

# Journal of the Arkansas Academy of Science

---

Volume 52

Article 5

---

1998

## Infrared Diode Laser Spectrometer for the Study of Jet Cooled Gases

Anthony Bednar  
*Arkansas State University*

Eric Barnett  
*Arkansas State University*

Candace Lindsay  
*Arkansas State University*

Trey Heath  
*Arkansas State University*

Philip Williams  
*Arkansas State University*

*See next page for additional authors*

Follow this and additional works at: <http://scholarworks.uark.edu/jaas>

 Part of the [Optics Commons](#)

---

### Recommended Citation

Bednar, Anthony; Barnett, Eric; Lindsay, Candace; Heath, Trey; Williams, Philip; Draganjac, Mark; and Reeve, W. (1998) "Infrared Diode Laser Spectrometer for the Study of Jet Cooled Gases," *Journal of the Arkansas Academy of Science*: Vol. 52 , Article 5. Available at: <http://scholarworks.uark.edu/jaas/vol52/iss1/5>

This article is available for use under the Creative Commons license: Attribution-NoDerivatives 4.0 International (CC BY-ND 4.0). Users are able to read, download, copy, print, distribute, search, link to the full texts of these articles, or use them for any other lawful purpose, without asking prior permission from the publisher or the author.

This Article is brought to you for free and open access by ScholarWorks@UARK. It has been accepted for inclusion in Journal of the Arkansas Academy of Science by an authorized editor of ScholarWorks@UARK. For more information, please contact [scholar@uark.edu](mailto:scholar@uark.edu).

---

# Infrared Diode Laser Spectrometer for the Study of Jet Cooled Gases

## **Authors**

Anthony Bednar, Eric Barnett, Candace Lindsay, Trey Heath, Philip Williams, Mark Draganjac, and W. Reeve

# An Infrared Diode Laser Spectrometer for the Study of Jet Cooled Gases

Anthony Bednar, Eric Barnett, Candace Lindsey, Trey Heath, Philip Williams  
M. Draganjac and Scott W. Reeve\*  
Department of Chemistry and Physics  
Arkansas State University  
PO Box 419, State University, AR 72467

\* Corresponding Author

## Abstract

We have constructed a tunable, high resolution, infrared diode laser spectrometer and combined it with a pulsed supersonic jet expansion. A modified version of the Perry multipass cell has been incorporated into the spectrometer to increase the effective absorption path length. Performance capabilities of the spectrometer are evaluated by examining ro-vibrational spectra for the carbon monoxide molecule in the five micron region of the infrared. From these measurements, an instrumental absorption sensitivity is determined. Finally, since one of our immediate goals is the infrared study of jet cooled transition metal carbonyls, we present high resolution data obtained by entraining the vapor above a solid metal carbonyl and injecting it into the pulsed jet expansion.

## Introduction

Infrared spectroscopy is a powerful method of analysis with a rich chemical history. Indeed, the application of this technique to identify functional groups in complex organic molecules by their characteristic infrared absorption band features is well known (see Silverstein et al., 1981). When a molecule absorbs an infrared photon an energy transition is induced from a rotational energy level in one vibrational state to a rotational energy level in a higher vibrational state (Atkins, 1983). In the gas phase, using an optical probe with sufficient resolution ( $\sim 0.003 \text{ cm}^{-1}$ ), it is possible to quantitatively measure the rotational energy spacing within a vibrational state. The measurement and subsequent analysis provides a plethora of fundamental information about the chemical and physical bonding interactions in the molecule. Details concerning molecular structure, the strength of chemical bonds, and the shape of molecular potential energy surfaces, for example, can all be extracted from the high resolution spectra (Atkins, 1983).

Over the past year, we have assembled a tunable, high resolution, infrared diode laser spectrometer at Arkansas State University and combined it with a supersonic jet expansion sample source. While this type of sample source introduces several experimental challenges, two important sensitivity improvements can be realized. Jet expansions not only provide a collision free environment to effectively isolate a gas phase molecule, they also produce rotationally cold gas samples (Levy, 1984; Miller, 1984). At typical jet temperatures (10-50 K), the lower rotational energy levels in a given vibrational state will be preferentially populated (Levy, 1984; Miller, 1984). The net result of this effect will

be spectra exhibiting greater intensity and less congestion. Moreover, this cooling will be critical in extending the investigation to include larger transient molecules which typically possess smaller rotational constants and larger rotational partition functions (Bernath, 1990).

Combined infrared diode laser/supersonic jet expansion spectrometers have now been built by several research groups worldwide (see De Piante et al., 1989; Heath et al., 1991; Hu et al., 1993; Juang et al., 1992; Low et al., 1996; McKellar et al., 1991; Schuder et al., 1991; Sharpe et al., 1988; Takami et al., 1986; Xu and McKellar, 1996). While we relied heavily on these instrumental descriptions during the construction phase of this work, we included several modifications (driven primarily by economic factors) in our spectrometer. The modifications have been evaluated through a series of diagnostic experiments performed to test the capabilities of our spectrometer. We were particularly interested in determining the sensitivity of our instrument since the success of future projects involving gas phase free radicals will depend on our ability to see small quantities of molecules. For the detection limit, or sensitivity determination, various isotopes of carbon monoxide ( $^{12}\text{C}^{16}\text{O}$ ,  $^{13}\text{C}^{16}\text{O}$ , and  $^{12}\text{C}^{18}\text{O}$ ) were observed in natural abundance. Carbon monoxide has been extensively studied in the microwave and infrared regions and so represented a natural choice for tuning up the instrument. In fact, a complete listing of every known carbon monoxide absorption in the five micron region can be downloaded from the National Institute of Standards and Technology (NIST) website (see <http://physics.nist.gov>). The table has several hundred entries and includes fundamental and hot band transi-

## An Infrared Diode Laser Spectrometer for the Study of Jet Cooled Gases

tions for several isotopic species. The NIST table has proven invaluable during these diagnostic experiments because gas cell spectra have been recorded that contain absorption lines for three different isotopic species. Here we present experiments performed to determine an instrumental absorption sensitivity and a detailed description of modifications made during the construction of the spectrometer.

and fine tuning mechanism for wavelength selection. Modulation of the laser can be selected manually through the controller. For example, a chopped modulation is used to monitor signal strength during optical alignment. With an externally applied ramp modulation the laser can be scanned through various regions in the infrared at rates of up to 0.2 wavenumbers ( $\text{cm}^{-1}$ ) per millisecond. The rapid scan infrared diode laser instruments described in the litera-

