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Modeling the CF_4 Laser

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Abstract

The CO_2-pumped CF_4 laser is a potentially useful source of line-tunable infrared radiation in the region 605-655 cm^{-1}, and the spectroscopy of CF_4 has been carried to the point that the laser frequencies that will result from any given pump line can be calculated to better than 0.01 cm^{-1}. We now report quantitative intensity and line-broadening studies on CF_4 and their application to modeling the laser gain. First, absorption measurements on isolated lines in the $\nu_2 + \nu_4$ pump band at a series of pressures yield an effective transition dipole moment for this band of 0.010 Debye. At the same time the transition moment for the $(\nu_2 + \nu_4) - \nu_2$ laser band has been calculated and agrees well with the results of laser self-absorption measurements. Finally, linewidths determined as a function of pressure yield a pressure-broadening coefficient of ca. 10 MHz/torr, significantly greater than that expected from a hard-sphere gas-kinetic model. From these data the gain of the CF_4 laser can be calculated at various pressures and temperatures; the results are in reasonable agreement with measured values.

Introduction

When $\nu_2 + \nu_4$ of CF_4 at 1066 cm^{-1} is pumped by a 9.4 μm CO_2 laser, stimulated emission occurs for the $(\nu_2 + \nu_4) \rightarrow \nu_2$ transition and produces many discrete laser lines in the 605 to 655 cm^{-1} region. A comprehensive program of Doppler-limited absorption spectroscopy of $^{12}CF_4$ has been carried out using tunable semiconductor diode lasers, and has led to a full understanding of the rovibrational energy levels and selection rules involved in the laser process.[1] From this spectroscopic analysis of the $\nu_2 + \nu_4$ absorption band, the pump and laser transitions have been identified; furthermore, the laser lines resulting from any given pump frequency have been predicted with ±0.003 cm^{-1} accuracy.[2,3]

However, in order to calculate either pump absorption or laser gain, it is first necessary to know the dipole moments associated with the specific rovibrational transitions for both absorption and emission. The purpose of this paper is to estimate the effective dipole moments for both the $0 \rightarrow (\nu_2 + \nu_4)$ and $(\nu_2 + \nu_4) \rightarrow \nu_2$ transitions and to put the understanding of the CF_4 laser on a more quantitative footing. We begin by describing the absorption of radiation by transitions from the ground state to the $\nu_2 + \nu_4$ band.

Transition Moments for $0 \rightarrow \nu_2 + \nu_4$

If the ν_2 (E symmetry type) and the ν_4 (F_2 symmetry type) component vibrations are strongly anharmonically mixed, the $\nu_2 + \nu_4$ combination band will have two vibrational subbands with the symmetry of the direct product $E \times F_2 = F_1$ and F_2 states. Only the F_2 subband can have an electronic dipole moment (F_1 transitions are symmetry forbidden) and transitions to this subband are exactly like transitions to a F_2 fundamental, exhibiting the same P, Q, and R structure. Furthermore, the line strength for transitions to the F_2 subband is the same as that for a spherical top infrared active fundamental, namely

$$S_{if} = \frac{8\pi^3 N}{hcZ} \nu_{if} |\mu_{if}|^2 g_i (2J_i + 1)$$

$$\times e^{-B_0 hcJ_i(J_i + 1)/kT}(1-e^{-hc\nu_{if}/kT}) \qquad (1)$$

Here N is the number of molecules per cm^3, $Z = Z_v Z_r$ is the product of the vibrational and rotational partition functions, and ν_{if} is the wavenumber (cm^{-1}) of the transition between the initial and final rovibrational states. The units in this equation are cm^{-2}. Since g_i is the nuclear-spin statistical weight and J_i the ground state total angular momentum, the product $g_i(2J_i+1)$ is the lower level degeneracy.

