

## Determination of the linewidth dependence on foreign-gas pressure for 3.4- $\mu\text{m}$ DF spectra\*

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Measurement of  $\nu=1-0$ ,  $P$ -branch 3.4- $\mu\text{m}$  DF absorption spectra is made for DF mixed with foreign gases at a temperature of 23–25°C. A cw DF laser is used as a light source, and laser intensity transmitted by the gas mixture is measured in order to determine the absorption. From the measured absorption, the ratio of cross sections  $Q_{AB}/Q_{AA}$  is determined, where  $Q_{AB}$  is the cross section for collision of DF (=A) with a foreign gas (=B) and  $Q_{AA}$  is for DF self-collisions. Results are obtained for the single line  $\nu=1-0$ ,  $P(8)$  in the case of  $\text{D}_2$ , He,  $\text{N}_2$ ,  $\text{CF}_4$ , and  $\text{SF}_6$  and for the lines  $\nu=1-0$ ,  $P(5-10)$  in the case of HF.

### I. INTRODUCTION

This paper reports a measurement of broadening by foreign gases of 3.4- $\mu\text{m}$  absorption spectra appropriate to the  $P$  branch of the  $\nu=1-0$  band of the DF molecule. This work is related to work done earlier by us where absorption measurements for pure DF were made.<sup>1</sup> The present measurements are important for two reasons. First, although our earlier self-broadening measurements confirm calculations of broadening based on Anderson's theory,<sup>2</sup> similar comparisons by others involving foreign-gas broadening yield unsatisfactory results. Examples of this are the first overtone band of HF broadened by  $\text{D}_2$  and the fundamental band of HF broadened by  $\text{CO}_2$ ,<sup>3</sup> and the fundamental band of HCl broadened by  $\text{H}_2$  and HCN.<sup>4</sup> Accordingly, further data which may serve to clarify such discrepancies are valuable. Second, linewidth broadening of spectra influences the intensity gain in corresponding laser media and hence determines in part the maximum possible output power.<sup>5,6</sup> Accordingly, the data herein are relevant to DF laser development in general.

### II. THEORY

Addition of a foreign gas  $B$  to a cell containing initially a gas  $A$  leads to an increase in the linewidth of spectra derived from  $A$  alone. This increase is given by<sup>7,8</sup>

$$\nu_{AB} = \nu_{AA} \left[ 1 + \left( \frac{M_A + M_B}{2M_B} \right)^{1/2} \frac{Q_{AB}}{Q_{AA}} \frac{p_B}{p_A} \right], \quad (1)$$

where  $\nu_{AA}$  is the linewidth for  $A$  alone,  $M_A$  and  $M_B$  are the molecular masses,  $Q_{AB}$  and  $Q_{AA}$  are broadening cross sections for  $A$  mixed with  $B$  and for  $A$  alone, respectively,  $p_A$  and  $p_B$  are the partial gas pressures, and  $\nu_{AB}$  is the linewidth (total) in the presence of  $A$  and  $B$ . The ratio  $\nu_{AB}/\nu_{AA}$  [and hence

$Q_{AB}/Q_{AA}$  from Eq. (1)] may be determined from the decrease in spectral absorption coefficient, at line-center frequency, for  $A$  alone when  $B$  is added to  $A$ . In the region of high absorber pressure where the rate of molecular collisions ( $=2\pi\nu_C$ ) significantly exceeds the corresponding rate associated with Doppler broadening ( $=2\pi\nu_D$ , where  $\nu_D$  is the Doppler width in Hz), the absorption coefficient for  $A$  alone is given by<sup>9</sup>

$$P_{AA} = S_A / \pi\nu_{AA}, \quad (2)$$

where  $S_A$  is the integrated line strength for a given line in the spectra of  $A$ . Since the addition of  $B$  does not affect  $S_A$ , the increase in linewidth causes the absorption coefficient to decrease in accordance with

$$P_{AB} = S_A / \pi\nu_{AB}. \quad (3)$$

Evidently then,  $\nu_{AB}$  may be determined from

$$\nu_{AB} = \nu_{AA} (P_{AA}/P_{AB}), \quad (4)$$

where  $\nu_{AA}$  and  $P_{AA}$  are taken from earlier measurements<sup>1</sup> and  $P_{AB}$  is determined from the present measurements.

### III. RESULTS AND DISCUSSION

The coefficient  $P_{AB}$  was measured for DF (=A) mixed with  $\text{D}_2$ , He, HF,  $\text{N}_2$ ,  $\text{CF}_4$ , and  $\text{SF}_6$ . With the exception of HF,  $P_{AB}$  was measured for only the  $\nu=1-0$ ,  $P(8)$  DF line. In the case of HF, measurements were made for the  $\nu=1-0$ ,  $P(5-10)$  lines. The results for the  $\nu=1-0$ ,  $P(8)$  line and the foreign gases studied are given in Table I. Results for broadening of DF lines by HF are given in Fig. 1.

