

**Investigations in the Infra-Red.\***

*Part I. Absorption Spectrum and Molecular  
Structure of Borates*

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ABSTRACT.

A study of the near infra-red absorption spectra of a few borates has been made in the region  $5\mu$ - $15\mu$ . The results are in agreement with the predictions of Cassie. The magnitude of the true force constant of the radical under investigation in comparison to that of  $\text{CO}_3$  and  $\text{NO}_3$  shows that the bond is not localised as in  $\text{BCl}_3$ . The slightly positive value of true rigidity reveals further that its plane configuration is not due to repulsion of the oxygen ions alone and follows the central quantisation more closely than  $\text{NO}_3$  or  $\text{CO}_3$  radical.

1. *Introduction.*

It is now well known that a radical or a molecule of the type  $\text{XO}_3$  may possess either a pyramidal or a planar configuration, and has six vibrational degrees of freedom but only four distinct fundamental frequencies. One of these corresponds to oscillation of the X atom relative to the  $\text{O}_3$  triangle along the

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line through the median point and normal to its plane. There are two fundamentals of double frequencies corresponding to the motion of the four atoms in the equilibrium plane. Another is due to simultaneous vibration of the three O atoms in phase towards or away from the X atom. This frequency plays an important role in deciding between the pyramidal and planar configurations. For a radical or molecule with the planar configuration it is inactive whereas in the case of a pyramidal one it is active.

A planar configuration has been ascribed to the nitrates, carbonates as well as the borates from crystal lattice data. In the case of the first two radicals, support to this view has been obtained from a study of their infra-red and Raman spectra. Pauling<sup>1</sup> however suggested that these radicals are slightly pyramidal in structure and the apparent planar configuration is due to the vibration of the N or C nuclei through the oxygen plane. From a consideration of their rigidity Cassie<sup>2</sup> has shown that the nitrate radical has a greater tendency to become pyramidal than the carbonate and that the plane configuration is maintained not through the central quantisation but through the repulsion of the oxygen ions. It is therefore, of interest to calculate the rigidity of  $\text{BO}_3$  as well as its force constants which will indicate the type of link in the BO bond. For this purpose a study of the infra-red and Raman spectra of the radical has been considered to be desirable.

The present paper deals with the infra-red investigations on a few inorganic borates. In view of the fact that the fundamentals of the carbonate<sup>3</sup> and nitrate<sup>4</sup> radicals lie between  $5\mu$  to  $15\mu$ , our observations are also confined to this region of the spectrum. Three fundamental frequencies have been located at  $7.5\mu$ ,  $11\mu$  and  $14\mu$ . The fourth fundamental which from a

<sup>1</sup> Pauling, *Jour. Amer. Chem. Soc.*, Vol. 53, p. 1882 (1931).

<sup>2</sup> Cassie, *Proc. Roy. Soc., "A"* Vol. 148, p. 87 (1935).

<sup>3</sup> Brester, *Zeits. f. Phys.* Vol. 24, p. 324 (1924.).

<sup>4</sup> Schafer and others, *Zeits. fur. Phys.* Vol. 45, p. 493 (1927).

comparison of the data for the above two radicals may be expected to be at about  $9\mu$  is definitely absent. This would correspond to the inactive fundamental frequency and would prove that the  $\text{BO}_2$  radical has a planar configuration. The true rigidity of the radical as distinct from its strain rigidity is slightly positive. Hence its planar configuration is not due to repulsion of the oxygen ions alone and follows the central quantisation more closely than  $\text{CO}_2$  and  $\text{NO}_2$ . The evaluation of the true force constant reveals further that the bond is not localised as in  $\text{BCl}_2$  investigated by Cassie (*loc. cit.*).

## 2. Experimental.

The source of radiation is a linear Nernst filament. A steady current from a battery of 72 storage cells of 250 amp.-hours capacity has been used to heat the filament. The current through the filament is maintained at 0.50 amps. with the help of a suitable resistance in series.

