Abstract

We report the observation of the spectrum of the $3\nu_3$ Q branch in UF_6 at both low (1.4 cm^{-1}) and high (0.004 cm^{-1}) resolution. The most prominent feature of the spectrum is the five sub-bandheads between 1875.4 and 1875.6 cm^{-1}. The transition strength for $3\nu_3$ is $\Gamma_{0,3} = 3.8\times10^{-2}$ km $mole^{-1}$.

THE $3\nu_3$ OVERTONE BAND IN UF_6 *

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We report the observation of the spectrum of the $3\nu_3$ Q branch in UF_6 at both low (1.4 cm^{-1}) and high (0.004 cm^{-1}) resolution. The most prominent feature of the spectrum is the five-sub-bandheads between 1875.4 and 1875.6 cm^{-1}. The transition strength for $3\nu_3$ is $\Gamma_{0,3} = 3.8 \times 10^{-2}$ km $mole^{-1}$.

1. Introduction

This paper reports the recent recording of a high resolution spectrum of the Q branch of the $3\nu_3$ overtone band in UF_6. The spectrum was obtained using a tunable diode laser with a resolution of approximately 0.004 cm^{-1}, and the measurements were carried out in a 10 m White cell described previously [1]. Prior to the diode laser spectroscopy, the band contour of $3\nu_3$ was obtained using a broadband light source, and these results are also presented herein.

Interest in the spectra of overtone and combination bands derives from the recent attempts to understand multiple photon absorption by molecules with octahedral and tetrahedral symmetry [2]. Detailed structures of the $3\nu_3$ Q branch provide information on the anharmonicity constants for this particular transition, and on the energy levels in the ν_3 ladder. Theoretical modeling of two-frequency infrared pumping and multilevel resonance pumping using a single infrared frequency are based on such detailed information about the low-lying vibrational energy states.

2. Experimental

The 10 m cell is described extensively in ref. [1]. A multipass mirror configuration was used to provide optical path lengths of up to 1 km. As the cross section for absorption in $3\nu_3$ was anticipated to be $\approx 10^{-22}$ cm^2, adequate absorption required pressures of 0.1–0.5 kPa. The cell was normally cooled to ≈260 K in order to provide a ground state population larger than that at room temperature (0.4% at 295 K) [3].

Low resolution band contours were obtained using an Ealing arc lamp source which was modified to hold a 650 W quartz–tungsten–halogen lamp. The size of the beam limited path lengths in the cell to 320 m. Dispersion was accomplished with a Spex 1 m monochromator, and detection was by an Infrared Associates Hg : Cd : Te detector. Because of the interference from atmospheric water bands near 1879 cm^{-1}, the entire optical path from the source to the 10 m cell and from the cell to the detector, including the monochromator, was purged with dry nitrogen.

For the high resolution spectra, the arc lamp source was replaced by a tunable diode laser supplied by Laser Analytics Inc. Path lengths of up to 1 km were used with UF_6 pressures of 0.5 kPa. The peculiarities of high resolution diode laser spectroscopy were recently reviewed along with other high resolution techniques by McDowell [4,5].

3. Broadband contour analysis

The infrared fundamental band contours of transition metal hexafluorides have been presented in several works [6–8] during the last ten years. Studies of the overtone bands are far less common, but three recent papers have dealt with the band contour of $3\nu_3$ for SF_6 [9–11]. The $3\nu_3$ overtone in UF_6 is included in a study

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of the general spectral features of this molecule by McDowell et al. [12].

Fig. 1 shows the band contour of $3\nu_3$ in UF_6. The light and dashed curves are spectra taken at a temperature of 258 K and 0.133 kPa with a path length of 320 m and resolution of approximately 1.4 cm^{-1}. The heavy line is a computer simulation of the spectrum under these conditions [13], and is based on the spectroscopic constants derived from the ν_3 fundamental transition. The calculated band contour is shifted on a frequency scale to match the experimental spectrum. From this fitting process, we derive an approximate band center of 1874.6 ± 1 cm^{-1}. This is in fairly good agreement with the value of 1870 5 ± 2 cm^{-1} reported by McDowell et al. in ref. [12]. A possible cause of the discrepancy is the shift in band center due to hot bands. The studies in ref. [12] were performed at room temperature and at moderately high sample pressures to overcome the small cross section. Even then the measured peak absorption was only a few percent which makes the determination of the band center uncertain. The present work substitutes long path length for high density, thus avoiding this problem.

