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## ROVIBRATIONAL SPECTROSCOPY OF ArCO VAN DER WAALS COMPLEX

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### INTRODUCTION

The information that can be obtained from the high resolution rovibrational spectra of small molecular clusters is very useful for determining intermolecular potentials and the effects of intermolecular interactions on intramolecular bonds. Recently, such spectra have been obtained via absorption measurements using F-center(1,2), frequency difference(3,4) and diode laser(5) sources. Because F-center and frequency difference lasers operate best in the 2-4  $\mu\text{m}$  region, studies using these laser sources have involved high frequency vibrational modes (H-X, X=C, F, Cl, Br) or overtones. Although diode lasers cover a much broader spectral range (3-20  $\mu\text{m}$ ), they are less convenient to use for doing survey spectroscopy. We have developed several new techniques which improve the sensitivity and convenience of absorption measurements using diode lasers for the study of molecular clusters in supersonic expansions. Here we describe these techniques and their application for the measurement of the rovibrational spectra of ArCO near 5  $\mu\text{m}$ .

### EXPERIMENTAL

A schematic diagram of the apparatus used in our experiments is shown in Fig. 1. The output of a Laser Analytics diode laser is collected with a parabolic mirror and passed through a Spex 1 meter monochromator to select a single laser mode. A portion of the laser output (~5%) is split off, passed through a Fabry-Perot etalon (0.015  $\text{cm}^{-1}$  FSR) and detected with an InSb detector. The signal from the detector is recorded by a transient digitizer, providing a relative frequency calibration for the spectra. The remaining radiation passes through a static gas cell and then into a vacuum chamber. Three spherical mirrors inside the vacuum chamber (r=450 mm), which are used in a White Cell(6) configuration, pass the laser radiation along the opening of a pulsed slit nozzle (2.5 mm x

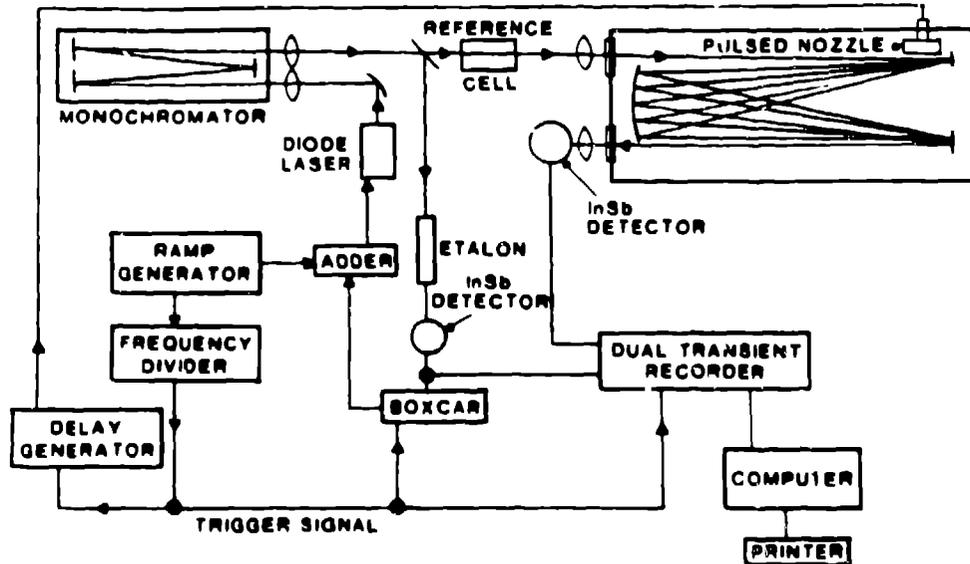


Figure 1. Schematic drawing of the experimental arrangement.

.005 cm). The radiation is mildly focused near the nozzle and passes 32 times within 1-2 cm of the nozzle slit. The path length in the high density region of the gas expansion is nearly a meter (Fig. 2). Under typical experimental conditions ( 75% Ar, 25% CO, 2 atm. backing pressure), the strongest ArCO features absorb 5-10 % of the laser radiation. The laser radiation passing through the expansion is detected by a second InSb detector and recorded by a transient digitizer.

The vacuum chamber is pumped by three mechanical pumps which have a total pumping speed of 1.5 m<sup>3</sup>/minute. Cluster absorption can be observed as long as the background pressure in the chamber is less than 0.6 torr. Typically during our experiments the pressure is below 0.2 torr. Absorption lines of reference gases placed in the static gas cell provide absolute frequency calibration for the spectra. Usually this cell is not required since CO monomer absorption in the vacuum chamber is strong and produces numerous reference lines in the ArCO data. To reduce noise produced by amplitude fluctuations in the diode laser output, the diode laser is scanned very rapidly (200 cm<sup>-1</sup>/sec). Signals from the ArCO absorption features which are about 0.003 cm<sup>-1</sup> wide appear at electronic frequencies greater than 10 kHz - far above the low frequency fluctuations in the diode laser output. By averaging 2000 laser scans, absorbances as small as 3 x 10<sup>-5</sup> can be detected.

