Abstract

Doppler-limited stimulated Raman spectra of the v_1 fundamental of CD_4 have been obtained both at room temperature in a static cell and at ~45 K in a molecular free-expansion jet. Spectral interferences due to overlapping hot-band transitions are significantly reduced in the molecular jet, thereby allowing an unambiguous assignment of the band origin at 2101.373 cm^{-1}. Analysis of the spectrum and determination of the relevant spectral constants leads to the conclusion that the v_1 band is strongly perturbed, probably by Coriolis interactions with the nearby $v_2 + v_4$ band.

Stimulated Raman Spectrum of the ν_1 Fundamental of CD$_4$ in a Molecular Jet

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Doppler-limited stimulated Raman spectra of the ν_1 fundamental of CD$_4$ have been obtained both at room temperature in a static cell and at $\sim$45 K in a molecular free-expansion jet. Spectral interferences due to overlapping hot-band transitions are significantly reduced in the molecular jet, thereby allowing an unambiguous assignment of the band origin at 2101.373 cm^{-1}. Analysis of the spectrum and determination of the relevant spectral constants leads to the conclusion that the ν_1 band is strongly perturbed, probably by Coriolis interactions with the nearby $\nu_2 + \nu_4$ band.

Introduction

The ν_1 band of CD$_4$ has been observed previously under low resolution[1,2] but since the rotational structure was unresolved, no assignment was possible. Recently, a high-resolution stimulated Raman spectrum was reported[3] by one of the authors (Owyoung) but no spectroscopic parameters were given because of the difficulties in assignment of the observed transitions.

These difficulties were caused, in part, by severe perturbations of the spectrum, especially for the higher J ($\geq$ 7) lines. The room temperature CD$_4$ ν_1 spectrum, which is spread out to a much larger extent than the ν_1 bands of the nondeuterated methanes studied previously,[4,5] is further complicated by the appearance of a number of unassigned weaker transitions. In particular these extra lines make it very difficult to unambiguously assign the Q(0) transition and the exact band origin.

In this paper we demonstrate how the use of a free-expansion jet has enabled us to obtain a spectrum of CD$_4$ at very low ($\sim$45 K) temperature which immediately clears up all ambiguity in the assignment of the Q(0) transition. In the low-temperature molecular jet spectrum, all hot-band transitions, and transitions from high-J rotational states, are frozen out. All that remains is a greatly simplified spectrum, involving only transitions from low-J levels of the vibrational ground state, from which the Q(0) transition is clearly identifiable.

Experimental Apparatus

The apparatus used for these experiments is essentially identical with that described previously.[6,7] The beams from a single-mode CW, Ar$^+$ ion probe laser and a tunable pulsed pump laser are overlapped in a focus in the gas sample. We then measure the transient signal induced on the probe by the pulsed pump.

The pump laser source is a single-mode CW dye oscillator (Coherent Model 599-021) which is pulse amplified to $\sim$1 MW by three dye amplifiers. These amplifiers are excited, in turn, by the 532-nm second harmonic of a specially modified, long-cavity ND:YAG laser (Quanta-Ray DCR-1). Although the line width of the CW oscillator is of the order 1 MHz, the pulse amplification process broadens the spectral width to at least the Fourier transform of the pulse width. For this particular oscillator/amplifier configuration we have measured a fwhm line width of 65 ± 5 MHz for the $\sim$12-ns fwhm pulsed output.

Since we are probing at a shorter wavelength (514.5 nm) than the $\sim$577-nm pump laser, this is an inverse Raman[8] experiment, i.e., the transient signal induced by the pump is an absorption at the probe laser frequency. By tuning the frequency difference (Stokes shift) between the two lasers we are able to map out the spectral profile of the Raman-induced absorption, and thereby display the Raman spectrum.

Precise values for the observed Stokes shifts were determined by using the same method described previously.[6,7] Because of the wide frequency range ($\sim$8 cm^{-1}) covered by the CD$_4$ spectrum, systematic calibration was essential in order to piece together the results of the several individual 1-cm^{-1} scans (limited by the scan range of the tunable oscillator) necessary to cover the full spectrum. Absolute wavenumber calibration is obtained from a CW wavemeter which simultaneously measures the frequencies of the Ar$^+$ ion probe laser and the CW dye oscillator, thereby providing us with a direct readout of their frequency difference (Stokes shift) with a precision of 0.001 cm^{-1}. For each spectral scan taken, frequency markers are recorded by monitoring the transmission of a portion of the CW dye oscillator output through a temperature-stabilized 150-MHz confocal etalon. Relative peak positions are obtained by measuring their positions with respect to the 150-MHz etalon frequency markers, using a linear interpolation between fringes.

