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Spectroscopic Investigation of Foreign Gas Effects upon CO_2 Laser Frequencies

Isao SUZUKI* and Shigeko SUZUKI**

* *Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo*
** *Department of Pure and Applied Sciences, College of General Education, The University of Tokyo, Komaba, Meguro-ku, Tokyo*

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The change in the oscillation frequencies of a CO_2 laser was examined when foreign gases were introduced into a cell placed inside the cavity. Several gases which have absorption bands around 10 μ region were investigated: sulfur hexafluoride, ammonia, ethylene, *trans*-dichloroethylene, methyl bromide, trichloroethylene, acrolein, and isopropyl alcohol. The CW laser oscillations in the P-branch of the 9.6 μ band as well as those in the R-branch of the 10.6 μ band were observed when some foreign gases with appropriate pressures were introduced in the cavity. It was also found that the presence of ammonia or methyl bromide even in a very low pressure suppressed the usually strong P(20) line of the 10.6 μ band. This is interpreted as due to a near coincidence of the laser line with one of the vibration-rotation transitions in these molecules.

Under ordinary CW operating conditions in a CO_2 laser, the laser action occurs on a few P-branch transitions of the 10.6 μ band of CO_2. Wood and Schwartz[1] reported that introduction of sulfur hexafluoride gas to a cell placed within the cavity causes the laser frequencies to shift to a few R-branch transitions. Similar phenomena occur in a wide variety of organic and inorganic gases,[2] and the oscillation frequencies are very sensitive to the pressures of given gases. We have also observed the CW laser action in a few P-branch lines of 9.6 μ band, a Fermi resonance partner of the 10.6 μ band. In the present paper, we describe the results of our spectroscopic investigation on the effect of foreign gases, which have some absorptions around the 10 μ region on a CO_2 laser system.

Experimental

The diagram for experimental setting is shown in Fig. 1. A mixture of CO_2 (9.9%), N_2 (15.8%) and He (74.3 %) with the total pressure of 8 mmHg was sealed in a pyrex tube of 1.2 m in length and inner diameter of 30 mm. The tube was cooled with water. The tube had a concave mirror of radius 3.5 m at one end and a potassium chloride plate at the other end. A 10 cm infrared gas cell with KCl windows was placed adjacent to the pyrex tube (see Fig. 1 (a)). The laser cavity was completed with a plane mirror with a 2 mm diameter hole in the center, through which the laser beam was coupled out. Both mirrors were aluminized. The gas mixture was excited by an ac-discharge at a current of 8 mA. The laser beam was scattered with a diffuse reflector, and a part of the emission radiation was introduced to the entrance slit of a spectrophotometer. With the evacuated cell placed inside the cavity, four or five lines distributed around the P(20) transition were normally observed. We have also examined a flow system, but no essential change was observed. In order to minimize the thermal extension effect of the pyrex tube due to discharge, the measurements were made after a certain equilibrium had been reached in the cavity length.

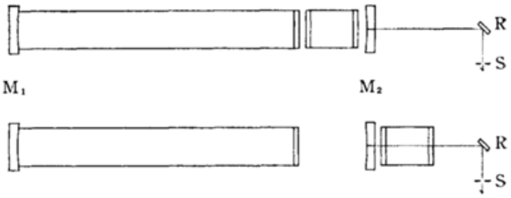

Fig. 1. Diagram for experimental setting: (a) an infrared gas cell was placed inside the cavity, and (b) the cell was placed just outside the cavity. M_1: Concave mirror (R=3.5 m), M_2: plane mirror with a 2 mm diameter hole in the center, R: reflector, and S: slit of the spectrophotometer.

We used a Perkin-Elmer 112G grating spectrophotometer with a KBr foreprism.[3] The 9—11 μ region was covered with the first order of a 75/mm grating. The gases which have absorption bands around 10 μ region were chosen. They are listed in Table 1 with the relevant absorption center and the approximate vibrational mode for each gas. We have also examined

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[1] O. R. Wood and S. E. Schwartz, *Appl. Phys. Letters*, **11**, 88 (1967).

[2] I. Suzuki and S. Suzuki, This Bulletin, **41**, 2549 (1968).

