 \cos (\omega_1 - \omega_2) t}{2(1 + m_1)(1 + m_2)}
\]

\[\text{(5)}\]

\[
A^*_0 \ \text{is the factor which contains the information about the molecular ions. Let's look at}
\]

the neutral molecular signals. The density modulation of neutral molecules is $2\omega_2$.

Changing $\omega_2$ to $2\omega_2$ in equation (5), we have

\[
P(t) = \frac{I_0}{1 + m_1(1 + \frac{1}{m_2})} \frac{m_1 I_0 \cos \omega_1 t}{1 + m_1}
\]

\[
= \frac{m_1 I_0 A^*_0 \cos \omega_1 t}{1 + m_1(1 + \frac{1}{m_2})} - \frac{m_2 I_0 A^*_0 \cos 2\omega_2 t}{(1 + m_1)(1 + m_2)}
\]

\[
- \frac{m_1 m_2 I_0 A^*_0 \cos (2\omega_2 + \omega_1) t}{2(1 + m_1)(1 + m_2)}
\]

\[
- \frac{m_1 m_2 I_0 A^*_0 \cos (2\omega_2 - \omega_1) t}{2(1 + m_1)(1 + m_2)}
\]

\[\text{(6)}\]

where $A^*_0$ is the absorption factor for neutral molecules. Comparing equation (6) with
(5), we know that if we detect the signals at $\omega_1 + \omega_2$ or $|\omega_1 - \omega_2|$, there are no neutral signals, and backgrounds from r.f. pick-up and emission. Detecting at $|\omega_1 - \omega_2|$, if $\omega_1 - \omega_2 \gg |\omega_1 - \omega_2|$, we have the double frequency technique. If we detect the signal at $\omega_1 + \omega_2$, we can have another choice, which is a sum frequency technique. The only problem for this is that when the frequency is very high, a fast response detector must be used, which is often less sensitive than the slow response detector. So we choose to detect the ion signal at difference frequency, $|\omega_1 - \omega_2|$. This is the basic idea of difference frequency spectroscopy.

C. Double Modulation Spectroscopy For Background Elimination

Basically, the double frequency modulation technique for background elimination, which will be discussed here, is the same as the difference frequency technique in part B above. Both techniques use two modulation frequencies to modulate both the discharge and the laser beam. The difference is that in the technique here $\omega_2 \gg \omega_1$, unlike the situation in part B, where $\omega_2 \approx \omega_1$. Similar equations to Eqs. (5) and (6) can be derived for this case. Because $\omega_2 \gg \omega_1$, $\omega_2 + \omega_1$ are two sidebands of $\omega_2$, which are very close to $\omega_2$. If we use a broadband lock-in amplifier as the first stage, the Fourier components at $\omega_2$ and $\omega_2 + \omega_1$ can pass through. The two sidebands are at $\sin(\omega_1 + \omega_2)t$ and $\sin(\omega_2 - \omega_1)t$. They beat together, producing a frequency component $\sin\omega_1 \sin\omega_2 t$. Using a second stage, narrow bandpass lock-in amplifier, the component at $\omega_1$ can be picked up. Neutrals and the backgrounds from r.f. pick-up and the emission light have only components at $\omega_2$. They can be eliminated by the second lock-in amplifier. Therefore, this is a technique which suppresses the background.
III EXPERIMENTAL APPARATUS

The experimental facilities we used include the diode laser system, monochromator, discharge system, the electronic frequency mixing circuit, and the detecting system.

A. Diode Laser System

The diode laser system we used is made by Laser Photonics, (formerly Laser Analytics), owned by Spectra Physics. It includes the closed-cycle refrigerator (model SP 5731), compressor (model SP 5710), cryogenic temperature stabilizer (model SP 5720), laser control module (model SP 5820), and SP 5600 series tunable diode lasers.

Fig. 6 is the block diagram of the diode laser system. The solid lines are electric control, and the dashed lines are heat transfer lines. The diode lasers are both temperature and current tuned. Temperature tuning provides coarse tuning, and current tuning provide fine tuning. Appendix I shows some specifications of the system.

