CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK 14850

The Infrared Spectrum and Vibrational Assignments of $H_2B_2O_3$[1]

BY F. A. GRIMM AND RICHARD F. PORTER

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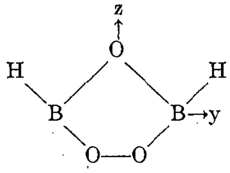
The infrared spectrum of cyclic $H_2B_2O_3$(g) has been obtained from 4000 to 250 cm^{-1}. A number of isotopic species, including $H_2B_2{}^{16}O_3$, $H_2B_2{}^{16}O^{18}O_2$, $H_2B_2{}^{18}O_3$, $D_2B_2{}^{16}O_3$, $H_2{}^{10}B_2{}^{16}O_3$, and $H_2{}^{10}B^{11}B^{16}O_3$, were prepared by allowing the appropriate isotopic combinations of oxygen to react with boroxine ($H_3B_3O_3$). A vibrational analysis indicates that the molecule exists in one major isomeric form with C_{2v} symmetry. Certain features of the spectrum arising from the mixed isotopic species are discussed.

Introduction

The compound $H_2B_2O_3$ is one of the few known cyclic molecules containing only boron, hydrogen, and oxygen. The infrared spectrum of gaseous $H_2B_2O_3$ was first observed by Ditter and Shapiro[2] as an unstable intermediate in the partial oxidation of pentaborane-9. At room temperature the gas decomposes into H_2 and B_2O_3(s) with a half-life of approximately 3 days. Microwave studies have shown the $H_2B_2O_3$ molecule to be a planar five-membered ring with C_{2v} symmetry.[3]



The microwave study did not rule out the existence of a highly symmetric isomer without a permanent dipole moment. However, a detailed analysis of the infrared spectrum should reveal the importance of another isomeric form.

It should be noted that although the pure isotopic species ($H_2{}^{11}B_2O_3$ and $H_2{}^{10}B_2O_3$) have C_{2v} symmetry, the mixed species ($H_2{}^{10}B^{11}BO_3$) has only C_s symmetry. Naturally occurring boron contains approximately 20% boron-10 and 80% boron-11. Therefore, in the spectrum of $H_2B_2O_3$ prepared from the natural isotopic abundance of boron, one has a combination of the pure isotopic species $H_2{}^{11}B_2O_3$ and $H_2{}^{10}B_2O_3$ and the mixed isotopic species $H_2{}^{10}B^{11}BO_3$ in the approximate ratio 16 : 1 : 8. In the present study the vibrational analyses of six pure and four mixed isotopic species have been considered.

Experimental Section

Gaseous $H_2B_2O_3$ was prepared, as previously reported,[4] from diborane and oxygen. In order to produce larger quantities of the compound a 3-l. bulb was used in place of the 2-l. bulb used in ref 4. *Caution should be exercised in the preparation as diborane–oxygen mixtures and condensed $H_2B_2O_3$ are explosive.* The method has been shown to produce very pure $H_2B_2O_3$, which may contain small amounts of hydrogen due to some decomposition. The method for the preparation of the isotopic species is described below.

$H_2{}^nB_2{}^{16}O_3$ (Where *n* Is Used to Indicate the Natural Abundance of Boron-10 and Boron-11).—Diborane was prepared from the reaction of anhydrous stannous chloride with sodium borohydride "*in vacuo*" at 250°.[5] Matheson reagent grade oxygen was used without further purification.

$D_2{}^nB_2{}^{16}O_3$ and $HD^nB_2{}^{16}O_3$.—Deuteriodiborane was prepared from sodium borodeuteride which contained better than 98% deuterium. Since it was observed that hydrogen or deuterium could exchange with the appropriate isotope of $H_2B_2O_3$, it was possible to obtain information on the mixed hydrogen–deuterium species by adding hydrogen to $D_2{}^nB_2{}^{16}O_3$ and then observing the infrared spectrum at intervals during the exchange, which occurs slowly over a period of days. The exchange of deuterium with the hydrogen species $H_2{}^{10}B^{11}B^{16}O_3$ was also observed.[6]

$H_2{}^{10}B_2{}^{16}O_3$.—Boron-10 diborane was prepared from $CaF_2{}^{10}BF_3$ (obtained from Oak Ridge National Laboratory) by heating with an excess of $LiAlH_4$. Impurities were removed by adding small quantities of ammonia to form an addition compound of the unreacted BF_3 and HBF_2 and then by vacuum distillation of the boron-10 diborane. The starting material contained 96% boron-10.

