

## Intensity Measurements in the Raman Spectrum of Carbon Dioxide\*

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A simple photographic method of measuring intensities in the Raman effect was devised. The ratio of the intensities of the strong Raman doublet of CO<sub>2</sub> was found to be 0.572 instead of 0.667 as roughly estimated by Dickinson, Dillon and Rasetti. This value (0.572) although in apparent disagreement with the calculations of Dennison and Adel is in fair agreement with Placzek's recent work. An exposure of 24 days brought out three lines in addition to the four commonly observed. They may be identified with three of the lines predicted by Dennison and Adel.

RECENT theoretical work on the Raman effect in CO<sub>2</sub><sup>1</sup> has brought out the need for accurate intensity measurements of the strong Raman doublet under ordinary conditions. No very satisfactory method of measuring intensities in the Raman effect has been devised. On account of the long exposure times necessary in the Raman effect the reciprocity law would not be expected to hold.<sup>2</sup> For the measurements to be of greatest possible accuracy it is desirable that the experiment be conducted in such a way that errors due to the failure of the reciprocity law may be avoided. To avoid these errors the density marks for comparison must be exposed for the same length of time as the lines whose intensities are to be measured. When the exposure times are from 40 to 120 hours as is usually the case for gases, it is not practical to expose the plate to the Raman scattering and the comparison consecutively. A means was devised therefore of exposing the two simultaneously.

The gas was sealed at a pressure of 6 atmospheres in a quartz tube about 10" long and  $\frac{3}{4}$ " in inner diameter with walls thick enough to withstand 15 atmospheres pressure. The back end of the tube was bent and blackened with aquadag to prevent reflection and diaphragms were so placed in the tube that no light reflected from the walls of the tube could reach the spectrograph. The front end of the tube was ground and polished to form a plane window. Gas was

taken from a commercial cylinder. It was introduced into the tube through a capillary sealed in the bent end of the tube to a pressure of 6 atmospheres. The tube was then immersed in liquid air, the gas frozen and the capillary sealed off.

Light was taken from a Hanovia Sc-2537 quartz mercury arc in spiral form surrounding the tube. The arc operated at a little above room temperature. The tube and arc were contained in a furnace. At higher temperatures the electrodes of the arc were water-cooled. The temperatures were measured with a thermocouple.

For comparison a Zeiss step filter of platinum sputtered on quartz in five layers of different transmissive powers was used. The transmissive power of each step for the 2537 mercury line was measured photoelectrically.

The slit of the Hilger E-1 quartz spectrograph which was used throughout was opened very wide and made as long as possible by removing the Hartmann diaphragm. The upper portion of the slit was narrowed with a piece of razor blade to a width such that the faint and strong Raman doublets of CO<sub>2</sub> were just resolved. The step filter was held over the slit with wax, the clear quartz area above the steps being placed over the narrowed part of the slit and the steps over the lower wider portion. The filter was illuminated by light from a small quartz mercury arc. This light was passed through a ground quartz plate to insure the uniformity of the beam and was made approximately monochromatic by passing through a monochromator. This uniform, approximately monochromatic (around 2537A) beam was reflected on to the slit by means of a silvered mirror. The light from the Raman tube

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<sup>1</sup> Dennison and Adel, *Phys. Rev.* **43**, 716 (1933).

<sup>2</sup> Harrison, *J.O.S.A. and R.S.I.* **19**, 267 (1929).

passed above this mirror, through the clear portion of the filter, and fell on the narrowed portion of the slit.

Although slow, Eastman 33 plates were used throughout because of their high contrast. Exposure times were from 35 to 115 hours.

The densities of blackening of the lines and comparison were measured with a Moll microphotometer.

At arc temperature the experimental error was around 2 percent but at high temperatures the error was greater, around 9 percent, because at higher temperatures the 2537 line in the Raman scattering was accompanied by a background which varied in intensity in the region of the Raman lines and it was difficult to determine the intensities of the lines from that of the background. The background was probably due to the presence of a small amount of gas not mercury vapor in the arc.

