CF₄ Combination Band Absorption Spectroscopy

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Absorption and linewidth measurements of the $R^+(29) (\nu_2 + \nu_4) A_1^+ + E^9 + F_1^{14}$ transition in CF₄ are reported as a function of gas pressure and temperature. From these a value for the Einstein A coefficient ($0.0185 \pm 0.0010 \text{ sec}^{-1}$) is deduced. A model for low temperature absorption and a detailed analysis of additional absorption lines are given. The Doppler width reported by Eckhardt *et al.* (*J. Mol. Spectrosc.* **90**, 321-326 (1981)) at 150 K is confirmed, while the homogeneous linewidth is found to be 10% smaller. The frequency displacement of the absorption feature from the CO₂ 9R(12) emission line center is found to be (34 ± 2) MHz independent of temperature and pressure as may be expected. The room temperature absorption measurements of Radziemski *et al.* (*Opt. Lett.* **3**, 241-243 (1978)) at three different pressures are confirmed but the absorption is not due to a single line and therefore the corresponding dipole moment calculated from those data (*Proc. Soc. Photo-Opt. Instrum. Eng.* **288**, 209-216 (1981)) is too large. © 1991 Academic Press, Inc.

I. INTRODUCTION

Through optical pumping of the $\nu_2 + \nu_4$ combination band of CF₄, lasing can be obtained in the midinfrared on many transitions near 16 μm . In view of the possible application of the CF₄ laser for UF₆ photochemistry and the scarcity of other high-intensity 16- μm sources, this laser has received much attention in the recent past (1-4). Part of this effort has been concentrated on the $\nu_2 + \nu_4$ absorption band which is used to pump the laser (5-7). To identify the many absorbing transitions, high-resolution diode laser spectroscopy measurements were carried out both at room temperature (5) and at 131 K (6). Absorption and linewidth measurements at 150 K as a function of gas pressure were reported by Eckhardt *et al.* (7) using a pulsed CO₂ laser the frequency of which could be tuned within the gain bandwidth of the 9R(12) CO₂ laser transition. At room temperature peak absorption measurements are reported by Radziemski *et al.* (5) for three pressures. The latter data were used by Patterson *et al.* (8) to calculate the transition dipole moment. Since the data of Ref. (5) showed an increase in the peak absorption as a function of pressure the simple approach in Ref. (8) to fit a Lorentzian absorption lineshape to the data in order to determine the transition dipole moment seems questionable. Moreover the origin of this increase in absorption was not investigated in Ref. (8). Other problems still not clarified include the exact position of the $R^+(29)$ absorption peak relative to the CO₂ 9R(12) line center and the consistently high value of the Einstein A coefficient determined from room temperature measurements on other transitions in the $\nu_2 + \nu_4$ combination band relative to the low-temperature data.

In view of the existing uncertainties, extensive measurements were made of the CF_4 absorption in the neighborhood of the $R^+(29)(\nu_2 + \nu_4) A_1^4 + E^9 + F_1^{14}$ transition as a function of both temperature and pressure. Following a description of the experimental setup and measurement procedures we will focus on the theory of absorption for single and multiline transitions in the presence of pressure broadening and on temperature effects on the absorption coefficients. Finally, the experimental results are presented and the data are then analyzed as described previously.

II. EXPERIMENTAL DETAILS

A sealed off, cw CO_2 laser, which was tuned to the $9R(12)$ emission line, was used as our pump. The CO_2 laser cavity consisted of an 80% reflectivity, concave mirror with a radius of curvature of 3 m and a grating (150 l/mm) mounted in a Littrow configuration to tune the laser. The grating was mounted on a piezo transducer to allow length tuning of the CO_2 laser. An optoacoustic cell could be used to lock the CO_2 laser to the absorption line which is shifted by approximately 30 MHz to the blue side of the $9R12$ line center. Alternatively we could sweep the frequency with the piezo to tune the laser through the absorption maximum. Frequency was calibrated against the drive voltage using the longitudinal mode spacing ($c/2L = 95$ MHz) of the CO_2 laser. Nonlinearities in the piezo displacement gave errors of less than 5% in the frequency determination.