$H_2{}^nB_2{}^{18}O_3$.—The sample of oxygen-18 used contained the following percentages: 86.3% $^{18}O_2$; 12.3% $^{16}O^{18}O$; 0.4% $^{16}O_2$.

$H_2{}^nB_2{}^{16}O^{18}O^{18}O$ (Where the Oxygen-18 Is in the Peroxide Position).—Boroxine was prepared from oxygen-16 and then oxygen-18 (see percentages above) was added to produce this as the major species.

Spectra were taken on a Perkin-Elmer 521 infrared spectrophotometer in a 10-cm cell equipped with CsI windows from 4000 to 250 cm^{-1}. Indene was used for wavelength calibration and the position of bands exhibiting very sharp Q branches could be located to better than 0.5 cm^{-1}. Reasonable limits for the center of the B-type bands would be ±2 cm^{-1}. Higher resolution spectra were also taken in order to resolve the many Q branches found in the 700–900-cm^{-1} region of the spectrum. These were obtained by using a programmed slit set at 200 μ at 925 cm^{-1}.

Attempts to obtain higher pressures by the techniques employed were thwarted by the unstable nature of the compound. It was found, for example, that the decomposition rate is greatly accelerated in a metal multi-path-length cell, and no improvement in the intensity of the spectrum is obtained. Also, attempts to obtain more material by condensing together various batches always resulted in decomposition upon warming to room temperature (noted by a flash in the storage bulb). The highest sample pressures (15–30 mm) were obtained by combining batches while still in the gas phase.

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[1] Work supported by the Army Research Office, Durham, N. C., and the Advanced Research Projects Agency.

[2] J. F. Ditter and I. Shapiro, *J. Am. Chem. Soc.*, **81**, 1022 (1959).

[3] W. V. Brooks, C. C. Costain, and R. F. Porter, *J. Chem. Phys.*, **47**, 4186 (1967).

[4] F. A. Grimm and R. F. Porter, *Inorg. Chem.*, **7**, 706 (1968).

[5] W. Jeffers, *Chem. Ind.* (London), 431 (1961).

[6] The sample contained 50% $H_2{}^{10}B^{11}B^{16}O_3$.

TABLE I

FREQUENCY LISTING (MAXIMA LISTED EXCEPT FOR THE B-TYPE BAND WHERE THE ITALICIZED FREQUENCY IS THE CENTRAL MINIMUM)

