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Determination of Einstein-A and linewidth dependence on pressure for 3.4-μm DF spectra. I. Absorption measurements for pure DF*

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Measurement of $v = 1\text{-}0$, P-branch 3.4-μm DF absorption spectra is made for a 0.1- to 500-Torr range of pressure. A cw DF laser is used as a light source, and laser intensity transmitted by DF gas is recorded in order to determine the absorption. The laser frequency is tunable over an interval which corresponds to a Doppler width. This permits measurement of the frequency dependence of transmitted light intensity for each line in the spectra, from which determination of absorption at precisely the absorption peak frequency is made. This latter determination permits evaluation of Einstein-A and linewidth ν_L^0 dependence on pressure. The results obtained for $v = 1\text{-}0$, $P(5)$ through $P(10)$ spectra are (A in sec^{-1}, ν_L^0 in cm^{-1} atm^{-1}): for $P(5)$, $A = 28 \pm 4$ and $\nu_L^0 = 0.46 \pm 0.08$; $P(6)$, $A = 34 \pm 4$ and $\nu_L^0 = 0.45 \pm 0.07$; $P(7)$, $A = 31 \pm 4$ and $\nu_L^0 = 0.29 \pm 0.05$; $P(8)$, $A = 35 \pm 4$ and $\nu_L^0 = 0.24 \pm 0.04$; $P(9)$, $A = 31 \pm 4$ and $\nu_L^0 = 0.17 \pm 0.03$; and $P(10)$, $A = 34 \pm 4$ and $\nu_L^0 = 0.13 \pm 0.02$. These values for A and ν_L^0 are in excellent agreement with corresponding theoretical values.

INTRODUCTION

This paper reports a precise measurement of 3.4-μm absorption spectra for the P branch of the $v = 1\text{-}0$ band of the DF molecule. A cw DF laser is used as a light source, and laser intensity transmitted by DF gas is recorded in order to determine absorption. The precisely defined wavelength of the laser permits resolution of absorption for individual vibrational-rotational lines in the band. Further, since the wavelength of the laser is tunable, the full frequency dependence of the transmitted light intensity for individual lines is measured. From this data Einstein A's and pressure broadening of the spectra are determined.[1]

Much earlier measurements of line strength (or equivalently the Einstein A) and pressure broadening of molecular spectra were done with conventional light sources.[2] In such cases, spectra were broadened by high absorber pressure in order to minimize instrumental modifications of the true spectra. The broadening, however, caused overlapping of adjacent lines in the spectra and necessitated measurement of the strength of the entire band. Individual line strengths were computed then from a theory which related their strengths to that of the total band. In the computation, it was assumed that: (i) All lines had a Lorentz frequency dependence; (ii) linewidths had no dependence on molecular rotational quantum number J. However, in many cases these latter assumptions were false. In light of this, it is desirable to measure absorption at low pressure and thereby determine directly the strength and width of individual lines and their variation with, e.g., J and pressure. The laser as a source gives a means of achieving this end since the use of it permits the elimination of instrumental modifications of the true spectra already mentioned.

The results of the present work are important with regard to understanding molecular structure and molecular interactions.[3] Calculation of the Einstein A's and comparison with experiment is a test of the dipole derivative function and wave functions used to describe the DF molecule. The line broadening of the spectra reflects the nature of the electrostatic multipole interactions as well as the molecular rotational energy transfer dynamics which occur during molecular encounters. The work is relevant also to the development of DF chemical lasers. Information concerning small signal-intensity gain at the laser frequency is of interest in the design and subsequent optimization of the performance of a laser.[4] Calculation of the gain requires as input, however, both Einstein-A and linewidth dependence on pressure.[5]

In 1950, Talley, Kaylor, and Nielsen[6] reported measurement of the fundamental and first overtone absorption bands of DF done by conventional spectroscopic methods. Wavelength measurements of spectra were made and molecular constants were determined. More careful measurements were made later by Spanbauer, Narahari Rao, and Jones.[7] To our knowledge, no further work along similar lines has been done for DF since then. Accordingly, the present line strength and broadening results are truly the first detailed measurements of their kind for DF.

