

RAMAN SPECTRA OF ORGANIC COMPOUNDS

Part II. Methyl Borate

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1. INTRODUCTION

IN continuation of the earlier work (Krishnan, 1961) the author has recorded the Raman spectrum of methyl borate B(OCH₃)₃ using ultra-violet excitation. This substance is a liquid at ordinary temperatures. The Raman spectrum of methyl borate was investigated by Joglekar and Thatte (1936), Ananthakrishnan (1936), Milone (1936), Kahovec (1938, 1939) and by Becher (1954). They had employed the 4046 and 4358 excitation. The maximum number of Raman lines reported so far is fifteen. Ananthakrishnan and Becher investigated the polarisation characteristics of the Raman lines also though their results were not in complete agreement.

The liquid used in the present investigation was pure Kahlbaum's sample. Since the liquid got easily decomposed due to the action of atmospheric water vapour, the Wood's tube containing the sample was kept carefully sealed. The liquid exhibited traces of fluorescence. The spectrum was recorded with a Hilger medium quartz spectrograph using Ilford Zenith Astronomical plates, the slit-width used being 0.02 mm. Exposures of about 40 hours were given to record a reasonably intense picture.

2. RESULTS

An enlarged photograph of the Raman spectrum of methyl borate is reproduced in Fig. 1 on Plate V, along with its microphotometer record. The frequency shifts of the Raman lines are marked in the microphotometer tracing. Thirty-four Raman lines have been recorded and the frequency shifts have been entered in column 1 of Table I. The figures given within brackets represent the visual estimates of their intensities. The intense 'wing' extending up to 110 wavenumbers from the exciting line is a new feature of the recorded spectrum. In column 2 of Table I are given the frequency shifts reported by Ananthakrishnan (1936). The frequencies corresponding

to the prominent maxima in the infra-red absorption spectrum of methyl borate taken by Becher (1954) are given in column 3 of Table I.

3. DISCUSSION

(a) *Structure of the molecule.*—From electron diffraction studies Bauer and Beach (1941) have definitely established that the boron and the three oxygen atoms of methyl borate are in one and the same plane with $\widehat{BOC} = 113^\circ$. On this basis one can have two possible structures for the methyl borate molecule. These two structures have the respective point-group symmetries C_3 and C_{3h} . The point-group C_3 could be eliminated as some of the vibrational modes which appear in Raman effect are not recorded in infra-red absorption and *vice versa*. Hence the only possible structure for methyl borate is the one having the symmetry of the point-group C_{3h} . The structure is indicated in Fig. 2. This conclusion is also supported by the investigations of Becher (1954).

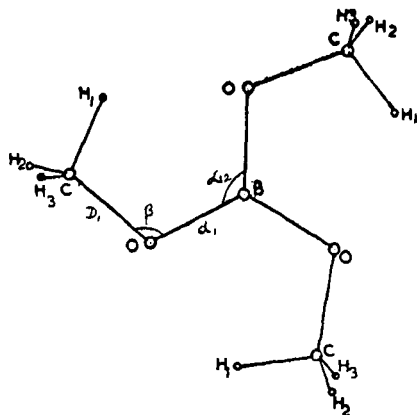


FIG. 2. The structure of methyl borate molecule: hydrogen atoms 1 are in the BO_3C_3 plane. The hydrogen atoms 2 and 3 are situated above and below the BO_3C_3 plane symmetrically.

(b) *Vibrational assignments.*—A molecule having the symmetry C_{3h} will have four species of vibrations— A' , A'' , E' and E'' . Of these A' , E' and E'' are active in Raman effect and A'' and E' are infra-red-active. Of the Raman-active species A' will give rise to polarised Raman lines, while the other two species produce depolarised Raman lines. Since $B(OCH_3)_3$ molecule contains sixteen atoms, it will have 42 fundamental modes of vibration distributed among the various species as follows:

$$8A' + 6A'' + 9E' + 5E'',$$

i.e., there will be 28 distinct fundamental frequencies. Of these 10 are due to the internal vibrations of the BO_3C_3 group and the rest due to the vibra-

tions of the CH_3 groups. Hence from a knowledge of the polarisation of the Raman lines and from the activity of the various frequencies, a satisfactory vibrational assignment could be made. Unfortunately only a trial polarisation picture was taken, and this is used in conjunction with Ananthakrishnan's data for making the assignments. The latter are indicated in column 4 of Table I. Column 5 of the same table gives the species of the vibrations.

Regarding the vibrations of the CH_3 groups, Ananthakrishnan observed six and the present author seven Raman lines in the C-H stretching region, whereas theoretically only five Raman lines—three polarised and 3 depolarised—are expected. Of the seven Raman lines observed, five are definitely polarised. The existence of a large number of Raman lines in this region could only be explained on the basis of Fermi resonance between the C-H stretching frequencies and the overtones of the C-H bending frequencies.