The square of the transition dipole $|\mu_{if}|^2$ in the above expression is

$$|\mu_{if}|^2 = \frac{2J_f+1}{3(2J_i+1)} |\mu_{0,24}|^2 \qquad (2)$$

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where we have averaged over the initial states and summed over the final states with the same external quantum numbers. The factor 1/3 arises since we are considering only one direction of polarization. Only transitions for which ΔJ = 0,±1 are allowed where we have the following designations:

$J_f = J_i - 1$ P branch

$J_f = J_i$ Q branch

$J_f = J_i + 1$ R branch

Our expressions for S_{if} and $\langle\mu_{if}\rangle$ differ from those of Fox and Person,[6] since they erroneously delete the denominator $3(2J_i+1)$ in $\langle\mu_{if}\rangle^2$ and put it in their expression for S_{if}. The exact form of the dipole moment is not important when calculating small signal absorptions, but is critical when calculating Rabi frequencies, absorption near saturation, or gains.

Unfortunately, the $\nu_2 + \nu_4$ combination band does not exhibit a simple P, Q, R structure. This is because the anharmonic interaction between the ν_2 and ν_4 vibrations is weak; hence, the F_1 and F_2 subbands are close and mix strongly by means of the Coriolis interaction. If we write the eigenstates of the Hamiltonian as $|(E\times F_2)J_f RC\rangle$, where $R = J_f + 1, J, J_f - 1$ for the three Coriolis sublevels of ν_4 and C is a rovibrational symmetry species, then the new body-fixed dipole moment becomes

$$|\langle\mu'_{0,24}\rangle|^2 = |\langle\mu_{0,24}\rangle|^2 f^2_{J_f,RC} \tag{3}$$

where

$$f^2_{J_fRC} = \sum_{C'} |\langle F_2 J_f C' | (E\times F)J_f RC\rangle|^2 \tag{4}$$

is just the sum of squares of expansion coefficients obtained by diagonalizing the Hamiltonian in the F_2 basis. For a given J_f, we have $J_i = J_f+1, J_f, J_f-1$ for the P, Q, R branches and $R = J_f+1, J_f, J_f-1$ for the +,0,- Coriolis sublevels, giving rise to nine possible subbranches as shown in Fig. 1. Each rovibrational state has a different dipole for each subbranch according to Eqs. (3) and (4).

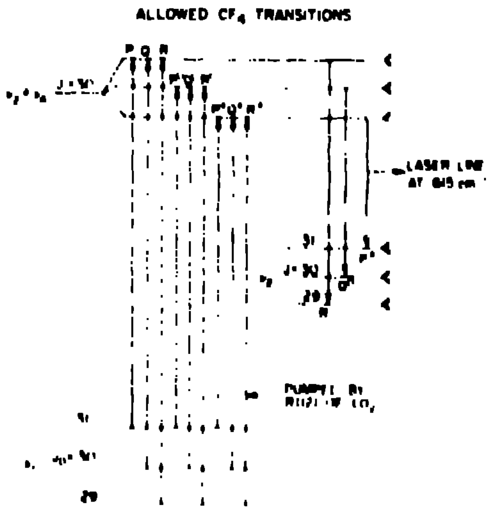

Figure 1. Typical energy level diagram for the CF₄ laser with arrows indicating allowed transitions.

Substituting Eq. (3) into Eq. (2) gives the new space-fixed dipole moment

$$|\langle\mu_{if}\rangle|^2 = \frac{2J_f+1}{3(2J_i+1)} |\langle\mu_{0,24}\rangle|^2 f^2_{J_fRC} \tag{5}$$

In our analysis of the $\nu_2 + \nu_4$ band of $^{12}CF_4$ the line strength dependence on $(2J_f+1)f^2$ was confirmed.

Continuing with our evaluation of the line strength in Eq. (1), the rotational partition function for an XY_4 spherical-top molecule is

$$Z_r = \frac{(2I_Y+1)^4}{12}\sqrt{\pi}\left(\frac{Bhc}{kT}\right)^{-3/2} e^{Bhc/4kT},$$

where I_Y is the nuclear spin of the Y atoms (1/2 for fluorine). The number density per cm³ is $N = N_0(pT_0/p_0T)$, where N_0 is the Loschmidt constant (2.687×10^{19} mol/cm³), $T_0 = 273.15$ K, and $p_0 = 760$ torr. With B = .191688 as determined in Ref. 1, we have from Eq. (1)

$$|\langle\mu_{0,24}\rangle|^2 = \frac{4.059\, T^{5/2} Z_v e^{0.2758(J_i+1/2)^2/T}}{f^2_{J_fRC}\, g_i(2J_f+1)\,\nu_{if}} \frac{S_{if}}{P} \tag{6}$$

