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Abstract

We describe software developed with LabVIEW to provide operational control for an *in-house* infrared diode laser spectrometer that has been combined with a pulsed supersonic jet expansion sample source. Data were collected with this instrument using a modified version of the rapid-scanning method. A prerequisite in employing the rapid-scan detection scheme is that the modulation used to scan the laser be synchronized in time with the electrical signal used to trigger the pulsed gas valve. Software performance was evaluated by examining a series of rotation vibration (ro-vibrational) spectra for the carbon monoxide molecule in the five micron region of the infrared.

Introduction

High resolution infrared laser spectroscopy is a proven experimental method for obtaining fundamental information about the chemical and physical properties of gas phase molecules (Hirota, 1992). Tunable lead salt semiconductor diode lasers are frequently used to make these high resolution measurements. Lead salt diodes are manufactured for the entire 3-30 micron region of the infrared and possess a narrow spectral width output which permits the resolution and measurement of rotational fine structure. Complete infrared diode laser spectrometers are available commercially, although these complete systems are quite expensive (~$50,000 for a liquid nitrogen cooled system). Over the last year, we have assembled an *in-house* infrared diode laser spectrometer from individual spectrometer components that can be purchased separately for approximately half the price of a complete commercially assembled system. In addition to the spectrometer, we have also constructed a supersonic jet expansion vacuum system from commercially available components. The combination of a supersonic jet sample source and an infrared diode laser spectrometer to perform direct absorption infrared measurements was first described about twenty years ago (Gough et al., 1978). Since that time, this instrumental combination has been used to investigate the properties of several stable gas phase molecules (see for example, Takami et al., 1988; Davies et al., 1990; Burie et al., 1991; Gang et al., 1992; Brown et al., 1993; and Davies et al., 1994), as well as weakly bound species such as van der Waals complexes (see for example,

Sharpe et al., 1988; De Piante et al., 1989; Schuder et al., 1991; McKellar et; al., 1992; and Hu et al., 1993). One challenge faced when combining two sophisticated scientific instruments is establishing and executing operational control for each instrument during an experiment. Operation and control for our infrared diode laser spectrometer, a supersonic jet expansion, and the peripheral detection electronics is accomplished via a Pentium personal computer (PC) equipped with the LabVIEW full development software package. LabVIEW is a graphical programming language commercially available through National Instruments. Following De Piante, Campbell, and Buelow (1989), we have optimized the software to increase instrument sensitivity and resolution and decrease laser source noise. In a companion paper submitted to these proceedings, we provide a detailed description of the instrument assembled at Arkansas State University. Here, we describe the development and optimization of a LabVIEW algorithm designed to control and operate the spectrometer.