From the band contour, we can derive the integrated band absorption, defined [14] as:

$$\Gamma_{n'',n'} = (1/nl) \int_{\text{band}} \ln(I_0/I)\, d\nu$$

$$= (8\pi^3 N/3hc)\, \langle n'|\mu|n''\rangle^2, \qquad (1)$$

where n is the density, l is the path length, N is Avogadro's number. $\Gamma_{n'',n'}$ is of interest because, as shown in eq. (1), it is simply proportional to the dipole moment for a transition between states with quantum numbers n' and n''. The integrated band absorption for $3\nu_3$ in UF_6 is $\Gamma_{0,3} = 3.8 \times 10^{-2}$ km $mole^{-1}$ so that the strength of the overtone band compared to the fundamental [15] is $\Gamma_{0,3}/\Gamma_{0,1} = 5.6 \times 10^{-5}$. In SF_6, $\Gamma_{0,3} = 4.8 \times 10^{-2}$ km $mole^{-1}$ [10] and the ratio to the fundamental is $\Gamma_{0,3}/\Gamma_{0,1} = 4.5 \times 10^{-5}$.

4. High resolution spectrum

The absorption spectrum of the $3\nu_3$ Q branch in UF_6 at 0.004 cm^{-1} resolution is shown in fig. 2. These data were taken at a pressure of 0 469 kPa, temperature of 257 K, and path length of 1 km. Also shown are $^{14}N^{16}O$ lines [17] of the 1—0 transition in the $X\,^2\Pi$ state, which were used for calibration. The resolution of this diode laser was about 0.004 cm^{-1}, established by its ability to resolve the splitting of the NO lines.

The most distinctive feature of the Q branch is the five sub-bandheads between1875.4 and 1875.6 cm^{-1}. This identifies the $3\nu_3$ Q branch as a fundamental-type band of case (ii) in the notation of Brock et al. [18] where the clustering parameter $\beta = v/g$ will have a value $2 < \beta < 5$. This situation also prevails in $3\nu_3$ of SF_6 [11], although it is not the most commonly observed type of Q branch. A detailed analysis of the positions of the sub-bandheads and evaluation of the anharmonic constants will be reported in a subsequent paper.

Another portion of the high resolution spectrum at lower frequency is shown in fig. 3, recorded under the

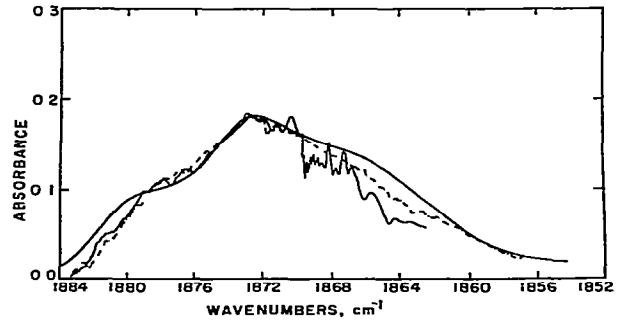

Fig. 1. The broadband absorption contour of $3\nu_3$ in UF_6. The light and dashed curves were measured at 258 K and 0.133 kPa with 320 m path length The heavy line is a computer simulation of the spectrum.