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where $\nu_{if} \gg kT/hc$. Here S_{if}/p is in cm^{-2}/torr and $\langle\mu_{0,24}\rangle$ is in Debye (1D = 10^{-18} esu-cm). The vibrational partition function Z_v is calculated using the following frequencies and degeneracies for the fundamentals of $^{12}CF_4$: ν_1 = 909.1(1)[7], ν_2 = 435.4(2)[7], ν_3 = 1283.2(3)[8], ν_4 = 631.2(3)[9].

Vibrational transition moments were calculated from Eq. (6) for two different lines:

1) $^{14}CF_4$, $R^+(25)$ $A_1^3+E^8+F_1^{12}$ (ι_i = 10), ν_{if} = 1068.7 cm^{-1}, f^2 = 0.723 .

These spectra were recorded for a series of pressures at each of two different temperatures. We were forced to use a diode that had seriously degraded resolution (ca. 0.002 cm^{-1}, or well above the Doppler limit), and consequently the spectra could not be analyzed on the basis of a Doppler-broadened contour. Instead, the line areas were estimated by taking the product of the peak absorbance and the half-width (fwhm on an absorbance scale). To account for absorption in the wings of the lines that is not included in this "triangular" approximation, a correction factor of 1.065 was applied (this correction of 6.5% is strictly applicable only to a Gaussian line, but it is not sensitive to the exact line shape assumed and will not significantly affect the results; in any case, the shape of a resolution-degraded line is not known with certainty).

A plot of the measurements of line area as a function of pressure for T = 297 K is shown in Fig. 2. A least-squares fit to the observed points yields a slope of (2.76 ± 0.09) × 10^{-4} cm^{-1} torr^{-1}; dividing by the path length of 120 cm gives S_{if}/p = (2.32 ± 0.08) × 10^{-6} cm^{-2} torr^{-1}. The transition moment obtained from this value and from a similar measurement at T = 163 K are summarized in Table I. The result at T = 297 is considered the more reliable because of pronounced resolution difficulties in the lower-temperature runs.

2) $^{12}CF_4$, $Q^+(20)$ $F_1^5+E^3+F_1^5$ (ι_i = 8),

ν_{if} = 1063.6 cm^{-1}, f^2 = .527.

These spectra were recorded at pressures from 10 to 20 torr. To account for absorption in the wings of this line a Voight lineshape was assumed with a pressure broadening coefficient given below, resulting in a correction factor of about 1.5. Because of the uncertainty of this factor, our estimated error is larger than above.

3) $^{12}CF_4$, $R^+(29)$ $A_1^4+E^9-F_1^{14}$ (ι_i = 10),

ν_{if} = 1073.3 cm^{-1}, f^2 = 0.718.

These data were taken by Radziemski et al. with a tunable CO$_2$ laser. From their original spectra at three different pressures (2.9 to 11.4 torr) and T = 296 K, the peak absorbances and half-widths were determined, and a Lorentzian (pressure-broadened) line shape was assumed, to yield a value for S_{if}/p. The resulting value of $\langle\mu_{0,24}\rangle$ is given in Table I.

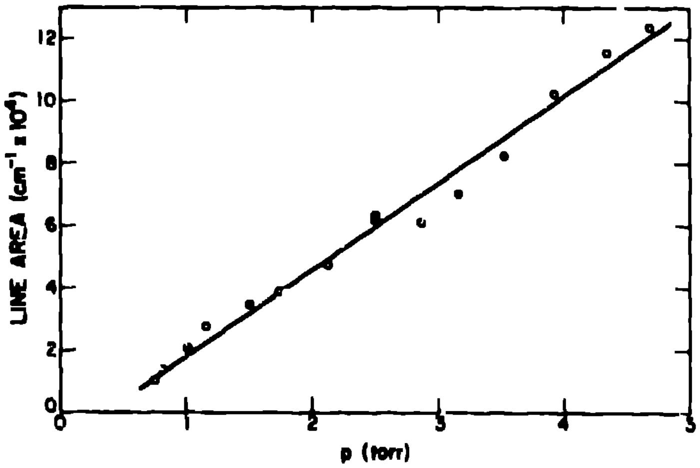

Figure 2. Line area of a $R^+(25)$ pump transition of $^{14}CF_4$ at 297 K vs pressure.