Materials and Methods

A schematic of our *in-house* infrared diode laser spectrometer is shown in Fig. 1. Experiments are performed by collimating infrared radiation from one of three Pb-salt diodes with an off-axis parabolic mirror (OAPM) and focusing the light with a 250 millimeter (mm) CaF_2 lens into a 0.5 meter monochromator for mode selection. Upon exiting the monochromator, the beam is collimated with a second 250
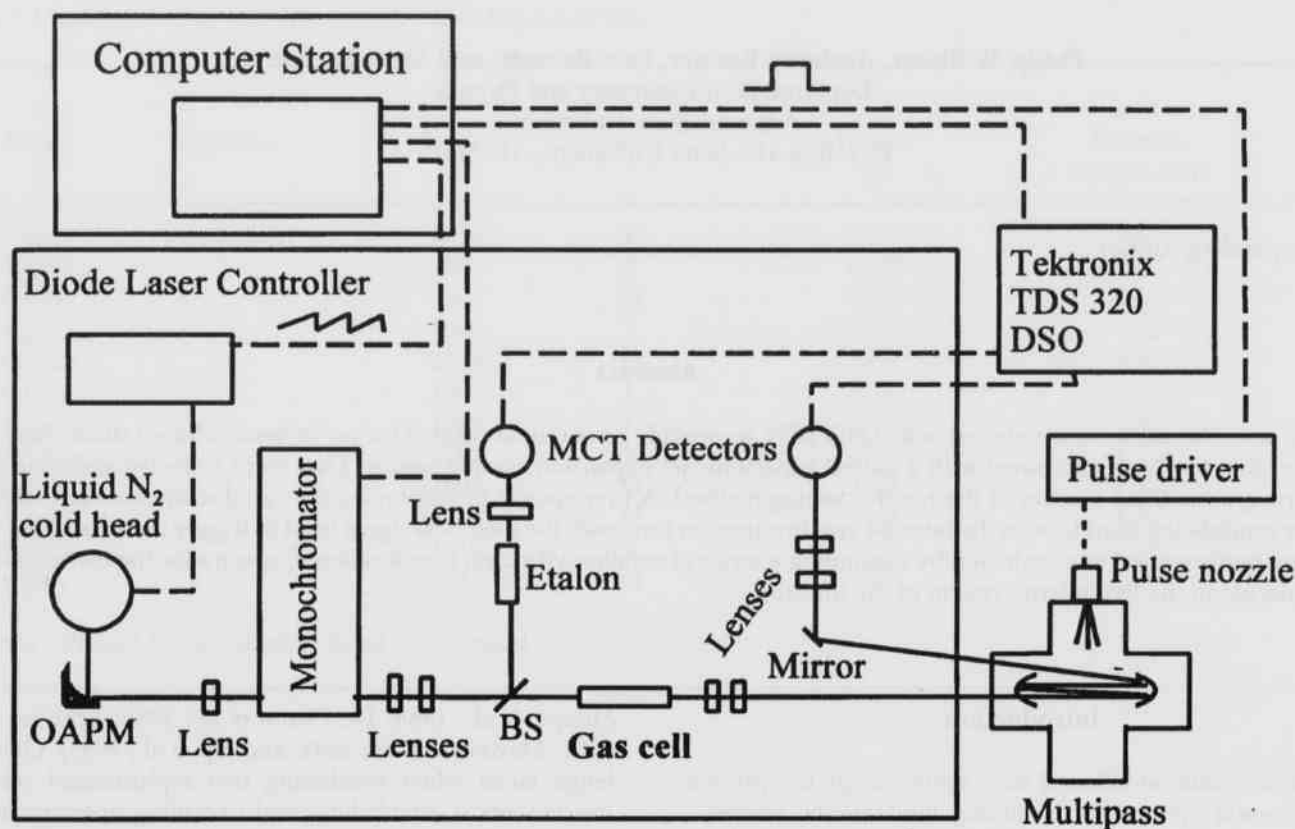
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Fig. 1. Tunable diode laser spectrometer. The solid line represents the optical path and the dotted line shows the electrical connections.

mm CaF_2 lens before intersecting a beamsplitter positioned to send 8% of the radiation through a tuning rate etalon for calibration. The remaining 92% first traverses the length of a reference gas cell before being focused into a multipass mirror arrangement inside the chamber where it will make 15-30 passes through a pulsed jet expansion about 1 cm downstream of the nozzle. The signal channel is finally focused with a CaF_2 f/2 lens onto a mercury cadmium telluride (MCT) infrared detector. MCT detectors produce a voltage that is proportional to the incident infrared radiation. This voltage is first amplified and filtered with an voltage amplifier before being displayed on a digital storage oscilloscope.

Pb-salt diode lasers can be specified to provide coverage of an approximately 150-200 wavenumber (cm^{-1}) window within the 300-3500 cm^{-1} spectral region. Individual diode lasers can be tuned or scanned through this ~200 cm^{-1} window by controlling the diode temperature and applied current. The nominal operating range for a Pb-salt diode is 80-140 Kelvin (K). Coarse tuning is accomplished through

changes in the diode temperature. As an example, we have tuned one of our diodes from 1870 cm^{-1} to 2015 cm^{-1} by varying the temperature from 83 K to 116 K. Fine tuning of the laser is done with the applied current. A nominal tuning rate for each of our diodes is ~0.04 cm^{-1} per milliamp (mA). High resolution scans for a given region are obtained by setting the temperature to an appropriate value and varying the current. We have opted to use a modified version of the rapid-scan method for data collection rather than the conventional slowscan boxcar based method. Originally described by De Piante and coworkers (De Piante et al., 1989), the rapid-scan method involves scanning the diode laser by applying an external modulation in the form of a voltage ramp to the diode laser controller. Here we apply a 0-5 volt (V) ramp at a frequency of 25-85 Hertz (Hz) with a step size of 5 millivolt (mV). The laser controller converts the applied voltage into a current applied to the diode. A modulation depth of 5 V corresponds to the current being scanned through a 100 mA region 50 mA on either side of some preset value, with a step size of 90 microamp (µA). To

