THE RAMAN SPECTRUM OF BORIC ACID

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1. INTRODUCTION

The Raman spectrum of boric acid has been studied by a number of authors. A summary of the results obtained by the earlier workers is given by Hibben (1939). Recently the Raman spectra of boric acid and its isotopic substitutes were studied by Servoss and Clark (1957) and by Goubeau and Hummel (1959). Though many of the investigators have studied the Raman spectrum of boric acid in the crystalline state, nobody has succeeded in recording the low frequency lattice lines so far. Moreover, a closer study of the results obtained by the various authors shows that these results are none too concordant. The present author has already recorded the Raman spectrum of the trimethyl ester of boric acid using the mercury $\lambda 2537$ excitation technique (1961). Since boric acid was also known to be transparent to this portion of the ultra-violet radiation, it was thought worthwhile to record its Raman spectrum by using the $\lambda 2537$ excitation. The results obtained from such an investigation are reported in this paper.

2. EXPERIMENTAL DETAILS

Crystalline boric acid in the form of flakes supplied by Merck was used as such for recording the Raman spectrum. The flakes were illuminated perpendicular to the cleavage plane by the ultra-violet radiation from a water-cooled, magnet by controlled quartz mercury arc. The scattered light was taken along the cleavage plane. The spectrum was recorded using a Hilger medium quartz spectrograph. Slit widths of about 0.04 mm. were used. Using Ilford Zenith Astronomical plates an exposure of about two days was necessary to record a satisfactory Raman spectrum. Fifteen Raman lines including three belonging to the lattice spectrum were recorded, their frequency shifts and visually estimated relative intensities being given as follows:—60 (4), 128 (4 $b$), 210 (4), 499 (4), 735 (0 $b$), 884 (10), 1085 (0 $b$), 1172 (1), 1384 (1), 1430 (0 $b$), 2530 (0 $b$), 2666 (0 $b$), 3165 (8), 3251 (8) and 3420 (1 $b$). The lattice lines are now being reported for the first time.
enlarged print of the Raman spectrum of boric acid together with its microphotometer record is reproduced in Fig. 1.

3. CRYSTALLOGRAPHIC DATA

The precise crystal structure of boric acid has been determined by Zachariasen (1954). The crystals are triclinic with space group C \textit{i} (\textit{P}\textit{\textbf{1}}), with four molecules in the unit cell. The cell dimensions are \(a_1 = 7.0394 \text{\AA}\), \(a_2 = 7.053 \text{\AA}\), \(a_3 = 6.578\), \(\alpha_1 = 92.58^\circ\), \(\alpha_2 = 101.17^\circ\) and \(\alpha_3 = 119.83^\circ\). The structure is built up of nearly planar layers, the distance between successive layers being 3.18 \text{\AA}. Hence the layers are held together by weak Van der Waal's forces and the crystal exhibits a cleavage plane parallel to the layers. The molecules in an individual layer are held together by hydrogen bonds of moderate strength, the \(\text{O} \cdots \text{O}\) distance being 2.72 \text{\AA}. According to Zachariasen, the hydrogen atoms lie on the \(\text{O} \cdots \text{O}\) line within experimental errors. Hence the structure in a single layer consists of hexagonal rings, whose sides are the \(\text{O} \cdots \text{H} \cdots \text{O}\) bonds and has the symmetry \(C_{6h}\). The site symmetry of the boric acid molecule in the layer is \(C_{6h}\).

4. ASSIGNMENTS

Detailed assignments of the observed vibrational spectra of boric acid have been discussed by various authors, e.g., Bethell and Sheppard (1955), Plumb and Hornig (1957), Servoss and Clark (1957) and Goubeau and Hummel (1959). Only a few minor changes are necessary from the assignments of the above authors in view of the additional lines recorded here and these will be briefly discussed here. Since, in the crystal structure, the neighbouring layers are held together only by weak Van der Waal's forces, the best way to start a vibrational analysis of the crystal will be to proceed from that of a single layer only. Any changes from the selection rules thus derived can then be explained on the basis of the breakdown of the selection rules due to interaction between neighbouring layers. The symmetry of an individual layer is \(C_{6h}\) and the 'layer unit cell' contains two boric acid molecules. Now, since there are fourteen atoms in the 'layer unit cell' there should be 3 \(N-3\), \textit{i.e.}, 39 vibrational frequencies. These are divided among the eight irreducible representations (species) of the symmetry group \(C_{6h}\) as follows:

\[
\Gamma = 4A_g + 2A_u + 3B_g + 4B_u + 2E_{1g} + 4E_{1u} + 5E_{2g} + 2E_{2u}
\]

(Mathieu, 1945, Herzberg, 1945).

Each of the species \(A_g\), \(B_u\), \(E_{1g}\) and \(E_{2u}\) contains one lattice oscillation of the rotatory type and each of the species \(B_g\) and \(E_{2g}\) contains one lattice oscillation of the translatory type. Species \(A_g\), \(E_{1g}\) and \(E_{2g}\) are Raman active, and