The absorption cell had double entrance and exit windows, separated by a vacuum space, to avoid temperature gradients inside the cell. Temperature was measured using Pt resistance thermometers along the length of the absorption cell, which was cooled using cold nitrogen gas. The CO_2 pump beam was coupled in by reflecting from the plane side of a planoconvex KCl lens in such a manner that the internal reflection at the convex side was separated from the measuring beam. The incident beam was monitored with a HgCdTe detector using a thick KCl flat beam splitter.

The beam transmitted through the absorption cell was monitored by a second HgCdTe detector after reflection off a planoconvex BaF_2 lens. A chopper and two phase sensitive lock-in amplifiers were used and their time averaged ratio was calculated with a computer. The absorption of the CF_4 gas could easily be determined for different pressures by calibrating the background ratio at zero pressure. At higher pressures measurements were taken while stabilizing the cavity length optoacoustically, instead of scanning the absorption line profile. The optoacoustic signal is in first-order proportional to the product of the pump power and the absorption. Tuning the frequency away from emission line center the absorption will increase to a maximum while the power of the pump laser will fall off causing the optoacoustic signal maximum to occur at a frequency which is shifted away from the absorption maximum toward emission line center. At the highest pressures the linewidths were so large that this slight shift in frequency had no effect on the measured absorption.

Linearity of both detectors was checked using absorption filters in incoming and transmitted beam. Saturation effects in the gas were avoided by using low light levels in the cell (approximately 100 mW/cm^2). An extra absorption filter in the main beam did not affect the measured absorption, thereby confirming the absence of gas saturation.

III. THEORY AND DATA ANALYSIS

A. Single Absorption Line

In the absence of contributions of neighboring lines the absorption coefficient for a single transition is given by

$$\alpha(\nu) = \frac{\lambda^2}{8\pi} AS(\nu, \nu_0) \left(n_0 - \frac{g_0}{g_1} n_1 \right) \quad (1)$$

with $\alpha(\nu)$ the absorption coefficient at frequency ν (1/m), λ the pump wavelength, A the Einstein coefficient for spontaneous emission, $S(\nu, \nu_0)$ the lineshape function of the absorption, $n_{0,1}$ the population density of ground and upper level, respectively, and $g_{0,1}$ the degeneracy of these levels.

Temperature and pressure are seen to influence the absorption through the dependence of the lineshape and population densities on these quantities.

(i) *Lineshape.* At low pressures the absorption line is Doppler broadened, giving rise to a Gaussian lineshape function S

$$S(\nu, \nu_0) = \frac{2}{\Delta\nu_D} \sqrt{\frac{\ln 2}{\pi}} \exp\left(-\frac{4 \ln 2 (\nu - \nu_0)^2}{\Delta\nu_D^2}\right) \quad (2)$$

with ν the frequency of the absorbed light (Hz), ν_0 the line center frequency (Hz), and $\Delta\nu_D$ the FWHM of the Doppler broadened line. For CF₄ (9)

$$\Delta\nu_D \approx 2.46\sqrt{T} \text{ MHz} \quad (3)$$

with T the temperature (K).

At higher pressures collision processes become more important and the linewidth becomes pressure broadened leading to a Lorentzian lineshape,

$$S(\nu, \nu_0) = \frac{\Delta\nu_p}{2\pi} \left[(\nu - \nu_0)^2 + \left(\frac{\Delta\nu_p}{2} \right)^2 \right]^{-1}, \quad (4)$$

where the homogeneous linewidth, $\Delta\nu_p$, has been measured by Eckhardt *et al.* (7) at a temperature of 150 K. Their data can be extended using an assumed inverse square root of the temperature dependence to give

$$\Delta\nu_p = \frac{0.992p}{\sqrt{T}} \text{ MHz} \quad (5)$$

with p , the pressure, in pascal¹ units and T in Kelvin.