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put this into more familiar spectroscopic terms, a 100 mA change corresponds to a scan through 4 cm^{-1} with a step size of less than 0.003 cm^{-1}. Unfortunately, diode lasers do not produce continuous radiation, but rather lase on several longitudinal modes for a given temperature and current setting. The longitudinal modes are typically 1-2 cm^{-1} in length and separated from one another by several wavenumbers. Thus, a scan of 100 mA represents a scan through one of these longitudinal modes. With a repetition rate of 25 Hz, the scan is completed in 40 milliseconds (ms) yielding a scan rate of ~0.1 cm^{-1}/ms. The primary advantage to the rapid scan technique is sensitivity. Absorption features with a full width at half maximum of 0.006 cm^{-1}, for example, are effectively modulated at electronic frequencies of 20 kilohertz (kHz). Source noise, laser 1/f noise, and noise from other sources generally occur at much lower frequencies. Thus, the noise can be electronically filtered before the absorption signal is recorded. Using the rapid-scan method, De Piante et al. (1989) have reported absorption measurements near the shot noise limit.

The sample source for this experiment is a pulsed supersonic jet gas expansion. The expansion is housed in a vacuum chamber that is evacuated with a six inch diffusion pump backed by a mechanical pump. The pumping throughput of this system is ~ 1200 liters/second with a liquid nitrogen cryotrap. Under load, the pumping system is able to maintain a chamber pressure of $< 5 \times 10^{-4}$ Torr. The jet expansion itself is created with a General Valve series 9 pulsed valve combined with a matched pulse valve driver. The pulse driver has a great deal of experimental flexibility in the sense that the valve can be opened and closed at repetition rates of 1 to 250 Hz. Duration or length of a gas pulse can be varied from 1 microsecond (μs) to 100 ms. Control for the pulse driver, and thus the pulse valve, is provided by sending a 5 V pulse to the driver. The length of time the nozzle remains open during an experiment is determined by the time duration of the 5 V pulse. For a molecular absorption to be observed, the gas pulse and laser voltage ramp must have the same repetition rate and be synchronized in time. The necessary synchronization is obtained via a Pentium 100 MHz PC equipped with a general purpose interface bus (GPIB) card, an eight channel-12 bit data acquisition card (DAQ), and the LabVIEW full development software package.

Results and Discussion

Analog electrical signals for the voltage ramp and the voltage pulse are generated as arrays in a LabVIEW virtual instrument (VI) or algorithm. Synchronization is accomplished by binding the two one-dimensional arrays together. The LabVIEW package comes complete with a large number of VI's to help minimize software development time. We have utilized many of these *built-in* VI's including a ramp generation VI, GPIB talk/listen VI's, serial read/write VI's, as well as VI's designed to configure and write analog electrical signals to the analog output ports on a DAQ card installed in the Pentium PC.

In addition to tuning the laser, the voltage ramp is also used to trigger a digital storage oscilloscope during data collection. Transient absorption waveforms are acquired on the oscilloscope and transferred to the Pentium PC via an IEEE 488 (GPIB) bus. An example of a single transient absorption obtained with our instrument is shown in Fig. 2. Both waveforms in Fig. 2 show a sequence of five laser ramps. The bottom trace represents a typical etalon spectrum. An etalon signal is recorded simultaneously with the signal channel and is used for calibration. Here a one inch solid piece of germanium etalon produces maxima spaced by 0.048 cm^{-1}. The top trace in Fig. 2 is the signal channel. The three apparent steps on each ramp correspond to three different laser modes (the monochromator in this case was set to pass all wavelengths). On the laser mode farthest to the right, two molecular absorptions are clearly seen. These two absorptions were obtained with a 10 cm gas cell containing reagent grade carbon monoxide at a pressure of ~2 Torr. Carbon monoxide was chosen as a test molecule during the software optimization phase of work because it has been extensively studied. 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 website, viz http://physics.nist.gov. The molecular absorptions in Fig. 2 represent rotationally resolved vibrational transitions for two different isotopic forms of carbon monoxide.

