Raman Effect of Gaseous and Liquid Sulphur Trioxide and of Mixtures of the Trioxide with the Dioxide

THE number of Raman frequencies to be expected for the molecule SO_3 is either three or four, according as it has the symmetry D_{3h} (plane form) or C_{3v} (pyramidal symmetry). The Raman spectrum of gaseous sulphur trioxide was determined with a Hilger E_1 spectrograph, but only the frequency $1068{\cdot}5 \pm 0{\cdot}5$ was found with certainty[1]. A decision on the structure is thus not possible, as the infra-red absorption of sulphur trioxide is, so far as we know, unknown.

Bhagavantam examined the Raman spectrum of the *liquid* trioxide and its change with temperature. The intensities of the frequencies 535, 1068 and

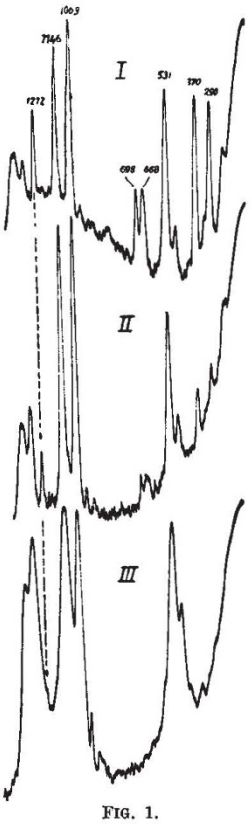

FIG. 1.

1403 as given by him increased with temperature, whereas the intensities of the other lines (290, 370, 666, 697, 1271 and 1489) diminished. His main results were confirmed by us; the changes in intensities with temperature, though very distinct, were found somewhat less pronounced. In long exposures the very weak lines 650 and 1516, mentioned by Venkateswaran[2], were also found.

The number of frequencies found for the liquid is far too large to be explained by the presence of only single molecules, SO_3, even if one takes into account the possibility of resonance degeneracy causing the splitting up of one line into two others; this has led Bhagavantam[3] to the hypothesis of the complexity of the liquid, a view put forward long ago for this substance by A. Smits on account of anomalies in the vapour pressure[4]. The group of lines the intensity of which increases with temperature is ascribed to $(SO_3)_1$; the other lines are thought to belong to a double molecule S_2O_6.

If in the liquid an inner equilibrium between SO_3 and polymerised molecules $(SO_3)_x$ exists, it would be interesting to study the influence on the Raman effect of the liquid trioxide, when diluting it with another liquid with which it is miscible in all proportions. For that reason the Raman spectrum (at 60°) was determined of mixtures of the trioxide with sulphur dioxide, containing respectively 75, 50 and 25 molecular per cent of trioxide. In all mixtures the three Raman lines of the dioxide were found in intensities determined by the concentration of sulphur dioxide in the mixture. The influence on the Raman lines of the trioxide of diluting it with the dioxide is, on the contrary, very marked, as may be seen from photometer records for the three mixtures reproduced here (Fig. 1) (I, 25 per cent; II, 50 per cent; III, 75 per cent sulphur dioxide respectively). The intensities of the Raman lines 290, 370, 650, 668, 699, 1271, 1490 and 1516 diminish strongly with dilution compared with the lines of the dioxide, whereas the intensities of the lines 530, 1068 and 1390 increase considerably, when one takes account of the relative decrease in concentration of the trioxide, when going from mixture I to mixture III.

The influence of dilution on the Raman spectrum of liquid sulphur trioxide is thus very striking, and in complete agreement with the conception of an inner equilibrium in the liquid between single and polymerised molecules, in the sense of Smits's theory. The dipole moment of the gaseous substance is being measured, as it may facilitate a decision about the symmetry of the molecule. In the case of a plane molecule, the electric moment would be zero.

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[1] The vapour contains only single molecules; compare A. Smits and N. F. Moerman, NATURE, **134**, 698 (1934).
[2] *Phil. Mag.*, (7), **15**, 263 (1933).
[3] *Ind. J. Phys.*, **5**, part 1, 49 (1930).
[4] A. Smits, *Versl. Kon. Akad. Amsterdam*, **32**, 349 (1923); NATURE, **113**, 855 (1924).

Raman Spectrum of the Ice-like form of Sulphur Trioxide

THE Raman spectrum of the ice-like form of solid sulphur trioxide (melting point 16·8°) was measured with the Hilger E_1 spectrograph and with a spectrograph of large aperture ($F/2$), but small dispersion, constructed by Kipp. The following lines were found: 292(1), 371(1*d*), 525(0), 662(½), 698(½), 1074(½, not sharp), 1273(2).

A comparison with the results obtained with the trioxide and with mixtures of it with the dioxide (see preceding letter) reveals the fact that the Raman lines of both the molecules $(SO_3)_1$ and $(SO_3)_x$ are present, those of $(SO_3)_x$ having here by far the greater intensities. This is in contrast to the liquid, as may be seen for the strongest frequencies 1068 ($(SO_3)_1$) and 1272 ($(SO_3)_x$) from two photometer records reproduced here (Fig. 2: I, liquid at 70°; II, solid at 12°). It is therefore necessary to assume that the lattice of the *solid* ice-like modification of sulphur trioxide consists of molecules $(SO_3)_x$ (for the larger part) and single molecules $(SO_3)_1$ (in small quantities); in agreement with the hypothesis of the complexity of