The results of the intensity measurements at arc temperature and at 200°C are contained in Table I.

TABLE I. *Intensity measurements.*

Temperature	$R_3/R_2$	$R_1/R_2$	No. mols. in 0101 state No. mols. in 0000 state
50°C	0.572	0.225	0.104
200°C	0.608	0.521	0.262

$R_1$ ,  $R_2$  and  $R_3$  represent the intensity of the lines 1409, 1388 and 1285  $\text{cm}^{-1}$ , respectively. The line 1409  $\text{cm}^{-1}$  arises in the 0101 state and the other two in the 0000 state. The ratio of the number of molecules in the two states was calculated for the two temperatures from the Boltzmann formula. The weight of the 0101 state was taken as 2 and of the 0000 state as 1.<sup>3</sup>

It may be seen that under ordinary conditions the ratio of the intensities of the strong Raman doublet is 0.572 instead of 0.667 as estimated by Dickinson, Dillon and Rasetti.<sup>4</sup> Dennison and Adel<sup>5</sup> used the latter value in their calculation of

<sup>3</sup> Dennison, *Rev. Mod. Phys.* **3**, 280 (1931).

<sup>4</sup> Dickinson, Dillon and Rasetti, *Phys. Rev.* **34**, 382 (1929).

<sup>5</sup> Dennison and Adel, *Phys. Rev.* **43**, 716 (1933).

$\Delta$  from the expression for the ratio of the intensities of the strong Raman doublet

$$(1 - \Delta/2^{\frac{1}{2}}|b|)/(1 + \Delta/2^{\frac{1}{2}}|b|)$$

in which  $b$  is a constant related to the separation of the strong Raman doublet and  $\Delta$  is a constant related to the difference between  $\nu_1$  and  $2\nu_2$  for  $\text{CO}_2$ . They obtained a preliminary value for  $\Delta=20$  and found the most probable value to be 14.7  $\text{cm}^{-1}$ . When the expression is set equal to 0.572 the value for  $\Delta$  obtained is 28 which is in disagreement with the most probable value found by Dennison and Adel. In a letter from Dr. Dennison he calls my attention to a very recent paper by Placzek<sup>6</sup> in which the latter takes into account the polarizability of the molecule and finds the expression for the ratio of the intensities of the strong doublet in  $\text{CO}_2$  to be more nearly

$$\frac{|(x - |\Delta|)^{\frac{1}{2}}\alpha_1 \mp (x + |\Delta|)^{\frac{1}{2}}\alpha_2|^2}{|(x + |\Delta|)^{\frac{1}{2}}\alpha_1 \pm (x - |\Delta|)^{\frac{1}{2}}\alpha_2|^2},$$

where  $x = 2^{\frac{1}{2}}|b|$  and  $\alpha_1$  and  $\alpha_2$  are related to the first and second derivatives of the polarizability. This expression is not completely correct, further measurements on the polarization of the lines being necessary in order to obtain an exact expression, but Placzek estimates that  $\alpha_1/\alpha_2$  should be approximately equal to  $\pm 10$ . If Dennison and Adel's value for  $b = 72.9 \text{ cm}^{-1}$  and  $\Delta = 14.7 \text{ cm}^{-1}$  are substituted and the expression set equal to 0.572 we find  $\alpha_1/\alpha_2 = \pm 14.8$  which is in fair agreement with Placzek's estimate.

The intensity of the weak Raman doublet increases with the temperature as would be expected from the Boltzmann distribution.

An exposure of 24 days brought out three lines in addition to the commonly observed four, corresponding to shifts  $1244 \pm 10$ ,  $1426 \pm 8$  and  $1528 \pm 15 \text{ cm}^{-1}$ . These may be identified with the lines predicted by Dennison and Adel at 1248, 1426 and 1517  $\text{cm}^{-1}$ .

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<sup>6</sup> Placzek, *Handbuch der Radiologie* VI, 2, 321 (1934).