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High-resolution Laser Spectroscopy of the ν_6 Fundamental Band of Jet-Cooled C_2F_6

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The ν_6 parallel band of C_2F_6 has been measured at high resolution by using diode laser absorption spectroscopy in a free jet expansion. A comparison of the rotational intensity distribution with simulated band profiles indicated a rotational temperature of between 2 and 3 K in the jet. In addition to the fundamental band, weak Q-branches of other bands were also found, both to the red and to the blue side of the ν_6 fundamental Q-branch. The band origin of the ν_6 mode was measured as 713.671 05(10) cm^{-1}. The B rotational constants were determined in different ways as described in the text. A preferred value of $B_0 = 0.061\,580\,6(22)$ cm^{-1} was selected for simulation purposes. This value is independent of the electron diffraction structure.

1. Introduction

Hexafluoroethane is of interest in fields as diverse as medicine, materials science, and, more recently, atmospheric chemistry. Although current concentrations of C_2F_6 in the troposphere are quite low, they are believed to be growing steadily.[1] The molecule may become an important greenhouse gas for two reasons. First, its lifetime in the atmosphere is >2000 years,[2] and, second, it has two intense fundamentals at 1116 cm^{-1} (ν_5) and 1250 cm^{-1} (ν_7) coinciding with an atmospheric window. The perfluorocarbons have received less spectroscopic attention than the chlorofluorocarbons (CFC's) despite their potential importance. The vibrational mode assignment of C_2F_6 was made some time ago based on IR and Raman spectra. For convenience the vibrational modes of C_2F_6 are collected in Table 1. One of the modes, ν_4, is formally both IR and Raman inactive but becomes active in the IR due to Coriolis effects.[3,4]

Structural data for C_2F_6 were obtained in an electron diffraction study by Gallaher *et al.*[5] The diffraction data are consistent with a staggered (D_{3d}) conformation with a barrier to internal rotation of 1290 cm^{-1} (3.7 kcal mol^{-1}). The barrier to internal rotation deduced from the observed torsional frequency[6] is 1367 cm^{-1} (3.9 kcal mol^{-1}). Recently Parra and Zeng[7] carried out a density functional theory (DFT) and molecular orbital (MP2) study of C_2F_6 and of some partially fluorinated ethanes. Both DFT and MP2 results gave a barrier height of 3.53 kcal mol^{-1}. Bond angles and bond lengths were in satisfactory agreement with the electron diffraction results and the staggered conformation was shown to have the minimum energy.

Because the molecule does not possess a permanent dipole moment, it has no microwave spectrum. Hence the only possibility of determining its structure from high-resolution spectroscopy is to obtain a rotationally resolved infrared or Raman spectrum. Even at high resolution, however, the room temperature IR spectrum is known to be highly congested due to hot bands, etc. In earlier work we obtained rotationally resolved spectra of both the ν_5 and ν_7 bands using diode laser spectroscopy of C_2F_6 in a jet.[8] These are intense CF stretching modes of the molecule. In the present study we describe the jet spectrum of the much weaker ν_6 band, which is a CF_3 deformation mode.[9] The results are intended to lay the foundation for assigning the more congested spectra in the ν_6 region, already recorded at higher temperatures.[10] Last, a comparison is made of the values of the B rotational constant of C_2F_6 derived by various methods.

TABLE 1: Wavenumbers of the Vibrational Modes of C_2F_6 from Infrared and Raman Measurements

mode	gas phase	liquid phase	activity
$\nu_1\,(A_{1g})$	1417[a]	1417[b]	R
$\nu_2\,(A_{1g})$	807.4[a]	807[b]	R
$\nu_3\,(A_{1g})$	348[a]	351[b]	R
$\nu_4\,(A_{1u})$	65.3[c]	*c*	inactive
$\nu_5\,(A_{2u})$	1116.9[d]	1111.5[b]	IR
$\nu_6\,(A_{2u})$	714.0[d]	713.7[b]	IR
$\nu_7\,(E_u)$	1250.5[d]	1244.0[b]	IR
$\nu_8\,(E_u)$	522.5[d]	522.7[b]	IR
$\nu_9\,(E_u)$	216.0[e]	*e*	IR
$\nu_{10}\,(E_g)$	1237.0[a]	1223[b]	R
$\nu_{11}\,(E_g)$	620[a]	620[b]	R
$\nu_{12}\,(E_g)$	380[a]	381[b]	R

[a] Reference 17. [b] Reference 18. [c] Reference 5. [d] Reference 16. [e] Reference 19.