A major difficulty in analyzing data obtained earlier under static cell conditions was the occurrence of numerous transitions arising from hot bands. Although none of these transitions were strong enough to confuse the assignment of the very strong ν_1 transitions near the peak of rotational distribution, they did lead to some ambiguity as to the assignment of the $J = 0$ band origin peak of the spectrum. We have been able to remove this difficulty by applying

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(6) P. Esherick, A. Owyoung, and C. W. Patterson, *J. Mol. Spectrosc.*, **86**, 250 (1981).

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(8) W. J. Jones and B. P. Stoicheff, *Phys. Rev. Lett.*, **17**, 1239 (1966).

the technique of pulsed molecular free expansions[9-11] to obtain an inverse Raman spectrum at a much lower temperature ($\sim$45 K) than is obtainable in a static cell. At these low temperatures all of the extraneous structure due to high-J transitions and vibrational hot bands is eliminated. One is then left with a very clean spectrum of the low-J transitions of the fundamental band.

A CW expansion version of the apparatus used here has been previously described in ref 11. For the work described here the apparatus was updated by the installation of a pulsed valve[9] which, by reducing the open-time duty cycle, allows for much higher molecular density operation while maintaining reasonable pumping speed requirements.

Basically, the molecular jet apparatus can be described as consisting of a nozzle, with a pulsed valve controlling the gas flow, a 25-cm diameter by 85-cm long chamber, and a modest (22 L/s) mechanical pumping system. The pulsed valve and nozzle were mounted on an externally adjustable three-way translation stage which greatly facilitated the alignment of the jet with the laser beams. By adjustment of the orifice size, backing pressure of the gas to be expanded, and the axial location of the probed region, both the density and the temperature of the "sample" could be controlled.

The pulsed valve, designed by Cross and Valentini,[12] is a modification of a commercial piezoelectric leak valve (Veeco, PV-10). The key elements are the addition of an interchangeable nozzle insert (with the desired orifice) which screws into the modified valve face plate, and a plunger which is cemented to the piezoelectric crystal. A Viton gasket at the tip of the plunger seals the orifice until a voltage is applied to the crystal. The applied voltage causes the crystal to buckle backward, opening the valve and allowing gas to flow through the body of the valve and out through the orifice. Since the device is piezoelectrically operated, the easily generated 150–350-V driving pulse draws very little current (<1 mA). The need for electromagnetic shielding and water cooling is thereby eliminated (even at high repetition rates <100 Hz).

The valve in our laboratory is typically operated with 450-μs (fwhm) pulses, although no observable change in beam intensity occurs down to approximately 250-μs widths. The day-to-day reproducibility and reliability of the valve has been exceptional, making it particularly useful to our molecular-jet/SRS studies.

Results

In Figure 1 we show the stimulated Raman spectrum of the ν_1 fundamental of CD₄ in the range 2101–2108 cm⁻¹. The ν_1 spectrum continues on to higher energy with additional complexity; however, we show here only the portion of the spectrum that we have assigned. The relative positions of the stronger lines are measured with a precision of $\pm 2 \times 10^{-3}$ cm⁻¹. The Doppler width (fwhm) at room temperature is 5.8×10^{-3} cm⁻¹.

The spectrum was analyzed by using the expression for the transition frequencies

$$\alpha = \alpha + (\beta - \beta^0)J(J+1) + (\gamma - \gamma^0)J^2(J+1)^2 +$$
$$(\pi - \pi^0)J^3(J+1)^3 + [(\epsilon - \epsilon^0) + (\rho - \rho^0)J(J+1)] \times$$
$$[(2J-3)\cdots(2J+5)]^{1/2}(-1)^J F^{(4JJ)}_{A_1pp} +$$
$$(\xi - \xi^0)[(2J-5)(2J-4)\cdots(2J+7)]^{1/2}(-1)^J F^{(6JJ)}_{A_1pp} \quad (1)$$

