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## The Infra-Red Spectrum of Borine Carbonyl and a Normal Coordinate Analysis of Axial $WXYZ_3$ Molecules\*

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The infra-red spectrum of borine carbonyl has been investigated in the region 2 to  $25\mu$ . Two perpendicular-type bands have been partially resolved, and indicate that the molecule is a symmetric top with symmetry  $C_{2v}$ . A normal coordinate analysis of axial  $WXYZ_3$  molecules has been carried out and applied to  $H_3BCO$ , the following values having been obtained for the force constants:  $k_{CO}=17.3$ ,  $k_{BC}=2.97$ ,  $k_{BH}=3.21$ ,  $k_{BCO}=0.142$ ,  $k_{HBC}=0.333$ ,  $k_{HBH}=0.363$ , all in units of  $10^6$  dynes/cm.

### INTRODUCTION

THE structure of the borine carbonyl molecule has, until recently, remained in some doubt. The two most likely alternatives are  $H_3BCO$ , in which all three hydrogen atoms are bonded to the boron atom, and  $H_2BCHO$ , with two hydrogen atoms bonded to the boron and the third hydrogen and one oxygen bonded to the carbon. The fact that borine carbonyl is unstable at room temperature and dissociates rather rapidly into diborane ( $B_2H_6$ ) and carbon monoxide favors the former structure,<sup>1</sup> as does an electron-diffraction investigation of the molecule.<sup>2</sup> However, the electron-diffraction results are not conclusive, and the dissociation of borine carbonyl could be the result of the transitory existence of  $H_3BCO$  or an equilibrium mixture of  $H_3BCO$  and  $H_2BCHO$ . A decision between these two possible structures is easily made from the infra-red spectrum of the compound, since the characteristic absorption of a C—H bond lies at about  $3000\text{ cm}^{-1}$  whereas that of a B—H bond lies in the region  $2400$  to  $2600\text{ cm}^{-1}$ . Since the completion of the experimental work on which this paper is based but before publication of preliminary results,<sup>3</sup> Gordy, Ring, and Burg<sup>4</sup> reported proof of the structure  $H_3BCO$  with symmetry  $C_{3v}$  from observations of the microwave spectrum.

### EXPERIMENTAL

The borine carbonyl was prepared by the method described by Burg and Schlesinger<sup>1</sup> from diborane and commercial carbon monoxide. It was purified by discarding those vapors which did not pass through a trap at  $-125^\circ\text{C}$  and those which did pass through one at  $-150^\circ\text{C}$ . The remaining vapor was frozen into a 10-cm Pyrex absorption cell with KBr windows. (It was sufficient in quantity to give a pressure in the cell of about 120 mm at room temperature.) To retard the decomposition of the borine carbonyl, carbon monoxide

was added to a partial pressure of 200 mm; in addition, whenever spectra were not being run, a side-tube connected to the cell was kept in a liquid nitrogen bath to freeze out the  $H_3BCO$ .

Spectra of the vapor were run with a Perkin-Elmer model 12B recording spectrometer, using LiF, NaCl, and KBr prisms. Spectra were obtained at pressures below 120 mm by connecting the cell to a vacuum line and allowing a portion of its contents to expand into the line. (The vapor in the line was then pumped through a trap at liquid nitrogen temperature, thus separating the  $H_3BCO$  from the CO, and the borine carbonyl was later frozen back into the cell and new carbon monoxide added ready for the next run.)

Over a period of eleven days, during which the borine carbonyl sample was kept in an excess of carbon monoxide, no appreciable decomposition of the former was noted. This is in contrast to later observations made after removing the CO: a measurable decrease in intensity of the borine carbonyl bands and an appreciable increase in intensity of the diborane bands was observed within fifteen minutes, and half of the carbonyl dissociated in two or three hours. (According to Burg and Schlesinger,<sup>1</sup> the half life of  $H_3BCO$  is about  $3\frac{1}{2}$  hours when starting with pure  $H_3BCO$  at a pressure of 105 mm.)

The fundamental band of carbon monoxide ( $2143\text{ cm}^{-1}$ ) nearly coincided with one of the borine carbonyl bands, but the latter was so extremely strong that the interference was not serious. Most of the absorption bands of diborane were also observed, but there was only one case of overlapping and that again involved a very strong band of borine carbonyl ( $2440\text{ cm}^{-1}$ ) so that no difficulty was experienced.

In addition to the diborane and carbon monoxide which were unavoidably present in the absorption cell, a third (unidentified) impurity was also detected. In the course of the observations which were made on the borine carbonyl spectrum with no added CO, it was found that two bands—one at  $215\text{ cm}^{-1}$  showing about ten percent absorption, and one at  $2057\text{ cm}^{-1}$  showing essentially 100 percent absorption at its center—remained constant in intensity while the borine carbonyl was decomposing. These bands were thus not due to

\* Work supported by Contract N6ori-20, T. O. IX, with the ONR.

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<sup>1</sup> A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.* **59**, 780 (1937).

<sup>2</sup> S. H. Bauer, *J. Am. Chem. Soc.* **59**, 1804 (1937).

<sup>3</sup> R. D. Cowan, *J. Chem. Phys.* **17**, 218L (1949).

<sup>4</sup> Gordy, Ring, and Burg, *Phys. Rev.* **74**, 1191L (1948).

$\text{H}_3\text{BCO}$  (nor to its decomposition products), as had been suspected also from the fact that they were only about half as wide as the other observed bands. Unfortunately, the observations on the dissociation of borine carbonyl were made with a rock salt prism, and so no check was obtained on the authenticity of the bands observed at  $622$  and  $423\text{ cm}^{-1}$ . The  $423\text{ cm}^{-1}$  band is probably also due to the impurity, since it is rather narrow. The compound responsible for the extraneous bands remains unidentified—the bands cannot be attributed to any of the impurities likely to be present in diborane, and no impurities were detected spectroscopically in the carbon monoxide used (run at a pressure of  $70\text{ cm}$  in a  $10\text{ cm}$  cell). It was considerably less volatile than borine carbonyl, as it was found to pass fairly readily through a trap at  $-85^\circ\text{C}$  whereas most of it was caught in a trap at  $-95^\circ\text{C}$ . It may have been produced by a side reaction in the absorption cell, or may have been present in the originally prepared sample and not completely removed during the purification process, which was carried out only once due to the fear that borine carbonyl was more unstable than it actually proved to be.