2. Experimental Section

Details of the mid infrared laser jet spectrometer have been given elsewhere[11] and only the features relevant to the present study are mentioned here. For the coldest rotational spectra, mixtures of 3% or 6% of C_2F_6 in Ar were prepared and left overnight in a reservoir prior to expansion. Spectra showing higher rotational temperatures were recorded from mixtures of 15% C_2F_6 in N_2 expanded from 3 bar pressure. C_2F_6 (>99% pure) was obtained from Fluorochem and used without further purification. The absorption signals in the jet were recorded by using a simple lock-in amplifier and boxcar arrangement (time constant 1 or 3 s). Line positions were measured against CO_2 reference lines,[12] using an evacuated confocal *etalon* for interpolation (free spectral range ~0.009 84 cm^{-1}). The estimated uncertainty in the measurement of line positions is $\sim 3 \times 10^{-4}$ cm^{-1}.

3. Results and Discussion

The ν_6 mode of C_2F_6 is of A_{2u} symmetry and is depicted in Figure 1. The nuclear displacements, D_{xyz}, shown in Figure 1

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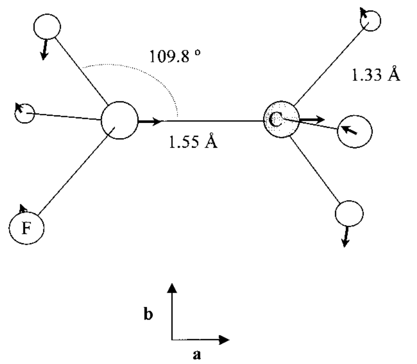

Figure 1. Calculated nuclear displacements in the ν_6 fundamental of C_2F_6 magnified 20 times for clarity. Bond angle and bond distances taken from ref 5.

have been calculated from

$$D_{xyz} = (\mathbf{B}^{+})^{-1}\,\mathbf{L} \tag{1}$$

where **L** (in symmetry coordinates) is the matrix of the eigenvectors of $\mathbf{H} = \mathbf{FG}$. The A_{2u} force constant matrix **F** has been calculated by Pace[13] and Carney et al.,[14] while the **G**-matrix is given by $\mathbf{G} = \mathbf{BM}^{-1}\mathbf{B}^{+}$. The symmetry coordinates in the A_{2u} symmetry species of C_2F_6 were chosen in the manner of Williams *et al.*[9] Fluorine atoms 1, 2, and 3 are attached to one carbon atom and 4, 5, and 6 to the other. Fluorine atom 1 points in the positive *x* direction and atom 4 in the negative *x* direction. The atoms 2 and 5 are on the same side of the *xz* plane. We then have[9]

$$S_{\nu 5} = (1/6^{1/2})(r_1 + r_2 + r_3 - r_4 - r_5 - r_6)$$

$$S_{\nu 6} = (d/12^{1/2})\,(\beta_1 + \beta_2 + \beta_3 - \beta_4 - \beta_5 - \beta_6 - (\alpha_{12} + \alpha_{13} + \alpha_{23} - \alpha_{45} - \alpha_{46} - \alpha_{56}))$$

In the symmetry coordinates given above, r_i is the change in the length of the C−F$_i$ bond, β_1 is the change in the C−C−F$_i$ angle, and α_{ij} is the change in the F$_i$−C−F$_j$ angle. The equilibrium C−F distance used in our calculation (d) is taken to be 1.326(2) Å, the C−C distance 1.545(6) Å, and the C−C−F$_j$ angle 109.75(0.12)°.[5]

The $\mathbf{M}^{-1}$ matrix is a diagonal matrix of the reciprocal of the masses of all the carbon and fluorine atoms. The elements of the B-matrix were calculated from the geometrical parameters of the molecule after defining 18 internal coordinates. Finally, since the transpose of the **B** matrix, $\mathbf{B}^{+}$, is not a squared matrix its inverse was obtained by

$$(\mathbf{B}^{+})^{-1} = \mathbf{M}^{-1}\,\mathbf{B}^{+}\mathbf{G}^{-1} \tag{2}$$