In the C-H bending region also five Raman lines—two polarised and three depolarised—are expected. But only two Raman lines—one very weak at about 1390 cm.^{-1} and another strong and broad at 1465 cm.^{-1} , both depolarised—are observed. There is a diffuse background extending over 200 wavenumbers. The other C-H bending frequencies might have overlapped with the one at 1465 cm.^{-1}

Of the CH_3 rocking frequencies the one at 1176 cm.^{-1} , which has a corresponding infra-red frequency, is definitely depolarised and has to be assigned to the species E' . The other assignments are indicated in Table I.

Restricting oneself to the BO_3C_3 group, one should expect to get eight Raman lines and two infra-red absorption bands not coinciding with the Raman lines below 1500 cm.^{-1} . Of these three should belong to the group A' and hence should be polarised and the other five should be depolarised. Also the in-plane vibrations, *viz.*, those belonging to the species E' , should be in general, stronger than the out-of-plane vibrations, *viz.*, those belonging to the species E'' . In the case of the BO_3C_3 group, there should be four vibrations belonging to species E' and one belonging to E'' . On this basis the assignments indicated in Table I are made. For the species A' and E' our assignments are in complete agreement with those of Becher (1954). However, a weak line at 575 cm.^{-1} observed by Becher has been assigned to species E'' . This line is not present in the spectrum recorded by the author. The depolarised Raman line appearing weakly at 546 cm.^{-1} has therefore been assigned to E'' instead.

There are two vibrations belonging to the species A'' , which are infra-red-active. One frequency has been given by Becher for the BO_3 out of plane

deformation at 664 cm.^{-1} The other frequency, *viz.*, the BOC out of plane bending could be at 575 cm.^{-1} This assignment is quite tentative since there are no infra-red data below 600 cm.^{-1}

There remain two more frequencies to be identified, which arise due to the twisting of the CH_3 group. The Raman-active CH_3 twisting frequency can be identified with the weak Raman line at 473 cm.^{-1} The other infra-red-active degenerate CH_3 twisting vibration is arbitrarily taken to give a frequency of 250 cm.^{-1}

TABLE I
Raman spectrum of methyl borate

Author	Anantha-krishnan	Becher (I.R.)	Assignment	Species
0-110	Wing	..
1. 200 (12)	..	197	BOC deformation	E'
2. 318 (12)	..	320	BOC deformation	A'
3. 473 (2)	CH_3 twisting	E''
4. 524 (8)	..	526	BO_2 deformation	E'
5. 546 (1)	BOC deformation out of plane	E''
..	664 BO_3 out of plane deformation	A''
6. 673 (1)	200 + 473	E' + E''
7. 726 (18)	..	728	B-O stretching	A'
8. 774 (12)	776 318 + 473	A' + E''
9. 815 (1)	815 524 + 318	A' + E'
10. 920 (1 b)	923 726 + 200	A' + E'
11. 1030 (16)	..	1030	1029 C-O stretching	E'
12. 1114 (10)	..	1117	.. C-O stretching	A'
13. 1175 (10)	..	1174	1176 CH_3 Rocking	E'

TABLE I (Contd.)

Author	Anantha- krishnan	(I.R.)	Assignment	Species	
14. 1224 (1)	E''	
..	..	1247	..	A''	
15. 1287 (1)	A'	
16. 1335 (1)	1347	B-O stretching	E'
17. 1390 (1 b)	1392	CH ₃ bending	E'
18. 1465 (15 b)	..	1460	E''
..	..	1511	A''
19. 2060 (1)	2 × 1030	2E'
20. 2139 (0)	2150	1030 + 1114	A' + E'
21. 2183 (0)	1030 + 1175	E' + E'
22. 2227 (0)	2220	2 × 1114	2 A'
23. 2330 (1)	2 × 1175	2 E'
24. 2528 (0)	2510	1347 + 1175	E' + E'
25. 2617 (5 b)	..	2614	2610	1465 + 1175	E' + E''
26. 2812 (16)	CH ₃ stretching	..
27. 2838 (16)	..	2838	..	CH ₃ stretching	A'
28. 2870 (20)	..	2870	2875	..	E' ?
29. 2905 (16)	..	2910
..	..	2925	A''
30. 2942 (20)	..	2940	A'
31. 2974 (16)	..	2974	2960	..	E'
32. 2996 (16)	..	2988	E''
33. 3480 (1)	2942 + 524	A' + E'
34. 3572 (1)	2870 + 726	A' + E'

There are a number of faint Raman lines which could be explained only as combinations and overtones of the fundamental frequencies and their assignments are also included in Table I. The fairly strong Raman line at about 776 cm.^{-1} may be the combination $318 + 473 \text{ cm.}^{-1}$ which has increased in intensity because of its nearness to the intense B-O stretching frequency at 726 cm.^{-1} . For the symmetry C_{3h} the following combinations are active in the Raman effect: $a' + e'$, $a' + e''$, $a'' + e'$, $a'' + e''$ and $e' + e''$. The combining species of the various combination lines are indicated in column 5 of Table I.