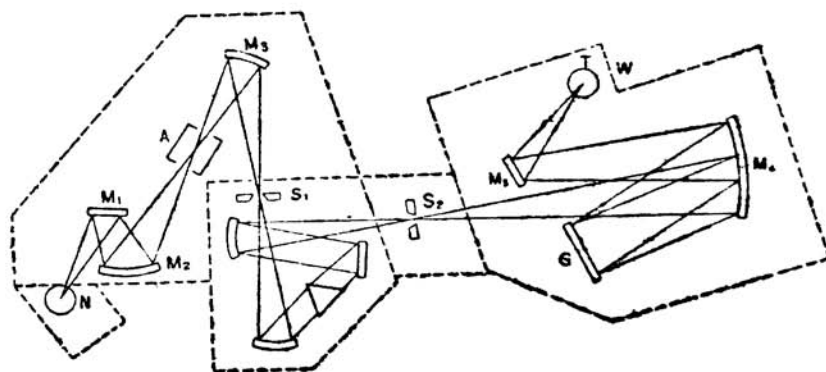


FIG. 1.

The general optical arrangement of the dispersive system is given in Fig. 1. This consists of three parts. The first part contains the condensing mirrors and the absorption chamber. Radiation from the source  $N$  after reflection at a plane mirror

$M_1$  is focussed at A within the absorption chamber by the concave mirror  $M_2$ . The beam then diverges and is again brought to a focus by the mirror  $M_3$ , on the slit  $S_1$  which is the entrance slit of the prism spectrometer. The second part consists of the prism spectrometer which is a Leiss monochromator having a rock salt prism, two concave mirrors placed at right angles and a prism table with a Wadsworth mirror mounted on it and capable of rotation from outside by worm wheel and pinion. The scale on the drum is directly graduated in wavelengths corresponding to rock salt prism.

The second slit  $S_2$  of the monochromator is the collimator slit of the grating spectrometer which constitutes the third part in the diagram.  $M_4$  is a single long focus concave mirror functioning both as the collimator and telescope. The last mirror  $M_5$  which is a plane one brings the focus to a convenient position for the thermopile T. The grating G is mounted on a goniometric table. In the present investigation, the grating spectrometer has not however been used.

A thermopile in conjunction with a Paschen galvanometer has been used for the detecting system and is of Hilger bismuth silver junction type. It has a symmetrical slit in its front and an eyepiece behind it. The latter along with a cross wire inserted in place of the pile is used for visual calibration. The Downing type Paschen galvanometer has a resistance of 13.56 ohms and gives a deflection of 1600 mms. per microampere on a scale placed at a distance of 1 meter. The sensitivity of the galvanometer can be varied by means of its control magnets. It has been made free from mechanical vibrations as far as possible by placing it on a concrete pillar on a foundation of about 9 ft. below the floor of the laboratory. Underneath the foundation there are shock absorbers consisting of 2 sheets of lead placed under 5 sheets of India rubber. The annular space around the pillar is filled with sand. To overcome the electrical disturbances on the connecting wires they are enclosed in composition tubing carefully earthed. Even with this arrangement the galvanometer vibrates

due to outside mechanical disturbances such as the passing of a heavy vehicle in the neighbourhood. The observations had therefore to be taken in the calm hours of the night.

The different sections of the apparatus are enclosed in separate boxes as indicated by dotted lines in Fig. 1. The Nernst filament with its asbestos housing is kept outside the chamber containing the absorption cells and the condensing mirrors. The enclosing chamber is provided with shutters to screen the rock salt prism from the influence of moist draughts while the instrument is not in operation. The box containing the grating spectrometer and the thermopile has its walls lined with asbestos. The open spaces are all packed with cotton wool to ensure a constancy of temperature inside.

The absorption chamber has been designed to hold vertically a rock salt plate on one side of which a thin layer of the solid under investigation is spread in the form of fine powder. Previous to this the rock salt plate is well ground and polished. To prevent moisture from depositing on the rock salt plates, the chamber, A is provided with a heater which consists of a small resistance coil carefully insulated. This enables us to maintain a slightly higher temperature than that of the room, the difference being nearly  $3^{\circ}\text{C}$ . A similar precaution is also taken to keep the monochromator prism dry. Drying agents are also placed inside the boxes to ensure further that the general atmosphere is free from moisture.