### RESULTS

A general view of the spectrum is shown in Fig. 1. The percent absorption plotted there was obtained with the aid of estimated background curves (such as the dashed line in Fig. 2); actual background runs with

an empty cell were not made since they would not have allowed for absorption by the carbon monoxide and diborane anyway. The frequencies of the absorption maxima are given in Table I. It will be noticed that there are no strong bands in the vicinity of  $3000\text{ cm}^{-1}$ , which indicates that at least the great majority of borine carbonyl molecules do not have the structure  $\text{H}_2\text{BCHO}$ .

In Figs. 2 and 3 are shown photographs of original records of the bands at  $809\text{ cm}^{-1}$  and  $2440\text{ cm}^{-1}$ . The structure of these bands is typical of perpendicular bands of a symmetric top molecule, and the maxima produced by successive  $Q$  branches show a distinct intensity alternation of the type *strong, weak, weak, strong . . .*, which indicates the presence of a threefold symmetry axis.<sup>5</sup> The observed intensity ratio agrees well with the value  $2:1$  to be expected for one set of three off-axis hydrogen atoms.<sup>5</sup> The infra-red evidence thus very strongly favors the structure  $\text{H}_3\text{BCO}$  (or  $\text{H}_3\text{BOC}$ ) with symmetry  $C_{3v}$  for borine carbonyl, in agreement with the microwave results.<sup>4</sup>

The positions and probable assignments of the maxima of the  $809$  and  $2440\text{ cm}^{-1}$  perpendicular bands are given in Tables II and III, respectively. (The assignments have been based on the requirement<sup>5</sup> that the strong maxima should correspond to values of  $K''$  of  $0, 3, 6, \dots$ . It may be noted that there are some irregularities in the  $2440\text{ cm}^{-1}$  band—due perhaps to interference from the corresponding band of  $\text{H}_3\text{B}^{10}\text{CO}$ .)

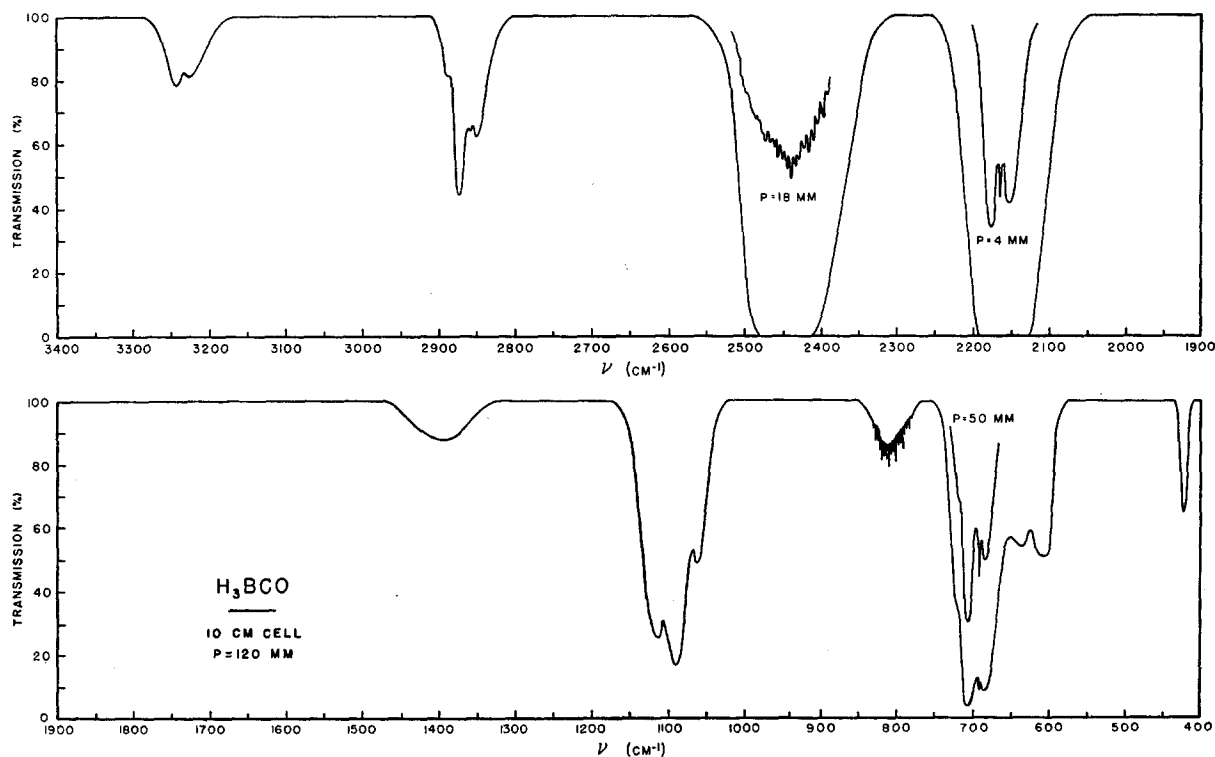


FIG. 1. The infra-red absorption spectrum of borine carbonyl.

<sup>5</sup> G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Co., Inc., New York, 1945), p. 432.