The temperature readout from the temperature stabilizer is the voltage across the semiconductor temperature sensor. We convert it to temperature (Kelvin) by a calibration curve displayed in Fig.7. The lowest temperature that can be obtained for this system is 10 K.

(1) Temperature Tuning

The temperature tuning rate is different for each diode. We have to measure it for each individual diode. In the experiments, we just used two diode lasers, #2 and #1 diode. The numbers correspond to the positions in the coldhead.

Fig.8 shows the temperature tuning curve of #1 diode at threshold currents. At low temperature, the tuning rate is small. When the temperature is higher than 20 K, the tuning rate is larger. The temperature tuning rate for #1 diode laser around 24 K is
Fig. 6  Block diagram of the diode laser system
Fig. 7 Conversion of sensor voltage to temperature (K) for the coldhead. Data were supplied by the manufacturer.
Fig. 8 Temperature tuning curve of #1 diode. The temperature was obtained from the sensor and converted via Fig. 7. The wavenumber was measured by the monochromator. The solid line is a computer fit to the data points using a quadratic function.
about 2.3 cm⁻¹/K.

Fig. 9 shows the temperature tuning curve for #2 diode at I=50 mA and I=250 mA. We can see that at I=50 mA, the temperature tuning curve is not a straight line. At I=250 mA, the temperature tuning curve is almost a straight line. When the temperature is higher than 60 K, the two curves have almost the same tuning rate, which is about 3.1 cm⁻¹/K.

(2) Current Tuning

Another property of a diode laser we have to know before we use it to do experiments is its current tuning rate. Current tuning is a fine tuning. We can find out approximately the wavelength of the diode laser by knowing this. Fig.10 is the plot of current tuning curves for #2 diode laser. The slopes of all the lines in the plot are almost the same. We derived from the figure that the average tuning rate for diode #2 is about 0.05 cm⁻¹/mA. For #1 diode laser, we measured the tuning rate to be 0.01 cm⁻¹/mA.

(3) Mode Structures

Diode lasers often oscillate in many spectral modes. The number of modes depends on the current applied on the diode laser and diode laser structure itself. Usually, the higher the current intensity, the more spectral modes. Knowing the spectral mode structure of an individual diode laser is important for doing spectroscopy. The separation between two modes is called the free spectral range. This is another important parameter for a diode laser. The free spectral range for #1 diode laser is 2 cm⁻¹. For #2 diode the free spectral range is 3.7 cm⁻¹.

B. Monochromator

The monochromator is a Digikrom model 240 (CVI Laser Corporation), which is a
Fig. 9  Temperature tuning curves of #2 diode laser, obtained in the same way as Fig. 8.
Fig. 10 Current tuning curves for #2 diode laser. The wavenumber was measured by the monochromator. Each curve is a computer fit to a quadratic function. The temperatures are indicated on each curve.
classical Czerny–Turner monochromator in its optical configuration, with a 240 mm focal length. The optical configuration is shown in Fig.11. As indicated in the figure, light from a source is focused on the entrance slit, E, and directed by the turning mirror, M1, to the collimating mirror, C. The focused beam is collimated and directed to the grating, G, which diffracts and reflects the radiation. A particular wavelength of the light, determined by rotating the grating, is directed to the focusing mirror, F, which focuses it onto the exit slit, X, via the second turning mirror, M2. The monochromator is totally computerized. The microcomputer is based on a Zilog Z–80 CPU, with 16 K PROM, 2 K RAM and four channel interrupts. The monochromator includes three gratings. It can be used from visible to far infrared. The parameters of the gratings are listed in Table.1.

<table>
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<th>lines/mm</th>
<th>width(mm)</th>
<th>N</th>
<th>range(nm)</th>
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<tr>
<td>1</td>
<td>1200</td>
<td>64</td>
<td>7.7x10^4</td>
<td>185–700</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>64</td>
<td>3.8x10^4</td>
<td>700–2800</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>64</td>
<td>9.6x10^3</td>
<td>2700–11000</td>
</tr>
</tbody>
</table>

