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NOTE

BAND STRENGTH AND LINE HALF-WIDTH OF THE 10·4 μ CO_2 BAND

S. R. DRAYSON and C. YOUNG*

High Altitude Engineering Laboratory,
Department of Aerospace Engineering,
University of Michigan

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Abstract—Experimental absorption data using a 10·4 μ CO_2 laser have been re-analysed. The band intensity of the 10·4 μ (10^00–00^01) CO_2 band is 0·0184 cm^{-1} $(atm\ cm_{273°K})^{-1} \pm 5\%$ at 300°K and the self broadened Lorentz half-width of the P(20) line is 0·096 $cm^{-1} \pm 5\%$ at 1 atm and 300°K.

THE ADVENT of the laser has made possible new techniques for determining intensities and collisional half-widths of lines in molecular absorption bands. MCCUBBIN *et al.*[1] have recently made measurements with a CO_2 laser on the P(20) line of the 10·4 μ band of CO_2. Using the laser as an essentially monochromatic source with the frequency of the line-centre, they measured the transmission of the beam through a CO_2 absorption cell. The cell was initially empty and small amounts of pure CO_2 were added until the pressure reached about 150 torr. The experiment was very carefully conducted, the data having only a small amount of scatter.

MCCUBBIN *et al.* analysed their data as follows. At all pressures the influence of neighbouring lines at the centre of the P(20) line is negligible. At very low pressures the line tends to the Doppler profile, and at the line-centre we have

$$\ln \tau = -\frac{S}{\alpha_D}\left(\frac{\ln 2}{\pi}\right)^{1/2} u_0 p$$

where τ is the transmittance, S the line intensity, α_D the Doppler half-width, u_0 the length of the absorption cell and p the pressure in atmospheres. The line intensity can be found from the slope of the plot of $\ln \tau$ against p, as the pressure tends to zero.

At much higher pressures collisional broadening dominates, and the expression for τ now becomes:

$$\ln \tau = -\frac{S}{\pi}\frac{u_0}{\alpha_0}$$

where α_0 is the Lorentz half-width at 1 atm. As the pressure increases, τ tends to a constant value and α_0 can easily be found using the value of S already determined.

The difficulty of this method lies in accurately determining the slope of the curve as p tends to zero. The problem is compounded by the fact that, even for pressures as low as

* Dr. Young is now at Dept. of Physics, University of New Brunswick, Fredericton, New Brunswick, Canada.

1 torr the absorption coefficient of the mixed Doppler–Lorentz (or Voigt) profile is about 10 per cent lower than the pure Doppler. At lower pressures the scatter of the experimental data, due to the small absorption, makes it very difficult to accurately determine the slope.

We have re-analysed the data using the mixed Doppler–Lorentz absorption coefficient. In this case

$$\ln \tau = -\frac{S}{\alpha_D}\left(\frac{\ln 2}{\pi}\right)^{1/2} u_0 p \frac{y}{\pi} \int_{-\infty}^{+\infty} \frac{e^{-t^2}}{y^2+t^2}\,dt$$

where $y = \dfrac{\alpha_0 p}{\alpha_D}(\ln 2)^{1/2}$.

Calculations using the values deduced by McCUBBIN *et al.* showed that the predicted absorption was consistently less than the experimental (see Fig. 1). Several larger values of