As the drum of the monochromator is calibrated in wavelength scale, it is expected that wave-length of any monochromatic radiation could be directly obtained, only if the prism is set in its minimum deviation for any known radiation. The green and yellow lines of mercury have been used for this purpose. A further check on the accurate setting of the prism spectrometer was made by identifying the fundamental bands of  $\text{BaCO}_3$ .

3. *Experimental Results.*

Merck's chemicals of extra pure quality were used in the investigation. Curves showing the absorption maxima for compounds are given in Fig. 2. It will be seen that in each case there are a number of absorption regions, some of which are evidently due to the presence of combination tones. In view of their intensities the mean band centres at  $7.5 \mu$ ,  $11 \mu$  and  $14 \mu$  select themselves as the active fundamentals. From an analogy with  $\text{CO}_2$  and  $\text{NO}_2$  radicals they have been ascribed to  $\nu_2$ ,  $\nu_1$  and  $\nu_3$ , respectively, while the remaining fundamental  $\nu_4$  which is optically inactive is assumed to lie at about  $9 \mu$ . The band centres of the observed fundamentals for the different compounds are collected in Table I.

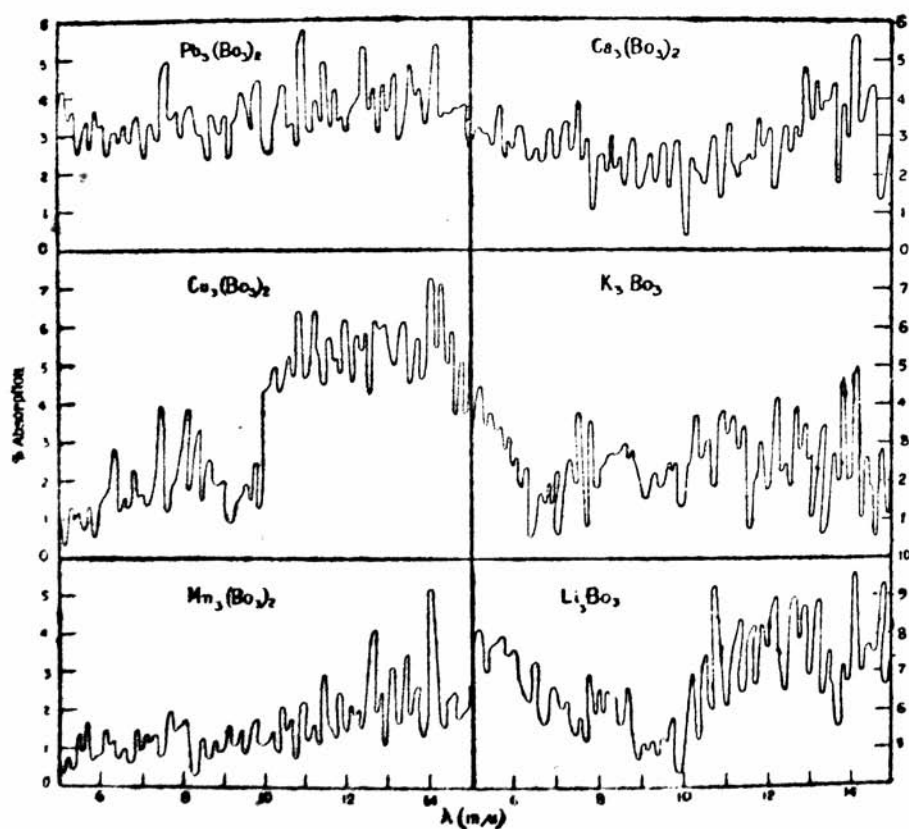


FIG. 2.

TABLE I.

Compound.	Bands.		
	$\nu_2$ ( $\mu$ )	$\nu_1$ ( $\mu$ )	$\nu_3$ ( $\mu$ )
Lithium Borate	7.6	10.7	14.0
Potassium Borate	7.5	10.9	14.1
Calcium Borate	7.5	11.0	14.1
Manganese Borate	7.6	10.8	14.0
Copper Borate	7.5	10.8	14.2
Lead Borate	7.6	11.0	14.1