Of course, a major objective in developing the LabVIEW software was to interface a supersonic jet expansion sample source with a tunable diode laser spectrometer. One of the experimental challenges, even with pulsed jet expansions, involves trying to deal with gas flows that can exceed the available pumping capacity. The major difference between our spectrometer and the instruments described by De Piante et al., and others (De Piante et al., 1989; Schuder et al., 1991; McKellar et al., 1992; Hu et al., 1993; Low et al., 1996) is how this problem of limited pumping capability is handled. The LabVIEW software described above allows us to vary the voltage ramp repetition rate from 1-100 Hz. A voltage ramp of 0-5 V with a step size of 5 mV and a repetition rate of 25 Hz will have a period of 40 ms. The gas pulse must of course be synchronized with the voltage ramp; however, a gas pulse of 40 ms would simply raise the background pressure in the expansion chamber to unacceptable levels. In fact, a realistic length for a gas pulse is on the order of 0.5-1.5 ms depending on the backing pressure of the gas in the reservoir. In other words, our pumping system requires that the gas pulse be shorter than

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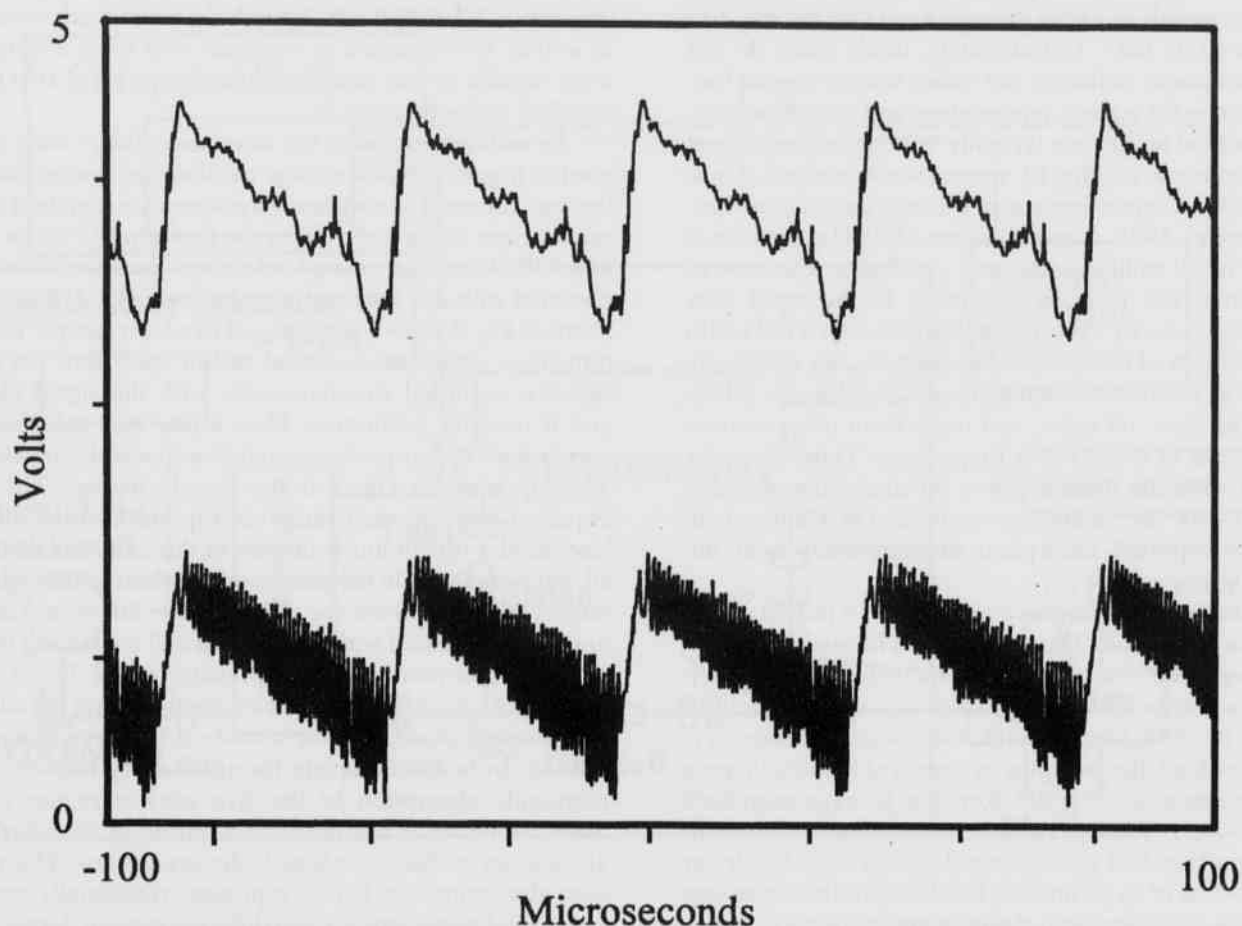### with a Pulsed Supersonic Jet Expansion

