Short Papers

Assignments of Optically Pumped Laser Lines of 1,1-Difluoroethylene

G. DUXBURY, T. J. GAMBLE, AND H. HERMAN

Abstract—**The submillimeter laser transitions of CF_2CH_2 have been assigned to pure rotation transitions in the ν_9, ν_4, and $\nu_5 + \nu_{10}$ vibrational states using results from laser Stark spectroscopy.**

I. INTRODUCTION

Submillimeter laser action has been obtained from 1,1 difluorethylene, CF_2CH_2, at a variety of wavelengths between 0.289 and 1.02 mm by Dyubko *et al.* [1], and by Hodges *et al.* [2]. However, the rotational transitions observed were not identified. The near coincidences between the pumping CO_2 lines and the absorption lines of CF_2CH_2 are mainly with lines of the two fundamental vibration–rotation bands of CF_2CH_2 which lie in this region, although there is a possibility that at least one near coincidence is with a vibration–rotation transition of a weak combination band which has its origin around 980 cm^{-1}. The two fundamentals are the A_1 symmetric CF stretch ν_4, at 926 cm^{-1}, and the B_1 in plane CH_2 rock ν_9, at 955 cm^{-1}. We have used three criteria to aid the assignment of the lines, the observed absorption of the P branch of the 10.6-μm CO_2 band by CF_2CH_2, the relationship between the vibration–rotation and the pure rotation lines which leads to an estimate of the band origin associated with the absorbing transition, and laser Stark spectroscopy of most of the coincidences and near coincidences in this band.

II. EXPERIMENTAL

The Stark spectrometer used for this work is based on those described by Freund *et al.* [3] and McKellar and Johns [4]. The CO_2 laser used has a 2-m cavity and is tuned using an original diffraction grating. The Stark cell has a length of 50 cm and a plate spacing of 0.9959 mm, which was determined by using the fields measured in the precise studies of methyl fluorides by Freund *et al.* [3]. The sinusoidal modulation of the field was at 5 kHz and the amplitude used was between 5 and 10 V peak to peak. Liquid nitrogen cooled Pb/Sn/Te detectors were used for these experiments.

III. RESULTS

The absorption experiments showed that almost all the P branch lines of the 10.4-μm CO_2 laser from $P4$ to $P40$ are strongly absorbed by CF_2CH_2, with particularly strong absorption in the region of $P22$ and $P30$. $P16$ is the only line showing only a small amount of absorption at a gas pressure of c.a. 5 torr.

The selection rules for the A_1 926-cm^{-1} band are the same as for pure rotation transitions $\Delta K_a = 0, (\pm 2)$, $\Delta K_c = \pm 1, (\pm 3)$. If one assumes that the pure rotation transitions are R-type transitions, and that in general the vibration–rotation transitions are R type or P type, the pure rotation transition frequencies can be added to or subtracted from the laser line frequencies to predict the band origins. Allowance must be made for the small differences in rotational constants between the states. The 955-cm^{-1} B_1 band is also a perpendicular band of a near oblate symmetric top, but the transitions take place to opposite asymmetry doublets, $\Delta K_a = \pm 1$, $\Delta K_c = \pm 1$, and so estimates made using the preceding method are a little more approximate.

Shimizu [5] has shown the power of the laser Stark technique in his extensive studies of $^{14}NH_3$ as his results have allowed many of the optically pumped laser lines of NH_3 to be identified. Similar studied of CH_3F have been carried out by Freund *et al.* [3]. The Stark experiments we have carried out have allowed us to discover many coincidences and near coincidences which all have characteristic patterns, and to verify the conclusions drawn from the absorption experiments that there are many more near coincidences than those for which laser action has been observed. An almost exact coincidence with $P(30)$ is shown in Fig. 1 and a low field coincidence with $P(38)$ in Fig. 2. Although some Stark experiments have been carried out previously on CF_2CH_2 by Hall *et al.* [6] and by Hall and Pao [7], no electric field spectra have been published previously for this molecule, and no systematic search appears to have been undertaken. Although CF_2CH_2 is a near oblate top, the permanent dipole moment lies along the least axis of inertia, the a axis. Consequently, since the Stark experiments tend to pick out the transitions with a fast, almost first order, Stark effect, only a few transitions are strongly field dependent. These "prolate" transitions have $J \simeq K_a$ and the dipole moment matrix element responsible for the near first order Stark effect couples the two halves of the prolate asymmetry doublet. For a given value of K_a, as J increases the asymmetry doubling rapidly increases as the switch over to oblate behavior occurs, and the Stark effect changes to a small second order one. Thus the Stark experiments only pick out a few of the many absorption lines close to the laser, and only coincidences within the Doppler width can be seen with the much smaller second order effect. N_2O laser lines have also been used to assist the low J assignments. Recently, Martin *et al.* [8] have observed the absorption spectrum at the $P(18)$ CO_2 laser line using their tunable laser spectrometer, and have commented on the poor amount of Stark modulation obtainable using this line. Unfortunately the line which they have chosen to study has almost the weakest absorption of all the CO_2 laser lines by CF_2CH_2. Whereas in the papers by Hall *et al.* [6] and Hall and Pao [7] which report the use of CH_2CF_2 as a modulator, the lines used for modulation include $P(22)$ which we have observed to have a very strong easily modulated zero field absorption line.