$H_2{}^{10}B_2{}^{16}O_3$[a]		$H_2{}^{10}B^{11}B^{16}O_3$[b]		$H_2{}^{n}B_2{}^{16}O_3$[c]			
Freq, cm^{-1}	Intens	Freq, cm^{-1}	Intens	Freq, cm^{-1}	Intens	Species	Assignment and remarks
....		421	sh	407, *425.5*, 444 PQR	m	$^{11}B_2$	ν_{10}
....		412, *429.5*, 447 PQR	m	....		$^{10}B^{11}B$	ν_{14} Q branch broad
431 Q		....		....		$^{10}B_2$	ν_{10} B-type band strongest Q branch taken as center
....		741	sh	724, *741*, 763	m	$^{11}B_2$	ν_{15}
....		726, *745*, 764	m	745	sh	$^{10}B^{11}B$	ν_{11}
730, *748*, 768	m	748	sh	749	vw, sh	$^{10}B_2$	ν_{15}
....		....		776 Q	w, sh	$^{11}B_2$	ν_6
....		778 b	w, sh	....		$^{10}B^{11}B$	ν_{10}
781 Q	w, sh	....		....		$^{10}B_2$	ν_6
....		....		829 Q	vw	$^{11}B_2$	ν_5 (?)
842 (?)	vw	....		....		$^{10}B_2$	ν_5 (?)
875 Q	w	875 Q	s	875 Q	m	$^{10}B^{11}B$	ν_{13}
....		883 Q	s	*883* Q	vs	$^{11}B_2$	ν_9 maximum of P and R obscure
895 Q	m	*895*, 911 QR	vs	895 Q	s	$^{10}B^{11}B$	ν_{12} maximum of P obscure
879, *899*, 915 PQR	vs	899 Q	s	899 Q	w	$^{10}B_2$	ν_9
....		....		961 Q	w, sh	$^{11}B_2$	ν_4
....		967 b	w, sh	967 Q	vw, sh	$^{10}B^{11}B$	ν_8
968	w, sh	....		....		$^{10}B_2$	ν_4
....		....		979	m	$^{11}B_2$	ν_{14} B-type band (broad B-type center)
....		979, *981*, 982	m	....		$^{10}B^{11}B$	ν_7
982	m	....		....		$^{10}B_2$	ν_{14} B-type band
....		1114 Q	vw	1114 Q	w	$^{11}B_2$	ν_3
....		1127 Q	w, sh	1127 Q	vw, sh	$^{10}B^{11}B$	ν_6
1132, *1145.5*, 1154 PQR	w, sh	1145.5 Q	vw, sh	....		$^{10}B_2$	ν_3
....		1167, 1168	s, sh	1166, *1169*, 1172	s, sh	$^{11}B_2$	ν_{13} B-type band
....		*1183*, 1185	s	*1183*	s	$^{10}B^{11}B$	ν_5
1179, 1185, *1192*, 1196, 1204	vs	1192	sh	1192	sh	$^{10}B_2$	ν_{13} B-type band
....		....		*1201* Q	s	$^{11}B_2$	ν_2
....		1218 Q	s, sh	1217 Q	sh	$^{10}B^{11}B$	ν_4
1237.5 Q		1237 Q	w, sh	....		$^{10}B_2$	ν_2
....		1363, 1374, *1375*	vs	1363, 1374, *1375*, 1385	vs	$^{11}B_2$	ν_{12} B-type band
1400	sh	1398, *1400*	vs	1398, *1400*	s, sh	$^{10}B^{11}B$	ν_3
1417, *1419*	vs	1417, *1419*	sh	*1420*	vw, sh	$^{10}B_2$	ν_{12} B-type band
....		1735	vw	1735	vw	$^{11}B_2$	$2\nu_9$ (1766)
....		1757	vw	1757	vw	$^{10}B^{11}B$	$2\nu_{12}$ (1790)
1780	vw	1778	vw	....		$^{10}B_2$	$2\nu_9$ (1798)
....		2135		~2135	w	$^{11}B_2$	$\nu_6+\nu_{12}$ (2151)
....		~2160 b	w	2160	w	$^{10}B^{11}B$	$\nu_3+\nu_{10}$ (2178)
~2180	w	2180		....		$^{10}B_2$	$\nu_6+\nu_{12}$ (2200)
....		....		~2350	w	$^{11}B_2$	$\nu_{12}+\nu_{14}$ (2354)
....		~2380	w	....		$^{10}B^{11}B$	$\nu_3+\nu_7$ (2381)
~2400	w	....		....		$^{10}B_2$	$\nu_{12}+\nu_{14}$ (2401)
....		~2535	vw	2537	w	$^{11}B_2$	$\nu_{12}+\nu_{13}$ (2544)
....		2575	m	2575	w	$^{10}B^{11}B$	$\nu_3+\nu_5$ (2583)
2587, *2607*, 2625 PQR	m	2605	w	....		$^{10}B_2$	$\nu_{12}+\nu_{13}$ (2611)
2635 (?) Q	w, sh	....		....		....	?
....		*2651*	s, sh	*2653*	vs	$^{11}B_2$	ν_{11} B-type center
....		2667	vs	....		$^{10}B^{11}B$	ν_2 (?)
2680, 2683	s	*2680*	s, sh	....		$^{10}B_2$	ν_{11} B-type center