The infrared spectrum of the ν_6 mode of C_2F_6 is that of a parallel band of a prolate symmetric top with allowed transitions given by $\Delta J = 0, \pm 1$ and $\Delta K = 0$. Neglecting the effects of centrifugal distortion the Q-branch transitions are given by[15]

$$\nu^{Q}_{J,K} = \nu_o + [(A' - B') - (A'' - B'')]K^2 + (B' - B'')J(J + 1) \tag{3}$$

and the P and R branches by,

$$\nu^{P,R}_{m,K} = \nu_o + (B' + B'')m + (B' - B'')m^2 + [(A' - B') - (A'' - B'')]K^2 \tag{4}$$

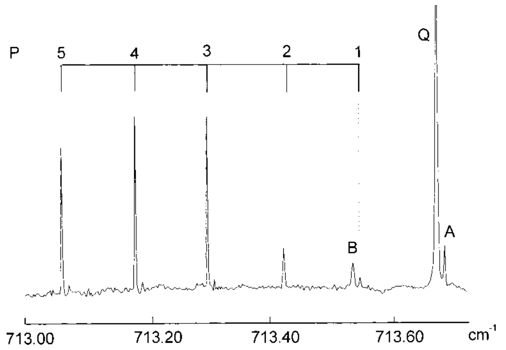

Figure 2. Q-branch and lower-*J* P-branch lines of the ν_6 fundamental of C_2F_6 recorded using 6% C_2F_6 in 4 bar of Ar.

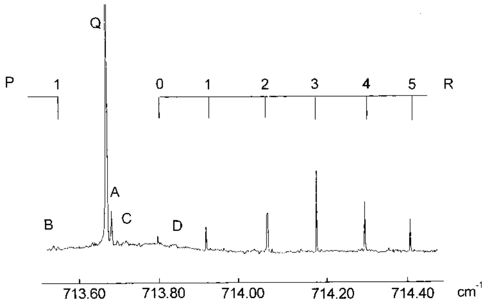

Figure 3. Q-branch and lower-*J* R-branch lines of the ν_6 fundamental of C_2F_6 recorded using 6% C_2F_6 in 3 bar of Ar. Four Q-branches of minor intensity (namely A, B, C, and D) have also been observed.

TABLE 2: Line Positions (cm^{-1}) of the ν_6 Fundamental Band of C_2F_6

line	observed ((o-c) × 10^4)	line	observed ((o-c) × 10^4)
P−branch		R−branch	
P(25)	710.5949(−1)	R(0)	713.7949(7)
P(24)	710.7183(4)	R(1)	713.9180(6)
P(23)	710.8405(−4)	R(2)	714.0410(5)
P(22)	710.9638(−4)	R(3)	714.1640(3)
P(21)	711.0862(−6)	R(4)	714.2871(2)
P(20)	711.2099(2)	R(5)	714.4102(1)
P(19)	711.3318(−9)	R(6)	714.5331(−2)
P(18)	711.4551(−6)	R(7)	714.6563(−3)
P(17)	711.5793(6)	R(8)	714.7790(−8)
P(16)	711.7008(−9)	R(9)	714.9031(0)
P(15)	711.8242(−5)	R(10)	715.0262(−1)
P(14)	711.9479(1)	R(11)	715.1495(−1)
P(13)	712.0701(−7)	R(12)	715.2730(2)
P(12)	712.1941(3)	R(13)	715.3954(−7)
P(11)	712.3171(3)	R(14)	715.5203(9)
P(10)	712.4393(−6)	R(15)	715.6424(−3)
P(9)	712.5624(−6)	R(16)	715.7664(4)
P(8)	712.6864(3)	R(17)	715.8894(1)
P(7)	712.8089(−2)	R(18)	716.0124(−2)
P(6)	712.9321(−1)	R(19)	716.1365(4)
P(5)	713.0551(−2)	R(20)	716.2592(−1)
P(4)	713.1784(0)	R(21)	716.3832(5)
P(3)	713.3013(−3)	R(22)	716.5063(2)
P(2)	713.4259(11)	R(23)	716.6298(3)
P(1)	713.5489(10)	R(24)	716.7525(−3)
		R(25)	716.8761(−1)
		R(26)	716.9996(0)
Q-branch		R(27)	717.1231(1)
Q(0)	713.6670	R(28)	717.2474(9)