(1) The resolution of the monochromator

The resolution of the monochromator is determined by the slit width and the maximum resolving power of the gratings R=mN, where m is the diffraction order and N is the number of grooves in the grating. N is given in Table 1. Once the grating is chosen, the maximum resolving power of the grating is fixed. The resolution then depends only on the slitwidths. For a certain slitwidth, there is a bandwidth so that only wavelengths within the bandwidth can pass through. Fig.12 gives the relation between the slitwidth and the FWHM of the bandwidth. This tells us the scan range for a certain slitwidth. As the slitwidth gets narrower, we get higher resolution until the diffraction
Optical configuration of the Digikrom 240
Fig. 12  Relation between the slitwidth and the resolution of the monochromator for #3 grating. Measurements were made on 633 nm line of a He–Ne laser in 8th order.
limit is reached. But because of diffraction through the slit, there is a maximum resolution of the monochromator. From Fig. 12, we know the maximum resolution is about 0.36 cm\(^{-1}\) for #3 grating.

(2) Calibration

The monochromator was not well calibrated when it first arrived. Using different orders of diffraction, we calibrated all three gratings with a He–Ne laser. When the monochromator was calibrated at one wavelength, we found that there were deviations between the reading and the real value when we made the measurement at other wavelengths, which are not the calibrating wavelengths. For example, passing the He–Ne laser through the monochromator, around the wavelength of the tenth order of the He–Ne 632.8 nm laser light, we saw the light spot passing through the monochromator. Then set the wavelength to 6.328 pm and calibrated it by the microcomputer. Then we measured the eighth order of He–Ne laser light, ninth order, eleventh order, and so on. We found that there were deviations between the true value and monochromator reading. Writing down and plotting these data, we get Fig. 13 which gives the deviations as a function of wavelength. By this plot, we can roughly know the correction of the reading wavelength. In order to check the results in Fig. 13, we passed the laser beam through a cell containing H\(_2\)O. By the pattern of the absorption spectra of H\(_2\)O vapor shown in Fig. 14, three H\(_2\)O lines have been recognized as i) 1884.56559 cm\(^{-1}\); ii) 1885.02120 cm\(^{-1}\); iii) 1885.30168 cm\(^{-1}\) [13] at 0.48 Torr H\(_2\)O pressure. By narrowing down the slitwidth to 100 µm and putting the #3 line on the top of the bandpass curve of the monochromator, we found that the monochromator reading was 5.294 µm, which would be 5.295 µm after vacuum correction, giving 1888.6 cm\(^{-1}\) before correction for monochromator calibration. The correction for the monochromator calibration was obtained by interpolating in the data plotted and Fig. 13, and is 0.006 µm. Making this correction gives a vacuum
Fig. 13  Correction curve for the monochromator. The curves are computer fit using quadratic function. Each curve is marked with the wavelength at which the calibration was performed. The deviation is the true wavelength minus the monochromator reading.
wavelength of 5.301 μm, which is 1886.44 cm⁻¹. This differs from the literature value, shown in Fig. 14, by 1.14 cm⁻¹, which is about three times larger than the resolution limit of the grating. Similar results were obtained near 3.5 μm region: The P(2) of \(^{35}\)HCl appears at a monochromator reading of 3.517 μm, which is 3.518 μm after vacuum correction, or 2842.5 cm⁻¹, compared with the true value of 2843.62 cm⁻¹. Again the absolute accuracy is 1.12 cm⁻¹.

C. Discharge System

The discharge system is a very important part in velocity modulation spectroscopy. Ions are produced inside the discharge cell. The system includes a plasma generator (a high power audio-frequency power supply), transformer, discharge cell, and a ballast resistor assembly. In some experiments, the ballast resistor was omitted. The block diagram is displayed in Fig. 15.

(1) Plasma Generator

In our experiment, a Plasmaloc 2 power supply was used to generate a gas plasma. The unit is capable of producing up to 1600 watts of power into an extremely wide variety of parallel plate reactor configurations, used in the semiconductor industry. Impedance matching between the Plasmaloc 2 and the gas plasma is accomplished by a built-in variable tap transformer network. The plasma power level is controlled by either the front panel level control or may be controlled by an external analog voltage (0 to 10 volts). The Plasmaloc 2 power output is level and held constant on either the forward power or the load power. In this load power level position, the unit will supply a constant plasma power regardless of changes in the load impedance occurring in the plasma reactor. In the forward power position, the Plasmaloc 2 will supply a fixed forward power and will allow the plasma power to vary as a function of its load impedance. Because perfect impedance matching is not obtained, a substantial fraction of the power is reflected back to the power supply. The Plasmaloc 2 has a self protect
Fig. 14 Absorption lines of H$_2$O vapor
Fig. 15 Block diagram of the discharge system. $R_b$ is the 7 kΩ ballast resistor and $R$ is a 10 Ω sensing resistor.
circuit, so the reflected power will not damage it, shown in the block diagram in Fig. 16. Appendix II shows the specifications of the Plasmaloc 2.