At intermediate pressures we have neither a Doppler nor a Lorentzian lineshape. The lineshape is a convolution of these two, resulting in a Voigt profile. Approximate analytical expressions for $S(\nu, \nu_0)$ can be found in Ref. (10) and are consistent with numerical results of the convolution in this pressure range. We also note that, contrary to the simple Voigt theory, Dicke narrowing (11) might also occur. Indications for Dicke narrowing in CF₄ were noticed in Ref. (7).

¹ Throughout the paper we use the SI unit for pressure, Pa. Since torr cells are still widely used, we note that 1 Torr = 133.3 Pa. In Eq. (5) the numerical factor is given by 132 if p is expressed in torr cells.

(ii) *Population density.* In Eq. (1) the population difference is given by (12)

$$\left(n_0 - \frac{g_0}{g_1} n_1\right) = \frac{\epsilon_0(2J_0 + 1)p \exp\left(\frac{-BhJ_0(J_0 + 1)}{kT}\right) \left(1 - \exp\left(\frac{h\nu_p}{kT}\right)\right)}{Z_r(T)Z_v(T)kT} \quad (6)$$

with ϵ_0 the nuclear spin statistical weight, J_0 the rotational quantum number of the lower pump level, ν_p the pump frequency, B the rotational constant of the CF_4 molecule, h, k Planck and Boltzmann constants, respectively, Z_r, Z_v the rotational and vibrational partition sums, respectively, and p the pressure (Pa). An additional temperature dependence of the absorption arises from the lineshape function, as is discussed above.

B. Multiple Closely Spaced Absorption Lines

In the case of several closely spaced, partially or nonresolved absorption lines the total absorption is

$$\alpha_{\text{tot}}(\nu) = \sum_{i=1}^m \alpha_i(\nu) = \left(\sum_{i=1}^m S_i(\nu, \nu_{0,i}) \left(n_{0,i} - \frac{g_0}{g_i} n_i \right) \right) \cdot \frac{\lambda^2 A}{8\pi} \quad (7)$$

with $\nu_{0,i}$ the center frequency for the i th absorption line and $(n_{0,i} - (g_0/g_i)n_i)$ the population difference for that transition. In Eq. (7) we assume that the transition dipole moment (i.e., A) is approximately constant. This should be a reasonable approximation for high J -values in the $\nu_2 + \nu_4$ combination band.

In our measurements we found strong indications that at least one and possibly more than one additional absorption feature is present close to the main transition. Such additional unknown absorption line(s) may be identified through a study of the pressure and temperature dependence of the absorption spectrum. To do this we must account for all known neighboring absorption lines which contribute to the absorption due to pressure broadening. Any extra measured absorption is then identified as arising from until now unknown transitions. For a single extra line we may write

$$\begin{aligned} \alpha_u(\nu) &= \alpha(\nu)_{\text{measured}} - \sum_{i=1}^m \alpha_i(\nu) = \frac{\lambda^2}{8\pi} AS(\nu, \nu_u) \left(n_{0,u} - \frac{g_{0,u}}{g_{1,u}} n_{1,u} \right) \\ &= \frac{\lambda^2}{8\pi} A \left[\frac{(\Delta\nu_p/2\pi)}{(\nu - \nu_u)^2 + \left(\frac{\Delta\nu_p}{2}\right)^2} \right] \left(n_{0,u} - \frac{g_{0,u}}{g_{1,u}} n_{1,u} \right), \end{aligned} \quad (8)$$

where the summation over i runs over the known absorption lines. Rewriting this we get

$$\begin{aligned} \frac{\Delta\nu_p * p}{\alpha(\nu) - \sum_{i=1}^m \alpha_i(\nu)} &= \frac{(\nu - \nu_u)^2}{\left(\frac{\lambda^2 A}{8\pi}\right) \frac{1}{2\pi} \left(\frac{n_{0,u} - (g_{0,u}/g_{1,u})n_{1,u}}{p}\right)} \\ &\quad + \frac{(\Delta\nu_p)^2}{4\left(\frac{\lambda^2 A}{8\pi}\right) \frac{1}{2\pi} \left(\frac{n_{0,u} - (g_{0,u}/g_{1,u})n_{1,u}}{p}\right)}. \end{aligned} \quad (9)$$