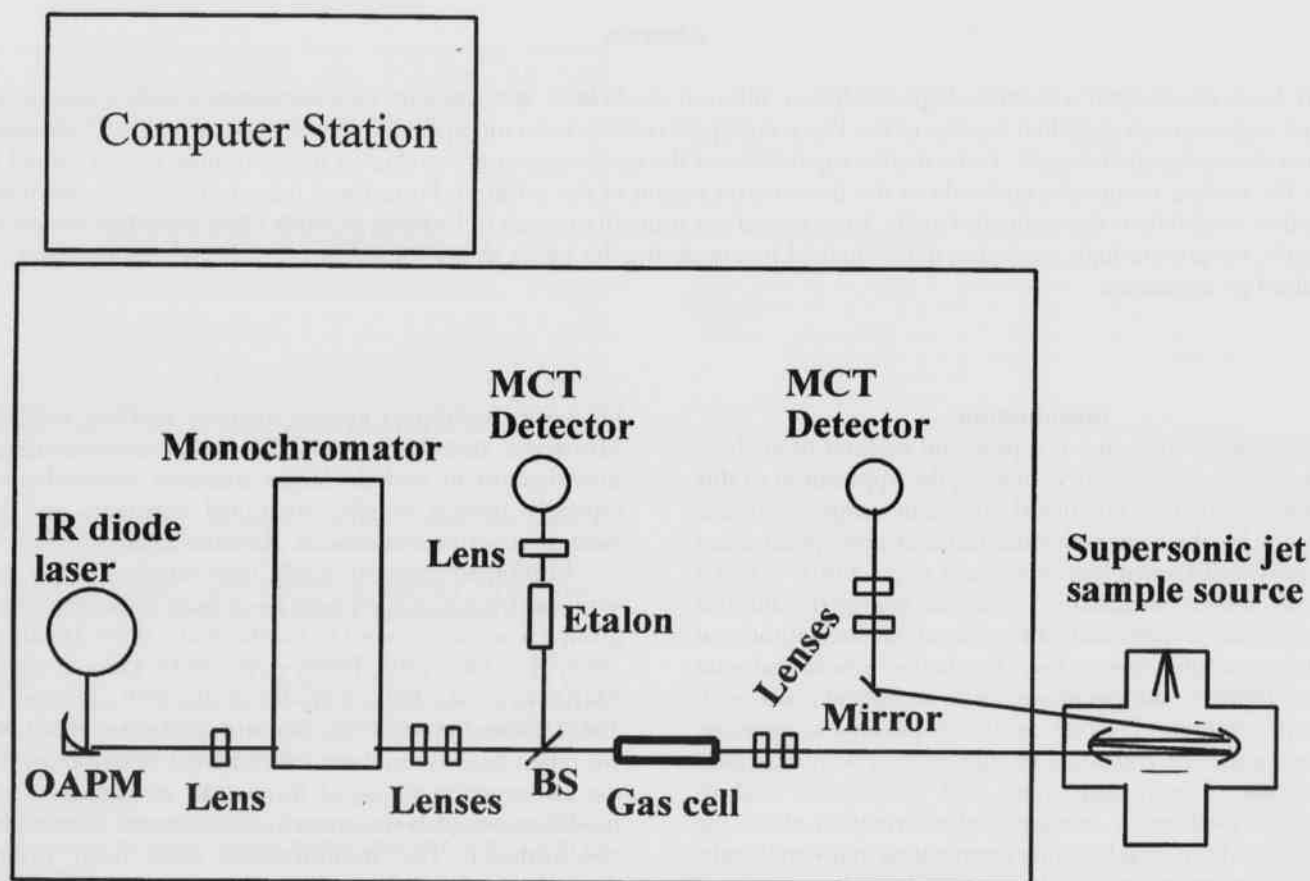


Fig. 1. Schematic of our infrared diode laser spectrometer.

### Materials and Methods

Figure 1 is a diagram of our instrument. The boxed area is a laser table of dimensions 122 cm wide x 182 cm long x 30 cm thick. Lead-salt tunable diode lasers (TDLs) are housed in a Laser Photonics, Inc. L5737 liquid nitrogen dewar that maintains the temperature of the diode at 80-120 K. The dewar can hold up to four TDLs, although at the moment only two are mounted for use. A Laser Photonics, Inc. L5830 laser controller provides manual adjustment of temperature and current to the diode which acts as a coarse

ture generally utilize a waveform generator to produce the voltage ramp to scan the laser and a delayed pulse generator to control the pulse driver. While these sophisticated electronic devices provide the required timing to synchronize a laser scan ramp with a sample gas pulse in a jet expansion (see below), they are quite expensive. For example, a Stanford Research Systems waveform generator with computer communication capability costs ~\$1500. A Stanford Research delayed pulse generator is ~\$4000. We have been able to achieve the same synchronization capability with LabVIEW software. Although we are using the

National Instruments full development LabVIEW package (academic price \$1300), the instrument synchronization could, in principle, have been controlled with the \$50 LabVIEW Student Edition package. A detailed description of the software we developed to provide the ramp modulation is given in a second paper submitted to these proceedings (Williams et al., accepted).

The beam of radiation produced by a TDL possesses an elliptical crosssection that diverges rapidly. To combat this problem, an aluminum Off-Axis Parabolic mirror (OAPM) is used to collimate the beam and direct it at a right angle towards a CVI Laser 482 DigiKrom 0.5 meter triple grating monochromator used for rough wavelength selection. At the time of purchase, CVI was offering a 0.5 m monochromator for the cost of a 0.25 m monochromator (this sale represents a savings of ~\$5000). Continuing with a description of the experiment, the radiation is focused into the monochromator with a 250 millimeter (mm) calcium fluoride ( $\text{CaF}_2$ ) lens.  $\text{CaF}_2$  lenses are required in the mid IR because glass lenses do not transmit infrared radiation above 2 microns ( $\mu\text{m}$ ). A

second set of lenses is positioned immediately after the monochromator to collimate and focus the beam onto an uncoated nitrocellulose beam splitter. The beam splitter directs 8% of the radiation through a 2.54 cm thick piece of solid germanium which serves as an étalon. After exiting the étalon, the radiation is focused onto a Grasby mercury cadmium telluride (MCT) detector with a  $\text{CaF}_2$  f/2 lens. The étalon possesses a free spectral range of  $0.048 \text{ cm}^{-1}$  and essentially creates an interference wave in the infrared signal. Maxima in the interference signal are spaced precisely at  $0.048 \text{ cm}^{-1}$ . Thus, the étalon signal is used for relative calibration. Absolute calibration of the infrared radiation is accomplished with a gas cell containing a reference gas with known spectral lines for the infrared region being examined.

The infrared radiation transmitted through the beam splitter constitutes the signal channel and is focused with a 500 mm focal length  $\text{CaF}_2$  lens into the supersonic jet chamber. By the way, all of the  $\text{CaF}_2$  lenses were purchased from International Scientific Products at a substantial savings ( $> \$100$  per lens in some cases depending upon focal length)