The average spacing between  $Q$ -maxima is  $3.1 \text{ cm}^{-1}$  for the  $809 \text{ cm}^{-1}$  band and  $6.7 \text{ cm}^{-1}$  for the other, the difference being attributable to Coriolis coupling between vibration and rotation. Since there should be four perpendicular bands and these have not all been resolved (nor even observed?), it is not possible to draw any conclusions regarding the moments of inertia of the borine carbonyl molecule. However, accurate values of the moments are available, and from these an estimate can be made of the spacings which should be observed in the other two perpendicular bands:

A straightforward extension of the calculation of Johnston and Dennison<sup>6</sup> for axially symmetric  $XYZ_3$  molecules has been carried out by the present author, the result obtained being that for axial  $WXYZ_3$  molecules, the sum of the  $\zeta$ -values for the fundamental vibrations of species  $E$  is

$$\zeta_5 + \zeta_6 + \zeta_7 + \zeta_8 = (I_A/2I_B) + 1 = (B/2A) + 1,$$

where  $I_A$  and  $I_B$  are the moments of inertia about axes along and perpendicular to the symmetry axis respectively, and  $A (=h/8\pi^2cI_A)$  and  $B$  are the corresponding rotational constants. The structure of borine carbonyl has been determined from the microwave spectra of the normal and deuterated compounds (for both  $B^{10}$  and  $B^{11}$ ) by Gordy, Ring, and Burg.<sup>7</sup> From their results, the calculated values of  $A$  and  $B$  are  $4.17$  and  $0.29 \text{ cm}^{-1}$ , respectively. This gives  $\sum \zeta = 1.03$ . From the theoretical expression  $\Delta\nu = 2(A-B) - 2A\zeta$  for the separation of successive  $Q$  maxima, one obtains  $\zeta = 0.13$  for the  $2440 \text{ cm}^{-1}$  band and  $\zeta = 0.56$  for the  $809 \text{ cm}^{-1}$  band,

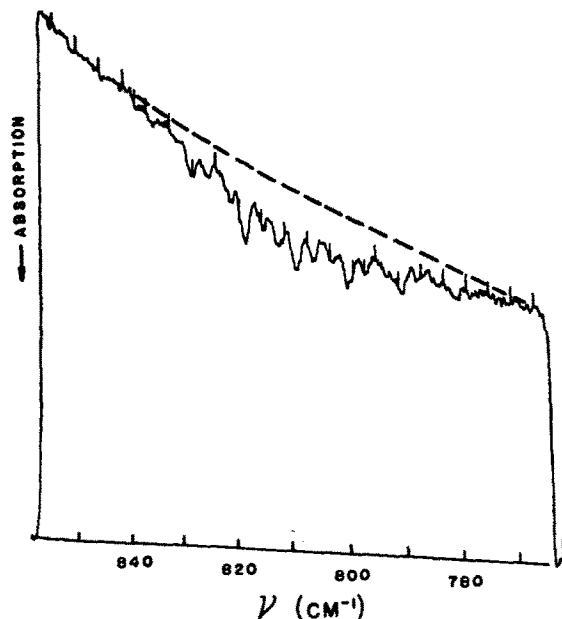


FIG. 2. Record of the  $809 \text{ cm}^{-1}$  band.

<sup>6</sup> M. Johnston and D. M. Dennison, Phys. Rev. 48, 868 (1935).  
<sup>7</sup> Gordy, Ring, and Burg, Phys. Rev. 78, 512 (1950). A copy of their manuscript was very kindly sent to the present author by Professor Gordy prior to publication.

TABLE I. Absorption bands of borine carbonyl.

$\nu_{\text{vac}}$	Type	Intensity*	Effective slit width
$423 \text{ cm}^{-1}$	(impurity?)	35	$4.5 \text{ cm}^{-1}$
$609 \left. \begin{array}{l} \text{635} \end{array} \right\}$	$\parallel ?$	45	4.5
$681 \left. \begin{array}{l} \text{692} \end{array} \right\}$	$\parallel$	230	1.8
$706 \left. \begin{array}{l} \text{809} \end{array} \right\}$	$\perp$	20	1.7
$1062 \left. \begin{array}{l} \text{1091} \end{array} \right\}$	$\parallel ?$	230	2.6
$1114 \left. \begin{array}{l} \text{c.1392} \end{array} \right\}$	$\perp ?$ (interf. $\text{H}_2\text{O}$ )	10	4.5
$2152 \left. \begin{array}{l} \text{2164} \end{array} \right\}$	$\parallel$	3300	2.5
$2176 \left. \begin{array}{l} \text{2440} \end{array} \right\}$	$\perp$	500	2.6
$2851 \left. \begin{array}{l} \text{2860} \end{array} \right\}$	$\parallel ?$	65	4.4
$2872 \left. \begin{array}{l} \text{3226} \end{array} \right\}$	$\parallel ?$	20	7.1
$(3231 \text{ min.}) \left. \begin{array}{l} \text{3242} \end{array} \right\}$			

\* The intensities given are rough values of the peak-absorption-coefficient  $\beta$  as calculated from the expression  $\ln(I_0/I) = 10^{-2}\beta l p$ , where  $l$  is the path length of the absorbing gas in centimeters,  $p$  is its pressure in millimeters of mercury, and the  $10^{-2}$  is an arbitrary factor.

leaving  $0.34$  as the sum of the  $\zeta$ -values for the other two perpendicular bands. Thus, if the two unknown  $\zeta$ -values were about equal ( $=0.17$ ), the spacings of the corresponding bands would be about  $6.3 \text{ cm}^{-1}$ , and therefore rather easily resolvable.

## VIBRATIONAL ASSIGNMENTS

Borine carbonyl, being a six-atomic molecule, has twelve normal vibration modes. Assuming the molecule

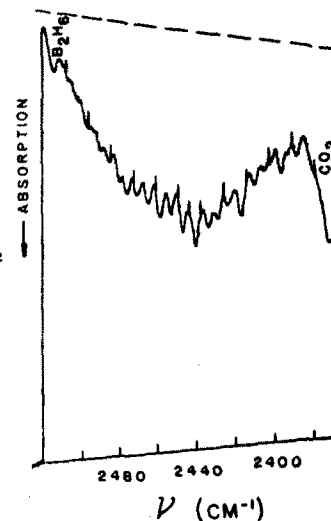


FIG. 3. Record of the  $2440 \text{ cm}^{-1}$  band.