(9) W. R. Gentry and C. F. Giese, *Rev. Sci. Instrum.*, **49**, 595 (1978).
(10) M. D. Duncan and R. L. Byer, *IEEE J. Quantum Electron.*, **15**, 63 (1979).
(11) J. J. Valentini, P. Esherick, and A. Owyoung, *Chem. Phys. Lett.*, **75**, 590 (1980).
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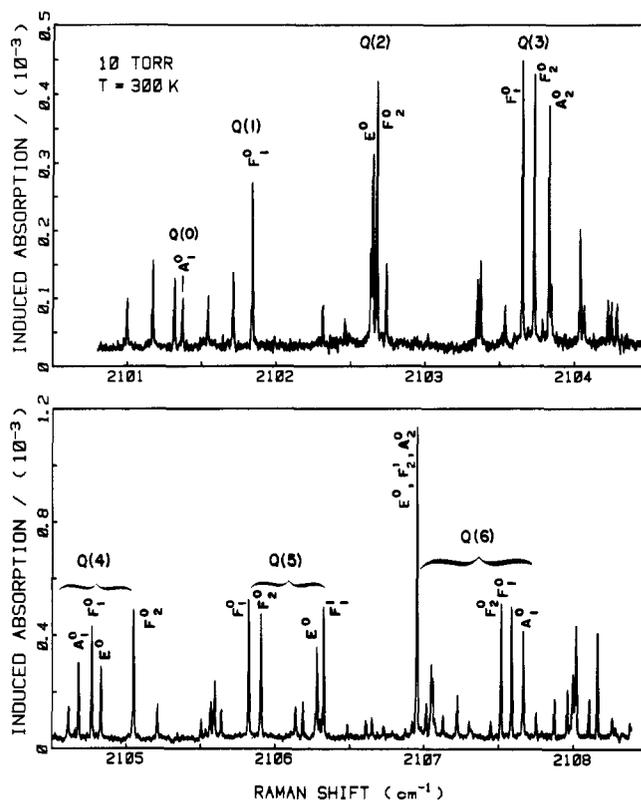
Figure 1. Inverse Raman spectrum of the ν_1 band of CD₄ taken in a room temperature cell at 10 torr pressure. Only the lower J, assigned portion of the spectrum is shown.

given by Moret-Bailly[13] which is accurate to fourth order in the Hamiltonian. The index p specifies C^n, where $C = A_1, A_2, E, F_1, F_2$ is the tetrahedral symmetry species and $n = 0, 1, 2, \cdots$ labels multiply occurring species C for a given J.

In our fit to the observed transition frequencies we have corrected for the effects of the off-diagonal $F^{(6JJ)}$ coefficients which are not included in Eq 1, as described in previous papers.[4,5]

The ground-state scalar constants of CD₄ have been determined by Brodersen et al.[2] from the ν_3 Raman spectrum. They find

$$\beta^0 = B_0 = 2.63264 \pm 0.00013 \text{ cm}^{-1}$$

$$\gamma^0 = -D_0 = (-2.74 \pm 0.15) \times 10^{-5} \text{ cm}^{-1}$$

$$\pi^0 \approx 0.0 \text{ cm}^{-1}$$

The ground-state tensor constant ϵ^0 has been determined previously by Poussigue et al.[14] to be $\epsilon^0 = -3.57 \times 10^{-7}$ cm⁻¹ from an infrared study of the ν_3 band.

Using eq 1, we arrived at the line assignments shown in Figure 1 except for the Q(0) A_1 assignment of the doublet near 2101.4 cm⁻¹. This doublet could only be unambiguously assigned by means of the jet-cooled spectrum shown in Figure 2 which eliminated the hot-band transitions. The rotational temperature $T = 43$ K was attributed to this spectrum by fitting the line intensities to the expression

$$I_R = g_c \frac{(2J+1)}{3} \exp[-\beta^0 J(J+1)hc/kT] \quad (2)$$

where g_C is the statistical weight factor given by $g_C = 15$, 15, 12, 18, 18 for $C = A_1, A_2, A_2, E, F_1, F_2$, respectively.

(13) J. Moret-Bailly, *Cah. Phys.*, **15**, 237 (1961); *J. Mol. Spectrosc.*, **15**, 344 (1965).
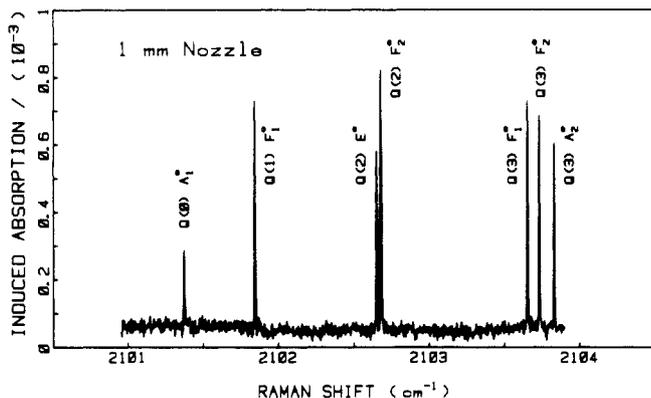(14) G. Poussigue, G. Tarrago, M. Dang-Nhu, and A. Valentin, *J. Mol. Spectrosc.*, **49**, 183 (1974).