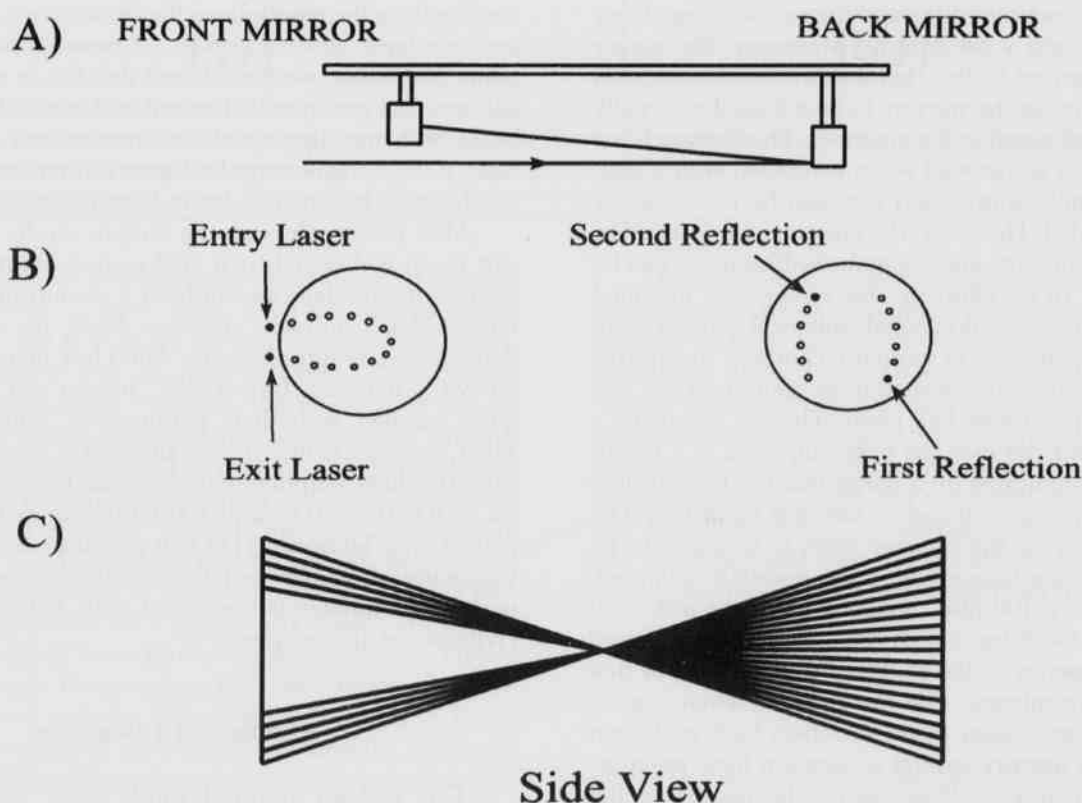


Fig. 2. Schematic showing A) how the two spherical mirrors are mounted on the ring stand rod relative to one another; B) dot patterns observed on each multipass mirror with the HeNe laser; and C) multipass pattern observed when viewing HeNe laser from a side viewpoint.



## An Infrared Diode Laser Spectrometer for the Study of Jet Cooled Gases

compared with equivalent optics from Oriel, Optics for Research, or Rocky Mountain Instruments. The chamber is a stainless steel six way cross with 15 cm diameter tubes from Kurt J. Lesker, Inc. . The chamber is evacuated with a CenCo 15 cm diffusion pump backed by a 500 liter per minute Welch model 1397 mechanical pump. The chamber can be isolated from the pump with a 15 cm gate valve and a Varian model 326 cryotrap is used to prevent back-streaming into the chamber. Parenthetically, both vacuum pumps, as well as the cryotrap, were purchased used from HK Equipment, again at a significant reduction in price (~40% of cost new). Without the cryotrap, the oil used for the diffusion pump would eventually coat the walls of the chamber and the multipass assembly located inside it. A General Valve Series 9 pulse valve mounted on one chamber flange creates the supersonic jet. The pulsed valve together with a pulse driver comprise the General Valve Iota One molecular beam system. The pulse driver can be operated manually with controls on its front panel or remotely through software.

Our multipass cell is a low cost version of the Perry cell (Kaur et al., 1990). While the original Perry cell utilized off-the-shelf commercial mirrors, the mirrors were mounted on kinematic mirror mounts with translation control capability in addition to x and y tilt control. Moreover, the mirror mounts were attached to the chamber flanges via vacuum feedthroughs allowing the mirrors to be adjusted externally once they were mounted in the chamber. The Perry cell is a proven design that works well when combined with a molecular beam sample source and can also be conveniently realigned as needed. However, the components, particularly the kinematic mounts and vacuum feedthroughs, can be quite expensive. In an effort to save money, we mounted two 2.54 cm diameter, gold-coated, spherical mirrors from Edmund Scientific in a set of standard Thorlabs, Inc. mirror mounts which in turn are attached to an aluminum rod (see Fig. 2) with two flex frame ball joints. The rod is actually a 1.25 cm ring stand rod that has been cut down to a length of ~25 cm and is mounted on a flange that has been drilled and tapped to the same thread as the ring stand rod. The mounting location on the six way cross is arranged to be perpendicular to the flange where the nozzle is mounted. The mirrors have a 100 mm radius of curvature with a 50 mm focal point. Gold has a high reflectivity in the infrared region and is superior to the standard silver coated or first surface aluminum mirrors. The two mirrors, when aligned properly will cause a laser beam to reflect back and forth between the two mirrors around a common focal point in-between the two mirrors. If the sample is centered at the focal point of the mirrors then the path length through the sample is increased by the number of reflections or passes between the two mirrors. In our instrument, the mirrors are spaced by ~9.5 centimeters, and the "back" mirror is translated to the right of the "front" mirror (Fig. 2a). This arrange-

ment allows the laser to miss the front mirror, reflect between the two mirrors, and then miss the front mirror exiting lower than the entry beam (Fig. 2b). The pattern created in the multipass can be examined with a helium-neon (HeNe) laser. Actually, the HeNe laser is used to align the mirrors and it is assumed the IR beam transverses the same path (Kaur et al., 1990). The number of passes are determined by counting the number of dots on the back mirror, multiplying the number of dots by two and then subtracting one.

Curiously, there are many possible dot patterns. Kaur and coworkers suggest the most desirable pattern is one that produces a parabola on each mirror (Kaur et al., 1990). The pattern is dependant on several factors including the angles of the mirrors, the angle of the entry laser, the distance that the mirrors are apart, and the location of the first reflection (or dot). We have chosen to use a slightly different dot pattern (see Fig. 2c). To achieve the multipass pattern in Fig. 2c, the first reflection must occur near the top left of the back mirror and it has to cross through the middle of the focal point. This pattern creates two vertical planes of reflections from the back mirror to the focal point. At the focal point, the planes rotate 90 degrees to create two horizontal planes coming from the parabola on the front mirror. With this pattern, we have observed up to 29 passes through the focal point. Moreover, we have found that this is one of the few patterns that generated a focused and controllable exit laser beam with no clipping of the front mirror upon exiting. Note, if the mirrors are pulled apart further, more passes can be obtained, but the exit beam becomes unfocused.

After passing through the sample via the multipass, the exit beam is directed by a gold coated flat mirror through another double lens assembly to a second nitrogen cooled Grasby MCT infrared detector. Note, the Grasby MCT detectors were approximately \$600 less than the comparable MCT detectors from EG&G Judson and we have been quite satisfied with their performance. Output from the MCT detector is first passed through a Stanford Research SR560 voltage amplifier (amplifier has 6 decibel (dB) points set at 100 Hertz (Hz) and 100 kiloHertz) before being displayed on a Tektronix TDS 320 digital storage oscilloscope. Communication between the oscilloscope and a Pentium personal computer is controlled with LabVIEW software (Williams et al., accepted).

### Results and Discussion

The *in-house* infrared diode laser spectrometer at Arkansas State is a versatile instrument capable of recording the vibrational spectra of gas phase molecules, free radicals, and molecular complexes at rotational resolution. The sample source for all of these molecular species is a supersonic jet expansion. To demonstrate some of the capability of our