TABLE II. Positions of the maxima of the 809  $\text{cm}^{-1}$  band.

Assignment	$\nu_{\text{vac}}$	$\Delta\nu$	Assignment	$\nu_{\text{vac}}$	$\Delta\nu$
$PQ_9$	782.1* $\text{cm}^{-1}$	2.5	$RQ_1$	812.0	3.4
$PQ_8$	784.6	3.4	$RQ_2$	815.4	3.1
$PQ_7$	788.0	2.7	$RQ_3$	818.5*	3.0
$PQ_6$	790.7*	2.9	$RQ_4$	821.5	3.5
$PQ_5$	793.6	3.3	$RQ_5$	825.0	3.3
$PQ_4$	796.9	3.0	$RQ_6$	828.3*	3.5
$PQ_3$	799.9*	3.0	$RQ_7$	831.8	3.4
$PQ_2$	802.9	3.0	$RQ_8$	835.2	3.7
$PQ_1$	805.9	3.3	$RQ_9$	838.9*	
$RQ_0$	809.2*	2.8			

to have asymmetry  $C_{3v}$ , the usual group-theoretical analysis indicates that four of these are totally symmetric and of species  $A_1$ , while the other eight correspond to four doubly degenerate vibrations of species  $E$ , both species being infra-red (and Raman) active. The  $A_1$  modes give rise to parallel bands, and may be described as a symmetrical BH stretching, a symmetrical BH bending ( $\text{BH}_3$  deformation), a BC stretching, and a CO stretching. The  $E$  modes produce perpendicular bands; and consist of an asymmetrical BH stretching, an asymmetrical  $\text{BH}_3$  deformation, a  $\text{BH}_3$  rocking, and a BCO bending.<sup>8</sup>

Tentative assignments of the observed bands are given in Table IV, where  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ ,  $\nu_4$  represent the totally symmetric vibrations and  $\nu_5$ ,  $\nu_6$ ,  $\nu_7$ ,  $\nu_8$  the degenerate vibrations, in the order of decreasing frequency in each case. A discussion of these assignments follows.

#### 2440 $\text{cm}^{-1}$ band

By comparison with the BH stretching frequencies of diborane (2522 and 2614  $\text{cm}^{-1}$  infra-red;<sup>9</sup> 2489 and 2523  $\text{cm}^{-1}$  Raman<sup>10,11</sup>) and of borazole (2519  $\text{cm}^{-1}$  infra-red; 2535  $\text{cm}^{-1}$  Raman),<sup>12</sup> the BH stretching frequencies of borine carbonyl may also be expected to lie in the vicinity of 2500  $\text{cm}^{-1}$ . Thus the 2440  $\text{cm}^{-1}$  perpendicular band can immediately be attributed to the asymmetrical BH stretching frequency.

#### 2164 $\text{cm}^{-1}$ band

The only strong parallel band above 1100  $\text{cm}^{-1}$  lies at 2164  $\text{cm}^{-1}$ , and has here been assigned to the CO

<sup>8</sup> The vibrational modes of  $\text{H}_3\text{BCO}$  may be compared with those of  $\text{H}_3\text{CCN}$ ; cf. reference 5, p. 332.

<sup>9</sup> W. C. Price, J. Chem. Phys. **16**, 894 (1948).

<sup>10</sup> T. F. Anderson and A. B. Burg, J. Chem. Phys. **6**, 586 (1938).

<sup>11</sup> See also: Webb, Neu, and Pitzer, J. Chem. Phys. **17**, 1007 (1949); Anderson and Barker, J. Chem. Phys. **18**, 698 (1950).

<sup>12</sup> B. L. Crawford and J. T. Edsall, J. Chem. Phys. **7**, 223 (1939).

TABLE III. Positions of the maxima of the 2440  $\text{cm}^{-1}$  band.

Assignment	$\nu_{\text{vac}}$	$\Delta\nu$	Assignment	$\nu_{\text{vac}}$	$\Delta\nu$
$PQ_7$	2389.5 $\text{cm}^{-1}$	7.3	$RQ_1$	2446.9	6.3
$PQ_6$	2396.8*	8.4	$RQ_2$	2453.2	5.6
$PQ_5$	2405.2	5.1	$RQ_3$	2458.8*	6.7
$PQ_4$	2410.3	6.3	$RQ_4$	2465.5	5.8
$PQ_3$	2416.6*		$RQ_5$	2471.3	5.8
$PQ_2$	2423.5		$RQ_6$	2477.1*	3.7
$PQ_1$	2428.7			2480.8	5.7
	2433.4			2486.5	4.8
$RQ_0$	2440.2*	6.7		2491.3	

\* The asterisks mark the strong lines.

stretching rather than to the symmetrical BH stretching vibration. According to Gordy, Ring, and Burg,<sup>7</sup> the CO distance in borine carbonyl is 1.13A, which is the same as the internuclear distance in carbon monoxide and nearly as short as the triple bond distance (1.11A). Thus borine "carbonyl" does not contain the carbon-oxygen double bond (internuclear distance about 1.24A) of a true carbonyl, and it is to be expected that the CO frequency will lie in the vicinity of 2100  $\text{cm}^{-1}$  rather than near the double-bond frequency 1740  $\text{cm}^{-1}$ .

The question remains as to the whereabouts of the symmetrical BH stretching frequency  $\nu_1$ . Ordinarily, a hydrogen vibration would be associated with quite a strong band; however, the electronic structure of borine carbonyl is sufficiently complex that it is difficult to predict what intensity should be expected. It is quite possible that the  $\nu_1$  band is rather weak, and was masked either by the 2440  $\text{cm}^{-1}$  band or by the atmospheric  $\text{CO}_2$  band at 2349  $\text{cm}^{-1}$  (which showed about 60 percent absorption at its maximum). If this is true, an investigation of the Raman spectrum might be of value in locating  $\nu_1$ .