Since $\Delta\nu_p$ is proportional to p , a linear fit of $\Delta\nu_p \cdot p / (\alpha(\nu) - \sum_{i=1}^m \alpha_i(\nu))$ versus p^2 directly gives us the population inversion density from the slope and the position of the line center of the unknown transition from the zero pressure intercept. For more than one unknown absorption line Eq. (9) is generalized to

$$\frac{\Delta\nu_p \cdot p}{\alpha(\nu) - \sum_{i=1}^m \alpha_i(\nu)} = \frac{1}{\sum_u \left[\frac{\lambda^2}{8\pi} \frac{A}{2\pi} \frac{(n_{0,u} - (g_{0,u}/g_{1,u})n_1)/p}{[(\nu - \nu_u)^2 + (\Delta\nu_p/2)^2]} \right]_u}, \quad (10)$$

where we once again assume the pressure broadening to be constant for all lines. At low enough pressures, however, the dominant contribution from any unknown transitions will come from the transition with the smallest frequency displacement relative to line center.

We may also study the temperature dependence of any additional absorption. Ignoring the upper state population (which gives corrections of less than 1% even at room temperature) one finds

$$\alpha_u(\nu) \approx \frac{\lambda^2 A}{8\pi} S(\nu, \nu_u) n_{0,u} = \frac{\lambda^2 A}{8\pi} S(\nu, \nu_u) \frac{f(E_u(J, \nu), T)p}{Z_r Z_v kT}. \quad (11)$$

Adjusting the pressure so as to keep the linewidth constant at all temperatures, Eq. (11) may be rewritten for a single additional transition as

$$\left(\frac{\alpha_u(\nu) \cdot T \cdot Z(T)}{p} \right)_{\Delta\nu_p = \text{cst.}} = \frac{\lambda^2 A}{8\pi k} S(\nu, \nu_u) f(E_u(J, \nu), T) \sim c \exp\left(-\frac{E_u}{kT}\right) \quad (12)$$

FIG. 1. Pressure dependence of the absorption linewidth at 122 K (a) and 294 K (b). Curves: (—) extrapolated from Ref. (7); (---) present determination.

FIG. 2. Pressure dependence of the absorption coefficient α at 122 K (a), 143 K (b), 169 K (c), 193 K (d), 230 K (e), and 294 K (f). Shown are the contribution of $R^+(29) A_1^4 + E^9 + F_1^4$ at the linecenter (----), the absorption due to all known absorption lines ($\cdots$), and the absorption including the newly determined absorption feature (—). In Fig. 2f measurements of Radziemski *et al.* (5) at 296 K are also included (O).

with E_u the energy of the lower state of the transition and $Z(T) = Z_r Z_v$.

Taking the logarithm we may write this as

$$\ln \left(\frac{\alpha_u(\nu) \cdot T \cdot Z(T)}{p} \right)_{\Delta\nu_p = \text{cst.}} = c' - \frac{E_u}{kT}. \quad (13)$$

If there is more than one absorption feature with equal lower state energy we can still use Eq. (13) since the contributions from the lines will behave in the same manner at constant homogeneous broadening.

FIG. 2—Continued

Analysis of the absorption measurements at several different values of $\Delta\nu_p$ should in principle give the same value of E_u . This enables us to check the consistency of the model and its results.

IV. RESULTS

Linewidth measurements at $T = 122$ K and at room temperature are given in Fig. 1. At the low pressure the Doppler linewidth (Eq. (3)) is confirmed. Solid curves correspond to the extrapolated literature (7) value for $\Delta\nu_p$ (Eq. (5)) while dashed curves correspond to a 10% smaller homogeneous linewidth

$$\Delta\nu_p = 0.895 p / \sqrt{T} \text{ MHz} \quad (14)$$

with p and T in pascal units and Kelvin, respectively.