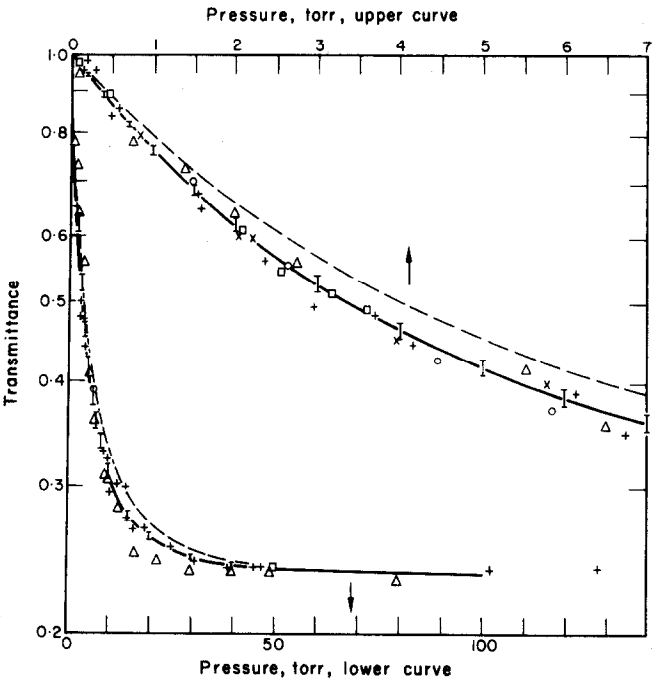

FIG. 1. Logarithmic plot of transmittance vs. pressure. Dashed line is theoretical curve of growth using parameters from McCUBBIN *et al.* Solid line uses re-estimated values, with error bars indicating ±5 per cent deviation in line intensity.
From Fig. 1, McCUBBIN *et al.*[1]

line intensity were tried. The value $S = 5{\cdot}6 \times 10^{-4}\ \text{cm}^{-1}\ (\text{atm cm}_{300\,°\text{K}})^{-1}$ gave a good fit to the experimental points over the entire range of pressure. This corresponds to a self-broadened Lorentz half-width of 0·096 cm^{-1} at 300°K. The curve is shown in Fig. 1, with error bars showing the effect of a 5 per cent change in S.

The value of band intensity for the 10·4 μ band (10^00–00^01) obtained is 0·0184 cm^{-1} (atm $cm_{273°K})^{-1} \pm 5\%$ at 300°K. This lies well within the range of values recently deduced by GRAY[2] (0·019 ± 0·004 cm^{-1} (atm $cm_{273°K})^{-1}$ at 300°K). MADDEN[3] has measured the variation of the self-broadened half-width with rotational quantum number for the (02^00–01^10) CO_2 band near 600 cm^{-1}. The optical collision cross-section varies with rotational quantum number and we would also anticipate some variations from band to band. However the latter effect is probably quite small. Madden obtained the value 0·102 cm^{-1} ± 10 per cent at 300°K for the P(21) line, which agrees with the laser determined value within experimental error.

A second paper by GERRY and LEONARD[4] used the same experimental technique and the mixed Doppler–Lorentz absorption coefficient discussed above. However, the larger scatter in their measurements makes it difficult to obtain an accurate fit to their data. In addition to this, both the Doppler and Lorentz half-widths vary by more than 15 per cent over their experimental temperatures. Using their best fit curve, the value of line intensity $2{\cdot}9 \times 10^{-4}$ cm^{-1} (atm $cm_{273°K})^{-1}$ at 273°K and $\alpha_0 = 0{\cdot}10$ cm^{-1} was obtained. Converted to 300°K, the line intensity becomes $4{\cdot}4 \times 10^{-4}$ cm^{-1} (atm $cm_{300°K})^{-1}$ at 300°K, some 20 per cent lower than the value from MCCUBBIN *et al.*

In addition Gerry and Leonard give a value for the optical collision cross-section which is close to the gas kinetic cross-section for CO_2. This is clearly incorrect, since the optical cross-section is appreciably larger than the gas kinetic values and only tends to the gas values for rather large rotational quantum numbers.

The laser method for the determination of line intensities and Lorentz half-widths of optically active molecules appears capable of a high degree of accuracy. Further measurements on foreign broadened gasses, particularly atmospheric constituents, should prove most useful. The band intensity 0·0184 cm^{-1} (atm $cm_{273°K})^{-1} \pm 5\%$ at 300°K and the self-broadened Lorentz half-width of the P(20) line 0·096 $cm^{-1} \pm 5\%$ at atmospheric and 300°K probably represent the most accurate determination to date.

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