4) There has also been a recent determination of the integrated band strength of $\nu_2 + \nu_4$ of $^{12}CF_4$ by Golden, Marcott, and Overend, who used a low-resolution grating spectrometer and pressure-broadened the CF$_4$. They obtained a strength of 0.80 ± 0.04 km/mole. Since

$$\sum_{Rc} f^2_{J_f Rc} = 1 ,$$

we may use Eqs. (10) and (11) of Fox and Person which relate the band strength S_M to the transition moment of a spherical top fundamental:

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$$\langle\mu_{0,24}\rangle = 0.3647\,(S_M/\nu_{0,24})^{1/2}$$

where $\nu_{0,24}$ is the band origin of $\nu_2 + \nu_4$ at 1066.4 cm^{-1}. From this equation we find $\langle\mu_{0,24}\rangle$ = (0.0100 ± 0.0003)D.

Table I. Vibrational Transition Moment of CF_4, $\nu_2 + \nu_4$.

	Line	T(K)	Z_v	S_{if}/p (cm^{-2} $torr^{-1}$)	$\langle\mu_{0,24}\rangle$ (D)
(1)	$^{14}CF_4$,R^+(25)	297 163	1.53 1.06	2.32(8) x 10^{-6} 7.8(3) x 10^{-6}	0.0099(2) 0.0091(2)
(2)	$^{12}CF_4$,Q^+(20)	294	1.50	1.36(13) x 10^{-6}	0.0102(5)
(3)	$^{12}CF_4$,R^+(29)	296	1.52	2.9(3) x 10^{-6}	0.0113(6)
(4)	Band intensity (Golden *et al.*)	300	--	--	0.0100(3)

The results in Table I are satisfying consistent, despite the very different approaches used in the three studies. We conclude that for $\nu_2 + \nu_4$ transitions in CF_4 $\langle\mu_{0,24}\rangle$ = (0.0100 ± 0.0002)D irrespective of the carbon isotope.

Pressure-Broadening Coefficient

Tunable-diode laser measurements of the self-broadening coefficient C_p were carried out for selected assigned and well-resolved lines in the P^-, Q^+, and R^+ branches of the $^{12}CF_4$ pump band at temperatures of approximately 110, 157, and 294 K and over a pressure range of 0.1 to 41 torr (10 Pa to 5.5 kPa). There was no significant difference in the coefficients for the various lines, and accordingly the data were combined to give the results in Table II. These are consistent with the more precise result of Eckhardt et al., who measured the linewidth of an R^+(29) transition with a tunable CO_2 laser at pressures of 0.5 to 50 torr, and obtained C_p = 11.1 MHz/torr at 150 K.

Table II. Pressure-broadening coefficients and derived optical collision diameters for CF_4 $\nu_2+\nu_4$ lines.

T (K)	C_p (MHz/Torr, fwhm)	σ(Å)[c]
294 ± 1[a]	6 ± 1	7.0 ± 0.6
157 ± 1[a]	8 ± 1	6.9 ± 0.4
110 ± 10[b]	11 ± 1	7.4 ± 0.4

[a] Mean of measurements on four lines of $^{12}CF_4$ belonging to the manifolds P^-(28), Q^+(20), and R^+(21,24) of $\nu_2 + \nu_4$.

[b] Measured for a line in R^+(25) of $^{14}CF_4$.

[c] Weighted mean 7.1 ± 0.3 Å.