[3] S. Mizushima *et al.*, A Report on the Perkin-Elmer Grating Spectrophotometer Model 112G. The Perkiln-Elmer Corp. (1959).

TABLE 1. THE GASES EXAMINED IN THE PRESENT STUDY WITH THE RELEVANT BAND CENTERS AND THEIR APPROXIMATE NORMAL MODES

		Band center		Approximate normal mode
(a)	NH_3	$\nu_2{}^a(a_1)$ $\nu_2{}^s(a_1)$	968.3 cm^{-1} 932.5 cm^{-1}	NH_3 deformation
(b)	CH_2=CH_2	$\nu_7(b_{1u})$	949.2 cm^{-1}	CH_2 wagging
(c)	SF_6	$\nu_3(f_{1u})$	940 cm^{-1}	SF deg. stretching
(d)	CHCl=CHCl (*trans*)	$\nu_6(a_u)$	898 cm^{-1}	CH out-of-plane bending
(e)	CH_3Br	$\nu_6(e)$	953.8 cm^{-1}	CH_3 rocking
(f)	CHCl=CCl_2	$\nu_{10}(a'')$	940 cm^{-1}	CH out-of-plane bending
(g)	CH_2=CHCHO	$\nu_{14}(a'')$ $\nu_{16}(a'')$	993 cm^{-1} 959 cm^{-1}	CH_2 wagging CH out-of-plane bending
(h)	$(CH_3)_2$CHOH	$\nu_{17}(a'')$	953 cm^{-1}	CH_2 rocking

(a)—(g) Taken from the table of fundamental frequencies in the ground electronic states in G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand, New York (1966), p. 583.

(h) C. Tanaka, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **83**, 657 (1962).

some liquids. In this case, liquid cells with thickness 1.0 mm and 0.1 mm with NaCl windows were used in place of the 10 cm gas cell.

Results and Discussion

The results of our present investigation are summarized in Table 2, in which the observed laser transitions for each foreign gas at various pressures are listed. With foreign gas present within the cavity, the laser output is usually distributed among several vibration-rotation transitions in one branch. However, under certain conditions simultaneous transitions in two branches are observed. The laser oscillations are usually too unstable, probably due to the competition effect among various vibration-rotation transitions, to allow quantitative measurements, but they are listed in Table 2 in approximate order of their intensities.[4] As in Table 2, a primed P hereafter refers to the P-branch transitions of the 9.6 μ band, while unprimed P and R refer, respectively, to the P- and R-branch transitions of the 10.6 μ band.

In most cases, their effects can be interpreted simply from the absorbances of given foreign gases in this region. Good examples are sulfur hexafluoride and *trans*-dichloroethylene: Both absorb strongly in the P-branch region of the 10.6 μ band, much less strongly in the R-branch region, and they have practically no absorptions in the P′-branch region. This explains rather remarkable changes in their oscillation frequencies with the gas pressures. This interpretation seems to hold for the case of liquids also, when a liquid sample was placed inside the cavity instead of gas. The results for several liquid samples are summarized in Table 3.

However, ammonia and methyl bromide seem to be exceptions. In Fig. 2(a), we show the absorption spectrum of 85 mmHg ammonia in a 10 cm cell superimposed with the emission lines of the CO_2 laser when the same cell was placed within the cavity, while in Fig. 2(b) similar spectra for the P-branch region are shown when the pressures of ammonia was reduced to 20 mmHg. No R-branch transitions were observed in the latter case. We note that the usually strong P(20) line was completely missing from the emission spectrum when ammonia was introduced into the cavity, whereas no strong absorption seems to be present at the corresponding frequency. We have shown in Fig. 2(c), the emission spectrum when the same cell containing 20 mmHg NH_3 was placed just outside the cavity (see Fig. 1(b)). The emission spectrum was almost unaffected by the presence of the outside cell.

As may be seen in Fig. 3 and Table 2(e), a similar effect was found when methyl bromide gas was introduced into the cavity. In this case the usually strong P(20) and P(22) lines are missing from the emission spectrum.[5] Even when the pressure of CH_3Br was reduced to 3 mmHg, the P(20) line was the weakest among the transitions in the P-branch region, which is rather unusual.