(c) *Calculation of force constants for methyl borate.*—Since a group theoretical analysis of the whole molecule of $B(\text{OCH}_3)_3$ will involve 8th and 9th degree equations which could not be solved here, the molecule is treated as a planar $\text{XY}_3 \text{Z}_3$ one the CH_3 group being considered as a single unit. This molecule will have 10 distinct fundamental frequencies distributed among the various species as follows:

$$3A' + 2A'' + 4E' + 1E''.$$

Also, since there is no infra-red data below 600 cm.^{-1} , the out-of-plane motions, *i.e.*, species A'' and E'' are not treated here. Wilson's (1939, 1941) F-G matrix method is used for calculating the force constants.

Internal co-ordinates.—The internal co-ordinates chosen for this problem are Δd_1 , Δd_2 , Δd_3 ; ΔD_1 , ΔD_2 and ΔD_3 , the changes in B-O and O-C distances respectively, and Δa_{12} , Δa_{23} , Δa_{31} ; $\Delta \beta_1$, $\Delta \beta_2$ and $\Delta \beta_3$, the changes in OBO and BOC angles. These are indicated on Fig. 2. As there are 12 internal co-ordinates, 12 symmetry co-ordinates can be constructed from these. Of these only eleven are genuine, and so one co-ordinate must be redundant. This is in the species A' . The symmetry co-ordinates for the various species are:

Species A'

$$R_1 = \frac{1}{\sqrt{3}} (\Delta d_1 + \Delta d_2 + \Delta d_3)$$

$$R_2 = \frac{1}{\sqrt{3}} (\Delta D_1 + \Delta D_2 + \Delta D_3)$$

$$R_3 = \frac{1}{\sqrt{3}} (\Delta \beta_1 + \Delta \beta_2 + \Delta \beta_3)$$

Species E'

$$R_{4a} = \frac{1}{\sqrt{6}} (2\Delta d_1 - \Delta d_2 - \Delta d_3)$$

$$R_{4b} = \frac{1}{\sqrt{2}} (\Delta d_2 - \Delta d_1)$$

$$R_{5a} = \frac{1}{\sqrt{6}} (2\Delta D_1 - \Delta D_2 - \Delta D_3)$$

$$R_{5b} = \frac{1}{\sqrt{2}} (\Delta D_2 - \Delta D_3)$$

$$R_{6a} = \frac{1}{\sqrt{6}} (2\Delta \alpha_{23} - \Delta \alpha_{31} - \Delta \alpha_{12})$$

$$R_{6b} = \frac{1}{\sqrt{2}} (\Delta \alpha_{31} - \Delta \alpha_{12})$$

$$R_{7a} = \frac{1}{\sqrt{6}} (2\Delta \beta_1 - \Delta \beta_2 - \Delta \beta_3)$$

$$R_{7b} = \frac{1}{\sqrt{2}} (\Delta \beta_2 - \Delta \beta_3).$$

Using these co-ordinates the elements of the G-matrices can be evaluated and are given below:

Species A':

$$G_{11} = \mu_0$$

$$G_{22} = \mu_0 + \mu_c$$

$$G_{33} = \frac{\mu_c}{D_0^2} + \mu_0 \left[\frac{1}{D_0^2} + \frac{1}{d_0^2} - \frac{2 \cos \beta}{d_0 D_0} \right]$$

$$G_{12} = \mu_0 \cos \beta$$

$$G_{13} = -\frac{\mu_0 \sin \beta}{D_0}$$

$$G_{23} = -\frac{\mu_0 \sin \beta}{d_0}.$$

Species E':

$$G_{44} = \mu_0 + \frac{3}{2} \mu_B$$

$$G_{55} = \mu_0 + \mu_c$$

$$G_{66} = \frac{3\mu_0}{d_0^2} + \frac{9\mu_B}{2d_0^2}$$

$$G_{77} = \frac{\mu_c}{D_0^2} + \mu_0 \left[\frac{1}{d_0^2} + \frac{1}{D_0^2} - \frac{2 \cos \beta}{d_0 D_0} \right] + \frac{3 \mu_B}{2 d_0^2}$$

$$G_{45} = \mu_0 \cos \beta$$

$$G_{46} = \frac{3\sqrt{3}}{2} \frac{\mu_B}{d_0}$$

$$G_{47} = -\mu_0 \frac{\sin \beta}{D_0}$$

$$G_{56} = 0$$

$$G_{57} = -\mu_0 \frac{\sin \beta}{d_0}$$

$$G_{67} = 0$$

where d_0 = equilibrium B-O distance = 1.38 Å, D_0 = equilibrium O-C distance = 1.43 Å, $\beta = \widehat{BOC} = 113^\circ$, and the μ 's are the inverse masses. μ_c is the inverse mass of the CH₃ group as a whole.