4. Evaluation of Force Constants.

Formulae showing the relationships between the fundamental frequencies and force constants of the  $XO_3$  type radical or molecule have been given by Nielson<sup>5</sup> and later by Menzies.<sup>6</sup> It may here be pointed out that their results are not in agreement due probably to approximation involved in transforming the potential function,

$$V = F(r) + f(a) + F'(r)(q_4 + q_5 + q_6) + \frac{1}{2}F''(r)(q_4^2 + q_5^2 + q_6^2) + f'(a)(q_1 + q_2 + q_3) + \frac{1}{2}f''(a)(q_1^2 + q_2^2 + q_3^2) \dots \dots \dots (1)$$

where  $r$  is the normal distance of X from O atom ;  $a$ , the length of the side of the triangle in the undisplaced state;  $q_1, q_2$  and  $q_3$ , the mutual displacements of O atoms in pairs;  $q_4, q_5$  and  $q_6$ , the relative displacements of the X and the O atoms.

Menzies' expression for the frequencies are

$$\nu_1 = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \sqrt{\beta\mu} \dots \dots \dots (2)$$

<sup>5</sup> Nielson, Phys. Rev., Vol. 32, p. 773 (1928).  
<sup>6</sup> Menzies, Proc. Roy. Soc. "A," Vol. 134, p. 265 (1931).

$$\nu_{2,3} = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \sqrt{\frac{1}{4}[\mu(1+\beta) + (1+3\alpha)] \pm \sqrt{\frac{1}{4}[\mu(1+\beta) + \frac{1}{4}(1+3\alpha)]^2 - \frac{1}{4}\mu \times [(1+3\alpha)(1+\beta) - (1-\beta)^2]}} \quad \dots \quad (3)$$

$$\nu_4 = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \sqrt{(1+3\alpha)} \quad \dots \quad (4)$$

where  $\mu = \frac{M+3m}{M}$  ( $M$  is the mass of X atom;  $m$ , the mass of O atom)

$$k = F''(r); \quad \alpha = \frac{f''(a)}{F''(r)}; \quad \beta = \frac{F'(r)/r}{F''(r)}$$

The value of  $F''$  is found out by eliminating  $\alpha$  and  $\beta$  from equations (3) and (4) as follows:—

$$[(\nu_2^2 + \nu_3^2)^2 - (\nu_2^2 - \nu_3^2)^2] \mu - \gamma(\nu_4^2 \mu - \gamma)] A^2 - 4\mu\gamma A + 4\mu^2 = 0 \quad \dots \quad (5)$$

$$\text{where } \gamma = [2(\nu_2^2 + \nu_3^2) - \nu_4^2]$$

Hence “A” can be evaluated by solving the above quadratic equation and is related to  $F''$  as  $A = \frac{4\pi^2 m}{F''}$ . Corresponding to the two values of “A” we have  $F'' = 4.3 \times 10^5$  and  $1.8 \times 10^5$  dynes/cm. Now substituting these values in equations (3) and (4)  $f''$  and  $F'$  are found to be as follows:

$f''$	$F'$
dynes/cm.	dynes.
$2.4 \times 10^5$	$1.9 \times 10^{-8}$
$3.4 \times 10^5$	$5.5 \times 10^{-8}$

On the other hand the value of  $F'$  corresponding to  $\nu_1$  is  $2.0 \times 10^{-8}$  dynes. This shows that  $F' = 1.9 \times 10^{-8}$  dynes corresponds to the case when the planar configuration could be maintained in the absence of repulsion between the atoms while  $F' = 5.5 \times 10^{-8}$  dynes to the case when the repulsion alone simulates its plane configuration.



The force constant  $F''$  of any link calculated as above from the observed vibrational frequencies should be corrected for deviation from the minimum of the potential energy curve to give its true value. It may here be noted that the value of  $F'' = \frac{d^2V}{dr^2}$  measures the curvature of the  $V:r$  curve for the link at its equilibrium separation and corresponds to the minimum in the curve for diatomic and non-closed triatomic molecules. But if the link is under strain as in the present case the equilibrium separation does not represent this minimum and the curvature measured by  $F''$  may be very different from that of the same link joining the same atoms in a diatomic molecule. The analytical expression for the potential energy curve of a diatomic molecule as given by Morse is

$$F = D e^{-2a(r-r_0)} - 2D e^{-a(r-r_0)} \quad \dots (6)$$

where  $D$  is the energy of dissociation of the bond,  $r_0$  the separation of the nuclei at the position of the minimum potential and  $a = 0.245 \sqrt{M_0 \omega_0 x}$  in  $\text{A}^{-1}$ ,  $\omega_0 x$  being the anharmonicity factor and  $M_0 = \frac{Mm}{M+m}$