The values of Table II yield C_p = $160/T^{([illegible])}$ MHz/torr, which shows the expected $T^{-1/2}$ dependence to within experimental error. Table II also gives the optical collision diameter, σ, calculated from $C_p = \Gamma_p/p$ where Γ_p (fwhm) = $1/\pi\tau$. Here τ is the mean lifetime between collisions: $\tau = 1/Z$ where the collision frequency is

$$Z = \sqrt{2}\,\pi\sigma^2 n\bar{v}, \quad (7)$$

the mean molecular velocity for a Maxwellian distribution is

$$\bar{v} = (8kT/\pi m)^{1/2}, \quad (8)$$

and the molecular density is

$$n = L(273p/760T) \quad (9)$$

(p in Torr, L = Loschmidt constant). The optical collision diameter of 7.1 ± 0.3 Å is to be compared with a gas-kinetic diameter of 4.70 Å obtained from the second virial coefficient, assuming a Lennard-Jones 6-12 potential. The larger optical cross section can be attributed to the many possible relaxation pathways in CF_4 which increase the probability for relaxation by intermediate-range potentials.

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Transition Moments for $\nu_2 + \nu_4 \rightarrow \nu_2$

By measuring the laser self-absorption, one can determine the vibrational dipole moment for the $\nu_2 \rightarrow \nu_2 + \nu_4$ transition. Since the ν_2 and ν_4 vibrations are only weakly coupled for $J_f > 5$, we expect the dipole moment $\langle\mu_{2,24}\rangle$ for the $\nu_2 \rightarrow \nu_2 + \nu_4$ transition to be approximately the dipole moment $\langle\mu_{0,4}\rangle$ for the $\nu_0 \rightarrow \nu_4$ transition. The later has been calculated by Fox and Person[5] based on averaged band strength measurements of Saeki *et al.*[16] and Levin and Lewis[17]:

$$\langle\mu_{2,24}\rangle \approx \langle\mu_{0,4}\rangle = .052 \text{ D} . \tag{10}$$

We assume that for $\nu_2 \rightarrow \nu_2 + \nu_4$ transitions the rovibrational dipole moment is

$$\langle\mu_{if}\rangle^2 = \frac{2J_f+1}{3(2J_i+1)} \langle\mu_{0,4}\rangle^2 . \tag{11}$$

We can now calculate line strengths in $\nu_2 \rightarrow \nu_2 + \nu_4$. First we must modify Eq. (1) so that it applies to a hot-band transition. We recall that the basic equation for the strength of a transition from state i to state f is

$$S = \frac{h\nu}{c} [B_{if}N_i - B_{fi}N_f] ,$$

where B_{if} and B_{fi} are the Einstein coefficients of absorption and induced emission, respectively, and N_i and N_f are the numbers of molecules in the two states. Now $N_i = Ng_i\exp(-E_i/kT)/Z$, and similarly for N_f, where g_i and g_f are the degeneracies of the two states. Since $B_{fi} = (g_i/g_f)\, B_{if}$ and $E_f - E_i = h\nu$, we have

$$S = \frac{h\nu N}{cZ} g_i\, B_{if}\, e^{-E_i/kT}(1-e^{-hc\nu/kT}) .$$

If state i is the vibrational ground state, then g_i is the rotational degeneracy [illegible]$_i(2J_i+1)$ and E_i is just the rotational energy; substituting B_{if} = [illegible] yields Eq. (1). For a rovibrational transition from ν_4, g_i = [illegible]$_i(2J+1)$ and $E_i = (hc\nu_4)$ + rotational energy, so the factor $\exp(-hc\nu_4/kT)$ must be added to the right hand side of Eq. (1). Making this change, we calculate the following line strengths for the $\nu_2 \rightarrow \nu_2 + \nu_4$ P(31) A_1 [illegible] F_1 transition of $^{12}CF_4$ (see Fig. 1) [ν = 615 cm^{-1}, [illegible]$_i$ = 10]:

$$S/p = \begin{cases} 1.27 \times 10^{-6} \text{ cm}^{-2}/\text{torr at } 130 \text{ K} \\ 4.88 \times 10^{-6} \text{ cm}^{-2}/\text{torr at } 300 \text{ K} \end{cases} . \tag{12}$$

From Eqs. (7)-(9) we find the peak absorption of $R^{4}(29)$ laser radiation for high pressures and a 200 cm path length is

$$\ln \frac{I_0}{I} = \alpha_0\,(200) = \begin{cases} .5 \text{ at } 130 \text{ K} \\ 1.9 \text{ at } 300 \text{ K} \end{cases} \tag{13}$$

At intermediate pressures the peak height is determined by a Voight profile when the pressure width is convoluted with the Doppler width. In Fig. 3 we compare the measured laser self-absorption of Eckhart, Hinsley, Piltch, and Rockwood[18] with our calculated Voight peak heights at 130 K and 300 K. Note that the calculated absorptions asymptotically approach the values given in Eq. (13) at high pressures.