#### 1392, 1091, and 809 $\text{cm}^{-1}$ bands

These bands have been assigned to the asymmetrical and symmetrical  $\text{BH}_3$  deformation and the  $\text{BH}_3$  rocking vibrations, respectively, which should produce a perpendicular, a parallel, and a perpendicular band, in that order. The width of the 1392  $\text{cm}^{-1}$  band is intermediate between the widths of the 809 and 2440  $\text{cm}^{-1}$  bands, and so is presumably a perpendicular band with a spacing of roughly 5  $\text{cm}^{-1}$ . (Compare the comments on  $\zeta$ -values at the end of the preceding section.) The fact that this band has not been resolved can be laid to the rather wide effective slit width of 4.5  $\text{cm}^{-1}$ , interference from the atmospheric water vapor band (which, though the latter showed only about seven percent maximum absorption, was still serious with a

weak band), and possibly also interference from the  $B^{10}$  isotopic molecule.

The envelope of the absorption in the vicinity of  $1091\text{ cm}^{-1}$  is rather peculiar, and has a width about twice the proper value for a parallel band. The boron isotope shift could well be sufficient to account for the width, but not for the fact that the high frequency maximum has a greater intensity than the low frequency one. Several combination frequencies can be found which lie close to  $1100\text{ cm}^{-1}$ , but none of these seems a very satisfactory explanation. If this absorption includes the  $\nu_3$  band as assumed, it seems likely that the center of the band lies at about  $1100\text{ cm}^{-1}$  rather than  $1091\text{ cm}^{-1}$ . This frequency might be compared with that of a somewhat analogous  $BH_2$  deformation vibration in diborane ( $1175\text{ cm}^{-1}$ ).<sup>9</sup>

#### 692 $\text{cm}^{-1}$ band

As the only possibility left for a strong parallel band, this is assigned to the boron-carbon stretching vibration  $\nu_4$ . This frequency is not excessively low in spite of the weak bond which might be expected from the instability of borine carbonyl.

#### 622 $\text{cm}^{-1}$ band

No central  $Q$  branch was observed for this band, due presumably to the low available resolution, but the separation of the two observed maxima is about right for a parallel band. For lack of anything better, it has been assigned to the second harmonic of the BCO bending vibration  $\nu_8$ , with intensity perhaps borrowed from the  $692\text{ cm}^{-1}$  band by Fermi resonance. If this assignment is correct,  $\nu_8$  is placed at about  $315\text{ cm}^{-1}$ , which may be compared with the frequencies  $380$  and  $290\text{ cm}^{-1}$  in  $H_3CCN$  and  $H_3CNC$ , respectively.<sup>8</sup>

#### 423 $\text{cm}^{-1}$ band

This band is too narrow to be either a parallel or perpendicular band of borine carbonyl, and is probably due to an impurity, as mentioned in the experimental section.

#### 2860 and 3231 $\text{cm}^{-1}$ bands

These are obviously combination bands. The assignments  $\nu_2 + \nu_4$  ( $=2856\text{ cm}^{-1}$ ) and  $\nu_2 + \nu_3$  ( $=3255\text{ cm}^{-1}$ ) fit fairly well and involve the strongest bands in the spectrum.

#### NORMAL COORDINATE ANALYSIS

On the basis of a valence-force field, the potential energy of a  $WXYZ_3$  molecule of symmetry  $C_{3v}$  can be written.

$$2V = k_a(\Delta a)^2 + k_b(\Delta b)^2 + k_c(\Delta c)^2 + k_{ab}(\Delta a)^2 + k_{bc}(\Delta b)^2 + k_{ca}(\Delta c)^2 + k_{abc}(\Delta a)(\Delta b)(\Delta c) + k_{\gamma}(\Delta \gamma)^2$$

where  $a$ ,  $b$ , and  $c$  are the internuclear distances  $r_{WX}$ ,

TABLE IV. Tentative vibrational assignments.

$\nu_{\text{vac}}$	Type	Intensity	Assignment
423 $\text{cm}^{-1}$		35	impurity
622	$\parallel?$	45	$2\nu_8?$ (BCO bending)
692	$\parallel$	230	$\nu_4$ (BC)
809	$\perp$	20	$\nu_7$ ( $BH_3$ rock.)
1091	$\parallel?$	230	$\nu_3$ ( $BH_3$ def.)
1392	$\perp?$	10	$\nu_8$ ( $BH_3$ def.)
2164	$\parallel$	3300	$\nu_2$ (CO)
2440	$\perp$	500	$\nu_5$ (BH)
2860	$\parallel?$	65	$\nu_2 + \nu_4$
3231	$\parallel?$	20	$\nu_2 + \nu_3$

$r_{XY}$ , and  $r_{YZ}$ , respectively;  $\alpha$  is the angle  $WXY$ ;  $\beta$  is the supplement of the angle  $XYZ$ ; and  $\gamma$  is the angle  $YZZ$ .

A normal vibration analysis using such a potential function has been carried out by expressing the various changes in bond lengths and angles in terms of a set of eighteen orthogonal mass-adjusted displacement symmetry coordinates. The five coordinates of symmetry  $A_1$  led in the usual manner to a fifth-order secular determinant with one zero root (corresponding to translation parallel to the  $z$  [symmetry] axis); the coordinate of symmetry  $A_2$  to a first-order determinant with zero root (rotation about the  $z$ -axis); and the twelve coordinates of species  $E$  to two identical sixth-order determinants, each having two zero roots (translation parallel to and rotation about the  $x$  or  $y$  axis). Thus from each of the  $A_1$  and  $E$  determinants there resulted a fourth-degree equation in  $\lambda = (2\pi\nu)^2$ , the solutions giving the fundamental vibration frequencies  $\nu_1, \nu_2, \nu_3, \nu_4$  in the one case and  $\nu_5, \nu_6, \nu_7, \nu_8$  in the other.

