Polarization and Intensity Measurements in the Raman Spectrum of Carbon Dioxide

A. Langseth, *University of Copenhagen* and J. Rud Nielsen, *University of Oklahoma*

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The relative intensities and the depolarizations (for unpolarized incident light) of the two principal Raman bands of carbon dioxide have been measured. The following results were obtained:

$$\rho_{1286} = 0.18, \quad \rho_{1389} = 0.14, \quad I_{1286}/I_{1389} = 0.61.$$

THE relative intensities of the two principal Raman bands of carbon dioxide were estimated visually by Dickinson, Dillon and Rasetti[1] and by Bhagavantam.[2] The latter also determined the depolarizations of the two bands. Recently, Isabel Hanson[3] has measured photometrically (at two different temperatures, 50°C and 200°C) the intensities of the 1286 cm^{-1}, the 1389 cm^{-1} and the 1410 cm^{-1} bands, excited by the 2537A mercury line.

The present work was carried out with an experimental arrangement previously employed to measure the depolarizations of the Raman bands of carbon disulphide.[4] The CO_2 gas was contained in a glass tube at a pressure of 20 atmospheres and a temperature of 25°C. The slit of the liquid-prism spectrograph was 0.1 mm wide, and the position of the Wollaston prism in the collimator tube was so adjusted that the "perpendicular" component of the 1286 cm^{-1} band, excited by the 4358A mercury line, fell nearly midway between the "parallel" components of the 1286 cm^{-1} and 1389 cm^{-1} bands. Two exposures were made lasting 48 hours and 144 hours, respectively, the density marks, produced by a step-weakener, being exposed one-third as long as the Raman spectrum.

Fig. 1 shows the intensity distribution, evaluated from a record taken with a Moll microphotometer of the plate exposed 48 hours. The correction for the continuous background, which varied somewhat from one band to the other, was very large, averaging 50 percent of the maximum intensity. The intensity distribution curve is analyzed into component bands as indicated by the dotted curves. It will be seen that whereas the ratio between the intensities of the parallel components of the principal bands as well as the depolarization of the 1389 cm^{-1} band can be determined with considerable accuracy, there is some difficulty in determining accurately the perpendicular component and, hence, the depolarization of the 1286 cm^{-1} band. This is due almost entirely to the broadening of the strong parallel components rather than to the presence of the weak satellites or to Raman bands excited by other mercury lines than 4358A. The dispersion was not large enough to separate the satellites from the principal bands. In Fig. 1, the arrows marked a and d indicate where the parallel components of the satellites, 1265 cm^{-1} and 1410 cm^{-1}, should appear. The observed intensity distribution curve shows no evidence of the presence of the 1265 cm^{-1} band but rather definite evidence, as indicated by the dotted curve, of the 1410 cm^{-1} band. The satellites are too weak and too far from the maxima of the principal bands to influence perceptibly the observed values for these maxima. Moreover, their presence would be a source of error only if they had depolarizations differing greatly from those of the principal bands.

The arrows marked b and c show where the parallel components of 1389 cm^{-1} excited by the 4339A and 4347A mercury lines should fall. There is evidence of the band excited by 4347A, although the maximum of the dotted curve seems shifted a little to one side. The low intensity of this band indicates that, for the light emitted by a quartz mercury arc, the value given

[1] R. G. Dickinson, R. T. Dillon and F. Rasetti, Phys. Rev. **34**, 582 (1929).

[2] S. Bhagavantam, Nature **127**, 817 (1931); Ind. J. Phys. **6**, 319 (1931).

[3] Isabel Hanson, Phys. Rev. **46**, 122 (1934).