Figure 2. Raman spectrum observed in pulsed free-expansion jet 2.8 mm downstream from a 1-mm diameter nozzle. Backing pressure was 50 psia and $T_{rot} \simeq 45$ K.

Using the ground-state constants above, and an analysis which includes the effects of off-diagonal $F^{(6JJ)}$ coefficients, we found the following $\nu_1 v = 1$ constants (in cm^{-1}) to give the best fit to the spectral data up through $J = 6$ transitions:

$$\alpha = 2101.392 \pm 0.012 \qquad \epsilon = (-1.072 \pm 0.051) \times 10^{-4}$$

$$\beta = 2.8610 \pm 0.0026 \qquad \rho = (6.49 \pm 0.80) \times 10^{-8}$$

$$\gamma = (-3.29 \pm 0.14) \times 10^{-3} \qquad \xi = (1.73 \pm 0.13) \times 10^{-6}$$

$$\pi = (2.76 \pm 0.1) \times 10^{-5} \tag{3}$$

The above constants and their standard deviations were obtained from a least-squares fit of the 21 lines shown in Figure 2. The overall standard deviation of the fit was 0.016 cm^{-1}.

The Table I we compare the experimentally observed transition frequencies with those values calculated from the ground- and excited-state constants above. The relative intensities I_R given in Table I are determined from eq 2.

Discussion

The large spectral extent of this band is clearly reflected in the magnitude of $\Delta\beta$ obtained from this analysis. In contrast with $^{12}CH_4$ and $^{13}CH_4$, which have very narrow ν_1 bands with $\Delta\beta$ values of 0.01 and 0.002 cm^{-1}, respectively,[4,5] the ν_1 band of CD₄ has a $\Delta\beta = 0.223$ cm^{-1}. Note that all three molecules have "abnormal" positive values for $\Delta\beta$, with the result that their ν_1 spectra all unfold toward higher energy with increasing J.

The unusually large and positive value for $\Delta\beta$, and the correspondingly large values for γ, π, and ϵ, leads one to believe that the ν_1 band of CD₄ is being perturbed strongly by another band. This conclusion is further supported by

TABLE I: Observed and Calculated Line Positions in the ν_1 Band of CD₄ (cm^{-1})

obsd	assignment	10^3(obsd $-$ calcd)	$I_R{}^a$
2101.373	Q(0) A$_1^0$	-20	5.0
2101.841	Q(1) F$_1^0$	5	17.6
2102.650	Q(2) E^0	9	18.6
2102.677	Q(2) F$_2^0$	19	27.8
2103.651	Q(3) F$_1^0$	-13	36.2
2103.730	Q(3) F$_2^0$	4	36.2
2103.830	Q(3) A$_2^0$	22	30.1
2104.679	Q(4) A$_1^0$	-21	35.1
2104.768	Q(4) F$_1^0$	-15	42.1
2104.830	Q(4) E^0	-13	28.1
2105.048	Q(4) F$_2^0$	-5	42.1
2105.823	Q(5) F$_1^0$	25	45.4
2105.905	Q(5) F$_2^0$	18	45.4
2106.281	Q(5) E^0	1	30.3
2106.327	Q(5) F$_1^1$	-8	45.4
2106.951	Q(6) E^0	-5	30.8
2106.951	Q(6) F$_2^1$	-4	46.2
2106.951	Q(6) A$_2^0$	-1	38.5
2107.515	Q(6) F$_2^0$	3	46.2
2107.586	Q(6) F$_1^0$	5	46.2
2107.664	Q(6) A$_1^0$	5	38.5

^{a} I_R is the relative intensity, calculated for $T = 300$ K.

the difficulty in assigning the spectral lines for $J > 6$. In earlier work[4,5] on $^{12}CH_4$ a Coriolis type interaction of ν_1 with the F$_1$ symmetry component of the nearby $\nu_2 + \nu_2$ band was suggested to account for the positive values of $\Delta\beta$ observed for these molecules. We note that this same interaction will occur in CD₄. In this case, however, the $\nu_2 + \nu_4$ band[1] (at about 2090 cm^{-1}) is approximately 8 times closer to resonance with ν_1 than in the nondeuterated methanes. Primarily because of this closeness of ν_1 to $\nu_2 + \nu_4$ we anticipate that this interaction will be stronger than an H$_{13}$-type interaction[15,16] with the ν_3 band at 2260 cm^{-1}. A complete understanding of the cause of the strong perturbations of this band, however, will require further study, including analysis of the higher-J transitions.

Registry No. CD₄, 558-20-3.

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