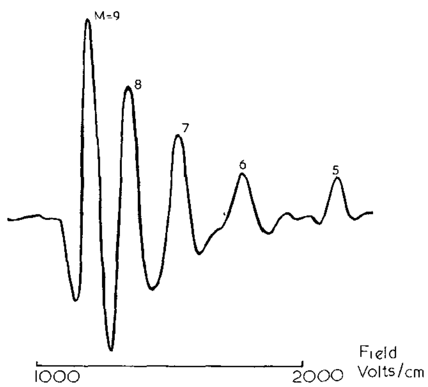

Fig. 1. Observed $\Delta M = 0$ transitions for the near coincidence between a Q branch CF_2CH_2 line and $P38$ of the 10.4-μm band of the CO_2 laser. Second derivative presentation is used. The sample pressure was about 100 μm and the time constant 3 s.

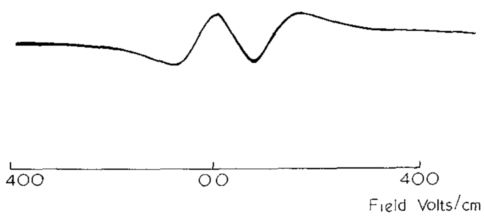

Fig. 2. Observed $\Delta M = 0$ transitions of the "zero-field" coincidence between a CF_2CH_2 line, and $P30$ of the 10.4-μm band of the CO_2 laser. First derivative presentation is used. The sample pressure was about 100 μm and the time constant 3 s.

Manuscript received May 6, 1974.
The authors are with the School of Chemistry, University of Bristol, Bristol, England.

Since CF_2CH_2 is a near oblate top, $A \simeq B \simeq 2C$, the subband spacing in the perpendicular A_1 and B_1 bands is approximately equal to twice the line spacing in the ${}^{P}P$ and ${}^{R}R$ branches. Lines in the ${}^{P}P$ and ${}^{R}R$ branches of the pure rotation spectrum therefore superimpose to give a regular fine structure. Rotational transitions with $K_c = J$ contribute the greatest intensity to the observed lines. We have therefore labeled each multiple transition (in Table I) by the limiting value of $J = K_c$, e.g., $J = 15$, $K_c = 0$, $\nu = 11.259$ cm^{-1}, $J = 30$, $K_c = 30$, $\nu = 11.228$ cm^{-1}, i.e., 16 transitions lie within 0.031 cm^{-1}. The measurement accuracy of the observed transitions is insufficient to allow a more specific assignment than that just given. Some of the lines which possess easily identifiable patterns have not as yet been used as laser sources. However, by the application of low tuning fields it can be seen, as shown in Table II, that many more millimeter lines of known pure rotation transitions can be generated than by relying on chance coincidences. This type of electric field tuned laser action has recently been demonstrated by Fetterman *et al.* [9] using several lines of NH_3. Since much lower fields are required for CF_2CH_2 than for most of the NH_3 lines it is possible that, by a combination of the zero field lines that have already been observed with electric field produced lines, a very wide frequency coverage will be available using one gas CF_2CH_2.

TABLE I
ASSIGNMENT OF LASER LINES

CO_2 line	CO_2 λμm	Type of zero Field coincidence	Absorbing transition		CF_2H_2 laser emission λμm	CF_2CH_2 laser assignment	Ref
P12	10.5131	strong	$\nu_5 + \nu_{10}$	P(97)	288.5	$J = K_c = 96$	a
P12			ν_4	R(73)	375.0	$J = K_c = 73$	a
P12			ν_9	Q	884	$J = K_c = 30$	b
			ν_4	R	415	$J = K_c = 66$	b
P14	10.5321	weak	ν_4?	R	554.4	$J = K_c = 49$	a
			ν_9	Q	1020	$J = K_c = 26$	b
P22	10.6114	very strong	ν_9	P	890.0	$J = K_c = 30$	a
P22			ν_9	P	890.1	$J = K_c = 30$	a
P22			ν_9	P	990.0	$J = K_c = 27$	a
P24	10.6321	weak	ν_4	R	568.0	$J = K_c = 48$	b
P24			ν_9	P	663.3	$J = K_c = 41$	a
P30	10.6964	very strong	ν_9	P(61)	458.0	$J = K_c = 60$	a
R20	10.2466	weak	ν_9	R(59)	464.3	$J = K_c = 59$	a

a [1].
b [2].