(2) The Stability of the discharge

The discharge frequency is 25 kHz to 125 kHz. Whether the discharge is stable or not is crucial for the experiment. In this range, the radiation interference problem is very serious. If the discharge is not stable, there will be a lot of big noise spikes, so the detection of small ion signals becomes impossible.

There are many factors which can influence the stability of the discharge: for example the mixture of gas, pressure, match of impedance, the shapes and separation of two electrodes, the dimensions of the discharge cell, and so on.

Because the dynamic impedance of a plasma is negative, it causes instability of the discharge. We put a ballast resistor assembly in the discharge circuit to make the discharge stable.

(3) The Designing of the Discharge Tube

The Pyrex discharge cell is one of the main parts of the whole discharge system. In the designing of the discharge tube, factors like the shape and dimensions of the electrodes, cooling, inlet and outlet of the gases, and many other technical problems should be considered. The tube which we are now using is shown in Fig. 17. Experimentally, we found two problems which should be solved to improve the performance of the tube. First, in the connection of the electrodes and the glass tube, there was no cooling. When the tube ran for a discharge for long period of time, this part would get very hot. The glass would crack and the electrodes would fall off. This cooling problem was solved by building a separate water cooling loop for the critical tube sections. Second, when running some discharges contain CH$_4$, N$_2$, and He to produce CN, there was a brown substance, probably polymerized C$_2$N$_2$ produced which
Fig. 16  Block diagram of Plasmaloc 2
Fig.17  Original design for the discharge tube
would stick on the windows, so that it would block the light passing through the cell. In order to solve these problems in a more satisfactory way, we designed a new tube as Fig. 18. The inlets 1, 6 and outlets 2, 5 are He gas inlets and outlets, so the CN or other contaminants can not reach the windows. The electrodes, the connections, and the discharge area are cooled by water as a whole. The new design of the discharge tube will very likely solve the problems we encountered before.

D. The Electronic Frequency Mixing Circuit

In the double frequency velocity modulation technique discussed here, we have to use an electronic frequency mixing circuit to obtain a frequency difference signal to be used as a reference for the lock-in amplifier. The idea of the circuit is to add two sine wave signals with different frequencies $\omega_1$ and $\omega_2$, mix them in a nonlinear circuit element and then use a low-pass filter to keep only the component at $|\omega_1 - \omega_2|$.

The circuit we used is shown in Fig. 19. $V_1$ and $V_2$ are two inputs with different frequencies $\omega_1$ and $\omega_2$ respectively. $K_1$ and $K_2$ are voltage followers to isolate the signal source $V_1$ from $V_2$. $R_1$ and $R_2$ are used to adjust the voltages to the inverting amplifier $K_3$, which acts as an adder here. If the input signals are sine functions, we have the output at point P as

$$V_p = V_0 \sin \omega_1 t + V_0 \sin \omega_2 t$$

$$= V_0 \sin \frac{\omega_1 - \omega_2}{2} t \sin \frac{\omega_1 + \omega_2}{2} t$$

If $\omega_1 \approx \omega_2$ >> $|\omega_1 - \omega_2|$

$$V_p = V_0 \sin \omega_1 t \sin \frac{\omega_1 - \omega_2}{2} t$$

(7)
Fig. 18 New discharge tube design. Separate inlets of helium keep the window clean.
Fig. 19  Frequency mixing circuit
It is an AM signal. The diode in $K_4$ acts as a mixer, and the combination $R_4C_1$ is a filter that only passes the lower frequency $|\omega_1-\omega_2|$ component. $K_5$ provides gain for the difference frequency component.