where $m = J + 1$ for R-branch components and $m = -J$ for P-branch lines. The *K* structure of the P- and R-branch lines was not resolved in the jet spectra and so each P- or R-branch component appeared as a narrow line-like feature as shown in Figures 2 and 3. The effect of nuclear spin statistics is rather modest and for $K \neq 0$ the weight of $K = 3p$ lines is 24 and $K \neq 3p$ is 20, where p is an integer. The assignment of the P- and R-branch lines was straightforward and in total 54 lines were used for fitting, Table 2. In the coldest rotational spectra the

TABLE 3: Parameters of C_2F_6 (in cm^{-1}) Obtained by Different Methods

	B_0	B_v	ν_0	rms
room temp			714.0[e]	
diode laser[a]	0.061 575 9 (fixed)	$B_6 = 0.061\,580\,6(3)$	713.671 01(10)	49×10^{-5}
	0.061 580 6(22)	$B_6 = 0.061\,585\,1(21)$	713.671 05(10)	47×10^{-5}
				54 lines fitted
	0.0615759[b]	$B_7 = 0.061\,508\,5(3)$[b]		
combination difference[a]	0.0615953(156)	$B_6 = 0.061\,580\,9(137)$		
band (A)[a]	0.0615806 (Fixed)	$B = 0.061\,602\,1(117)$	713.683 83(38)	49×10^{-5}
				6 lines fitted
		$\bar{B}$		
electron diffraction[c]		$B = 0.061\,768$		
		(av ^{12}C-^{13}C)		
ab initio[d]				
MP2		$B = 0.061\,842$	722	
B3LYP		$B = 0.060\,889$	705	

[a] This work. [b] Reference 8. [c] Reference 5. [d] Reference 7. [e] Reference 16.

slightly red shaded Q- branch was remarkably narrow (full width at half-maximum height of ~0.01 cm^{-1}), suggesting a small change in $A(\Delta A)$. This was estimated to be $\sim -2.5 \times 10^{-4}$ cm^{-1}.

The B rotational constants determined in various ways were examined for differences. In the first method used B_0 was fixed at the value used to analyze the ν_5 and ν_7 fundamentals,[8] and B_6 and the band origin floated. Essentially this value of B_0 comes from the electron diffraction structure.[5] In the second method B_0 and B_6 and also the band origin were floated. Last, the method of combination differences was used. The results are given in Table 3.

From comparisons with simulated spectra the rotational temperatures of the coldest spectra, such as those in Figures 2 and 3, were deduced to be about 3 K. Four additional Q-branches were observed near the origin of the ν_6 fundamental and are labeled A, B, C, and D in Figures 2 and 3. It is well-known that the vibrational temperature in the jet is considerably higher than the rotational temperature. Hence at least one of these features must involve hot bands by comparison with jet spectra of other molecules possessing low-frequency vibrations. A few P-branch lines associated with the band A were also recorded and the fitted parameters from the P-branch and Q-branch of band A are given in Table 3.

The ν_6 band origin determined here, 713.671 05(10)cm^{-1}, is red shifted by 0.329 cm^{-1} from its reported room-temperature value.[16] The DFT and MP2 calculated harmonic values for the D_{3d} conformation are 705 and 722 cm^{-1}, respectively. Whichever procedure is used in the present study to determine B_v, the change in the B rotational constant for the ν_6 band is even smaller than for the other bands. The fitted value of ΔB_6 ($B_6 - B_0$) is 4.7×10^{-6} cm^{-1}, which compares with $\Delta B_5 = -1.3 \times 10^{-4}$ cm^{-1} and $\Delta B_7 = -6.6 \times 10^{-5}$ cm^{-1}.[8] A small change is expected qualitatively from considering the nature of the vibration in Figure 1. The fitted values of B_0 (Table 3) are substantially larger than the electron diffraction value, which is understandable because the electron diffraction bond lengths are averages over several vibrational states corresponding to larger overall moments of inertia. The ab initio values of B bracket the experimental jet results (Table 3). The preferred value of B_0 is $B_0 = 0.061\,580\,6(22)$ cm^{-1}, which is independent of the electron diffraction results.