The results with ammonia and methyl bromide may be related with a near coincidence of the laser line with one of vibration-rotation transitions of a foreign gas. Recently, Ronn and Lide have investigated an infrared-microwave double resonance of methyl bromide using a CO_2 laser.[6] They

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[4] When the laser oscillations occur simultaneously among the lines in two branches, the laser action seems to become very unstable. A number of other weaker lines than those listed in Table 2 appear spasmodically in such cases.

[5] The absence of the P(22)line may be explained from the fact that the line is located close to the fairly strong ${}^PQ_2$ line of CH_3Br: the P(22) line is at 942.54 cm^{-1} and the ${}^PQ_2$ is reported to locate at 942.25 cm^{-1}. E. W. Jones, R. I. L. Popplwell and H. W. Thompson, *Spectrochim. Acta*, **22**, 647 (1966).

[6] A. M. Ronn and D. R. Lide, Jr., *J. Chem. Phys.*, **47**, 3669 (1967).

TABLE 2. THE EFFECT OF FOREIGN GASES ON THE OSCILLATIONS OF CO_2 LASER[a,b]

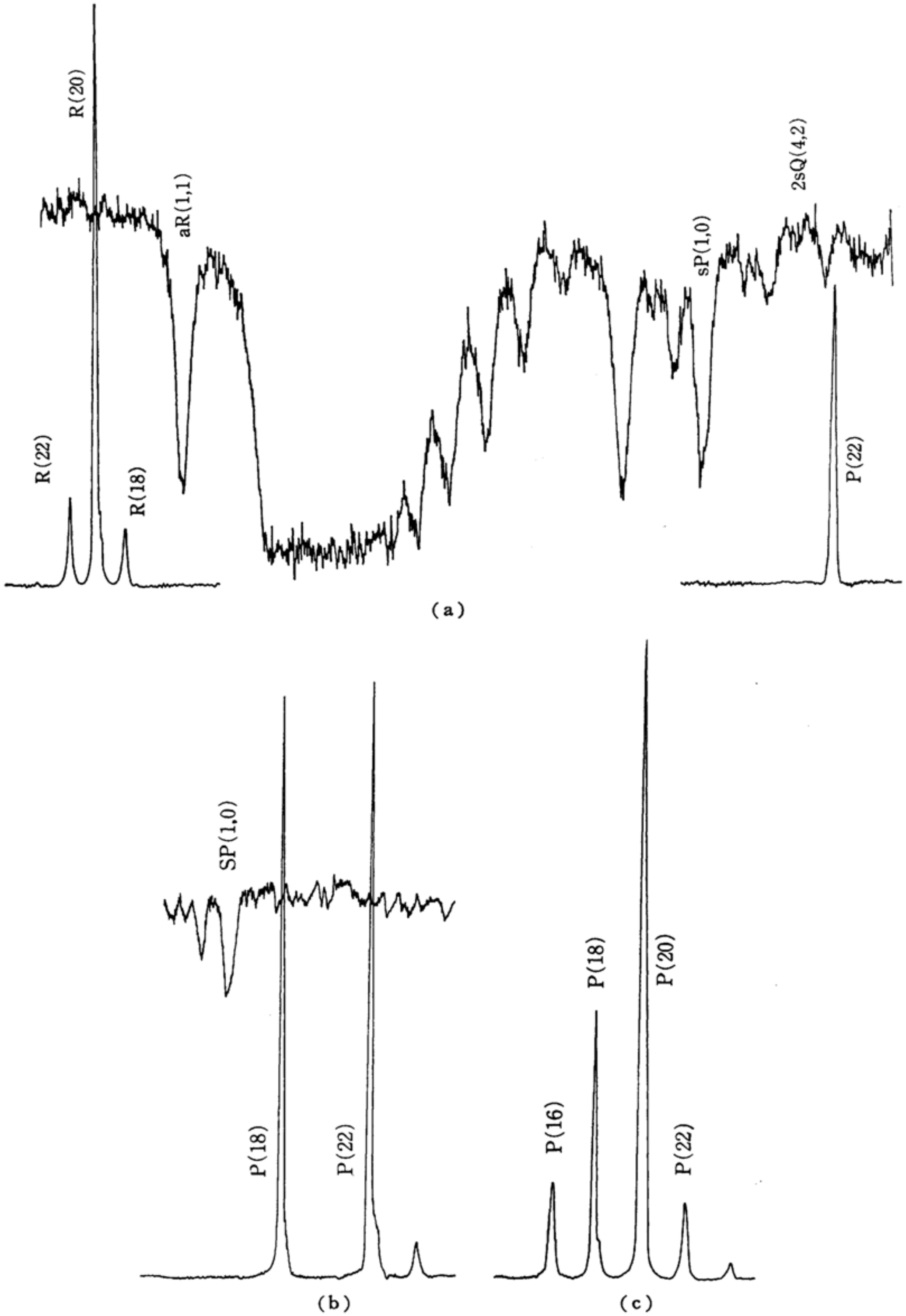
Pressure (mmHg)	P-branch	R-branh	P′-branch[d]
(a) NH_3			
170		20, 22.	
100		20, 22, 18.	
85	22.	20, 22, 18.	
50	22, 18.	20, 22, 18.	
30	22, 18.		
20	22, 18, 24, 16.		
10	22, 18, 24, 16.		
7	22, 18, 20.		
5	20, 22, 18.		
3	20, 22, 18.		
(b) CH_2=CH_2			
50		18.	
40		18.	20.
25		18.	
10		18, 20, 16.	
8		18, 20, 14.	
5	20.	18, 14, 16, 20.	
4	20, 18, 24.	20, 16.	
2	20, 18, 24.		
(c) SF_6			
20			20, 22, 24, 18, 26, 16, 14.
13			20, 22, 24, 18, 16.
8			20, 22, 24, 18, 16,
5.3		16, 18, 14.	18, 20, 22.
3.3		16, 18, 14, 20.	22, 20, 18.
2.4		16, 14, 18, 12, 20.	22, 20, 18, 16.
1.4		16, 18, 12.	