The parameters for the circuit are followings:

- $R_1=R_2=1.2 \text{ k}\Omega$
- $R_3=800 \Omega$
- $R_4=480 \Omega$
- $R_5=221 \Omega$
- $R_6=530 \text{ k}\Omega$
- $C_1=0.22 \mu\text{F}$
- $C_2=0.05 \mu\text{F}$
- $q = 0.22 \text{ pF}$
- $C_2=0.05 \text{ pF}$
- Op amplifiers: 3140E

This circuit was used in an experiment which successfully demonstrated that difference frequency spectroscopy does work.

In our experiments we used two independent frequency sources $\omega_1$ and $\omega_2$. If these sources are not very stable, then the difference frequency will vary. In our experiments, that was a problem. This could be fixed by using more stable sources.

Alternatively, another circuit was designed which will give a stable difference frequency even if the primary frequency sources are not very stable. The idea is to start with a 25 kHz source and a 0.5 kHz source, and generate a 25.5 kHz signal. The two frequencies used in the experiment are 25 kHz and 25.5 kHz. The diagram of the new circuit is shown in Fig.20. At the point $A$, a sine wave signal $\sin(a)$ at 500 Hz is input. The carrier is $\sin(b)$ at 25 KHz. After the audio $90^\circ$ phase shift network, we have $\sin(a)$ and $\cos(a)$. After the carrier $90^\circ$ phase shift network we have both $\sin(b)$ and $\cos(b)$ signals. Mixing them together in the balanced modulator, both $\sin(a)\cos(b)$ and $\cos(a)\sin(b)$ signals are obtained. At the output we have $\sin(a+b)$ at 25.5 kHz. The point is that the 500 Hz signal will not "wander" with this circuit.

E. The Detecting System

(1) Lock—in Amplifier

A lock—in amplifier is a key part in a system for detecting weak signals. Because
Fig. 20 Improved frequency mixing circuit
of the difficulty in making d.c. measurements due to zero drifts, amplifier instabilities, and flicker noise, the signal of interest should be at a frequency sufficiently high that the dominant noise is white noise. Hence in detecting weak signals often a mechanical chopper is used to convert a d.c. or low frequency signal to a high frequency one. Narrowing the bandwidth by a filter will reduce the noise and the signal—to—noise ratio will be enhanced accordingly. A simple block diagram of a lock— in amplifier is shown in Fig.21. The synchronous rectifier and low—pass filter will substantially narrow the bandwidth. This rectifier acts like a switch that is opened and closed in synchronization with the chopper. Since the phase relations for each of the noise components are random, they will tend to cancel each other when averaged.

The lock— in amplifier we used in our experiments was EG&G PARC model 5209. It has automatic operation, choice of a flat or tuned signal channel (lowpass, bandpass, or notch). It has voltage and current input modes. Input frequency range is 0.5 Hz to 120 kHz. The typical input noise is 5 nV per root Hz at 1kHz.

(2) Detectors

The detectors we used were photovoltaic InSb detectors made by Infrared Associates Inc. The photovoltaic process involves measuring an external voltage produced by infrared photons detected at the PN junction. Typically, these devices at 300 degree K exhibit low resistance of approximately 2 Ohms. A PPA—15—IS matched preamp was used with the InSb detector. The noise level is 0.85 µV. The spectral response of the detector is shown in Fig.22. The peak wavelength is at 5 µm. The cut—off wavelength is at about 5.5µm. A Silicon window prevents visible light from striking the detector.
Fig. 21  Simple block diagram of lock-in amplifier
Fig. 22 Spectral response of the InSb detector. The plot was provided by the manufacturer.
IV. EXPERIMENTAL RESULTS

A. The Observation of HeH$^+$ transition by Double Frequency Modulation
With Background Elimination

HeH$^+$ was first discovered by Hogness and Lunn[14] in 1925 with a mass spectrometer. The spectrum of HeH$^+$ was completely unknown in any spectral region until 1979, when Tolliver, Kyrala and Wing [15] observed five transitions in the fundamental band (1–0) and the vibrational hot band (2–1) using a coaxial ion beam–laser beam apparatus and a CO laser. Carrington and co–workers [16] used the same technique to make measurements near the dissociation limit. In 1982 Bernath and Amano [11] used a difference frequency laser system (with frequency modulation of the source) in a dc discharge cell to observe the fundamental band. In 1987, Blom, Moller and Filgueira reported observations of the (2–1) hot band [17]. Oka and co–workers [18] used a difference–frequency laser system and a velocity–modulated discharge to report measurements in the isotopes $^4$HeH$^+$, $^4$HeD$^+$, $^3$HeH$^+$, and $^3$HeD$^+$.