During an experiment the diode laser is repeatedly scanned over a laser mode (.75 to 1.5 cm<sup>-1</sup>) every 5 milliseconds. The transient digitizers are triggered at the start of every hundredth laser scan. After this initial scan is completed, the nozzle is opened and a second laser scan is recorded on the second half of the transient recorder output (Fig. 3). The first scan is subtracted from the second, helping to correct for laser amplitude changes due to varying laser output over the mode and interference effects that can occur in the optics. Due to

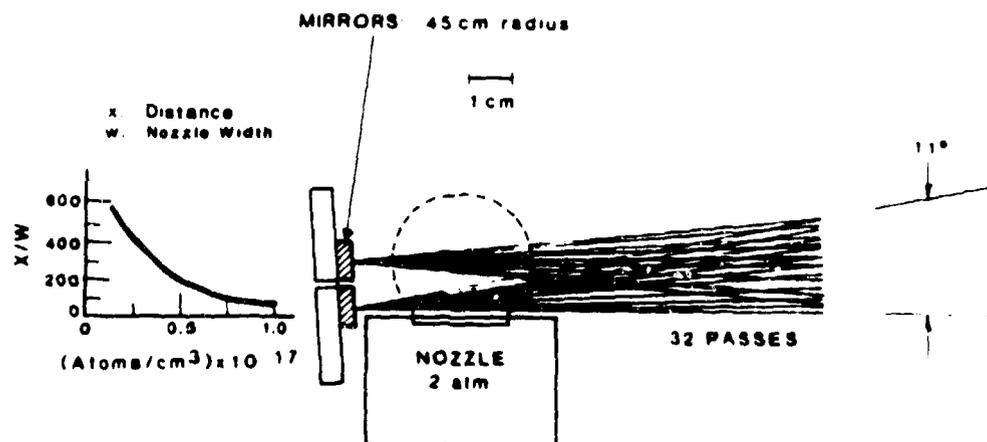


Figure 2. Scale drawing showing multipassing of diode laser radiation through nozzle expansion.

omnic heating, the diode laser requires 10-15% of the scan time to return to the original lasing frequency at the end of each voltage ramp. It is during this time that the nozzle opens and reaches a steady state flow. The nozzle is kept open for a total of 7 milliseconds.

Although signal to noise can be quite high on a single scan ( $> 30$ ), it is often necessary to average many scans to observe weak spectral features. To prevent drifting of the diode laser scan region during averaging, the scan region is stabilized using a boxcar integrator and voltage summing device. This is accomplished by sampling the etalon signal with a boxcar integrator at a specific time in the scan. If at this time the etalon signal is not at a zero crossing, the output voltage of the boxcar will be non-zero. This output voltage is summed with the ramp voltage scanning the diode laser, shifting the spectral region scanned by the laser so that a zero crossing of the etalon trace occurs at the sampling time of the boxcar. Thus the boxcar produces an error signal which prevents drifting of the diode laser. The linewidths<sup>(1)</sup> of the CO monomer features recorded in a single 5 millisecond scan of the diode laser are  $0.0023 \text{ cm}^{-1}$ . When 2000 such scans are averaged, the linewidths increase to  $0.0028 \text{ cm}^{-1}$ . Thus, once locked to a zero crossing, the spectral region scanned by the laser drifts less than  $0.0005 \text{ cm}^{-1}$ .

The slit nozzle is capable of producing linewidths<sup>(4)</sup> less than  $0.0015 \text{ cm}^{-1}$ , therefore, the resolution in our experiments is currently limited by the diode laser. Although the diode laser beam does not cross the expansion perpendicularly, the multiple crossing angles contribute less than  $0.0005 \text{ cm}^{-1}$  to the total linewidth.

(1.) For this measurement, the vacuum chamber was pumped by two diffusion pumps (5000 liter/sec) to a pressure of  $10^{-4}$  torr to minimize absorption by background CO.