There are a number of reasons for the discrepancies between the measured and calculated values. At low pressures the mode hopping of the CO$_2$ results in an oscillator gain off line center with a reduction in absorption. At higher pressures this effect is not as important since the line is broadened, and there will also be absorption from the tails of nearby lines. As a result, for high pressure the absorption is not constant but increases linearly with pressure.

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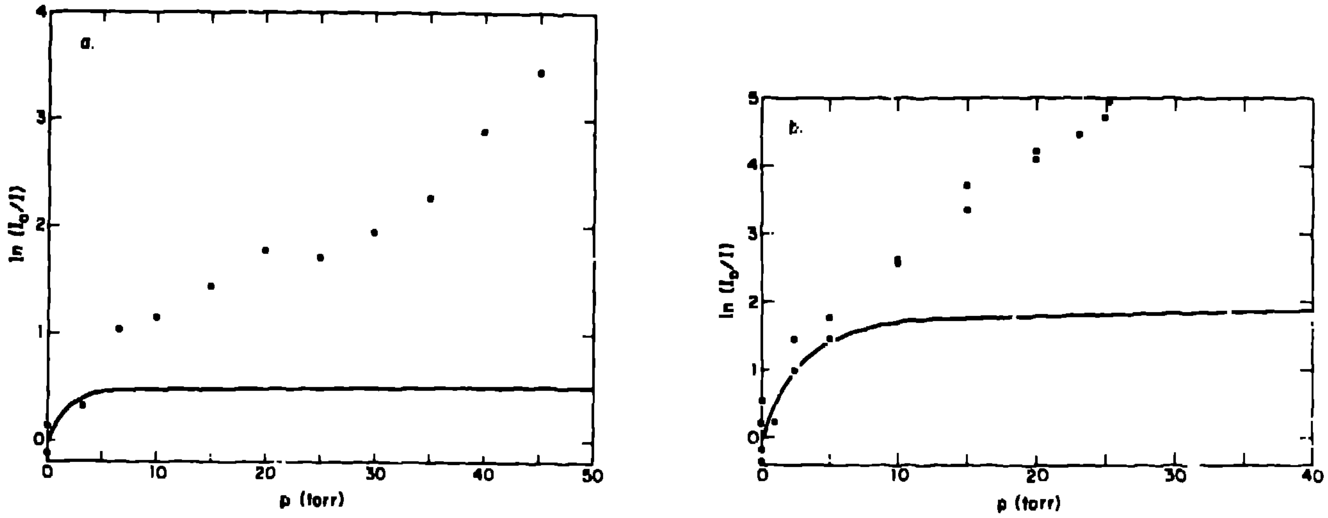

Figure 3. Peak absorption of the ^{1}[illegible]CF$_4$ laser line at 615 cm^{-1} vs pressure for a 200 cm path at a) 130 K and b) 300 K.

In Fig. 4 we show the spectrum of ^{1}[illegible]CF$_4$ near the 615 cm^{-1} laser line with the P(31) [illegible] ground state and [illegible] + [illegible] hot band transitions identified.[illegible] The laser emission line P(31) F_1^{1} + E^{1} + A_1^{1} at 615.030 has an unidentified shoulder which contributes substantially to the absorption of laser radiation seen in Figs. 3. This shoulder and the effects of the nearby tails account for the discrepancy between the calculated and observed laser absorption in Figs. 3.