F-matrices.—Only a simple valence potential function is employed taking into account a few interaction terms. The F-matrices for the two species are then as follows:

Species A'

$$\begin{bmatrix} F_d + 2F_{dd} & 0 & 0 \\ 0 & F_D & 0 \\ 0 & 0 & d_0^2 [F_\beta + 2F_{\beta\beta}] \end{bmatrix}$$

Species E'

$$\begin{bmatrix} F_d - F_{dd} & 0 & 0 & 0 \\ 0 & F_D & 0 & 0 \\ 0 & 0 & d_0^2 F_\alpha & 0 \\ 0 & 0 & 0 & d_0^2 [F_\beta - F_{\beta\beta}] \end{bmatrix}$$

where the F's have the usual significance. The secular equation for each species is then separately got as $(FG - E\lambda) = 0$ where E is a unit matrix. Thus we get a cubic equation for the species A' and quartic one for the species E'. Using the frequencies 726, 1114 and 318 cm.⁻¹ for species A' and 1347, 1030, 524 and 200 cm.⁻¹ for species E' the force constants could be found by a method of successive approximations. They are found to be;

$$F_d = 4.579 \times 10^5 \text{ dynes cm.}^{-1}$$

$$F_D = 5.315 \times 10^5 \text{ dynes cm.}^{-1}$$

$$F_a = 0.130 \times 10^5 \text{ dynes cm.}^{-1}$$

$$F_\beta = 0.527 \times 10^5 \text{ dynes cm.}^{-1}$$

$$F_{dd} = -0.088 \times 10^5 \text{ dynes cm.}^{-1}$$

$$F_{\beta\beta} = 0.037 \times 10^5 \text{ dynes cm.}^{-1}$$

(d) *Calculation of thermodynamic quantities.*—Since all the 42 fundamental frequencies of methyl borate could be identified, the statistical thermodynamic functions of the molecule could be computed following the methods outlined by Herzberg (1945) and Taylor and Glasstone (1946). These are given in Table II for temperatures from 300° K. to 1,000° K. The moments of inertia of the molecule are:

TABLE II

T° K.	$\frac{H_0 - E_0}{T}$	$\frac{F_0 - E_0}{T}$	S	C
300	16.315	61.840	78.152	28.352
400	20.363	67.100	87.459	36.562
500	24.367	72.083	96.448	43.957
600	28.177	76.897	105.071	50.268
700	31.703	81.426	113.127	55.608
800	34.989	85.927	120.913	60.143
900	37.998	90.240	128.235	63.966
1000	40.783	94.391	135.171	67.253

All the values are given in calories per mole per °C.

$$\frac{H_0 - E_0}{T} = \text{Total heat capacity.}$$

$$\frac{F_0 - E_0}{T} = \text{Total free energy.}$$

S = Total entropy.

C = Total heat content.

$I_A = 561.682 \times 10^{-40} \text{ gm./cm.}^2$ (about the principal 3-fold axis)

$I_B = I_C = 280.841 \times 10^{-40} \text{ gm./cm.}^2$ (about axes in the molecular plane).

The error, introduced by the uncertainty in the BOC out-of-plane vibration frequency and CH_3 twisting frequency in the infra-red absorption, will be only very small. Table II has been calculated on the assumption that there is no free or hindered rotation of the CH_3 groups. In the liquid state at least there seems to be no evidence for free or hindered rotation of the methyl groups.

4. SUMMARY

The Raman spectrum of methyl borate has been recorded using mercury $\lambda 2537$ excitation. Thirty-four Raman lines are recorded of which eighteen are reported for the first time. A complete vibrational assignment has been attempted by a comparison of the infrared and Raman spectra of methyl borate on the assumption that the molecular symmetry is C_{3h} . Using Wilson's F-G matrix method, the force constants for the in-plane vibrations of the BO_3C_3 part of the molecule have been calculated. Also, the entropy, heat content, heat capacity and free energy of the molecule have been evaluated from the spectroscopic data, on the assumption that the methyl groups exhibit no free or hindered rotation.

5. ACKNOWLEDGMENTS

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