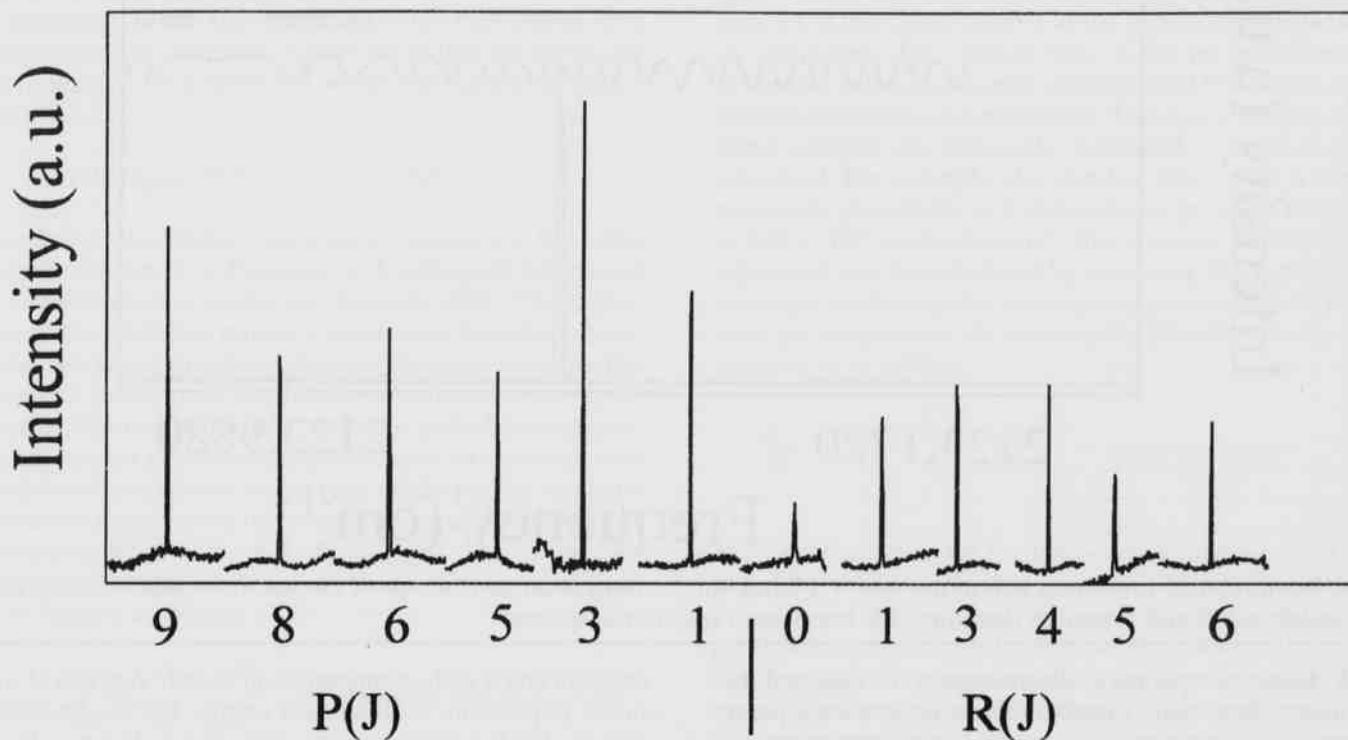


Fig. 3. Twelve rovibrational transitions of the  $v=0 \rightarrow 1$  band for carbon monoxide. The intensity of each line is plotted as a function of the P and R branch assignments.

instrument, several rovibrational transitions of carbon monoxide ( $v=0 \rightarrow 1$ ) have been observed and identified both in the jet and in a 10 cm gas cell. As described above, the laser is scanned over an approximately 1-2  $\text{cm}^{-1}$  region by ramping the current. Actually, the diode laser can be continuously scanned across a longitudinal mode, which is typically 1-2  $\text{cm}^{-1}$  in length. The modes are separated from one another by several wavenumbers and this non-continuous tunability gives rise to "snippets" of spectra. A series of twelve  $v=0 \rightarrow 1$  carbon monoxide transitions, acquired in the jet, are shown in Fig. 3. No attempt to scan a large portion of the 2100-2200  $\text{cm}^{-1}$  region was made. We simply searched and found laser modes corresponding to known carbon monoxide frequencies. The laser power for each mode is different and the intensities of the lines in Fig. 3 have been corrected to show relative intensities. Although all the spectral lines shown have a frequency or wavelength assigned to them, the signal as it is received from the scope is time based. Frequency is assigned by examining maxima in the étalon signal which is recorded simultaneously. An expanded view of the P(5) transition with calibrated frequency is given in Fig. 4.

The rotational temperature for carbon monoxide at conditions in our jet expansion can be obtained through an intensity analysis of the individual rovibrational transitions (Steinfeld, 1986). The analysis procedure involves converting the intensity of each rovibrational transition to a population by dividing the appropriate corrected intensity by the degeneracy,  $(2J+1)$ , and the line strength or Hönl-London factor (Hertzberg, 1950). For rotational levels observed in P and R branch spectra, an average population for the level was calculated and used in the determination. An approximate temperature can be obtained from the expression

$$J_{\max} \cong 0.59 \sqrt{\frac{T}{B}} \quad (1)$$

where  $J_{\max}$  corresponds to the rotational level with the greatest population fraction  $T$  is the temperature in Kelvin, and  $B$  is the rotational constant in  $\text{cm}^{-1}$  (Bernath, 1995). An observed  $J_{\max}$  of 3, for example, yields a rotational temperature of 50 Kelvin (K) for an expansion of neat carbon monoxide in our apparatus.

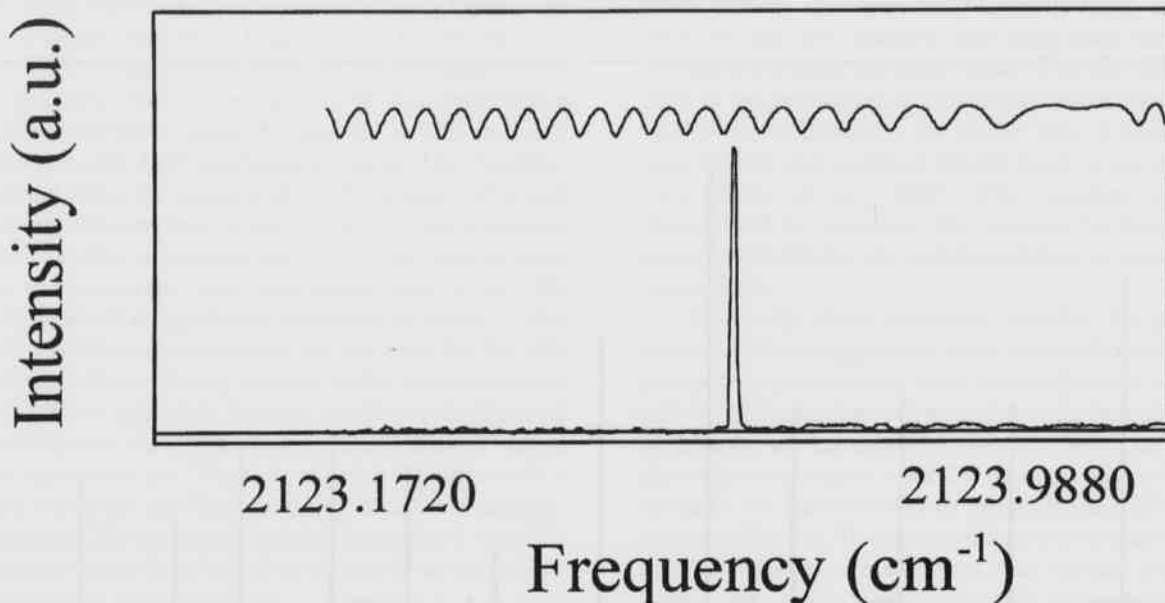


Fig. 4. Rovibrational transition, P(5) of the  $v=0 \rightarrow 1$  band, for the most abundant isotope of carbon monoxide. The top trace is an etalon signal and is used to determine the frequency range of the spectra.