TABLE II
ZERO FIELD COINCIDENCES AND POSSIBLE ZERO AND LOW ELECTRIC FIELD LASER TRANSITIONS

CO_2 line	CO_2 λμm	Type of zero field coincidence	Assigned low field line		Resonant field for pumping kV/cm	Possible laser transition J'-J"	Possible λmm
P_4	10.4406	medium					
P_6	10.4582	medium					
P_8	10.4762	strong	${}^{R}Q9$	ν_9	1.14	9 - 8	1.39
			${}^{R}Q6$	ν_9	3.33	6 - 5	1.96
P10	10.4945	strong	${}^{P}Q9$	ν_9	1.19	9 - 8	1.80
			${}^{P}Q11$	ν_9	2.14	11 - 10	1.44
			${}^{P}Q13$	ν_9	3.76	13 - 12	1.19
P20	10.5910	weak			zero		0.93
P36	10.7641	weak			zero		2.51
P38	10.7874	medium	${}^{S}Q9$	ν_4	1.16	9 - 8	1.39
P40	10.8111	medium	${}^{Q}Q9$	ν_4	0.07	9 - 8	1.35

IV. CONCLUSIONS

The main conclusions that we have drawn from this study are the following.

1) That the lines observed have high J values, and in many cases the pump lines belong to the band whose center is furthest from the laser line.

2) That it should be possible using electric field tuning and less lossy cavities to observe many more strong laser lines in the 0.5–3-mm region.

REFERENCES

[1] S. F. Dyubko, V. A. Svich, and L. D. Fesenko, "Submillimeter-band gas laser pumped by a CO_2 laser," *JETP Lett.*, vol. 16, pp. 418–419, Dec. 1972.

[2] D. T. Hodges, R. D. Reel, and D. H. Barker, "Low-threshold CW submillimeter- and millimeter-wave laser action in CO_2-laser-pumped $C_2H_4F_2$, $C_2H_2F_2$ and CH_3OH," *IEEE J. Quantum Electron.* (Notes and Lines), vol. QE-9, pp. 1159–1160, Dec. 1973.

[3] S. M. Freund *et al.*, "Laser Stark spectroscopy in the 10 μm region: the ν_3 bands of CH_3F," *J. Mol. Spectrosc.*, to be published.

[4] J. W. C. Johns and A. R. W. McKellar, "Stark spectroscopy with the CO laser: The ν_2 fundamentals of H_2CO and D_2CO," *J. Mol. Spectrosc.*, vol. 48, pp. 354–371, Oct. 1973.

[5] F. Shimizu, "Stark spectroscopy of NH_3 ν_2 band by 10μ CO_2 and N_2O lasers," *J. Chem. Phys.*, vol. 52, pp. 3572–3576, Apr. 1970.

[6] D. R. Hall, Y. H. Pao, and P. C. Claspy, "Stark effect modulation of a passively Q-switched CO_2 laser," *Appl. Opt.*, vol 10, pp. 1688–1689, July 1971.

[7] D. R. Hall and Y.-H. Pao, "High-efficiency driven Q switching of the CO_2 laser using the Stark effect in molecular gases," *IEEE J. Quantum Electron.* (Corresp.), vol. QE-7, pp. 427–429, Aug. 1971.

[8] J. M. Martin, V. J. Corcoran, and W. T. Smith, "Identification of absorption lines in gases used to modulate the CO_2 laser," *IEEE J. Quantum Electron.* (*Special Issue on 1973 IEEE/OSA Conference on Laser Engineering and Applications, Part II of Two Parts*), vol. QE-10, pp. 191–195, Feb. 1974.

[9] H. R. Fetterman, H. R. Schlossberg, and C. D. Parker, "C.W. submillimeter laser generation in optically pumped Stark tuned NH_3," *Appl. Phys. Lett.*, vol. 20, pp. 684–686, Dec. 1973.

Plasma Modulation of an HCN Gas Laser

G. D. TAIT, L. C. ROBINSON, AND D. V. BARTLETT

***Abstract*—A transient plasma is located within the Fabry–Perot resonator of a dc hydrogen cyanide laser. Plasma tuning sweeps the resonator modes through the emission line of the HCN molecules and produces pulses of far-infrared output radiation. Pulse production by hydrogen, nitrogen, helium, and argon pulsed plasmas is discussed.**

I. INTRODUCTION

The electrical discharge of a hydrogen cyanide gas laser produces molecules in a state of population inversion and, in addition, a plasma of positive ions and free electrons. When the discharge is pulsed the plasma electron density varies with time, its spatial distribution changes, and the nature of the laser radiation is markedly affected. In particular, "spikes" of submillimeter radiation can be produced [1].

In the experiment to be described in this short paper we have separated the effects of the transient plasma from the processes of HCN molecule formation and population inversion by using two physically separate discharges both located within the Fabry–Perot laser resonator. One is a dc discharge through a mixture of nitrogen and methane and the other is a pulsed discharge through a different gas.

Manuscript received June 5, 1974.
The authors are with the School of Physics, University of Sydney, Sydney, Australia.