0.8		16, 18, 14, 20, 12.	
0.5		18, 20, 16.	
0.1_7		20, 18, 16. 12.	
0.0_3	20, 18, 22.	18.	
(d) CHCl=CHCl (*trans*)			
110[c]			18, 20, 16, 22.
85			18, 20, 16, 22.
30		20.	18, 20, 22. 22.
20		20, 16.	18, 20, 16, 22.
10		24, 20, 16, 14.	18.
5	20, 18.	20, 18, 16.	
2.5	20, 18.	18, 14.	
1	20, 18, 22.	14, 22.	
(e) CH_3Br			
100			20.
60	18, 24.		20, 18.
30	16, 18, 24, 26.		
18	16, 18, 24, 26.		
3	16, 18, 24, 26, 20.		
1	16, 18, 24, 26, 20.		
0.5	20, 18, 22, 16, 24.		
(f) CHCl=CCl_2			
41[c]		14, 18, 20.	20, 22, 18, 16.
20		18, 14, 16.	16.
9		16, 18, 20, 12.	20.
3.5		14, 16, 18.	
1		20, 18, 14, 16.	
(g) CH_2=CHCHO			
55[c]			22.
13			20, 16.
7			20, 16.
3		16.	
(h) $(CH_3)_2CHOH$			
7		18, 20.	
3		22.	
1	20.	22, 20.	

a) In each branch, the emission lines are arranged in the approximate order of their intensities, which have been determined from the average of several runs.

b) Extremely weak or unstable emission lines are omitted from the table.

c) Gas pressures are only approximate owing to the adsorption of the gas to the wall.

d) P′ refers to the P-branch transitions of the 9.6 micron band.



(a)

(b)

(c)

Fig. 2. Absorption spectrum of NH_3 (10 cm cell, spectral slit width 0.5 cm^{-1}) superimposed with emission lines from the CO_2 laser when the same cell was placed inside the cavity. (a) 85 mmHg NH_3. (b) 20 mmHg NH_3. (c) 20 mmHg NH_3, the cell was placed just outside the cavity (see Fig. 1 (b)). The positions of the laser lines are as follows: 947.80, 946.00, 944.19 and 942.35 cm^{-1} for P(16) through P(22), and 974.57, 975.84 and 977.20 cm^{-1} for R(18) to R(22). The sP(1, 0) and aR(1, 1) bands in ammonia were found at 948.27 and 971.90 cm^{-1}, respectively.