THEORY

The spectral absorption coefficient $P(\nu)$ is defined by[8]

$$I(\nu) = I_0(\nu) \exp[-P(\nu) l] . \quad (1)$$

In Eq. (1), $I(\nu)$ and $I_0(\nu)$ are light intensities after and before transmission by an absorber which has an absorption coefficient $P(\nu)$ in cm^{-1} and path length l in cm. As indicated, $P(\nu)$, $I_0(\nu)$, and $I(\nu)$ have a dependence on ν, where ν is in cm^{-1} ($\nu \equiv \lambda^{-1}$).

The integrated line intensity S_{ul} is related to $P(\nu)$ by

$$S_{ul} = \int P(\nu) d\nu , \tag{2}$$

and, further, is related to the Einstein A_{ul} by[9]

$$S_{ul} = \frac{1}{8\pi c \nu_{ul}^2} N_l A_{ul} \frac{g_u}{g_l} \left[1 - \exp\left(-\frac{hc\nu_{ul}}{kT} \right) \right] . \tag{3a}$$

The quantity S_{ul} has a linear dependence on pressure p which is given by

$$S_{ul} = S_{ul}^0 p , \tag{3b}$$

where S_{ul}^0 is independent of pressure and is described in units of $\mathrm{cm}^{-2}\,\mathrm{atm}^{-1}$. In Eq. (2), the integration of $P(\nu)$ is performed over the width of the spectral line the center of which is at ν_{ul}. In Eq. (3a) c is the speed of light; N_l the population density of the absorbing, lower molecular level[10]; A_{ul} the Einstein-A for the transition $u \to l$ in sec^{-1}; g_u and g_l quantum degeneracies of the upper and lower levels for the transition $u \to l$; h is Planck's constant; k is Boltzmann's constant; T is absorber temperature in degrees Kelvin.

At low absorber pressure, where the line shape is determined primarily by Doppler effect and not by molecular collision frequency,[11] S_{ul} is given by[12]

$$S_{ul} = P_{ul} (\pi / \ln 2)^{1/2} \nu_D , \tag{4}$$

where P_{ul} is the absorption coefficient at ν_{ul} (i.e., at absorption maximum) and $\nu_D = (2kT \ln 2 / mc^2)^{1/2} \nu_{ul}$ is the Doppler width; m is the molecular mass. Accordingly, from a measurement of P_{ul}, A_{ul} may be determined from Eqs. (4) and (3a).

At high absorber pressure, where molecular collision frequency primarily determines the line shape and not Doppler effect,[11] the integrated line intensity is given by[13]

$$S_{ul} = \pi P'_{ul} \nu_L , \tag{5a}$$

where P'_{ul} is the absorption coefficient at ν_{ul} and appropriate to the high pressure region, and ν_L is one half the full width at one-half the maximum intensity of a pressure-broadened line which has a Lorentzian shape. The quantity ν_L has a linear dependence on pressure p which is given by

$$\nu_L = \nu_L^0 p , \tag{5b}$$

where ν_L^0 is independent of pressure and is described in units of $\mathrm{cm}^{-1}\,\mathrm{atm}^{-1}$. Since S_{ul}^0 has the same value at low and high pressure, from a measurement of P'_{ul} and S_{ul}^0 determined from Eqs. (3b) and (4), ν_L^0 may be determined.

EXPERIMENT

A schematic diagram of the apparatus used to measure absorption coefficients and their pressure dependences is shown in Fig. 1. The DF laser is a cw source which yields individually the $v = 1$-0, $P(5)$ through $P(10)$ lines required. The laser operates in a single lowest-order transverse circular mode, and for a given line its frequency may be varied within its Doppler line profile. Hence, the laser frequency may be set to coincide with the exact molecular absorption frequency as required. The tuning is done by changing the laser cavity length. This is achieved by attaching one of the laser mirrors to a transducer. The light from the laser is intercepted by a beam splitter. Fifty percent of the light is reflected by the beam splitter and mirror, passed through an absorption cell, and is incident upon an infrared detector. The other 50% of the light, after transmission by the beam splitter, is incident directly upon a second detector identical to the first in its operating characteristics. The light is mechanically interrupted before striking the detectors which permits lock-in amplifier detection of the signals $I(\nu)$ and $I_0(\nu)$ and resultant enhancement of signal-to-noise ratio, etc., in the usual way. The intensities $I(\nu)$ and $I_0(\nu)$ versus cavity tuning are plotted simultaneously by two x-y recorders, where $I(\nu)$ is the light intensity transmitted by the cell which reduces to $I_0(\nu)$ in the limit of zero absorption.