[a] At 14 mm, the 10-cm cell contained 92.2% $H_2{}^{10}B_2{}^{16}O_3$, 7.7% $H_2{}^{10}B^{11}B^{16}O_3$, and 0.1% $H_2{}^{11}B_2{}^{16}O_3$. [b] At 12 mm, the 10-cm cell contained 50% $H_2{}^{10}B^{11}B^{16}O_3$, 25% $H_2{}^{10}B_2{}^{16}O_3$, and 25% $H_2{}^{11}B_2{}^{16}O_3$. [c] At 27 mm, the 10-cm cell contained 65.9% $H_2{}^{11}B_2{}^{16}O_3$, 30.6% $H_2{}^{10}B^{11}B^{16}O_3$, and 3.5% $H_2{}^{10}B_2{}^{16}O_3$.

Results

A frequency listing of the spectra of the various isotopic species of $H_2B_2O_3$ is given in Tables I and II. Included in the listing is the isotopic species to which the band is attributed. This information was obtained by observing the change in band intensities of spectra containing different percentages of the various isotopes. Figures 1–3 give an example of the spectra obtained showing only the major features and are intended only for display of qualitative band shapes and intensities; the actual spectra obtained are more detailed and in some cases were more intense than those shown. No bands were observed in the region above 3000 cm^{-1} or in most cases below 400 cm^{-1} so these regions have been omitted in the figures.

Vibrational Analysis of Species with C_{2v} Symmetry

For the isotopic species of C_{2v} symmetry group theory predicts the following fundamental vibrations: $\Gamma_{vib} = 6A_1 + 2A_2 + 2B_1 + 5B_2$. All of the vibrations would be active in the infrared spectrum except the A_2 species, which would be active only in the Raman spectrum. The molecule has an asymmetric top and, except for the deuterated species, has its smallest moment of inertia coincident with the symmetry axis. From the microwave results,[3] sufficient information was available to estimate band shapes for the fundamental vibrations.[7]

Six isotopic species with C_{2v} symmetry have been partially analyzed. These include $H_2{}^{10}B_2{}^{16}O_3$, $H_2{}^{11}B_2{}^{16}O_3$, $H_2{}^{11}B_2{}^{16}O^{18}O_2$, $H_2{}^{11}B_2{}^{18}O_3$, $D_2{}^{10}B_2{}^{16}O_3$, and $D_2B_2{}^{11\text{-}16}O_3$. For convenience in the discussion of the analysis it is necessary to choose one isotopic species as an example. The natural choice is $H_2{}^{11}B_2{}^{16}O_3$. Therefore, unless otherwise noted, all frequencies quoted below will be those of $H_2{}^{11}B_2{}^{16}O_3$.

The analysis of the pure isotopic species (C_{2v} symmetry) was based on the following reasoning.

Out-of-Plane Vibrations

B_1 Species.—The two vibrations of this symmetry were readily assigned at 883 and 425.5 cm^{-1}. Isotopic shifts using the Redlich–Teller product rule and band shapes support the assignments. The results of the product rule calculations are summarized in Table III. The out-of-plane BH bending mode at 883 cm^{-1} may be compared to the one found at 918 cm^{-1} in both borazine[8] and boroxine.[9] The ring mode at 425.5 cm^{-1} is found to be somewhat higher than in borazine where an analogous band is found at 394 cm^{-1}. The analogous fundamental has not been observed for boroxine. There seems to be little doubt about the assignment of the B_1 species for any of the isotopic species.