Putting  $b = e^{-a(r-r_0)}$

$$F = -2aDb^2 + 2aDb \quad \dots (7)$$

$$F'' = 4a^2Db^2 - 2a^2Db \quad \dots (8)$$

For  $r = r_0$  the true force constant,

$$F_0'' = 2a^2D \quad \dots (9)$$

Now  $D$  can be determined from equations (7) and (8) as follows :—

$$D = \frac{(4F' + F'')^2}{8(2F' + F'')} \quad \dots (10)$$

Corresponding to  $F'' = 4.3 \times 10^5$  dynes/cm and  $F' = 1.9 \times 10^{-3}$  dynes the energy of dissociation  $D$  is 13.7 volts. Substituting the value of  $D$  in equation (9) one can evaluate the true force constant  $F''_0$  provided "a" is known. From the analysis of the bands associated with the diatomic molecule of boron monoxide<sup>7</sup> one finds that in the ground state,  $^2\Sigma$ , of the molecule,  $\omega_0 x$  is  $10.7 \text{ cm.}^{-1}$  so that  $a$  comes out to be nearly  $2\text{A}^{-1}$  and the true force constant  $F''_0$  is  $17.4 \times 10^5$  dynes/cm.

### 5. Calculation of Rigidity.

Of the four fundamental frequencies  $\nu_1$  is assumed to arise only from the strain of the radical and as we have already remarked it corresponds to motion of the B atom in the perpendicular plane. On the other hand, the frequencies  $\nu_2$ ,  $\nu_3$  and  $\nu_4$  involve only motions in the plane of the triangle. Hence  $\beta$  should have two different values, their difference giving a measure of the rigidity of the plane configuration which can be calculated as follows from the observed fundamental frequencies:—

If  $\theta$  is the angle between the displaced link and its equilibrium position, the potential energy associated with a deviation of one BO bond from the plane configuration is given by,

$$V = \frac{1}{2} K_\theta (r^2 \theta^2) \quad \dots (11)$$

where  $K_\theta$  is the tangential restoring force constant.  $\nu_1$  is then given by

$$4\pi^2 \nu_1^2 = \frac{1}{m} K_\theta \mu \quad \dots (12)$$

But from Menzies' expression,

$$4\pi^2 \nu_1^2 = \frac{1}{m} \cdot \frac{F'}{r} \cdot \mu \quad \dots (13)$$

<sup>7</sup> Jevons, Report on Band Spectra of Diatomic Molecules.

Hence assuming  $r$  to be  $1.35\text{\AA}$  as found by Zachariassen<sup>8</sup> one can calculate from the above relation the value of  $F'/r$  and thus of  $K_0$  which must be corrected for the strain of the radical. The frequencies of the normal modes confined to the plane of the radical give  $F'/r$  as  $1.4 \times 10^5$  dynes/cm. and this is due to strain alone. On the other hand  $F'/r$  calculated from  $\nu_1$  is  $1.5 \times 10^6$  dynes/cm. This shows that the true rigidity of each bond is given by tangential restoring force constant of approximately  $1 \times 10^4$  dynes/cm; in other words the rigidity associated with the central B atom in  $\text{BO}_2$  radical is  $3 \times 10^4$  dynes cm.

### 6. Conclusions.

The results are in agreement with the prediction of Cassie. The magnitude of the true force constant of the radical under investigation in comparison to that of  $\text{CO}_2$  and  $\text{NO}_2$  shows that the bond is not localised as in  $\text{BCl}_2$ . The slightly positive value of true rigidity reveals further that its plane configuration is not due to repulsion of the oxygen ions alone and follows the central quantisation more closely than  $\text{NO}_2$  or  $\text{CO}_2$  radical.

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<sup>8</sup> Zachariassen, Jour. Amer. Chem. Soc., Vol. 53, p. 2124 (1931).