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ON THE RAMAN SPECTRUM OF ANTIMONY TRICHLORIDE AT -195°C

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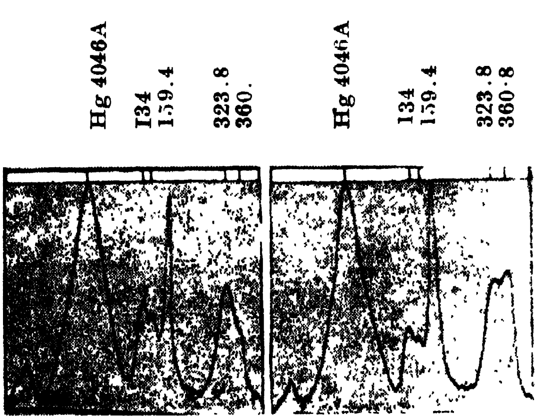
The Raman spectrum of antimony trichloride in the liquid state was first studied by Braune and Engelbracht (1932) who reported the four lines 134, 165, 320 and 360 cm^{-1} and these were assigned to vibrations ω_4, ω_2, ω_3 and ω_1 respectively by Howard and Wilson (1934) who calculated the force constants assuming the bond angle to be 94°. According to the above assignment the lines 134 and 320 cm^{-1} should be totally depolarised and the other two lines should have a factor of depolarisation much less than 6/7 as in the case of PCl_3. The value of ρ the factor of depolarisation of the line 195 cm^{-1} of $AsCl_3$ due to ω_2 is, however, much greater than that of the line 260 cm^{-1} of PCl_3. The nature of polarisation of the lines due to $SbCl_3$ had not been reported by previous workers, and therefore, the polarisation of these lines have been studied in order to understand the difference in the values of ρ mentioned above. It was also thought worthwhile to study the Raman spectrum of the molecule in the solid state at −195°C to find out the changes in the spectrum due to intermolecular field in the crystal.



(a) (b)

Figure 1. (a) Horizontal component (b) Vertical component.

Microphotometric records of the horizontal and vertical components of the spectrum recorded simultaneously with the help of a double-image prism in the path of the scattered rays are reproduced in figures. 1 (a) and 1(b) respectively.

Similar record of the spectrum due to the crystal at −195°C is reproduced in figure 2. The Raman frequencies of the crystal are given in table 1.

Table 1

Raman spectra of $SbCl_3$ ($\Delta\nu$ in cm^{-1})

Liquid at 80°C	Solid at 4°C	Solid at −195°C (Boiling N_2)
		43.0 (1)
	55.0 (2)	58.0 (2)
	72.0 (2)	76.0 (3)
	98.0 (2)	102.0 (1)
134.0 (5)		
	145.0 (2)	143.0 (2)
159.4 (3)		155.0 (2)
	171.0 (2)	179.0 (3)
323.8 (8b)	318.0 (5)	319.0(5)
360.3 (10b)	339.0 (8)	339.0 (8)

It will be seen from figures.1(a) and 1(b) that only the line 360 cm^{-1} is highly polarised while the line 165 cm^{-1} besides the other two lines are totally depolarised. Theoretically, the line 165 cm^{-1} should be highly polarised. The clue to the ex-

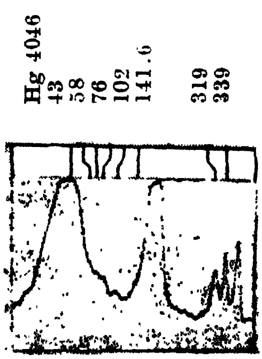


Figure 2. Raman spectrum of $SbCl_3$ at −195°C.

planation of this anomaly has been provided by the spectrum due to the crystals shown in figure 2 which shows four new lines at 43, 58, 76 and 102 cm^{-1} respectively. The unit cell of the crystals of antimony chloride is orthorhombic (Lindqvist and Niggli, 1956) and it contains four molecules, two of which are situated almost on the *c*-axis but displaced vertically from each other with a centre of symmetry between them. The other two are also similarly situated with respect to an axis parallel to *c*-axis and passing through the centre of the (001) face. The distance between the Sb-atom of the lower molecule on the

c-axis and the nearest Cl atom of the upper one is 3.48A and therefore there is possibility of formation of a weak bond between these two atoms. A similar bond may exist also between the Sb atom of the upper molecule and the Cl atom of the lower molecule. In fact the crystal consists of such vertical rods of molecules passing through the corners and the centres of faces of the unit cell.

The four new lines given in table 1 are due to intermolecular oscillations in such 'rods', the line 102.0 cm^{-1} being probably due to torsional oscillation about the c-axis in which both the bonds mentioned above are involved. The line 76 cm^{-1} may be due to an angular oscillation of the molecule about the horizontal Sb-Cl bond and the other two lines may be due respectively to such oscillations about a horizontal axis bisecting the angle between the other two Sb-Cl bonds and the three-fold axis of the molecule.

The liquid state probably consists of dimers formed in the same way as in the crystal. In that case in ω_2 the bonding of one of the Sb-Cl bonds is less than that of the ther two free bonds and therefore the mode becomes asymmetric to the three-fold axis and the Raman line becomes totally depolarised. In ω_1 no such influence of the intermolecular bonds is expected.

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ON THE METHOD OF MEAN VALUES AND CENTRAL LIMIT THEOREMS

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In the usual method* of mean values (Darwin and Fowler 1922), as in the theory of singular series of Hardy and Littlewood (Bellman 1961) for Waring problems

*In the text of the note, these will be referred to as the usual method and the modified method