A better temperature determination is obtained by assuming a Boltzmann distribution for the rotational population and then plotting the rotational level population versus the rotational energy. The points are fit to a linear expression with a slope of  $-1/kT$ , where  $k$  is the Boltzmann

constant and  $T$  is the temperature in Kelvin. A graph of rotational population vs. rotational energy for the transitions observed in the supersonic jet expansion is shown in Fig. 5. We have included populations determined from both P and R branch spectra in this analysis. Rotational temperature for

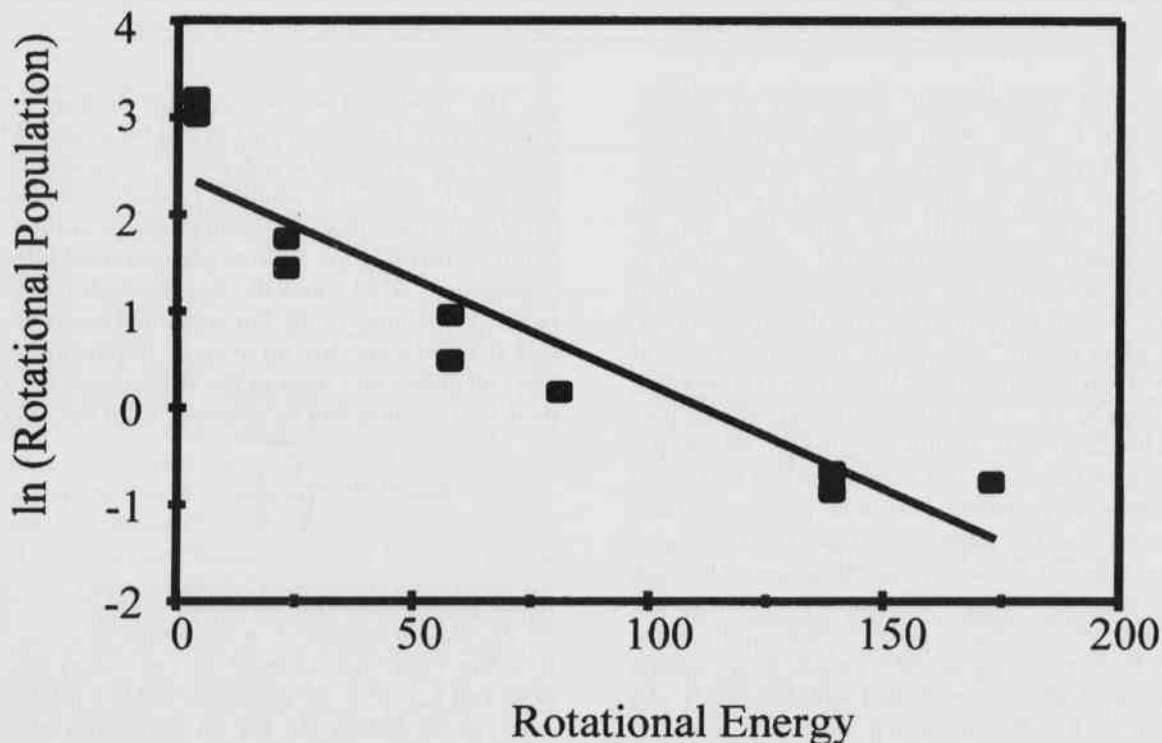


Fig. 5. Boltzmann plot showing relationship between the natural log of the rotational population and the rotational energy.



a neat carbon monoxide expansion in our jet, determined from the slope of the line, is  $66 \text{ K} \pm 10 \text{ K}$ .

**Detection Limit Determination.**—Our experiment is a typical infrared absorption experiment in that the molecular absorption can be understood within the context of Beer's Law, viz

$$I(\nu) = I_0(\nu) e^{-\gamma(\nu)L} \quad (2)$$

where  $I_0(\nu)$  is the incident intensity at frequency  $\nu$ ,  $I(\nu)$  is the transmitted intensity at frequency  $\nu$ ,  $L$  is the path length and  $\gamma(\nu)$  is the absorption coefficient (Bernath, 1995). The importance of the multipass mirror arrangement described above is now clearly evident; the multipass effectively increases the absorption path length which increases the observed signal intensity. The interaction of a molecule with electromagnetic radiation can produce absorption, induced emission, and spontaneous emission if the energy of the photon happens to coincide exactly with the energy difference between two eigenstates  $|m\rangle$  and  $|n\rangle$ ,  $E_m - E_n$ , for the molecule. Neglecting spontaneous emission, the absorption coefficient can be written as (Kroto, 1992)

$$\gamma(\nu) = \frac{8\pi^3}{3hc} \nu \left( \frac{N_m}{g_m} - \frac{N_n}{g_n} \right) |\langle n|\mu|m\rangle|^2 \delta(\nu, \nu_0). \quad (3)$$

The term  $\delta(\nu, \nu_0)$  in equation (3) is a line shape function, typically represented by either a Gaussian or Lorentzian function, centered at the frequency corresponding to  $(E_m - E_n)/h$ ,  $\nu_0$ . The lineshape function is sensitive to a given set of experimental conditions and is molecule dependent only in terms of linewidth. The absorption coefficient, and thus the intensity of a vibrational transition, is also directly proportional to the square of the transition dipole moment,  $|\langle n|\mu|m\rangle|^2$ . For rovibrational transitions, the transition dipole moment is, to a first order approximation, directly proportional to  $d\mu/dr$  (Bernath, 1995). The absorption coefficient is also a function of the difference in population between the two energy states,  $(N_n/g_n - N_m/g_m)$ . In this expression,  $N_i$  represents the number of molecules in the ground state  $m$ , the excited vibrational state  $n$ , and the degeneracy of each state is indicated by  $g$ . Assuming the sample is at equilibrium, the population difference can also be expressed in terms of a Boltzmann distribution, viz.

$$\frac{N_m}{g_m} - \frac{N_n}{g_n} = \frac{N_m}{g_m} \left( 1 - e^{-\frac{E_m - E_n}{kT}} \right) \quad (4)$$

The terms in the exponential denominator above are the Boltzmann constant,  $k$ , and the temperature in  $T$ . From Equation (4), the population difference will be largest, for a

given rovibrational transition  $E_m - E_n$ , when  $kT$  is small. Or in other words, the population difference will be largest for samples at low temperatures, as are produced in supersonic jet expansions. The cooling effect in the jet has allowed us to observe carbon monoxide rovibrational transitions at low carbon monoxide concentrations. The concentration of gas phase samples are frequently expressed in units of molecules/cm<sup>3</sup>. For example, the number density for a carbon monoxide gas sample at 2 atmospheres pressure and 25°C is  $5.38 \times 10^{19}$  molecules•cm<sup>-3</sup>. The number density in the expansion can be calculated by assuming the expansion is isentropic and using the isentropic equation of state for an ideal gas to generate the relationship (Smalley et al., 1977; Lubman et al. 1982)

$$\left( \frac{T}{T_0} \right) = \left( \frac{P}{P_0} \right)^{\frac{\gamma-1}{\gamma}} = \left( \frac{\rho}{\rho_0} \right)^{\frac{\gamma-1}{\gamma}} = \frac{1}{1+(1/2)(\gamma-1)M^2}. \quad (5)$$

Here  $T_0$ ,  $P_0$ , and  $\rho_0$  are the temperature, pressure and density of the gas located in the reservoir behind the nozzle,  $T$ ,  $P$ , and  $\rho$  are the temperature, pressure and density for the gas in the expansion, and  $\gamma$  is the heat capacity ratio  $C_p/C_v$ . The quantity  $M$  in equation (5) is the Mach number ( $M = \text{speed of molecules}/\text{speed of sound}$ ). Mach numbers of 50-100 (supersonic levels) are routinely achieved in jet expansions. The Mach number can be calculated from equation (6) below (Smalley et 1977)

$$M = A \left( \frac{X}{D} \right)^{\frac{\gamma-1}{\gamma}} \quad (6)$$

and the appropriate constants for argon ( $A = 3.26$  and  $\gamma = 5/3$ ). The quantity  $X$  in equation (6) is the distance from the nozzle (downstream) and  $D$  is the nozzle diameter. Of course, the Mach number cannot increase forever and will asymptotically approach a terminal value. In our system, for example, a terminal Mach number of  $\sim 50$  is predicted based on a nozzle diameter of 0.4 mm (Smalley et al., 1977). Keep in mind, that even at high Mach numbers the molecules still travel at speeds of only  $\sim 1500$  m/s. The local speed of sound however is proportional to  $(T)^{1/2}$ . Thus high Mach numbers are reached in the expansion because of the cooling effect of the jet rather than an increase in molecular speed.