[4] A. Langseth, J. Utoft Sørensen and J. Rud Nielsen, J. Chem. Phys. **2**, 402 (1934).
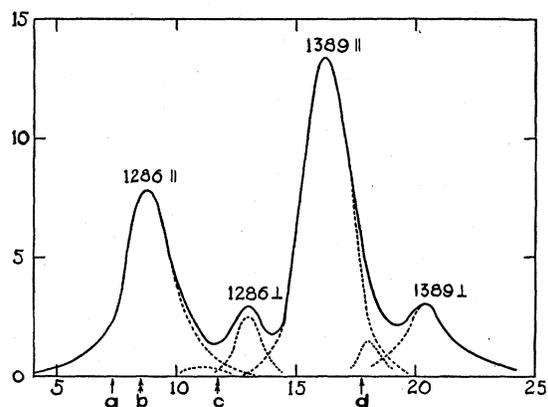
FIG. 1. Energy distribution curve.

in most spectral tables for the ratio between the intensities of the 4347A and the 4358A lines is not even of the right order of magnitude. As shown by the position of the arrow b, the parallel component of 1389 cm^{-1}, excited by the 4339A mercury line, lies rather close to the parallel component of 1286 cm^{-1} excited by 4358A. This will tend to make the observed intensity of the latter band too high. However, although no data are available to permit a quantitative estimate, it is evident from the low intensity of the band at c, together with the fact that the line 4339A is much weaker than 4347A, that this error is very small.

The results obtained are listed in Table I.

TABLE I. *Depolarizations and intensity ratio.*

Exposure time	ρ_{1286}	ρ_{1389}	I_{1286}/I_{1389}
48 hours	0.20	0.14	0.60
144 hours	0.16	0.14	0.63
Average:	0.18	0.14	0.61

The depolarizations are for unpolarized incident light. Because of the greater broadening of the parallel components, the data derived from the 144 hour exposure are somewhat less accurate than those obtained from the shorter exposure. The error in the average value of ρ_{1286} may be as high as 15 percent. The depolarization of the

1389 cm^{-1} band is probably correct to within 8 percent, and the intensity ratio to 5 percent.

The observed depolarizations are lower than the value 0.2 obtained by Bhagavantam[2] for both bands by a visual method. As in the case of carbon disulphide, for which similar values were found for the depolarizations,[4] the stronger band is more highly polarized than the weaker band. However, in view of the aforementioned errors, which influence the measurement of the perpendicular component of 1286 cm^{-1}, it is possible that the difference in the depolarizations of the two bands is less than observed.

A calculation of the depolarization of the Raman band associated with the totally symmetrical vibration of CO_2, based upon previous work of Ramanathan[5] and others, has been made by Bhagavantam.[6] He obtained a value 0.3 that is roughly twice as high as the observed depolarizations. Also for other molecules, this method of calculation leads to too high values for the depolarization.[7]

The observed intensity ratio confirms remarkably the value 10 : 15 estimated visually by Dickinson, Dillon and Rasetti but differs considerably from the values 1 : 3 and 1 : 2 obtained by Bhagavantam by a more elaborate method. The average value 0.61 for the intensity ratio is in exact agreement with that found by Hanson at 200°C but is somewhat higher than the supposedly more accurate value 0.57 found by her at 50°C. The values for the intensity ratio listed in Table I have been evaluated by multiplying the ratio between the intensities of the parallel components of the 1286 cm^{-1} and 1389 cm^{-1} bands by $1.18/1.14 = (1+\rho_{1286})/(1+\rho_{1389})$. Even if it be assumed that the observed difference between the depolarizations of the two bands is due entirely to experimental errors, we find a value 0.59 for the intensity ratio which is higher than the lower of the two values obtained by Hanson.

[5] K. R. Ramanathan, Proc. Roy. Soc. **A107**, 684 (1925).
[6] S. Bhagavantam, Ind. J. Phys. **6**, 557 (1932).
[7] Cf. G. Placzek, *Rayleigh-Streuung und Raman-Effekt*, Marx: *Handbuch der Radiologie*, p. 365, 2nd Ed., Vol. 6, Part II, Braunschweig, 1934.