The laser used in this experiment is essentially the same as the laser described elsewhere by Hinchen.[14] The optical cavity consists of a diffraction grating and coated mirror. The grating is used to achieve laser oscillation for individual $v = 1$-0 lines. It is a Bausch and Lomb 35-53-05-820 plane reflectance grating having 240 grooves/

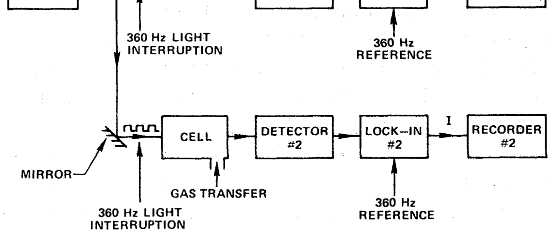

FIG. 1. Schematic diagram of apparatus.

mm and a 3.75-μm wavelength blaze. The mirror radius of curvature is 1.0 m and is 98% reflecting at 3.5-μm. With a mirror-to-grating spacing of 25 cm and with two intracavity irises to suppress off-axis mode oscillation, single-mode oscillation is readily achieved. Typical output power for a given line is 50–100 mW. This output is attenuated by a factor of 10 before the light enters the absorption region. This is done to ensure absence of saturation of absorption for the range of absorber pressure studied. The mirror is attached to a Lansing 21.917 piezoelectric translator. The transducer voltage is derived from a Kepco FG-100A function generator and a Lansing 80.310 high-voltage dc amplifier. The mirror and grating are held in Davidson D-622 mounts, and are held separated by four 2.5-cm-diam Invar rods. This latter construction aided the long- and short-term stability of the laser.

In order to transfer pure DF to and from the cell a high-vacuum gas handling system is used. The cell and component parts of this system are of mixed Kel-F, Monel and stainless-steel construction. Prolonged observation of absorption indicated no change of absorption and hence no DF decomposition or reaction in our system. The gas pressure is measured with a MKS Instruments 90H-30 pressure-sensing head and 90M-XRP electronic indicator. This is a capacitance-manometer-type measuring instrument. For pressures which exceed 30 Torr, a Wallace and Tiernan FA-145 gauge is used. The DF used in this experiment is purchased in quantities of 10–15 g, in Monel cylinders, from the Ozark-Mahoning Company of Tulsa, Oklahoma.

The infrared detectors are room-temperature operated PbSe having a (2×2)-mm element size. Two Princeton Applied Research 128A lock-in amplifiers are used, these being tuned to a signal frequency of 360 Hz.

The result of a representative absorption measurement is given in Figs. (2a) and (2b) for the $v=1\text{-}0$, $P(8)$ laser line. Figure (2a) is light intensity versus cavity tuning in the absence of absorption and represents that portion of the incident light which is transmitted by the beam splitter. The frequency scale is determined from the known translational characteristics of the transducer. The lock-in amplifier time constant for this measurement was 0.01 sec. Figure (2b) is transmitted light intensity versus cavity tuning in the presence of absorption, and represents that part of the incident laser light which is reflected in succession by the beam splitter and mirror. In this case, the data are for light transmitted by a 3.975-cm-long cell which contained 0.8 Torr of DF. Hence, from Figs. (2a) and (2b) and Eq. (1), it follows that in this case $I(\nu=\nu_{ul})/I_0(\nu=\nu_{ul})=0.24$ and $P_{ul}=0.36$ cm^{-1}. This particular measurement yields then one point in a plot of P_{ul} versus pressure.

A very large number of measurements of the type given in Figs. (2a) and (2b) were made. These measurements of P_{ul} covered a pressure range of 0.1–500 Torr and the DF lines $v=1\text{-}0$, $P(5)$ through $P(10)$. Three cells were used. A 3.975-cm-long cell was used at low pressure where P_{ul} is small and sufficient path length was required in order to achieve a measurable absorption, whereas at higher pressures where P'_{ul} is correspondingly larger, shorter 0.51- and 0.15-cm-long absorption cells were used.