Diode lasers have almost never been used to study this species: of the 62 transitions in all isotopes listed by Oka [18], only one was observed with a diode laser. The basic reason is that, because of their poor collimation properties, it is difficult to send a laser beam many times through a cell. Oka made two passes through a one–meter cell in the same direction, and Bernath and Amano had a path length of 32 meters. They used frequency–difference laser systems, whose beams are better collimated. To see a line in HeH$^+$ with a diode laser is therefore a good test for a sensitive spectroscopic technique.

As shown in Fig.23, the laser beam was collimated by an off–axis parabolic mirror $M_1$, then passed through a mechanical chopper, discharge cell, and monochromator, finally falling upon a detector $D_1$. Another beam was split by the CaF$_2$
Fig. 23  Experimental setup for double modulation spectroscopy with background elimination
beam splitter (BS) with about 4% reflectivity, passed through a HCl gas reference cell, and detected by a second detector D2. The output of D1 which contained the ion signal, was connected to lock—in #1 with the reference frequency at 24.5 kHz. The output of lock—in #1 then became the input of lock—in#2, which derived its reference from the 25 Hz mechanical chopper. The output of lock—in#2 went to a three—pen recorder. The signal from D2 was also referenced to the mechanical chopper. Its output was connected to the three—pen recorder.

We used the HCl$^{35}$ fundamental P(2) line as our frequency calibration. Its frequency is 2843.62 cm$^{-1}$ [19]. From Bernath and Amano's paper, we know that HeH$^+$ v=1-0 P(1) line is at 2843.904 cm$^{-1}$. So HCl P(2) line is a perfect frequency marker for the observation of HeH$^+$ v=1-0 P(1) line. Another advantage to use HCl as a frequency marker here is that HCl has only two lines in the region. Another line is isotope HCl$^{37}$ line. Its frequency is about two wavenumbers lower than the HCl$^{35}$ P(1) line. We found both of them. So we were very sure the HCl line we used as a frequency marker is at 2843.62 cm$^{-1}$.

The difficulties of using a diode laser to look for ion lines are (1) the single mode scanning range is small, about 2 cm$^{-1}$, (2) diode lasers have multimode structure, and (3) mode hops occur frequently. In order to find a line, we have to set one mode so that the line we are looking for is in the scanning range of this mode. The HCl P(2) line is a very strong line and its transition frequency is very close to the HeH$^+$ P(1) line (about 0.28 cm$^{-1}$ away). Once we find the neutral HCl P(2) line, the HeH$^+$ P(1) line should be within the scanning range of the diode laser mode. The HCl P(2) line is at 3.516 μm. We set the center wavelength of the monochromator to 3.517 μm, with the slitwidth of 100 μm. We found the HCl line as shown in Fig.24. The FWHM linewidth of HCl is 0.4 mA of laser current, corresponding to 0.025 cm$^{-1}$.

The ac discharge was operated at 25.2 kHz with a sine wave voltage. The peak—to—peak discharge current was 350 mA. The discharge power was 160 W in the
Fig. 24 Observation of the P(2) line of $^3\text{H}^\text{Cl}$. The sloping background is due to the variation in the laser power with injection current. The frequency increases to the left.
load; the "forward power" was 400 W, with the difference reflected back into the plasma generator. The gas mixture of He:H$_2$ was about 100:1 at a total pressure of 2.1 Torr. We used a flowing system with continuous pumping to maintain a clean discharge tube.