The jet cooled spectra acquired for the detection limit determination were all obtained using one of three gas mixtures, 30%, 10%, or 5% carbon monoxide in argon, respectively. As the argon carrier represents the major component of the mixture, the calculations are approximated by using values for  $\rho$  and  $A$  appropriate for argon. For a Mach number of 37 (calculated for a position 1.5 cm downstream of the nozzle) and a reservoir number density of  $5 \times 10^{19}$  molecules/cm<sup>3</sup>, an expansion number density of  $\rho \sim 5 \times$

## An Infrared Diode Laser Spectrometer for the Study of Jet Cooled Gases

$10^{15}$  molecules/cm<sup>3</sup> is obtained. In most cases,  $v=0 \rightarrow 1$  ro-vibrational transitions for the  $^{12}\text{C}^{16}\text{O}$  species were observed at 100% absorbance, even for gas mixtures of 10% carbon monoxide in argon. The carbon-13 isotopic form of carbon monoxide,  $^{13}\text{C}^{16}\text{O}$ , has also been observed with all three gas mixtures. Figure 6 shows the  $v=0 \rightarrow 1$  R(0) line of  $^{13}\text{C}^{16}\text{O}$ . Given that the carbon-13 isotope is present at a 1% level in natural abundance, a number density corresponding to  $\sim 5 \times 10^{12}$   $^{13}\text{C}^{16}\text{O}$  molecules/cm<sup>3</sup> is obtained with equation (5). The third isotopic form of carbon monoxide we have observed in natural abundance is  $^{12}\text{C}^{18}\text{O}$ . Figure 7 shows the  $v=0 \rightarrow 1$  R(1) transition recorded with a 30% gas mixture. Note, the signal to noise ratio for the absorption in Fig. 7 is  $\sim 3$  or 4. We have also observed this transition with a 10% gas mixture; however, the signal to noise ratio was  $\sim 1$ . Oxygen-18 is present at a 0.2% level in natural abundance corresponding to a number density for the 30% gas mixture of  $\sim 3 \times 10^{12}$  molecules/cm<sup>3</sup>.

website), a peak absorption coefficient of  $0.00776 \text{ cm}^{-1}$  is calculated for the  $v=0 \rightarrow 1$  R(0) line of  $^{13}\text{C}^{16}\text{O}$ . This particular transition was observed with a 5 dot pattern on the front multipass mirror. We will assume the absorption path length for one pass through the expansion is approximately 1 cm at a distance of 1.5 cm downstream of the pulsed nozzle. A peak absorption coefficient of  $0.00776 \text{ cm}^{-1}$  combined with a total absorption path length of  $\sim 9 \text{ cm}^{-1}$  will give rise to an 8% absorption. At best, the signal to noise in Fig. 6 is 25:1, suggesting the absorption sensitivity of our instrument is 0.003 with the current experimental parameters. This sensitivity level should be sufficient, however, to examine both radicals and van der Waals complexes in the jet as nominal concentrations for such species is  $\sim 10^{13}$  molecules $\cdot\text{cm}^{-3}$  (Bernath, 1990; Schuder et al., 1991).

Finally, there is some interest in comparing the absorption sensitivity of our instrument with other instruments described in the literature. In their paper describing the

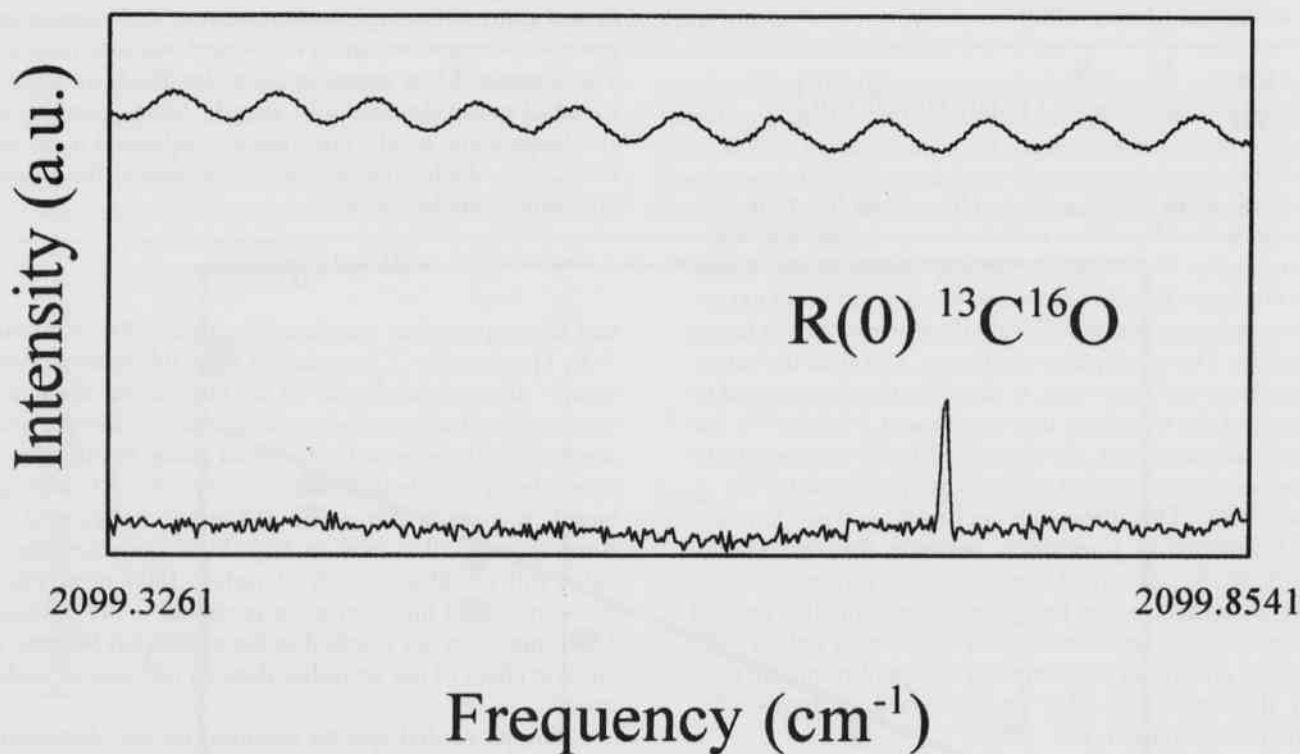


Fig. 6. Spectrum obtained with a 10% gas mixture of carbon monoxide in argon. The gas pulse has been triggered to optimize the intensity of this peak. Spectral assignment is made using a NIST table of carbon monoxide frequencies.