Fig. 2. Single transient absorption waveform collected with the infrared diode laser spectrometer at Arkansas State University. Five laser lamps are shown for the signal channel (top trace) and the etalon calibration channel (bottom trace).

the voltage ramp, even at higher frequencies (e.g., a 100 Hz rep rate shortens the ramp period to 10 ms). To deal with this issue, the software has been developed with the flexibility to allow the gas pulse to be positioned anywhere along the voltage ramp. Figure 3 provides a pictorial description of this idea. The top trace in Fig. 3 was obtained using a gas mixture consisting of 30 % reagent grade carbon monoxide in argon, and the two absorption features correspond to two different isotopic species of carbon monoxide, $^{12}C^{16}O$ and $^{12}C^{18}O$, respectively. The peak to the left is P(11) for the v = 0→1 band of $^{12}C^{16}O$. The smaller peak is R(1) for the v = 0→1 band of $^{12}C^{18}O$. Rotationally resolved spectra such as those shown in Fig. 3 are generated by the coaddition, in real time, of transient absorption waveforms over many gas pulses. For the spectrum in Fig. 3, 500 waveforms were averaged and a background subtraction performed before the data were recorded. The bottom half of Fig. 3 illustrates the

relationship between the gas pulse, the voltage ramp, and the frequency of the infrared radiation. For this particular spectrum, the gas pulse was positioned on the ramp to optimize the intensity of the $^{12}C^{18}O$ peak. The larger line from the $^{12}C^{16}O$ species is visible under non-optimized gas pulse conditions because it is a strong line. If we had recorded the spectrum with the gas pulse optimized on the more intense feature, the smaller peak would not be observed.

To cover a particular infrared region then, several spectra, differing only in the gas pulse position along the ramp, must be recorded. For example, a series of three spectra for the same ~1 cm^{-1} region in the infrared (2099.0827-2100.1366 cm^{-1}), acquired at different gas pulse positions along the voltage ramp, are displayed in Fig. 4. The three lines in Fig. 4 represent rovibrational transitions for the v = 0 → 1 band of three different isotopic species of carbon monoxide. The P(11) line of $^{12}C^{16}O$, the most abundant iso-

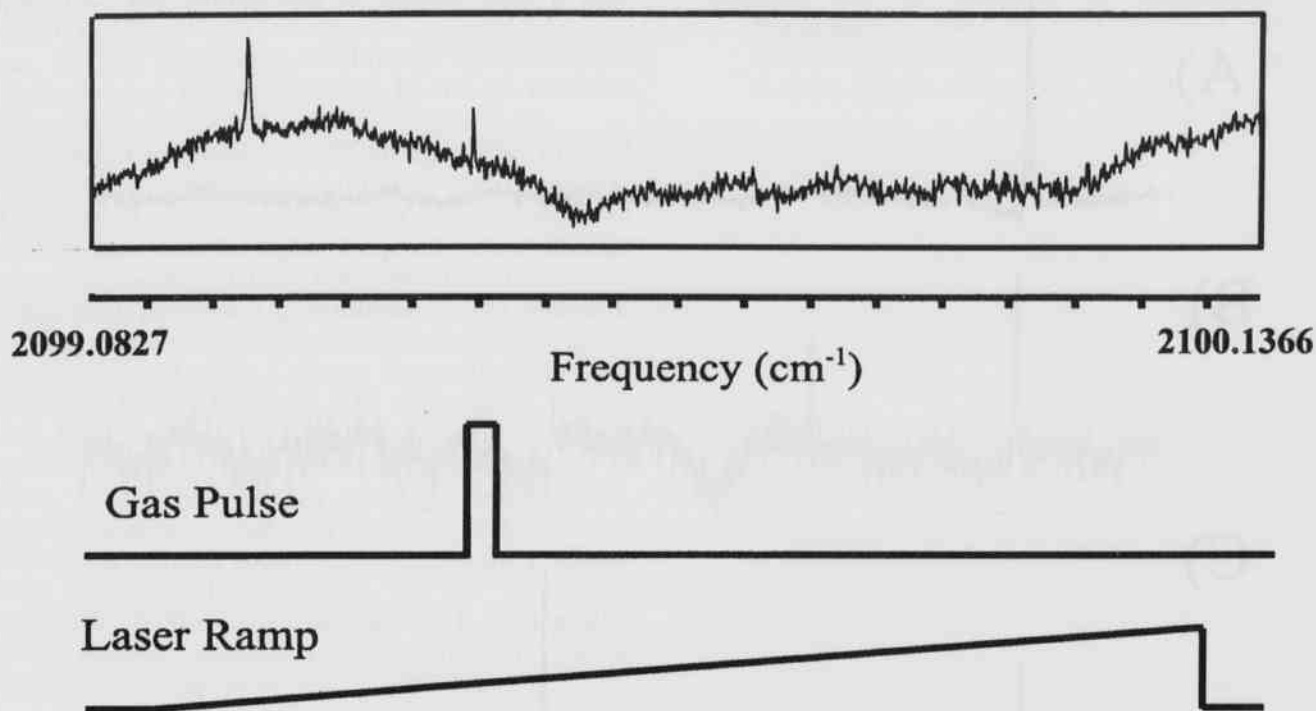Philip Williams, Anthony Bednar, Eric Barnett, and Scott W. Reeve