We used the monochromator as shown in Fig. 23 to make sure the laser frequency passed through the range where we expected the HeH$^+$ signal to be. Then, to find the line, we removed the monochromator and focused the laser beam on the detector. This gives the maximum signal. The time constant on lock-in #1 was 1 ms and the time constant of lock-in #2 was 1 s. We want the first time constant to be small to pass the side bands on the signal to the second lock-in. We can also adjust the sensitivities of lock-in #1 and lock-in #2 to obtain suitable amplification.

The resulting spectrum of HeH$^+$ is shown in Fig. 25. The dispersion-shaped line is the HeH$^+$ v=1-0 P(1) line. The separation of the lines in Figs. 24 and 25 is 5.4 mA, or 0.27 cm$^{-1}$ (with a current tuning rate 0.05 cm$^{-1}$/mA), which agrees well with previous data which is 0.28 cm$^{-1}$. The linewidth of the HeH$^+$ resonance, defined as the FWHM of a single lobe, is 0.3 mA, or 0.015 cm$^{-1}$.

The double modulation technique for background elimination play an important role in detecting the HeH$^+$ fundamental P(1) line. Fig. 26 shows an attempt to find the line using the regular velocity modulation technique. All other conditions were identical to those of Fig. 25, and the scan was made within a minute of Fig. 25. A changing background level made detection of a signal impossible.

**B. Difference Frequency Spectroscopy**

There is another double frequency velocity modulation technique, in which two different frequencies are used to modulate both the discharge and the laser beam. This is different from the double modulation technique described earlier, because here we use two high frequencies instead of using one high and one low frequency.
Fig. 25  HeI$^+$ v=1-0 P(1) line at 2843.904 cm$^{-1}$

Laser diode current (Amperes)
Fig. 26 Search for HeH$^+$ P(1) v=1-0 line using conventional velocity modulation spectroscopy. The scan covers the same range as Fig. 23 but the signal is obscured by a changing background.
In practice, it is very hard to mechanically chop the laser beam at 25 kHz. One way to do this is to use an electro-optic modulator, but that is expensive and cumbersome. Fortunately, our diode laser current can be modulated at 25 kHz.

(1) Observation of H$_2$O line in a passive absorption cell using difference frequency spectroscopy

In order to make sure that this technique and everything worked well, we tried to find the H$_2$O line which we knew before by double frequency modulated passive absorption. As shown in Fig.27, the current of the diode laser was chopped at 1kHz and the laser beam was modulated by a mechanical chopper at 900 Hz. Input of these two signals into an electronic frequency mixing circuit produces a reference signal for the lock—in amplifier at 100 Hz. The passive absorption cell was one meter long. The pressure of H$_2$O was about 0.5 Torr. From Fig.14, we knew the exact wavelength of the three H$_2$O lines. We then chose the first line and narrowed down the slitwidth of the monochromator to 100 μm. The center readout wavelength was at 5.296 μm, which is the readout wavelength of the first H$_2$O line.

The result is shown in Fig.28. The H$_2$O line was found at the center of the bandpass curve of the monochromator. This result means that the double frequency technique can be used to find a line in a discharge.

(2) Difference Frequency Spectroscopy of a discharge

The experimental setup for the difference frequency spectroscopy experiment is shown in Fig.29. The frequency of the discharge was 23.4 kHz and the laser current modulation frequency was 23.8 kHz. A function generator was used to modulate both the laser current and to send the 23.8 kHz signal to the input of the frequency mixer. Both modulation functions were sine. The frequency difference from the mixing circuit was 418 Hz. The mixture of H$_2$:O$_2$ was 1:1. The total pressure was 40 mTorr. The
Fig. 27  Experimental setup for the difference frequency spectroscopy in a passive cell
Fig. 28  Spectrum of H₂O using the difference frequency spectroscopy in a passive absorption cell
Fig. 29  Experimental setup for the difference frequency spectroscopy of a discharge
discharge current was 300 mA. The time constant of the lock-in amplifier was 300 ms. The slitwidth of the monochromator was 2000 μm and the center wavelength was 5.341 μm. The laser scanning speed was $2.5 \times 10^{-4}$ A/sec, which was equivalent to 0.0025 cm$^{-1}$/sec. We found a line, shown in Fig.30. The line was repeatable, so this is definitely a real line. It could be either an ion or an excited neutral line.