In view of our result (discussed below) that more than one transition is involved at the higher temperatures the reduced value of $\Delta\nu_p$ has been used in the determination of other quantities (e.g., the Einstein A coefficient, the transition dipole moment).

The frequency displacement, $\Delta\nu_0$, from the center of the 9R12 CO₂ line was measured at 122 and 294 K. The frequency displacement was found to be independent of temperature and pressure: $\Delta\nu_0 = 34 \pm 2$ MHz. This result seems obvious. Earlier work, however, suggested a strong temperature dependence (5).

For a CO₂ pump frequency fixed to the center of the absorption line, the absorption was measured as a function of pressure for six different temperatures (Fig. 2). The absorption at room temperature as measured by Radziemski at three different pressures was confirmed by our measurements. Contrary to Ref. (7) no indication was found for the occurrence of a Dicke minimum at any temperature from these measurements, nor did we find any dips in the linewidths in Fig. 1. The results could be fitted at the low pressure side where no contributions of other lines were expected using a Voigt

TABLE I
Absorption Lines Near the $R^+(29) F_1^{14} + E^9 + A_1^4$ transition

Branch	Symmetry Species	Degeneracy	Detuning from $R^+(29)$ line center at 1073.270 cm^{-1} (GHz)	cf. Ref.
$R^+(29)$	$F_1^{14} + E^9 + A_1^4$	(10)	0	(13)
$R^+(28)$	$F_2^8 + E^6 + F_1^8$	(8)	0.430	(13)
$R^+(29)$	$F_1^{13} + F_2^{14}$	(6)	1.17	(14)
$R^+(29)$	$F_1^{15} + F_2^{15}$	(6)	1.38	(14)
$R^+(28)$		(5)	1.44	(6)
$R^+(28)$		(3)	1.56	(6)
$R^+(28)$		(3)	1.64	(6)
$R^+(28)$		(5)	1.80	(6)
$R^0(17)$	$F_1^4 + E^3 + F_2$	(8)	1.70	(6)
$R^+(29)$		(10)	2.31	(6)

line shape. We found an excellent fit using the Einstein coefficient $A = (0.0185 \pm 0.0010) \text{ sec}^{-1}$.

At higher pressures we modeled the absorption while accounting for 10 known neighboring absorption lines (Table I). Contributions from all other known absorption lines were always less than 1% in the pressure/temperature range under study. Since the line separations are large compared to the Doppler widths we only consider contributions from neighboring transitions due to homogeneous pressure line broadening.

Using our new value for A , the model gives a very good description of the absorption measurements for the absorption at the lowest two temperatures (122 and 143 K) even at the highest pressures measured. At these temperatures far away absorption lines are expected to contribute more than at elevated temperature due to the larger pressure broadening (cf. Eq. (5)). Above 200 K, however, the measured absorption exceeded the predicted absorption by a factor of 2 or more for pressures larger than 5 kPa.

To identify possible unknown transitions we analyzed the temperature dependence of this excess absorption at constant linewidth in the manner discussed in Section IIIB. Results are given in Fig. 3. A value of $E_u/k = 910 \pm 50 \text{ K}$ was found. Attention is drawn to the internal consistency of the data, which we believe to give additional confirmation for the existence of additional transition(s) with the same lower state energy. If the lower state involved is an excited rotational state of the ground vibrational

FIG. 3. Temperature dependence of the additional absorption for homogeneous linewidths 100 MHz (—), 200 MHz (···), 300 MHz (---) and 400 MHz (-·-·-).

state, this would imply a rotational quantum number $J = 57 \pm 2$. Alternatively this might be a hot band transition from the ν_2 vibrational state with $J = 31 \pm 3$. The latter possibility seems very plausible if anharmonicity effects are small. This could occur if a $\nu_2 (+\nu_4)$ vibration is excited in the transition that is perpendicular to the ν_2 vibrational state of the molecule.