If these equations are written

$$A_1: \lambda^4 - A\lambda^3 + B\lambda^2 - C\lambda + D = 0$$

and

$$E: \lambda^4 - F\lambda^3 + G\lambda^2 - H\lambda + I = 0$$

then the results obtained for the various coefficients are as follows, where the following abbreviations have been used:

$$\begin{aligned} k_{\gamma}' &= k_{\gamma} / \cos^2(\gamma/2) \\ 1/m_1 &= 1/m_W + 1/m_X \\ 1/m_2 &= 1/m_X + 1/m_Y \\ 1/m_3 &= 1/m_Z + 3 \cos^2\beta / m_Y \\ 1/m_4 &= 1/m_Z + 3 \sin^2\beta / m_Y \\ 1/m_5 &= 1/m_Z + 3/m_Y \\ 1/m_6 &= 1/m_Z + 3 \cos^2\beta / 2m_Y \\ 1/m_7 &= 1/m_Z + 3 \sin^2\beta / 2m_Y \\ 1/m_8 &= 1/m_Z + 3/2m_Y \\ 1/m_9 &= b/am_W + b(1+a/b)^2/am_X \\ f &= 1 + \cos^2\beta. \end{aligned}$$

$$\begin{aligned} A &= \lambda_1 + \lambda_2 + \lambda_3 + \lambda_4 \\ &= k_a/m_1 + k_b/m_2 + k_c/m_3 + (k_{\beta} + 3 \cos^2\beta k_{\gamma}')/m_4. \end{aligned} \quad (1)$$

$$\begin{aligned}
 B &= \lambda_1 \lambda_2 + \lambda_1 \lambda_3 + \lambda_1 \lambda_4 + \lambda_2 \lambda_3 + \lambda_2 \lambda_4 + \lambda_3 \lambda_4 \\
 &= k_a k_b \{ 1/m_1 m_Y + 1/m_W m_X \} \\
 &\quad + k_a k_c / m_1 m_3 + k_a (k_\beta + 3 \cos^2 \beta k_\gamma') / m_1 m_4 \\
 &\quad + k_b k_c \{ 1/m_3 m_X + 1/m_Y m_Z \} \\
 &\quad + k_b (k_\beta + 3 \cos^2 \beta k_\gamma') \{ 1/m_4 m_X + 1/m_Y m_Z \} \\
 &\quad + k_c (k_\beta + 3 \cos^2 \beta k_\gamma') / m_6 m_Z. \quad (2)
 \end{aligned}$$

$$\begin{aligned}
 C &= \lambda_1 \lambda_2 \lambda_3 + \lambda_1 \lambda_2 \lambda_4 + \lambda_1 \lambda_3 \lambda_4 + \lambda_2 \lambda_3 \lambda_4 \\
 &= k_a k_b k_c \{ 1/m_1 m_Y m_Z + 1/m_3 m_W m_X \} \\
 &\quad + k_a k_b (k_\beta + 3 \cos^2 \beta k_\gamma') \{ 1/m_1 m_Y m_Z + 1/m_4 m_W m_X \} \\
 &\quad + k_a k_c (k_\beta + 3 \cos^2 \beta k_\gamma') / m_1 m_3 m_Z \\
 &\quad + k_b k_c (k_\beta + 3 \cos^2 \beta k_\gamma') \{ 1/m_6 m_X m_Z + 1/m_Y m_Z \}. \quad (3)
 \end{aligned}$$

$$\begin{aligned}
 D &= \lambda_1 \lambda_2 \lambda_3 \lambda_4 \\
 &= k_a k_b k_c (k_\beta + 3 \cos^2 \beta k_\gamma') \{ 1/m_1 m_Y m_Z^2 \\
 &\quad + 1/m_6 m_W m_X m_Z \}. \quad (4)
 \end{aligned}$$

$$\begin{aligned}
 F &= \lambda_6 + \lambda_7 + \lambda_8 \\
 &= k_c / m_7 + k_\alpha \{ 1/m_9 + a/b m_Y \} \\
 &\quad + k_\beta \{ 3c^2/2b^2 m_2 + 1/m_6 + 3c \cos \beta / b m_Y \} \\
 &\quad + k_\gamma' \{ 9 \sin^4 \beta / 8 m_Y + 3f/4 m_Z \}. \quad (5)
 \end{aligned}$$

$$\begin{aligned}
 G &= \lambda_6 \lambda_7 + \lambda_6 \lambda_8 + \lambda_7 \lambda_8 + \lambda_6 \lambda_7 + \lambda_6 \lambda_8 + \lambda_7 \lambda_8 \\
 &= k_a k_\alpha \{ 1/m_7 m_9 + a/b m_Y m_Z \} + k_c k_\beta \{ 1/m_3 m_Z \\
 &\quad + (3c^2/2b^2) (1/m_7 m_X + 1/m_Y m_Z) + 3c \cos \beta / b m_Y m_Z \} \\
 &\quad + k_c k_\gamma' \{ 9 \sin^2 \beta / 4 m_Y m_Z + 3f/4 m_Z^2 \} \\
 &\quad + k_a k_\beta \{ 1/m_6 m_9 + 3c \cos \beta / a m_1 m_Y + a/b m_Y m_Z \\
 &\quad + (3c^2/2ab) (1/m_1 m_Y + 1/m_W m_X) + 3c \cos \beta / b m_X m_Y \} \\
 &\quad + k_a k_\gamma' \{ 9 \sin^4 \beta / 8 m_3 m_Y + 3f/4 m_9 m_Z + 3af/4 b m_Y m_Z \} \\
 &\quad + k_\beta k_\gamma' \{ 9c^2 f/8 b^2 m_2 m_Z + 27c^2 \sin^4 \beta / 16 b^2 m_X m_Y \\
 &\quad + 9(f + 4c \cos \beta / b) / 8 m_Y m_Z + 3/4 m_Z^2 \}. \quad (6)
 \end{aligned}$$