TABLE 3. THE LASER OUTPUT WHEN THE LIQUID SAMPLES IN 0.1 mm CELL WERE PLACED INSIDE THE CAVITY[a)]

Sample	P-branch	R-branch	P′-branch
(i) $CHCl_3$		18, 16, 14, 20, 12.	
(ii) CH_2ClCH_2Cl		18, 16, 20, 14.	
		18.[b)]	18.[b)]
(iii) $CHCl{=}CCl_2$			20, 18, 16, 22, 14.
(iv) $CHCl{=}CHCl$ (*trans*)			22, 20, 18.
(v) CH_3NO_2	20(only)		

a) CCl_4, C_6H_5, and CH_2Cl_2 have little effect upon the laser oscillation pattern.
b) 1.0 mm cell.

interpreted the results as due to a very near coincidence between the P(20) line and the $^PP(9)$ line of the ν_6 fundamental within 0.001 cm^{-1}. The ^PP lines of a symmetric top molecule are usually very weak in intensity,[7)] however, such a close matching in frequency may suppress the laser oscillation of the particular line involved.

The spectrum of ammonia in this region was studied extensively by Garing, Nielsen, and Rao under high resolution.[8)] In the spectrum of ammonia, a number of weak bands are found in the P-branch region. However, the 2sQ(4,2) line[9)] which Garing *et al.* reported at 944.14 cm^{-1} is most likely to coincide with the P(20) line at 944.18 cm^{-1}.

Although the present study is rather qualitative, it opens some interesting possibilities in the study and the application of the CO_2 laser system. Mixtures of foreign gases may be used, for example, and we may be able to control the oscillation frequencies of a CO_2 laser by changing the ratios of the gases as well as their pressures.

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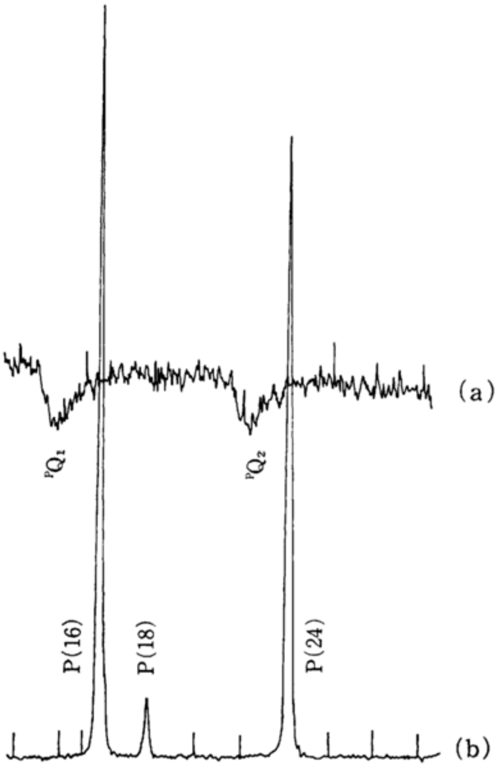

Fig. 3. (a) Absorption spectrum of 18 mmHg CH_3Br in a 10 cm gas cell superimposed with (b) the emission lines from the CO_2 laser when the same cell was inserted in the cavity. The $^PQ_1$ and $^PQ_2$ bands are at 949.14 and 942.25 cm^{-1}, respectively.

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7) We see in Fig. 3 two successive Q branches, $^PQ_1$ at 949.65 cm^{-1} and $^PQ_2$ at 942.25 cm^{-1}. Jones, Popplewell and Thompson reported six weaker bands between these two Q-branches, which they assigned to the $^PP_1(10)$. (see Footnote 5). They are too weak to be seen in Fig. 3.

8) J. S. Garing, H. H. Nielsen and K. N. Rao, *J. Mol. Spectry.*, **3**, 496 (1959).

9) We have used the notation in Ref. 8. The transition is related to the hot band $\nu_2^s \to 2\nu_2^a$ with $J=4\to4$ and $K=2\to2$.