From the result in Fig.30, we can see that the noise level was very high. For this noise level, it is very hard to find an ion signal. After checking the system again, we found the problems coming from the instability of the reference frequency for the lock-in amplifier. The instability could be as high as 30 Hz. It was about 10% in our experiment at 400 Hz.

The drawback of this experiment is that we used two high frequency function generators to get a low frequency difference signal. Suppose their instabilities are within 0.1%. It is about 24 Hz. But that is 5% of 400 Hz. We could solve this problem by using more stable frequency sources.

Alternatively, with a low stability source to improve the experiment, we could use only one function generator. Then use a frequency divider to obtain a low frequency signal, say 500 Hz. Mixing them together, the highest frequency signal can be obtained. This improvement can solve the problem.

The difference frequency technique shows promise and has been demonstrated in principle. It can be especially useful for slow detector such as PbS, whose time constant is more than 1 ms.
Fig. 30  Spectrum of $\text{H}_2 + \text{O}_2$ discharge using the difference frequency spectroscopy
V. CONCLUSION

A HeH\(^+\) \(v=1-0\) P(1) line at 2843.904 cm\(^{-1}\) was found by using a diode laser and the double modulation spectroscopy with background elimination. In our discharge, the conventional velocity modulation technique did not work. The experimental results have proven that the new double—modulation technique is a very sensitive method for spectroscopy of molecular ions, and it is reasonable to expect the application of this technique to other molecular ion lines, including negative ions. The frequency difference spectroscopy has also been tried, and the principle has been demonstrated.

The two above techniques, double frequency and double modulation, are still based on an a.c. discharge, which is the source of r.f. pick—up and emission background in the velocity modulation technique. Obviously, if we change the a.c. discharge to d.c. discharge, the problem will be solved completely.

When a discharge is d.c. instead of a.c., positive or negative molecular ions will have fixed moving directions. By the conventional absorption spectroscopy, it is impossible to suppress the neutral signals. If we pass two laser beams through the discharge tube in opposite directions, the resonance frequency for one beam is red shifted and for another beam is blue shifted. Therefore, when we tune the laser, use two detectors and an electronic subtractor, the neutral signals will be canceled and the ion lines will have dispersion shapes like those in velocity modulation spectra. The diagram of the technique is shown in Fig.31. The experiments are planned.
Fig. 31 Diagram of the proposed double beam technique
VI. APPENDIX I

Specifications of the diode laser system

Output current range........ 0–2.0000 A, positive or negative, floating with respect to ground

Current readout accuracy... 100 μA

Noise plus ripple.......... <50 μA Peak–to–peak

Long–term drift............ <100 μA/day (after 30 min)

Temperature stability...... <20 μA/°C

Line voltage stability..... <10 μA change for line voltage change up to ±10%

Output impedance (typical). >20 KΩ at d.c.

Automatic sweep range.... ± 200 mA

Automatic sweep rate....... 0.01—10 mA/sec.

Automatic sweep recorder reference................ 50 mV/mA

Internal waveform generator:

Waveforms available..... ±sawtooth, triangular

Frequency................ 50 Hz to 1 kHz

Amplitude.............. 0–200 mA

External generator input:

Input impedance........... >50 kΩ

Response................. 20 mA/V

Frequency range......... D.C. to 10 kHz

Maximum amplitude....... ±200 mA

Chopped mode:
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency</td>
<td>50 Hz to 1 kHz</td>
</tr>
<tr>
<td>Amplitude</td>
<td>Set by manual and sweep controls</td>
</tr>
</tbody>
</table>
VII. APPENDIX II

Specifications of Plasmaloc 2

Frequency coverage........ 25 kHz to 125 kHz
Frequency stability........ Better than 0.1% from 0 to +45 °C ambient
                           after 5 minutes warm up.
Maximum leveled power     1600 Watts, forward or load
output.....................  
Mismatch protection........ The unit will tolerate 400 Watts of power
                           reflected from the load (gas plasma), subject
                           to operation of the thermal protection.
                           Instantaneous overload protection is provided
                           the load impedance exceed allowable limits.
Thermal protection......... Thermostatic protection provides automatic
                           cut–out should the power transistors overheat
                           due to load mismatch or cooling system failure.
REFERENCES