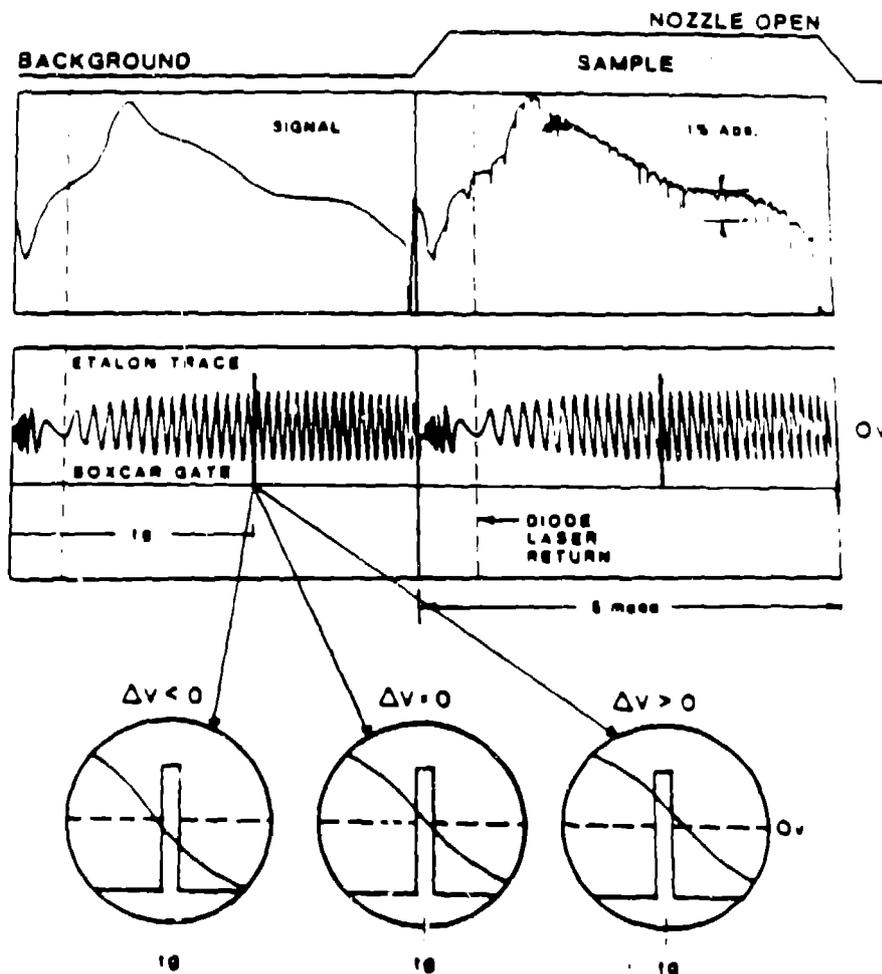


Figure 3. Traces of transient recorder output. Top panel shows signal from radiation passing through vacuum chamber. First half of trace corresponds to scan taken before nozzle opens. Note that cluster absorbances are clearly visible on second scan recorded after the nozzle opens. Middle panel shows etalon signal ( $FSR=0.03 \text{ cm}^{-1}$ ). Bottom figures show enlarged view of etalon trace near boxcar sampling gate.

## RESULTS AND DISCUSSION

We observe over 300 absorption lines near the CO monomer band center at  $2143.27116 \text{ cm}^{-1}$  (7) which can be attributed to the ArCO complex. The spectral region between  $2130$  to  $2160 \text{ cm}^{-1}$  also contains many lines for pure CO clusters. Although the number of pure CO clusters in our Ar/CO expansions can be reduced by reducing the proportion of CO in the Ar/CO gas mixtures, they cannot be completely eliminated. Since the scan region of the diode laser can be locked very accurately, it is possible to first take a spectrum with an Ar/CO gas mixture, repeat the scan using only CO, then subtract the two. Although the temperatures of the expansions may

not be exactly the same, the spectral features due to pure CO clusters reproduce quite well. The linewidths of features attributed to the ArCO complex are all less than  $0.003 \text{ cm}^{-1}$ . Within the limits of our resolution, we find no evidence of line broadening due to vibrational predissociation of the ArCO complex.

The ArCO spectrum is similar to one produced by a *b*-type transition in a nearly prolate, symmetric-top molecule. No lines are observed that can be attributed to an *a*-type transition. The most prominent features in the spectrum, two sub-bands corresponding to the  $K=0 \rightarrow 1$  and  $K=1 \rightarrow 0$  transition regions ( $K=K_{-1}$ ), are found in the null gap of the CO monomer. The Q-branch of the  $K=0 \rightarrow 1$  region is shown in Fig. 4. A preliminary, least-squares analysis of these P, Q, and R sub-branches yields rotational constants for the  $K=0,1$  sub-levels. They are presented in Table 1. Since the bending motion of the CO subunit and rotation of the CO about the Ar-CO bond axis may be strongly coupled, the energy levels can be represented by the expression (8)

$$E_K = v_K + \bar{B}_K J(J+1) - D_K [J(J+1)]^2 + \delta_{K,1} [1/4(B_1 - C_1)J(J+1) - \delta J^2(J+1)^2]$$

where  $\bar{B}_K = (B+C)/2$  and the term following the Kronecker delta accounts for the asymmetry splitting in the  $K=1$  states. The spectrum contains a progression of such *K*-type sub-bands on each side of the CO monomer line center. The P, Q and R branches of the  $K=1 \rightarrow 2$  and  $K=2 \rightarrow 1$  transition