In Fig. 3, the absorption coefficient versus DF pressure is plotted for the $v=1\text{-}0$, $P(9)$ line. The 3.975- and 0.51-cm-long cells were used. Using the procedure outlined in detail above, from Fig. (3) it follows that $A=31(\pm 4)$ sec^{-1} and $\nu_L^0=0.17$ ± 0.03 cm^{-1} atm^{-1}. These results are appropriate to a cell temperature of 23 °C. The results of the

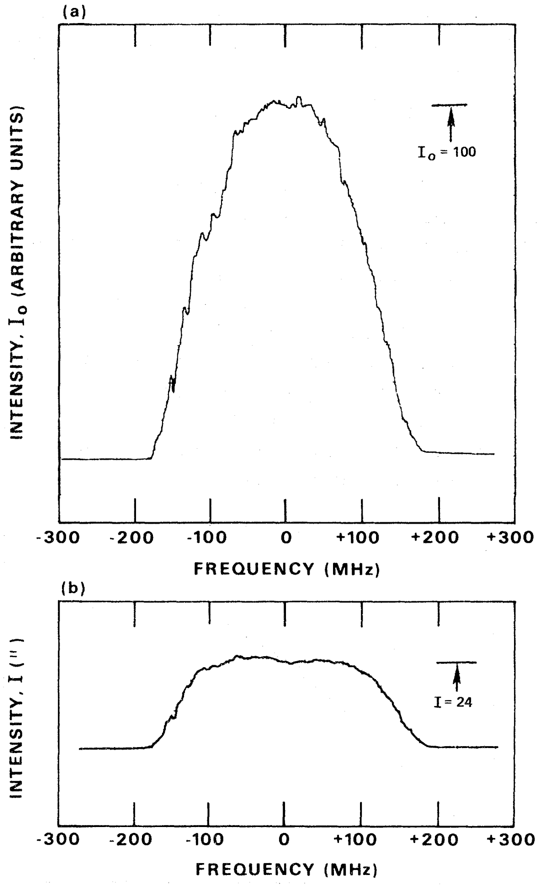

FIG. 2. (a) Plot of $v=1\text{-}0$, $P(8)$ laser intensity vs cavity tuning frequency for empty cell. (b) Plot of $v=1\text{-}0$, $P(8)$ laser intensity vs cavity tuning frequency for 0.8-Torr DF in 3.975-cm-long cell.

determinations of A and ν_L^0 for $v=1$-0, $P(5)$ through $P(10)$ are summarized in Table I and Fig. (4). (The notation used in this work to identify the molecular transitions is taken from Ref. 7 below, wherein the associated wavelengths also are given.)

DISCUSSION

The results which are given in Table I are computed on the basis of values of P_{ul} and P'_{ul} taken from Fig. 3 and similar plots. The value of P_{ul} is determined by fitting a straight line to points such as those given in Fig. 3 in the region of pressure 0–1 Torr. This region is appropriate to nearly pure Doppler linewidth broadening, and the absorption coefficient is linearly proportional to pressure. The value of P'_{ul} is determined by finding the asymptotic value of the absorption coefficient in the region of pressure exceeding 100 Torr. This region is appropriate to nearly pure collisional linewidth broadening, and the absorption coefficient is independent of pressure. Another approach to arriving at values for A and ν_L^0 is to computer fit the data to the so-called Voigt profile by variation of the parameters A and ν_L^0.[15] This profile is given by

$$P_{ul}=\frac{S_{ul}}{\nu_D}\left(\frac{\ln 2}{\pi}\right)^{1/2}[1-\mathrm{erf}(a)]e^{a^2}, \tag{6}$$

where $a=\nu_L(\ln 2)^{1/2}/\nu_D$ and erf is the "error function."[16] The use of a computer was unnecessary. The values in Table I, determined as described above, when substituted into Eq. (6) describe curves of absorption coefficient versus pressure which fit the data very well. The curve drawn in Fig. 3 is derived from values given in Table I and from Eq. (6). In summary, the values which we give for A and ν_L^0 are consistent with a Voigt fit to the data, although a formal variation-of-parameters procedure was not used.