To find the center frequency of this new transition we plot in Fig. 4 $\Delta\nu_h \cdot p / (\alpha(\nu) - \sum \alpha_i(\nu))$ versus p^2 (see Section IIIB). For pressures below 2.5 kPa a linear fit can be made to the data. The resulting population density and center frequency displacement from the main absorption are given in Table II, along with the degeneracy of the lower level. The large value of the degeneracy $\epsilon_0 = 43 \pm 7$ is also suggestive of a hot band transition. Averaging these data a value of $\Delta\nu_0 = 40 \pm 7$ MHz is found. In fact in Ref. (7), Fig. 1, a small side peak is shown which was interpreted as statistical error. Its position coincides within the errors with our determination.

Above 2.5 kPa systematic deviations from linear behavior are observed in Fig. 4. This corresponds to the extra unexplained absorption in Fig. 2. Other new single transitions could, however, not be identified, either from the temperature behavior at constant linewidth or from the p^2 dependence of $\Delta\nu_h \cdot p / (\alpha - \sum \alpha_i(\nu))$ (where we include our newly identified transition in the sum over all known transitions). In view of the many possible hot band transitions this is hardly surprising.

These results show that a determination of the dipole moment by Patterson *et al.* (8) from absorption measurements of Radziemski *et al.* (5) at room temperature for pressures of 386, 785, and 1516 Pa cannot be justified in view of the contribution from the extra line(s). Also at 386 Pa the Doppler width, $\Delta\nu_D = 42$ MHz, exceeds the homogeneous linewidth $\Delta\nu_p = 22$ MHz, so a Lorentzian fit is incorrect. The transition dipole moment should therefore be corrected. Using our value for the Einstein A coefficient we find $\langle \mu_{0,24} \rangle = 0.0080$ D. This value is somewhat lower than other

FIG. 4. Determination of the additional absorption line position and strength. See Section IIIB for a discussion on the quantity $Y = \Delta\nu_p * P / (\alpha(\nu) - \sum_i \alpha_i(\nu))$.

absorption features in the $\nu_2 + \nu_4$ band, but room temperature measurements always seem to give higher values than at lower temperature (8), which we think is due to contributions of other absorption lines at room temperature.

SUMMARY

Using a CO_2 laser pump the absorption of the $R^+(29) \nu_2 + \nu_4$ combination band transition in CF_4 was studied as a function of temperature and pressure. The Einstein

FIG. 4—Continued

coefficient for spontaneous emission was determined to be $A = 0.0185 \pm 0.0010 \text{ sec}^{-1}$. The increased absorption at high pressures is explained by additional absorption lines which have a strong temperature dependence suggesting high rotational numbers and/or hot band transitions. One of these features is very close to the $R^+(29)$ line (distance: $40 \pm 7 \text{ MHz}$, $\epsilon_0 = 43 \pm 7$). At the highest pressures a single line model cannot explain the measurements, presumably several additional lines all contribute to the absorption.

The dipole moment for ground state to $(\nu_2 + \nu_4)$ transitions is corrected to $\langle \mu_{0,24} \rangle \approx 0.0080 \text{ D}$. The homogeneous linewidth is determined to be 10% smaller than the value given by Eckhardt *et al.* Their results may, however, have been influenced by the existence of the additional absorption.

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TABLE II

Characteristics of the Additional Absorption as Determined by the Pressure Dependence

T(K)	$\frac{N_{\text{diff}}}{P} (10^{17} \text{ m}^{-3} \text{ Pa}^{-1})$	$(\nu - \nu_0) (\text{MHz})$	ϵ_0
122	0.7 ± 0.1	42 ± 10	31 ± 4
143	2.1 ± 0.2	34 ± 6	51 ± 5
169	2.9 ± 0.3	27 ± 5	42 ± 4
193	4.1 ± 0.5	35 ± 6	45 ± 6
230	5.3 ± 0.3	43 ± 4	46 ± 3
294	5.2 ± 0.4	44 ± 5	45 ± 3

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