With the number densities in hand, we proceed with a detection limit or sensitivity calculation. Given a carbon monoxide transition moment of 0.1078 Debye (see NIST

rapid scan method for obtaining high resolution infrared spectra, De Piante and coworkers reported an instrumental sensitivity of 0.0003 (De Piante et al., 1989). The only other

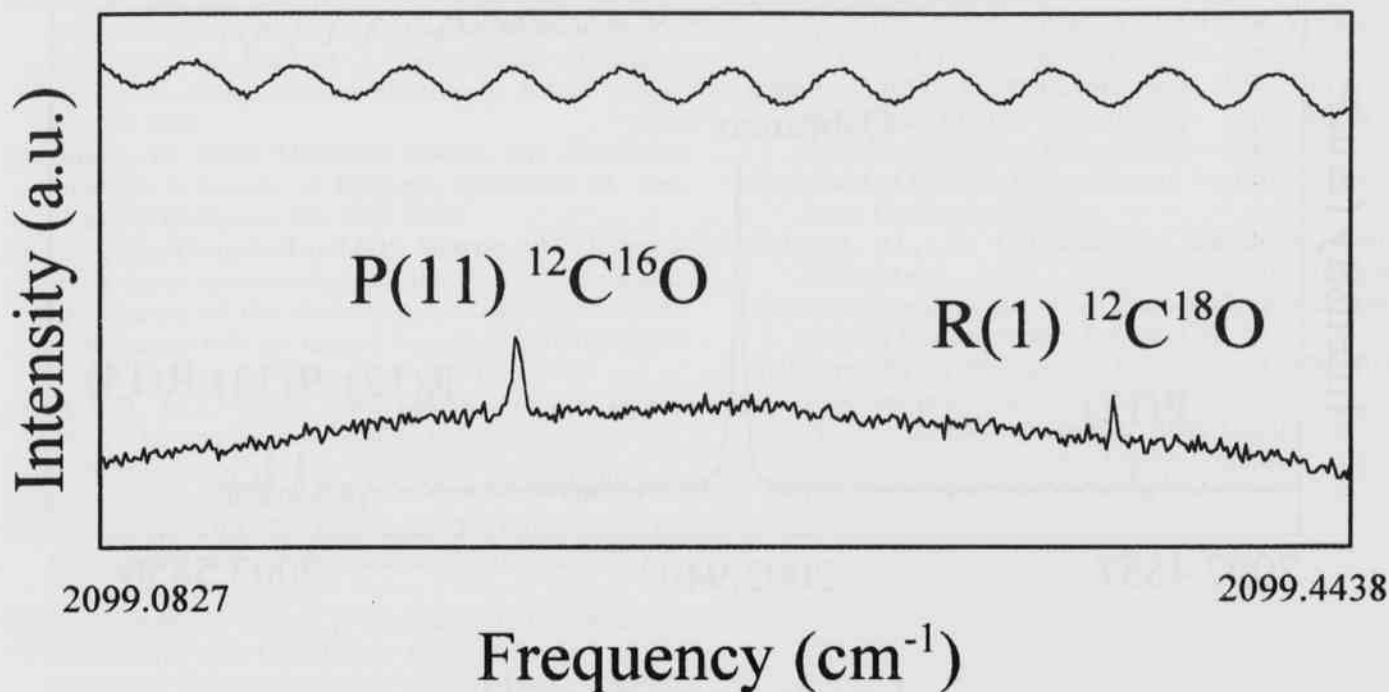


Fig. 7. Spectrum obtained with a 30% gas mixture of carbon monoxide in argon. The gas pulse has been triggered to optimize the intensity of the <sup>12</sup>C<sup>18</sup>O peak. Spectral assignment is made using a NIST table of carbon monoxide frequencies.

reported instrumental sensitivity value for an infrared diode laser spectrometer coupled with a supersonic jet expansion that we are aware of is 0.0006 (Schuder et al., 1991). While these two values represent comparatively better figures of merit, we need to point out that both of these instruments utilize a 10 cm slit nozzle design where we have a pinhole nozzle. Slit jet nozzles offer several advantages including greater path lengths along the axis collinear with the slit and greater column densities (Nesbitt, 1994). For example, the effective path length for these two instruments is 80 cm (De Piante et al., 1989) and 24 cm (Schuder et al., 1991), respectively. Because the relationship between absorbance and path length is linear, we do plan to incorporate a slit nozzle in the future. In fact, General Valve does offer a commercial 2.54 cm slit jet nozzle for \$1500 (the General Valve IOTA ONE system we are using comes standard with a pinhole nozzle). With the appropriate increases in path length, our instrument should match the absorption sensitivity reported by others.

**Transition Metal Carbonyl Studies.**—One of our long range goals is the high resolution infrared investigation of transition metal monocarbonyl radicals. Before we can realistically begin this work several experimental issues will

need to be dealt with. We intend to produce metal monocarbonyl radicals by passing the vapor from a parent carbonyl through a gas discharge formed by attaching electrodes to the end of the pulsed nozzle. Iron monocarbonyl, for example, has been studied in the microwave region using a 2% iron pentacarbonyl in argon gas mixture (Kasai et al., 1995). Many of the metal monocarbonyl radicals we are interested in will need to be produced from solid parent carbonyl compounds. Thus, one potential experimental problem involves entraining the vapor above a solid into an argon carrier so that it can be injected into a supersonic jet/electric discharge expansion. Following the work of Paul Davies at Oxford (see for example, Burie et al., 1991), a pulsed valve with a 1.5 ml reservoir machined into the valve body has been incorporated into our supersonic jet vacuum chamber. This particular valve can also be heated with an external band heater to temperatures of ~100°C to further increase the amount of vapor pressure of the compound of interest. With this new valve, we have observed an intense Q branch and several rovibrational transitions for the  $\nu_6$  band of chromium hexacarbonyl, Cr(CO)<sub>6</sub> (see Fig. 8). The spectrum in Fig. 8 represents several individual laser scans over the 2002.4557-2003.5856 cm<sup>-1</sup> region, each with a dif-

## An Infrared Diode Laser Spectrometer for the Study of Jet Cooled Gases

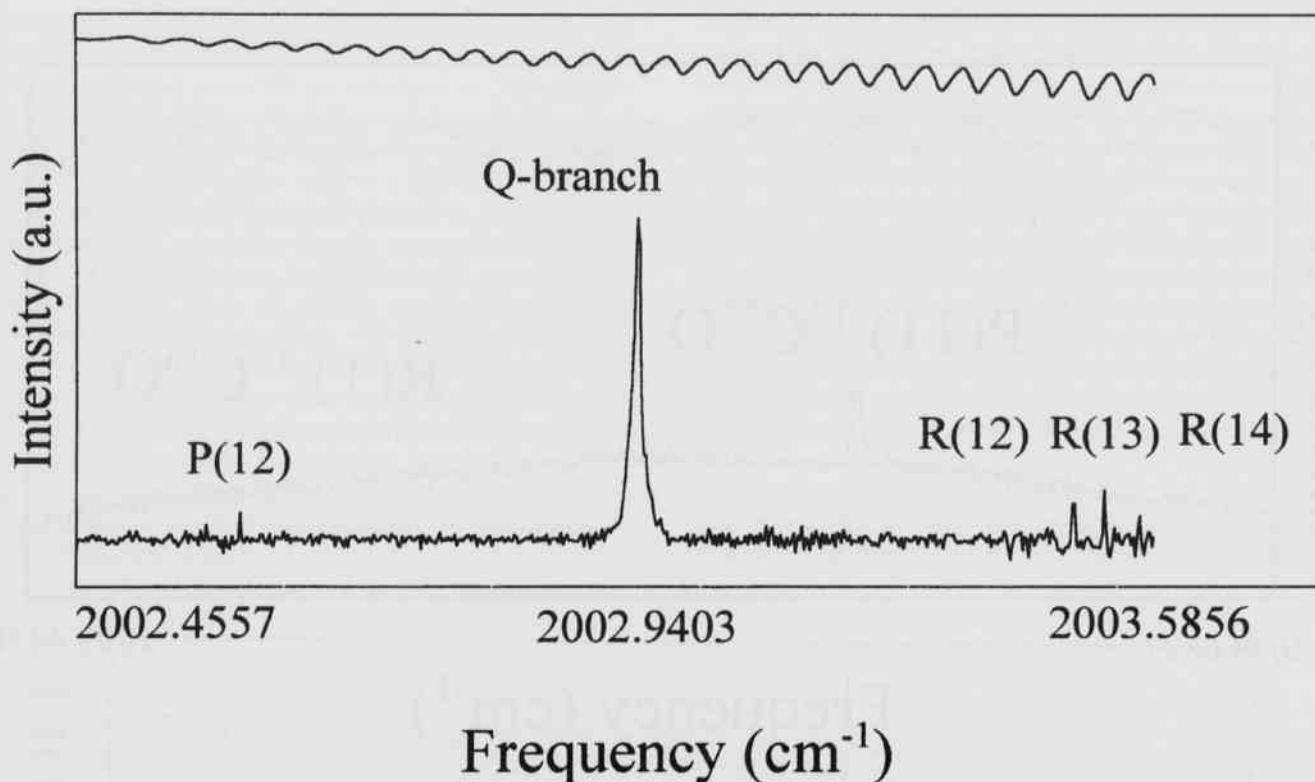


Fig. 8. Observed infrared absorption spectrum for chromium hexacarbonyl in the 5 micron region. Assignments were made following Burie, et. al., 1991.