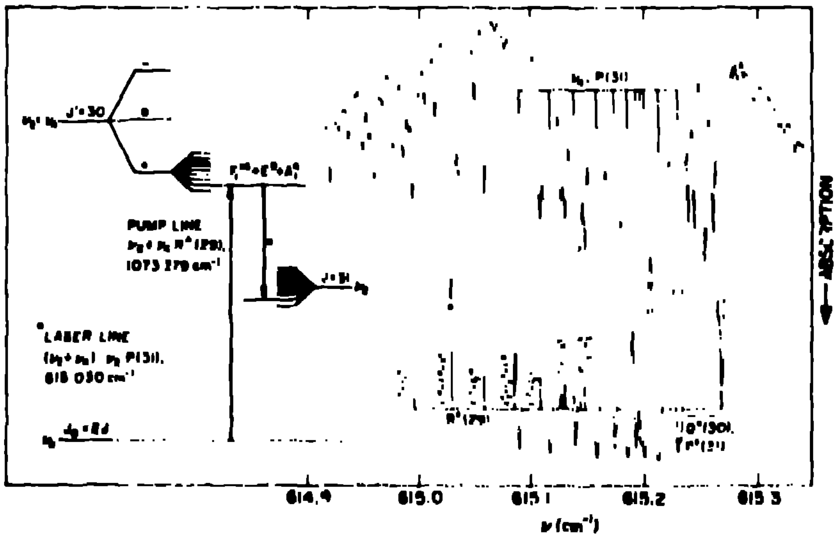

Figure 4. The upper "comb" indicates the strong [illegible] P(31) lines; the lower comb designates the transitions of ([illegible] + [illegible]) [illegible] P(31) with those components accessible by pumping R^{0}(29) of [illegible] explicitly identified. The schematic to the left shows the origin of the 615 cm^{-1} laser line, indicated by a star.

The spectrum in Fig. 4 was recorded at pressures of 1 to 10 torr. Since the P(31) F_1^{1} + F_2^{1} line at 615.059 is relatively isolated, it was used to determine the [illegible] + [illegible] [illegible] dipole moment. From the line area and pressure we determined the dipole moment to be [illegible] = 0.0565 ± 0.006 D. Because of the large error in this measured dipole moment we shall continue to assume [illegible] = [illegible] 0.52 D.

Since the dipole moments for all laser transitions are known, we are now in a position to estimate gain.

CF$_4$ Laser Gain

Let α_p be the absorption coefficient for the CO$_2$ 9R12 line at 1073 cm^{-1} and α_g be the gain at 615 cm^{-1}. If we assume the pump pulse varies little in the collisional period (4 ns at 6 torr) and the pressure width is greater than the inhomogeneous Doppler width, we may use the formula for gain at line center given by Panock and Temkin[illegible]

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$$\alpha_s = |\alpha_p| \frac{\langle\mu_{2,24}\rangle^2}{f^2\langle\mu_{0,24}\rangle^2} \frac{615}{1073} \frac{3\Omega^2/\gamma_p^2}{(1+4\Omega^2/\gamma_p^2)(1+\Omega^2/\gamma_p^2)} \qquad (14)$$

where Ω is the Rabi frequency of the pump given by

$$\Omega(\mathrm{cm}^{-1}) = 4.6 \times 10^{14} \langle\mu_{if}\rangle \sqrt{I} .$$

Here I is the pump intensity in W/cm² and

$$\langle\mu_{if}\rangle = \frac{2J_f+1}{3(2J_i+1)} \langle\mu_{0,24}\rangle^f$$

$$= 4.9 \times 10^{-21} \text{ esu-cm for } R^+(29)\ F_1^{14}+E^9+A_1^4$$

Using the CO_2 power given by Eckhardt, et al.[12] of 1.3 MW/cm² we find

$$\Omega = 2.6 \times 10^{-3} \mathrm{cm}^{-1}$$

Substituting this into Eq. (14), we find that at 5 torr and 130 K α_s = .082 cm^{-1} in contrast to their measured value of .035 cm^{-1}. Actually the maximum gain occurs at lower power when the $\nu_2 + \nu_4$ level is not Stark-split. The maximum possible gain occurs when $\Omega^2/\gamma_p^2 = 1/2$ in which case α_s = .11 cm^{-1}.

The discrepancy between the calculated gain and the measured gain could be explained by the fact that the CO_2 laser is not stable and is not always on line center of the $\nu_2 + \nu_4$ absorption feature. From Fig. 4 we see that the shoulder near the P(31) $F_1^{14}+E^9+A_1^4$ transition could account for an absorption of α = .5/200 cm = .0025 cm^{-1} at 5 torr and 130 K which should be insignificant compared to the laser gain.

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