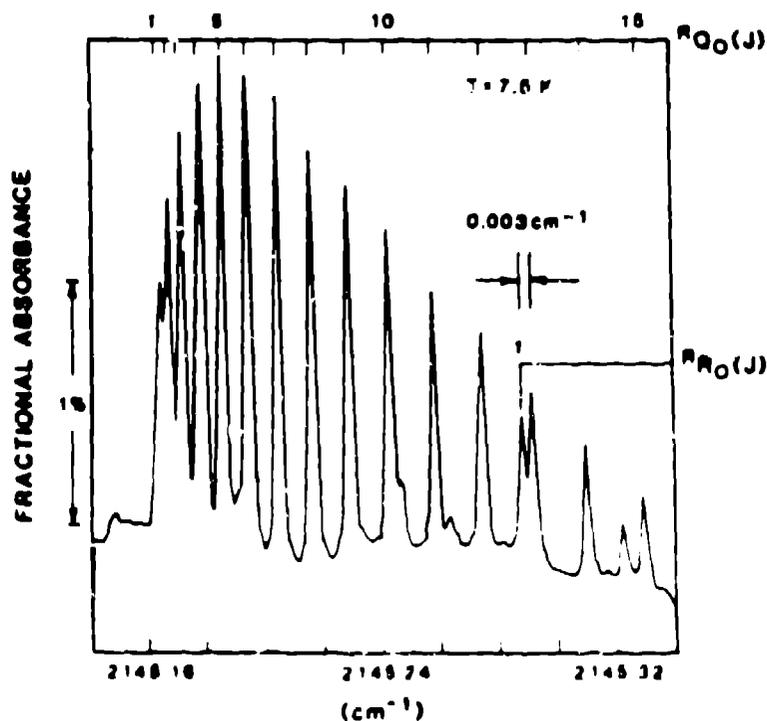


Figure 4. ArCO  $R_{00}$  band located in the CO monomer null gap. Spectrum is an average of 300 5 millisecond scans.

Table 1. Effective Parameters for ArCO

	v=0		v=1	
	K=0	K=1	K=0	K=1
B (MHz)	2072.2(7) <sup>a</sup>	2064.6(1.3)	2074.1(1.3)	2062.5(7)
B-C (MHz)		128.5 (6)		130.5(6)
D/10 <sup>-2</sup> (MHz)	6.3(3)	7.3(3)	7.0(3)	6.4(3)
δ/10 <sup>-3</sup> (MHz)		-3.2(4)		-1.9(4)
A-B (MHz)	71643(12)		70973(12)	
Δv (cm-1)	2142.8322(8)			
Δ <sub>K</sub> (MHz)	1287(3)			

<sup>a</sup>Numbers in parentheses denote one standard deviation and apply to last digits of constants.

regions are all split by the asymmetry of the complex. Assuming that the origins,  $v_K^0$ , of the various K sub-levels can be expressed as

$$v_K^0 = v + (A-B)K^2 + \Delta_K K^4,$$

we can solve for  $\Delta v = v' - v''$ ,  $(A-B)'$ ,  $(A-B)''$  and  $\Delta_K = \Delta_K' - \Delta_K''$  from the K=2→1, K=1→0, K=0→1 and K=1→2 sub-band origins, where the primes and double primes refer to the excited and ground states respectively. Values for these constants are also given in Table 1.

Calculations of potential surfaces (9) for the ArCO complex suggest that the CO subunit may not be strongly oriented in the complex. The calculations predict that only small-to-intermediate-sized barriers restrict the rotation of the CO in the plane of the complex. Although there have been no published studies of the spectra of ArCO, there have been several experimental and theoretical studies of the very similar ArN<sub>2</sub> complex (10,11). This complex possesses both localized bending states as well as nearly free-rotor states of the N<sub>2</sub> sub-unit. For low K states, the energy level spacings resemble those of a slightly asymmetric top, while for very high K states, the energy level spacings are closer to those of a free rotor. Similar behavior is observed in our data. The energy level spacings for transitions involving K>1 levels bear a decreasing resemblance to those of a slightly asymmetric top. Preliminary analysis indicates that for the higher K levels, a

Hamiltonian for a semi-rigid molecular structure will not reasonably reproduce our ArCO spectra. In conclusion, we feel that to obtain meaningful structural information, it will be necessary to analyze the data using a hindered rotor Hamiltonian.

#### ACKNOWLEDGMENTS

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