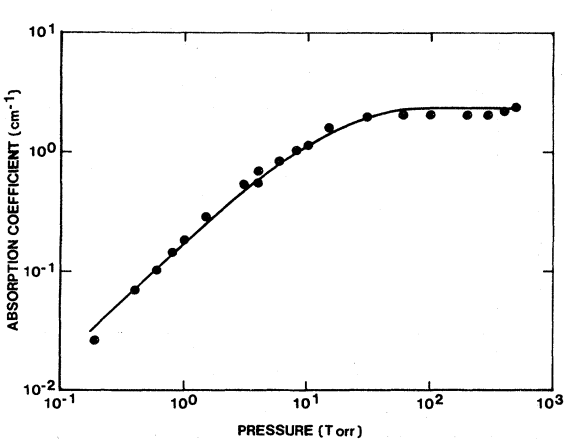

FIG. 3. Absorption coefficient vs DF pressure for $v=1$-0, $P(9)$ laser line.

TABLE I. Summary of A_{ul} and ν_L^0 results appropriate to a 23 °C absorber temperature. The theoretical values of ν_L^0 and A_{ul} are taken from Refs. 17 and 19, respectively.

Transition ($v=0\leftarrow 1$)	A_{ul} (sec^{-1}) Expt.	Theory	ν_L^0(cm^{-1}/atm) Expt.	Theory
$P(10)$	34(±4)	32	0.13±0.02	0.14
$P(9)$	31(±4)	32	0.17±0.03	0.18
$P(8)$	35(±4)	32	0.24±0.04	0.24
$P(7)$	31(±4)	32	0.29±0.05	0.33
$P(6)$	34(±4)	32	0.45±0.07	0.44
$P(5)$	28(±4)	32	0.46±0.08	0.53

The sources of uncertainty associated with the values for A and ν_L^0 in Table I are (a) lack of precision regarding absorber pressure; (b) instability in $I(\nu=\nu_{ul})/I_0(\nu=\nu_{ul})$. With regard to (a) above, repeated use of DF caused the capacitance manometer pressure sensor to behave erratically, owing to reaction of DF with materials within the sensor. This problem was avoided by partial use of other sensors of different construction, but being inherently less accurate with regard to absolute pressure determination. With regard to (b) above, the instability in $I(\nu=\nu_{ul})/I_0(\nu=\nu_{ul})$ was due to variation in laser spot positions with respect to their respective detectors. Thermal gradients in the laser cavity and elsewhere caused these variations. The significance of the magnitudes of the experimental uncertainties in Table I is that these magnitudes define a range of values for A_{ul} and ν_L^0 which yield equally satisfactory Voigt fits to the data. These uncertainties were determined by a variation-of-parameters procedure without, however, the use of a computer.

Theoretical values are available for the pressure dependence of linewidths associated with DF

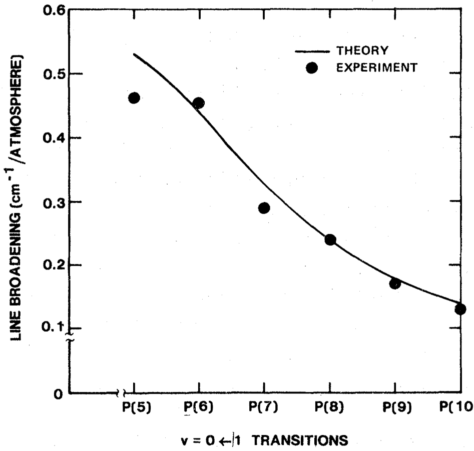

FIG. 4. Line broadening for $v=1$-0 P-branch transitions.

spectra.[17,3] The results of these linewidth calculations are given in Table I and Fig. 4, and are taken from Ref. 17. The results are appropriate to a 23 °C absorber temperature. The good agreement between theory and experiment gives support to the Anderson theory[18] and the dipole-dipole interaction as a means of describing line broadening due to collisions involving polar diatomic species. The somewhat poorer agreement between theory and experiment at lower values of J is due to increased experimental uncertainty caused by instability of the laser source. Theoretical values of A are taken from Ref. 19.

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