$$\begin{aligned}
 H &= \lambda_6 \lambda_7 \lambda_8 + \lambda_6 \lambda_7 \lambda_8 + \lambda_6 \lambda_7 \lambda_8 + \lambda_6 \lambda_7 \lambda_8 \\
 &= k_a k_\alpha k_\beta \{ (3c^2/2ab + 3c \cos \beta / a) / m_1 m_Y m_Z \\
 &\quad + 3c^2/2ab m_7 m_W m_X + 1/m_3 m_9 m_Z \\
 &\quad + 3c \cos \beta / b m_X m_Y m_Z + a/b m_Y m_Z^2 \} \\
 &\quad + k_c k_\alpha k_\gamma' \{ 3f(1/m_9 + a/b m_Y) / 4 m_Z^2 \\
 &\quad + 9 \sin^2 \beta / 4 m_9 m_Y m_Z \} \\
 &\quad + k_c k_\beta k_\gamma' \{ 9c^2 f/8 b^2 m_2 m_Z^2 + 3/4 m_5 m_Z^2 \\
 &\quad + 27c^2 \sin^2 \beta / 8 b^2 m_X m_Y m_Z + 9 \cos \beta / 2 b m_Y m_Z^2 \} \\
 &\quad + k_a k_\beta k_\gamma' \{ (9c^2 f/8ab m_Z) (1/m_1 m_Y + 1/m_W m_X) \\
 &\quad + 9c \cos \beta / 2a m_1 m_Y m_Z + 9f/8 m_9 m_Y m_Z \\
 &\quad + 3(1/m_9 + a/b m_Y) / 4 m_Z^2 \\
 &\quad + 27c^2 \sin^4 \beta / 16ab m_W m_X m_Y + 9c \cos \beta / 2b m_X m_Y m_Z \}. \quad (7)
 \end{aligned}$$

$$\begin{aligned}
 I &= \lambda_6 \lambda_7 \lambda_8 \\
 &= k_a k_\alpha k_\beta k_\gamma' \{ 9c^2 f(1/m_1 m_Y + 1/m_W m_X) / 8ab m_Z^2 \\
 &\quad + 9c \cos \beta / 2a m_1 m_Y m_Z^2 + 3/4 m_5 m_9 m_Z^2 \\
 &\quad + 27c^2 \sin^2 \beta / 8ab m_W m_X m_Y m_Z \\
 &\quad + 9c \cos \beta / 2b m_X m_Y m_Z^2 + 3a/4b m_Y m_Z^3 \}. \quad (8)
 \end{aligned}$$

In addition to the internal checks in the calculations afforded by the occurrence of zero roots, the absence of any terms which were not linear in each of the force constants, etc., the above equations have been partially checked as follows:

The expressions for  $A$ ,  $B$ ,  $C$ , and  $D$  have been compared with the corresponding ones given by Glockler and Wall<sup>13</sup> for methylacetylene ( $\text{HCCCH}_3$ )—the appropriate special cases having been taken in each instance, and complete agreement having been obtained.

Since Glockler and Wall do not give expressions for the degenerate frequencies, partial checks on the expressions for  $F$ ,  $G$ ,  $H$ , and  $I$  were obtained by comparison with equations given by Herzberg<sup>14</sup> for linear  $WXY$  molecules, by Wagner<sup>15</sup> for axial  $XYZ_3$  molecules, and by Slawsky and Dennison<sup>16</sup> for axial  $XCH_3$  molecules—the appropriate special cases again being used. The following discrepancies were noted:

(1) In place of the  $k_\beta$  in Eqs. (1) to (8) above, the corresponding expression in Wagner's results is  $ck_\beta/b$ . Since this difference is present in the non-degenerate as well as the degenerate equations, it is probably due to a mistake in Wagner's expression for the potential energy of the molecule.

(2) A single term in the coefficient of  $k_c k_\beta$  in Eq. (6) above disagrees completely with the corresponding term given by Wagner, but agrees with that given by Slawsky and Dennison; hence it is presumably Wagner's which is in error.

(3) Slawsky and Dennison appear to have made a typographical error in their potential energy function, omitting what corresponds to the  $c^2$  coefficient of  $k_\gamma$  in the potential function given above.

The numerical calculations described below have provided further checks on the algebra.

#### APPLICATION TO BORINE CARBONYL

The equations given above have been used to calculate force constants of the  $\text{H}_3\text{B}^{11}\text{CO}$  molecule, the values used for the various parameters being those obtained by Gordy, Ring and Burg:<sup>7</sup>  $a = 1.131\text{\AA}$ ,  $b = 1.540\text{\AA}$ ,  $c = 1.194\text{\AA}$ ,  $\beta = 75^\circ 23'$ ,  $\gamma = 113^\circ 52'$ .

On the surface, it would appear that Eqs. (1)–(8) could be used with the known values of  $\nu_2$ ,  $\nu_3$ ,  $\dots$ ,  $\nu_7$  to calculate the six force constants and the unknown values of  $\nu_1$  and  $\nu_8$ . However, due to the approximations involved in using a valence-force potential (and in neglecting anharmonicities), the eight equations cannot be expected to make up a consistent set of functions of the six force constants. Correspondingly, an attempt to solve these equations exactly in the manner just mentioned would most likely lead to highly erroneous values of  $\nu_1$  and  $\nu_8$  and to values of the force constants which had little physical significance. It was therefore felt that it would be better to assume values for  $\nu_1$  and  $\nu_8$  and then determine values of the force constants which would satisfy all eight equations as closely as possible. The resulting indeterminacy in the values for the force constants (except possibly for  $k_\alpha$ ) is probably no greater than the errors inherent in the use of a valence-force treatment.