Fig. 3. Relationship between gas pulse, laser ramp, and observed spectra.

topic species of carbon monoxide, is shown in Fig. 4a. Figure 4b is another view of the spectral region shown in Fig. 3 and the line assignments are described in the text above. Finally, in Fig. 4c, the R(0) line of $^{13}C^{16}O$ is observed at 2099.7101 cm^{-1}. The gas pulse in Fig. 4c was positioned to optimize the intensity of the $^{13}C^{16}O$ transition.

Each of these individual spectra is saved in spreadsheet form complete with a header containing all the information for the scan, e.g., laser current, laser temperature, oscilloscope settings, pulse duration, pulse position along the voltage ramp, voltage ramp repetition frequency, and voltage ramp period, which is automatically recorded by the scanning program before the file is saved. Because the spectra are saved in spreadsheet form, a *complete* spectrum, containing all the molecular absorptions in a particular infrared region, can be obtained by simply summing the individual files together. We have performed this spreadsheet summation manually with the three spectra shown in Fig. 4. Thus, the complete absorption spectrum for carbon monoxide in the 2099.0827 - 2100.1366 cm^{-1} region of the infrared appears in Fig. 5. Generally speaking, the spreadsheet summation for a molecule with a previously unobserved rotationally resolved vibrational spectra will normally include

more than three individual files. Consider the following experimental situation. A voltage ramp with a 25 Hz repetition rate will have a 40 ms period. If a 1 ms gas pulse length is used, 40 experiments will need to be performed, each with an incrementally different gas pulse position along the laser ramp, to completely cover an infrared region with a single longitudinal lasing mode. The acquisition time at a single gas pulse position is about four minutes. The total scan time to cover a ~1-2 cm^{-1} region then, is approximately 2 1/2 hours. Keep in mind, however, a 0.003 cm^{-1} instrumental resolution (determined from the step size of the voltage ramp) will allow us to make rotationally resolved vibrational measurements for a large number of gas phase molecular systems. In other on-going research, we are attempting to obtain high resolution infrared spectra for several transition metal carbonyl compounds. These compounds are particularly challenging to study in a jet as most are solids at room temperature. In a companion paper, we also describe efforts to entrain the vapor pressure above a solid and inject it into a supersonic jet expansion.