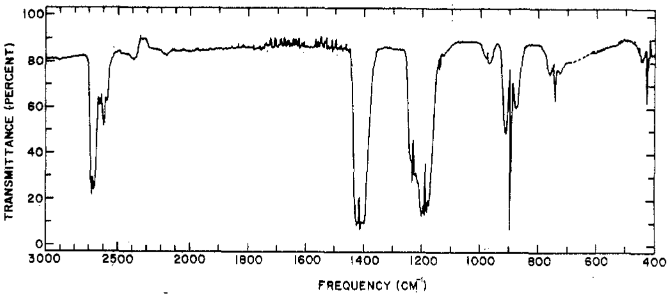

Figure 1.—Spectrum of $H_2{}^{10}B_2{}^{16}O_3$. The sample had a pressure of 14 mm and contained 92.2% $H_2{}^{10}B_2{}^{16}O_3$, 7.7% $H_2{}^{10}B^{11}B^{16}O_3$, and 0.1% $H_2{}^{11}B_2{}^{16}O_3$.

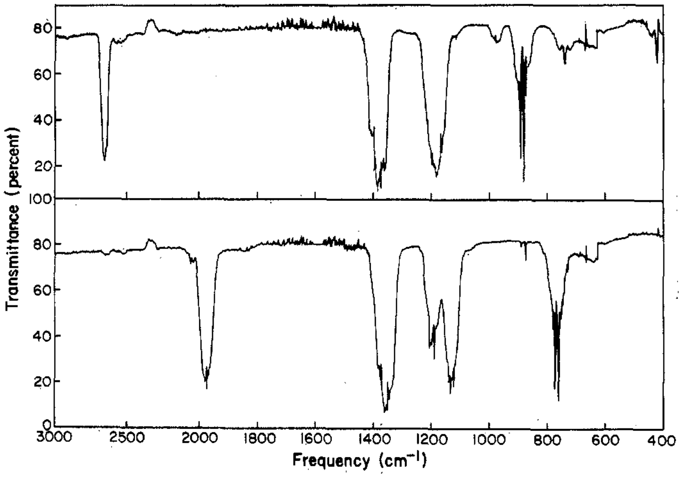

Figure 2.—Spectra of $H_2{}^nB_2{}^{16}O_3$ (top) and $D_2{}^nB_2{}^{16}O_3$ (bottom). Sample pressures were 11 and 12 mm, respectively. (For percentages of isotopic species see footnotes *b* and *c* in Table I.)

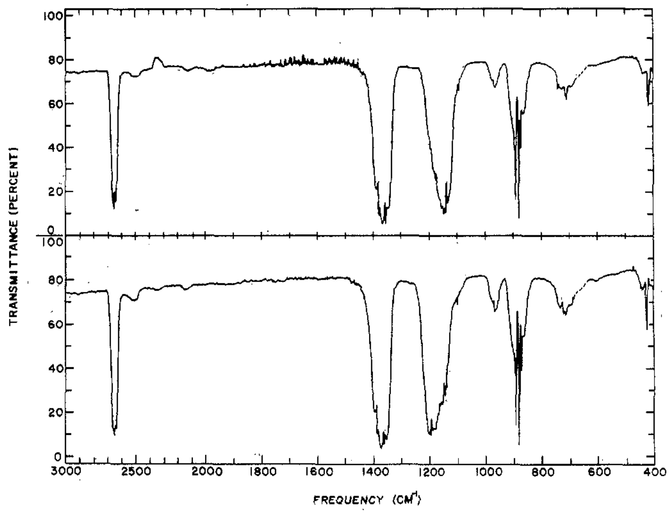

Figure 3.—Spectra of $H_2{}^nB_2{}^{16}O^{18}O_2$ (bottom) and $H_2{}^nB_2{}^{18}O_3$ (top). Sample pressures were 15 and 13 mm, respectively. (For percentages of isotopic species see footnotes *b* and *c* in Table II.)

In-Plane Vibrations

B_2 Species.—Group theory predicts two vibrations involving predominantly BH motion and three ring motions. These bands might be expected to be more intense than the corresponding symmetric in-plane A_1 vibrations. Thus, the intense band at 2653 cm^{-1} is

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[7] H. C. Allen, Jr., and P. C. Cross, "Molecular Vib-Rotors," John Wiley & Sons, Inc., New York, N. Y., 1963.

[8] K. Niedenzu, W. Sawodny, H. Watanabe, J. Dawson, T. Totani, and W. Weber, *Inorg. Chem.*, **6**, 1453 (1967).