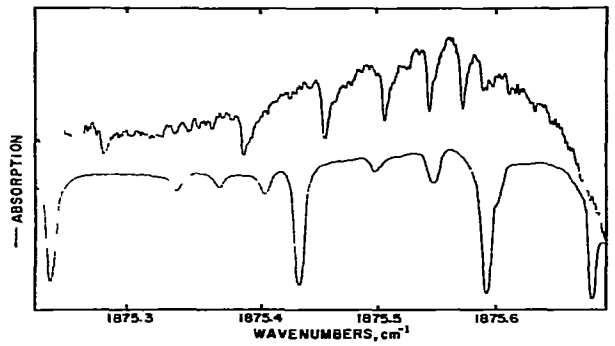

Fig. 2. High resolution (0 004 cm^{-1}) of $3\nu_3$ in UF_6. This spectrum was obtained at 0.469 kPa and 257 K with a 1 km path length. The lower curve is the $^{14}N^{16}O$ reference gas

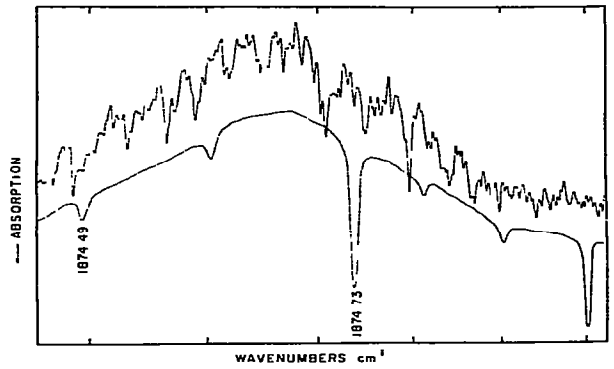

Fig. 3 Spectrum under high resolution of the hot band ($\nu_6 + 3\nu_3$) − ν_6 Experimental conditions are the same as in fig. 2.

same experimental conditions. This spectrum shows structures and intensities typical of Q branches, but there is no regular pattern visible in the absorption lines. These may represent several hot band transitions of the nature ($\nu_t + 3\nu_3$) − ν_t which have significant populations at this temperature.

References

[1] K C. Kim, E Griggs and W B Person, Appl Opt. 17 (1978) 2511.
[2] C D. Cantrell and H.W. Galbraith, Opt. Commun. 21 (1977) 374
[3] D. Jackson, Statistical Thermodynamic Properties of Hexafluoride Molecules, Los Alamos Scientific Laboratory Report LA-6025-MS (August, 1975).
[4] R.S. McDowell, in. Vibrational spectra and structure, Vol. 10, ed. J.R. Durig (Elsevier, Amsterdam, 1980).
[5] R S. McDowell, in· Laser spectroscopy, Vol. 3, eds. J.L. Hálland and J.L. Carlsten (Springer, Berlin, 1977).
[6] R S McDowell, R J. Sherman, L.B. Asprey and R C. Kennedy, J. Chem. Phys. 62 (1975) 3974.
[7] R S. McDowell and L.B Asprey, J. Mol. Spectry. 45 (1973) 491.
[8] J C. Cummings, J. Mol. Spectry., to be published.
[9] H. Kildal, J. Chem. Phys 67 (1977) 1287.
[10] J.R. Ackerhalt, H. Flicker, H.W Galbraith, J. King and W B. Person, J. Chem. Phys. 69 (1978) 1461.
[11] A S. Pine and A.G. Robiette, to be published
[12] R.S. McDowell, L.B. Asprey and R.T. Paine, J. Chem. Phys. 61 (1974) 3571.
[13] K C. Kim, R F. Holland and H. Filip, Appl. Spectry. 32 (1978) 287.
[14] J. Overend, in Infrared spectroscopy and molecular structure, ed. M Davies (Elsevier, Amsterdam, 1963) pp. 345–376.
[15] K.C. Kim and W.B. Person, private communication.
[16] P.N. Schatz and D F. Hornig, J. Chem. Phys. 21 (1953) 1516.
[17] C. Amiot, R. Bacis and G Guelvachvili, J. Chem. Phys. 56 (1978) 251.
[18] E.G. Brock, B.J. Krohn, R S. McDowell and C W. Patterson, J Mol. Spectry 76 (1979) 301.