2099.0827   **2100.1366**
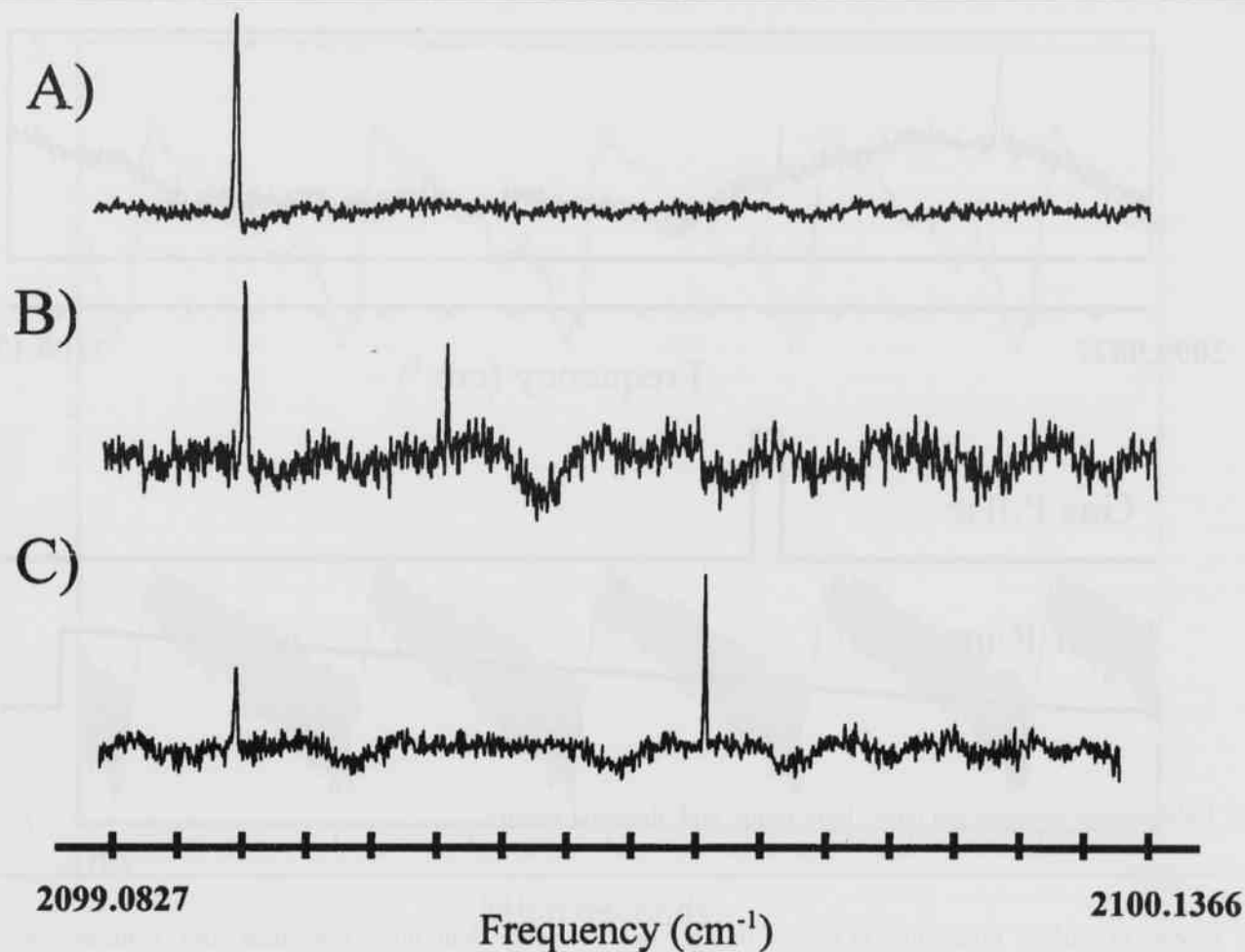
Frequency (cm⁻¹)

Fig. 4. Rovibrational spectra for the carbon monoxide molecule collected at different gas pulse positions along the voltage ramp.

Literature Cited

Brown, P.R, P.B. Davies, G.M. Hansford, and **N.A. Martin.** 1993. Diode laser jet spectroscopy of 1,4-Dioxane. J. Mol. Spect. 158:468-478.

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.

Davies, P.B., N.A. Martin, M.D. Nunes, D.A. Pape, and **D.K. Russell.** 1990. Diode laser and Fourier transform infrared spectroscopy of jet-cooled nickel carbonyl. J. Chem. Phys. 93:1576-1582.

Davies, P.B., G.M. Hansford, and **T.C. Killian.** 1994. Diode laser jet spectroscopy of Hexafluorbenzene in the 10-µmRegion. J. Mol. Spect. 163:138-158.

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.

Gang, J., M. Pennington, D.K. Russell, P.B. Davies, G.M. Hansford, and **N.A. Martin.** 1992. Infrared laser spectroscopy of jet-cooled methyl manganese pentacarbonyl. J. Chem. Phys. 97:3885-3891.

Philip Williams, Anthony Bednar, Eric Barnett, and Scott W. Reeve

Gough, T.E., RE. Miller, and G. Scoles. 1978. J. Mol. Spect. 72:124.

Hirota, E. 1992. Microwave and Infrared Spectra of Free Radicals and Molecular Ions. Chemical Reviews. 92:141-173.