In Table I the quantity  $\nu_{AB} - \nu_{AA}$ , which is the contribution to the linewidth due to broadening by  $B$  alone, is determined from Eq. (4), together with the appropriate self-broadening results. Similarly, the  $Q_{AB}/Q_{AA}$  are determined from Eq. (1). In de-

TABLE I. Summary of foreign-gas broadening of  $\nu = 1-0$ ,  $P(8)$  DF transition.  $\nu_{AB} - \nu_{AA}$  gives the broadening due to  $B$  alone. The broadening due to  $A (=DF)$  alone for the above transition is given in Ref. 1.

A	B	$\nu_{AB} - \nu_{AA}$ ( $10^{-1} \text{ cm}^{-1}/\text{atm}$ )	$Q_{AB}/Q_{AA}$
DF	He	$0.04 \pm 0.01$	$0.010 \pm 0.002$
DF	CF <sub>4</sub>	$0.45 \pm 0.10$	$0.24 \pm 0.10$
DF	N <sub>2</sub>	$0.54 \pm 0.10$	$0.24 \pm 0.06$
DF	SF <sub>6</sub>	$0.54 \pm 0.10$	$0.30 \pm 0.02$
DF	D <sub>2</sub>	$0.64 \pm 0.15$	$0.15 \pm 0.02$
DF	HF	$2.33 \pm 0.50$	$0.96 \pm 0.06$

termining  $Q_{AB}/Q_{AA}$  for a given gas, several different values of  $p_B/p_A$  were used from which a mean value of  $Q_{AB}/Q_{AA}$  was computed. For SF<sub>6</sub>, for example,  $p_A$  was 40 Torr and  $p_B$  was 150, 300, 450, and 600 Torr. This gave values of  $Q_{AB}/Q_{AA}$  consistent with  $0.28 < Q_{AB}/Q_{AA} < 0.32$ .

Since calculations of broadening of DF  $\nu = 1-0$ ,  $P$  branch lines by HF have been carried out,<sup>10</sup> measurements were made for six DF lines in order to compare theory with experiment. Theoretical values of  $\nu_{AB} - \nu_{AA}$  from Fig. 1 are consistently greater than the given experimental values. This is similar to broadening of the first overtone band of HF by H<sub>2</sub> and D<sub>2</sub> at 373 °K.<sup>3</sup> In this latter case, theoretical values exceed experimental ones, where the relevant theories are those of Anderson<sup>2</sup> and Fiutak and Van Kranendonk,<sup>11</sup> and the broadening agents are nonpolar H<sub>2</sub> and D<sub>2</sub>. Similar disagreement exists for HCl spectra broadened by H<sub>2</sub> and HCN.<sup>4</sup> What is of particular interest in the present case is the inadequacy of the above theories when applied as well to the case of broadening by polar HF.

The present results are also relevant to DF chemical lasers. Linewidth broadening of the laser transition influences the unsaturated gain for a wave propagating in the laser medium in a manner which is identical to that given by Eq. (6)

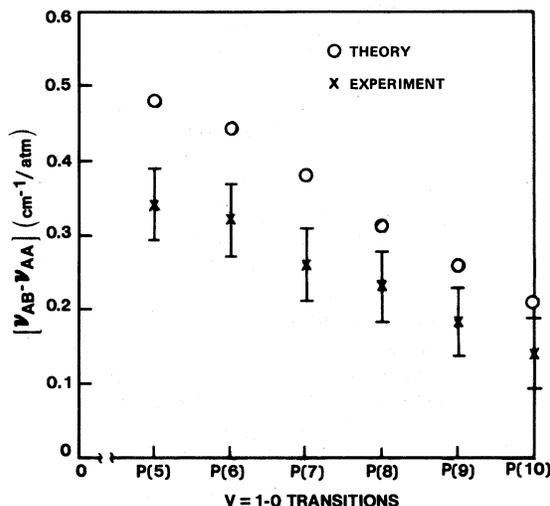
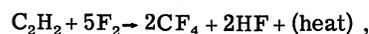


FIG. 1. Broadening of  $\nu = 1-0$ ,  $P(5-10)$  DF transitions owing to molecular collision of active DF ( $=A$ ) with perturbing HF ( $=B$ ).

of Ref. 1, where for inverted population density appropriate to laser media the  $P_{ul}$  is interpreted not as an absorption, but rather as an amplification coefficient valid for any value of  $\nu_C/\nu_D$ . With the exception of He and N<sub>2</sub>, the gases studied by us occur commonly as either fuels or fuel products in DF lasers. For example, CF<sub>4</sub> and HF are of particular interest since these occur as products of the reaction



which is a reaction associated with F-atom production for DF chemical laser operation. The large broadening of DF spectra by HF, per Fig. 1, suggests the desirability of using fuels that burn other than C<sub>2</sub>H<sub>2</sub>, such as C<sub>2</sub>F<sub>4</sub>. The SF<sub>6</sub> and D<sub>2</sub> data in Table I are relevant to DF chemical lasers in which F atoms are produced by electrical discharge of the SF<sub>6</sub> fuel and then reacted with D<sub>2</sub>.<sup>12</sup>

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