The frequencies used in the calculations were those

<sup>14</sup> See reference 5, p. 173.

<sup>15</sup> J. Wagner, *Zeits. f. physik. Chemie* **B40**, 36 (1938).

<sup>16</sup> Z. I. Slawsky and David M. Dennison, *J. Chem. Phys.* **7**, 522 (1939).

<sup>13</sup> George Glockler and F. T. Wall, *J. Chem. Phys.* **5**, 813 (1937).

given in Table V. By more or less trial and error procedures the following set of values of the force constants was found to satisfy each of Eqs. (1)–(8) to within an error of 1.2 percent or less: CO stretching:  $k_a = 17.3 \times 10^5$  dynes/cm, BC stretching:  $k_b = 2.97 \times 10^5$ , HB stretching:  $k_c = 3.21 \times 10^5$ , BCO bending:  $k_\alpha = 0.142 \times 10^5$ , HBC bending:  $k_\beta = 0.333 \times 10^5$ , HBH bending:  $k_\gamma = 0.363 \times 10^5$  dynes/cm.

The frequencies calculated from these force constants and Eqs. (1)–(8) are given in Table V, along with the percent difference between observed and calculated values. The agreement is probably as good as can be expected with a simple valence-force potential function. (The close agreement between observed and calculated values of  $\nu_8$  does not of course imply that the assumed value  $315 \text{ cm}^{-1}$  is accurate, since  $\nu_8$  is determined primarily by the value of  $k_\alpha$ , and the latter has little effect on the other frequencies. Any future revision in the value of  $\nu_8$  will entail a corresponding change in  $k_\alpha$ .)

The CO stretching force constant,  $17.3 \times 10^5$  dynes/cm, may be compared with that of the CO molecule (18.5) and with the CN force constant<sup>17</sup> in the isoelectronic molecule  $\text{H}_3\text{CCN}$  (17.5). The author is aware of no other available values of the BC force constant; however, the internuclear distances calculated with the aid of Badger's rule<sup>18</sup> from the values  $k_a = 17.3 \times 10^5$  and  $k_b = 2.97 \times 10^5$  are  $a = 1.15 \text{ \AA}$  and  $b = 1.54 \text{ \AA}$ , respectively, and the latter especially is in good agreement with the microwave data.

The BH stretching force constant,  $3.21 \times 10^5$  dynes/cm, is about six percent smaller than the value  $3.42 \times 10^5$  given by Crawford and Edsall for borazole<sup>12</sup> and by Bell and Longuet-Higgins for diborane.<sup>19</sup> This can probably be ascribed to the difference between an

H—B—bond in the former case and an H—B=

bond in the latter ones, analogous to the corresponding CH bonds where the difference in force-constant values ( $4.79$  and  $5.1 \times 10^5$ )<sup>20</sup> is also 6 percent. A point of some interest in connection with the HBC and HBH bending force constants is the fact that  $k_\beta$  is smaller than  $k_\gamma$ , whereas the opposite is the case with methyl radicals;<sup>20</sup> this may correspond to the relatively weak boron-carbon bond in borine carbonyl.

In summary, it may be said that although  $k_c$  and especially  $k_\alpha$  may require some revision when  $\nu_1$  and  $\nu_8$  are determined more accurately, the values of the force

TABLE V. Calculated frequencies of borine carbonyl.

Mode	$\nu_{\text{obs}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{calc}}$ ( $\text{cm}^{-1}$ )	Difference
$A_1: \nu_1$	(2360 est.)	2350	−0.4 percent
$\nu_1$	2164	2135	−1.3
$\nu_2$	1105	1152	+4.2
$\nu_4$	692	674	−2.6
$E: \nu_6$	2440	2479	+1.6
$\nu_6$	1392	1346	−3.3
$\nu_7$	809	822	+1.6
$\nu_8$	(315 est.)	316	+0.3

constants which have been calculated appear to be quite reasonable, and a valence-force function seems to represent the potential energy of the borine carbonyl molecule with fair accuracy.

### ELECTRONIC STRUCTURE

A very good discussion of the electronic structure of borine carbonyl has been given by Gordy, Ring, and Burg<sup>7</sup> on the basis of resonance among the following five structures: I.  $\text{H}_3\text{B}^--\text{C}\equiv\text{O}^+$ ; II.  $\text{H}_3\text{B}^--\text{C}^+=\text{O}$ ; III.  $\text{H}_3^+\text{B}^--\text{C}=\text{O}$ ; IV.  $\text{H}_3^+\text{B}^--\text{C}^+-\text{O}^-$ ; V.  $\text{H}_3\text{B CO}$ ; the latter being essentially free  $\text{BH}_3$  and  $\text{CO}$ . They conclude that the departure of the angle HBC from the tetrahedral value, the known internuclear distances, and the small permanent dipole moment of borine carbonyl (1.80 debye)<sup>21</sup> can be accounted for by assuming the ground state to consist of a resonant mixture of these five structures in the following order of importance: V, II, III, I, and IV—the contributions being about 50 percent structure V, about 30 percent I and II combined, and about 20 percent III and IV combined. The predominance of V (which provides no formal BC bond) explains the chemical instability of the molecule; at the same time, the reasonably large value of the BC force constant obtained from the infra-red data is understandable from the contribution of the double-bond structures III and IV.

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<sup>17</sup> J. W. Linnett, *J. Chem. Phys.* **8**, 91 (1940).

<sup>18</sup> R. M. Badger, *J. Chem. Phys.* **3**, 710 (1935).

<sup>19</sup> R. P. Bell and H. C. Longuet-Higgins, *Proc. Roy. Soc. A* **183**, 357 (1945).

<sup>20</sup> See reference 5, p. 193.

<sup>21</sup> Strandberg, Pearsall, and Weiss, *J. Chem. Phys.* **17**, 429 (1949).