

### On a New Line in the Raman Spectrum of Solid Carbon Dioxide.

THE Raman spectrum of solid carbon dioxide was first investigated successfully by McLennan and Smith<sup>1</sup> who observed two Raman lines at  $1285 \text{ cm.}^{-1}$  and  $1388 \text{ cm.}^{-1}$  respectively. No particular care, however, appears to have been taken by these authors to investigate whether there are any Raman lines lying very close to the Rayleigh line. The investigation has, therefore, been repeated by the present authors, using suitable experimental arrangements for recording Raman lines in the neighbourhood of the Rayleigh line. Commercial "Dry Ice" was locally obtained in the form of heavy solid blocks, which, when washed with ether and kept in an unsilvered Dewar vessel, remained as a translucent mass for a long time. The Raman spectrum of one of these blocks was photographed. The spectrograph used in the present investigation is the same as used previously in this laboratory for similar investigations. The dispersion is about  $11.5 \text{ A.U. per mm.}$  in the neighbourhood of the Hg line  $4047 \text{ \AA}$ . With an exposure of about 4 hours, a new line with  $\Delta\tilde{\nu} = 58 \text{ cm.}^{-1}$  was observed, besides the two lines  $1285 \text{ cm.}^{-1}$  and  $1388 \text{ cm.}^{-1}$ . The new line is at least twice as strong as the intense line  $1388 \text{ cm.}^{-1}$ .

The appearance of this new line with such a large intensity in the Raman spectrum of solid carbon dioxide is significant in view of the fact that in this case, the lattice being cubic,<sup>2</sup> and the molecule centro-symmetrical, Raman lines due to lattice oscillations cannot have appreciable intensities. It has already been pointed out by one of the present authors<sup>3</sup> (S.C.S.) that lattice oscillations cannot produce Raman lines of appreciable intensities unless there is an asymmetry of arrangement of the molecules around any particular molecule. The results of investigation of the Raman spectra of ammonium halides at different temperatures by Menzies and Mills lead to this conclusion. Since, in the crystals of solid carbon dioxide (accepting the molecule to be centro-symmetrical), no such asymmetry can be postulated, it is evident that the origin of this new line is other than lattice oscillation. This line may be due to intermolecular oscillations in loosely polymerised groups formed at the low temperature.

Details of the investigation will be published later.

The authors are indebted to Prof. D. M. Bose for providing facilities for the work in his laboratory.

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November 6, 1937.

<sup>1</sup> McLennan, J. C., and Smith, H. D., *Canad. J. Res.*, 1932, **7**, 551.

<sup>2</sup> Wycoff, *The Structure of Crystals*, 1931, p. 230.

<sup>3</sup> Sirkar, S. C., *Ind. J. Phys.*, **11**, Part V (in the Press).

<sup>4</sup> Menzies and Mills, *Proc. Roy. Soc.*, 1935, **146**, 407.

### A Convenient and Rapid Method for Determining Compressibilities of Gases and Vapours.

AN accurate method of determining compressibilities of gases and vapours by studying the variation of refractive index with pressure has been recently<sup>1</sup> reported. The usual method of determining the refractive index is to count the number of bands for various pressures or changes in pressure. This involves considerable time and trouble, particularly in the case of vapours, where quite a large number of bands have to be patiently counted. During the course of my work, I have found that accurate results can also be obtained by an alternative method, where the pressures corresponding to known refractive indices are determined. The reference standard of refractive index is provided by any gas, such as methane, whose refractive index has been already determined for various pressures by the usual method of counting the bands, and white light is used for the comparison (as in testing the purity<sup>2</sup> of the different samples of gas or vapour) instead of monochromatic radiation.

From the observed pairs of values of pressure and refractive index, the compressibility is determined in the usual way. This method is particularly useful in the case of vapours with high refractive indices and also for work at high temperatures.

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<sup>1</sup> H. E. Watson and K. L. Ramaswamy, *Proc. E. Soc.*, (A), 1936, **156**, 130-43.

<sup>2</sup> K. L. Ramaswamy, *ibid.*, 1936, **4**, 108-33.