ferent gas pulse position (in time) along an externally voltage ramp used to scan the diode laser. Thus, Fig. 8 is actually a composite obtained by summing together the individual scans and performing a baseline correction (see Williams et al., for a description of this process).

In conclusion, we have constructed an *in-house* high resolution, tunable, diode laser spectrometer from commercially available components. The spectrometer has been combined with a pulsed supersonic jet expansion to produce supercooled gas samples for spectroscopic study. Spectrometer capabilities were evaluated with a carbon monoxide gas sample and an absorption sensitivity for our instrument was determined. Continuing work will focus initially on observing high resolution spectra for several transition metal carbonyl halides. The goal here will be to develop procedures for reliably injecting vapor from the carbonyl compounds into the jet expansion.

**ACKNOWLEDGMENTS.**—Support for this project has been provided by the Arkansas Science and Technology Authority, the Arkansas Space Grant Consortium (Undergraduate Research Awards for Philip Williams, Candace Lindsey and Anthony Bednar), the Arkansas NASA EPSCoR Program, a Cottrell College Science Award

from Research Corporation, the Arkansas Science Information Liaison Office (SURF Award for Anthony Bednar and Candace Lindsey), and Arkansas State University. In addition, acknowledgment is made to the donors of The Petroleum Research Fund, administered by the ACS, for partial support of this research.

#### Literature Cited

- Atkins, P.W.** 1983. *Molecular Quantum Mechanics*, Second Edition, Oxford University Press, New York.
- Bernath, P.F.** 1990. High Resolution Infrared Spectroscopy of Transient Molecules, *Ann. Rev. Phys. Chem.* 41:91-122.
- Bernath, P.F.** 1995. *Spectra of Atoms and Molecules*, Oxford University Press, New York.
- Burie, J.-R., P.B. Davies, G.M. Hansford, J. Gang, and D.K. Russell.** 1991. Diode laser infrared spectroscopy of jet-cooled hexacarbonyls of chromium, molybdenum, and tungsten, *Mol. Phys.* 74:919-922.
- De Piante, A., E.J. Campbell, and S.J. Buelow.** 1989. Pulsed molecular beam, diode laser spectrometry using



- rapid scanning techniques, *Rev. Sci. Instrum.* 60:858-862.
- Heath, J.R., and R.J. Saykally.** 1991. Infrared laser absorption spectroscopy of the  $\nu_4(\sigma_u)$  fundamental and associated  $\nu_{11}(\pi_u)$  hot band of  $C_7$ : Evidence for alternating rigidity in linear carbon clusters. *J. Chem. Phys.* 94:1724-1729.
- Hertzberg, G.** 1950. *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules.* D. Van Nostrand Company, Inc. New York.
- Hu, T.A., E.L. Campbell and S.W. Sharpe.** 1993. Infrared diode laser spectroscopy of the Ar- $N_2O$  complex: Observation of the intermolecular bending mode in combination with the highest frequency intramolecular stretching mode. *J. Chem. Phys.* 98:6162-6169.
- Juang, Y.D., M.A. Walsh, A.K. Lewin, and T.R. Dyke.** 1992. The structure of  $N_2-SO_2$  from diode laser and molecular-beam electric resonance spectroscopy. *J. Chem. Phys.* 97:832-840.
- Kasai, Y., K. Obi, Y. Ohshima, Y. Endo, and K. Kawaguchi.** 1995. Pure rotational spectrum of FeCO. *J. Chem. Phys.* 103:90-95.
- Kaur, D., A.M. de Souza, J. Wanna, S.A. Hammad, L. Marcocelli, and D.S. Perry.** 1990. Multipass cell for molecular beam absorption spectroscopy, *Applied Optics* 29:119-124.
- Kroto, H.W.** 1992. *Molecular Rotation Spectra.* Dover, New York.
- Levy, D.H.** 1984. The Spectroscopy of Supercooled Gases. *Scientific American*, February, 96-108.
- Low, R.J., M.D. Brookes, C.J. Whitham and B.J. Howard.** 1996. A high resolution spectroscopic study of the open-shell complex Ar- $NO_2$ , *J. Chem. Phys.* 105:6756-6770.
- Lubman, D.M., C.T. Rettner, and R.N. Zare.** 1982. How Isolated are Molecules in a Molecular Beam? *J. Phys. Chem.* 86:1129-1135.
- McKellar, A.R.W., Y.P. Zeng, S.W. Sharpe, C. Wittig, and R.A. Beaudet.** 1991. Infrared Absorption of the CO-Ar Complex. *J. Mol. Spect.* 153:475-485.
- Miller, T.A.** 1984. Chemistry and Chemical Intermediates in Supersonic Free Jet Expansions. *Science* 223:545-553.
- Nesbitt, D.J.** 1994. High Resolution, Direct Infrared Laser Absorption Spectroscopy in Slit Supersonic Jets: Intermolecular Forces and Unimolecular Vibrational Dynamics in Clusters. *Ann. Rev. Phys. Chem.* 45:367-399.
- Schuder, M.D., D.D. Nelson and D.J. Nesbitt.** 1991. Investigation of internal rotor dynamics of NeDCl and ArDCl via infrared absorption spectroscopy. *J. Chem. Phys.* 94:5796-5811.
- Sharpe, S.W., R. Sheeks, C. Wittig, and R.A. Beaudet.** 1988. Infrared Absorption Spectroscopy of  $CO_2$ -Ar Complexes. *Chem. Phys. Lett.* 151:267-272.
- Silverstein, R.M., G.C. Bassler, and T.C. Morrill.** 1981. *Spectrometric Identification of Organic Compounds.* 4<sup>th</sup> Edition, J. Wiley & Sons, New York.
- Smalley, R.E., L. Wharton, and D.H. Levy.** 1977. Molecular Optical Spectroscopy with Supersonic Beams and Jets. *Acc. Chem. Res.* 10:139-145.
- Steinfeld, J.L.** 1986. *Molecules and Radiation.* The MIT Press, Cambridge, MA.
- Takami, M., Y. Oshima, S. Yamamoto and Y. Matsumoto.** 1986. Free-jet Infrared Absorption Spectroscopy of Stable and Unstable Molecular Species, *Faraday Discuss. Chem. Soc.* 86:1-12.
- Williams, P., A. Bednar, E. Barnett, and S.W. Reeve.** 1998. (in press) *Arkansas Acad. Sci.*
- Xu, Y. and A.R.W. McKellar.** 1996. Continuous slit-jet infrared spectrum of the CO- $N_2$  complex, *J. Chem. Phys.* 104:2488-2496.