The positions of the weaker Q-branches and the ν_6 Q-branch merits comment. The most likely hot band structure from the viewpoint of vibrational level populations is one involving the ν_4 torsional mode, namely $(\nu_6 + \nu_4) - \nu_4$. In the spectrum of the ν_5 fundamental in the jet, this hot band, $(\nu_5 + \nu_4) - \nu_4$, has been assigned as a shoulder on the red side of the ν_5 Q-branch.[8] The absence of a similar feature near the ν_6 Q-branch may be due to differences in the ζ parameters coupling the torsional mode to ν_5 or ν_6. Eggers et al.[6] have shown that the calculated $\zeta^2{}_{4,i}$ is considerably larger for $\zeta^2_{4,6}$ than $\zeta^2_{4,5}$ regardless of the force field used. The position of the ν_6 fundamental may itself be influenced by a perturbation. We have examined possible perturbing states and a number of candidates exist. One of them is the difference band $(\nu_5 - \nu_3)$ at 768 cm^{-1}, which has the correct A_{2u} symmetry for a Fermi interaction and was observed by Nielsen *et al.*[16] in the low-resolution spectrum. A more detailed interpretation of the hot bands in the jet spectra and their relationship to the more congested higher temperature spectra will be described later.[10]

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References and Notes

(1) Roehl, C. M.; Boglu, D.; Bruehl, C.; Moortgat, G. K. *Geophys. Res. Lett.* **1995**, *22*, 815.

(2) Ravishankara, A. R.; Solomon, S.; Turnipseed, A. A.; Warren, R. F. *Science* **1993**, *259*, 194.

(3) Lord, R. C.; Nielsen, E. *J. Chem. Phys.* **1951**, *19*, 1.

(4) Weiss S.; Leroi, G. E.. *J. Chem. Phys.* **1968**, *48*, 962.

(5) Gallaher, K. L.; Yokozeki, A.; Bauer, S. H. *J. Phys. Chem.* **1974**, *78*, 2389.

(6) Eggers, D. F., Jr.; Lord, R. C.; Wickstrom, C. W. *J. Mol. Spectrosc.* **1976**, *59*, 63.

(7) Parra, R. D.; Zeng, X. C. *J. Phys. Chem.* A **1998**, *102*, 654.

(8) Hansford, G. M.; Davies, P. B. *J. Mol. Spectrosc.* **1996**, *180*, 345.

(9) Williams, D. G.; Person, W. B.; Crawford, B., Jr. *J. Chem. Phys.* **1955**, *23*, 179.

(10) Ward, K. M.; Duxbury, G.; Loroño, M.; Henze, W.; Davies, P. B.; Newnham, D. A. *J. Mol. Spectrosc.*, submitted.

(11) Davies, P. B.; Hansford, G. M.; Killian, T. C. *J. Mol. Spectrosc.* **1994**, *163*, 138.

(12) Guelachvili, G.; Rao, N. *Handbook of Infrared Standards*; Academic Press: New York, 1986.

(13) Pace, E. L *J. Chem. Phys.* **1948**, *16*, 74.

(14) Carney, R. A.; Piotrowski, E. A.; Meister, A. G.; Braun, J. H.; Cleveland, F. F. *J. Mol. Spectrosc.* **1961**, *7*, 209.

(15) Herzberg, G. *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra*; Van Nostrand Reinhold: New York, 1964.

(16) Nielsen, J. R.; Richards, C. M.; McMurry, H. L. *J. Chem. Phys.* **1948**, *16*, 67.

(17) Nielsen, J. R.; Gullikson, C. W. *J. Chem. Phys.* **1953**, *21*, 1416.

(18) Lewis, A.; Pace, E. L. *J. Chem. Phys.* **1973**, *58*, 3661.

(19) Mann, D. E.; Plyler, E. K. *J. Chem. Phys.* **1953**, *21*, 1116.