Hu, T.A., E.L. Campbell and S.W. Sharpe. 1993. Infrared diode laser spectroscopy ofthe 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.

Low, RJ., 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.

McKellar, A.RW., Y.P. Zeng, S.W. Sharpe, C. Wittig, and RA. Beaudet. 1992. Infrared Absorption ofthe CO-Ar Complex. J. Mol. Spect. 153:475-485.

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.

Takami, M., Y. Oshima, S. Yamamoto and Y. Matsumoto. 1988. Freejet Infrared Absorption Spectroscopy of Stable and Unstable Molecular Species. Faraday Discuss. Chem. Soc. 86:1-12.
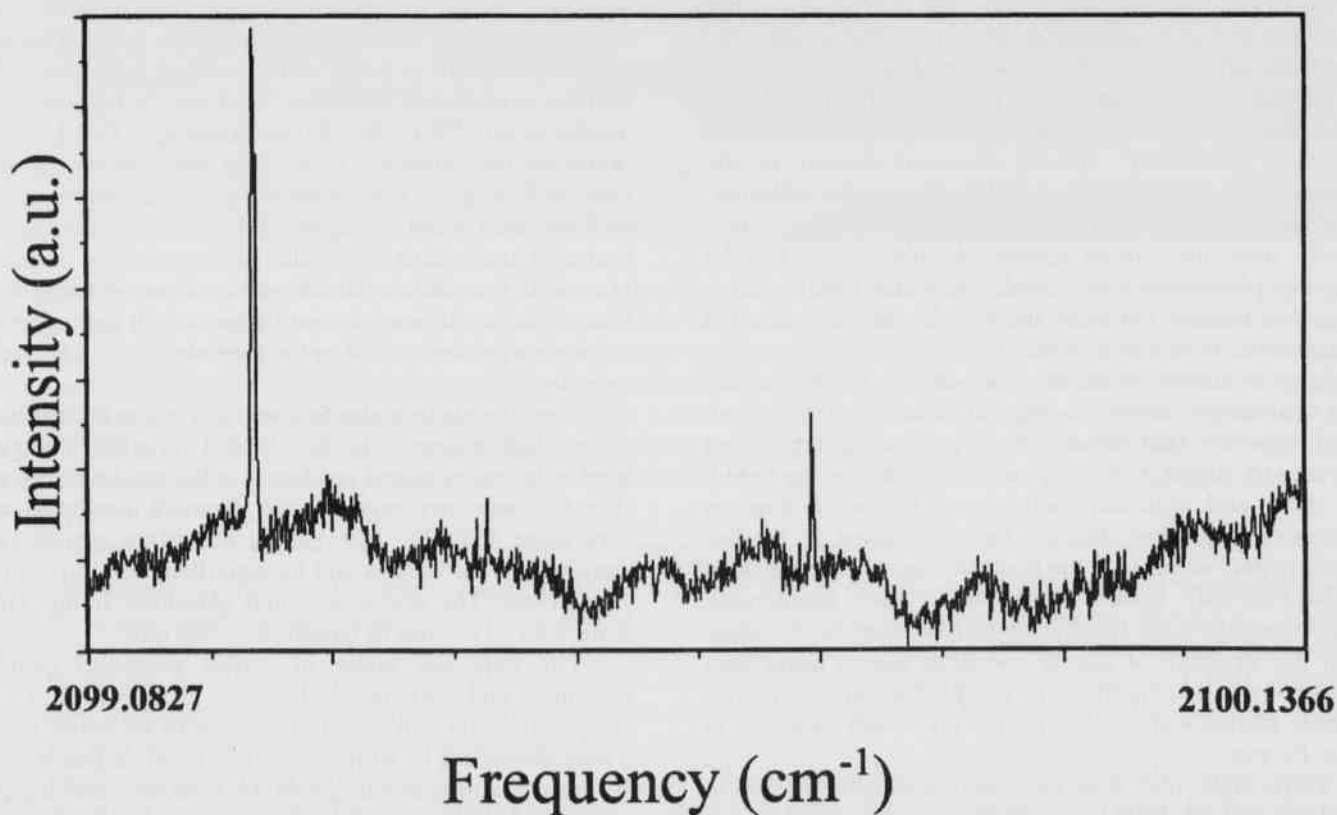
Fig. 5. Spectrum obtained by summing together the files shown in Fig. 4.