[9] F. A. Grimm, L. Barton, and R. F. Porter, *ibid.*, in press.

TABLE II

FREQUENCY LISTING OF MAXIMA

Freq, cm^{-1}	Intens	Species	Assignment and remarks
		$D_2{}^nB_2{}^{16}O_3$[a]	
335, *359*, 381 PQR	m	$D_2{}^{11}B_2$	ν_{10}
733 Q	w	$D_2{}^{11}B_2$	ν_{15}
745 Q	vw, sh	HD	$D^{11}B$ motion
750 Q	w, sh	$D_2{}^{11}B_2$	ν_4
757, *759*,[d] 762	vw	$D_2{}^{11}B_2$	ν_{14}
765[d] Q	vs	$D_2{}^{11}B_2$	ν_9
777[d] Q	vs	$D_2{}^{10}B^{11}B$	ν_{12}
785 Q	m	$D_2{}^{10}B_2$	ν_9
816 Q	w, sh	$D_2{}^{11}B_2$	ν_5
878 Q	m	HD	$H^{11}B$ motion
893.5 Q	vw	HD	$H^{10}B$ motion
1069	w	$D_2{}^{11}B_2$	ν^3
1083	vw, sh	$D_2{}^{10}B^{11}B$	ν_6
1125.5, *1127*[d]	s	$D_2{}^{11}B_2$	ν_{13} other maxima obscure
1137, *1139*[d]	m, sh	$D_2{}^{10}B^{11}B$	ν_5 other maxima obscure
1193 Q	s	$D_2{}^{11}B_2$	ν_2
1208 Q	sh	$D_2{}^{10}B^{11}B$	ν_4
1346, *1350*,[d] 1352	vs	$D_2{}^{11}B_2$	ν_{12}
1375,[d] 1377	s, sh	$D_2{}^{10}B^{11}B$	ν_3
1490	vw	$D_2{}^{11}B_2$	$2\nu_9$ (1530)
1850 b	vw	$D_2{}^{11}B_2$	$\nu_{13} + \nu_{14}$ (1884)
1975, *1977*,[d] 1985	vs	$D_2{}^{11}B_2$	ν_{11}
2050, *2067*, 2085	w	$D_2{}^{11}B_2$	$\nu_6 + \nu_{12}$ ($\nu_6 \sim 735$
		$H_2{}^nB_2{}^{16}O^{18}O_2$[b]	
~405, *425*, 442 PQR	m	$^{11}B_2$	ν_{10}
694, 714, 738	m	$^{11}B_2$	ν_{15} B-type band, center taken as strongest Q branch
724	sh	$^{10}B^{11}B$	ν_{11}
738, *744*, 748 PQR	w, sh	$^{11}B_2$	ν_6
874 Q	m	$^{10}B^{11}B$	ν_{13}
868, *882* PQ	vs	$^{11}B_2$	ν_9 position of R maxima obscure
894 Q	vs	$^{10}B^{11}B$	ν_{12}
898 Q	m	$^{10}B_2$	ν_9
954 b Q	vw, sh	$^{11}B_2$	ν_4
969, *971*[d]	m	$^{11}B_2$	ν_{14} B-type band
1101 Q	w	$^{11}B_2$	ν_3
1110 Q	vw	?	ν_6 (?) ($H_2{}^{10}B^{11}B^{16}O^{18}O_2$)
1149, *1151.5*,[d] 1154	s, sh	$^{11}B_2$	ν_{13} B-type band
1166[d]	m	$^{10}B^{11}B$	ν_5 B-type band
1197 Q	s	$^{11}B_2$	ν_2
1213 Q	sh	$^{10}B^{11}B$	ν_4
1357, 1365, *1366*,[d] 1369, 1374	vs	$^{11}B_2$	ν_{12} B-type band

[a] At 17.5 mm, the 10-cm cell contained 61.4% $D_2{}^{11}B_2{}^{16}O_3$, 30.7% $D_2{}^{10}B^{11}B^{16}O_3$, 3.8% $D_2{}^{10}B_2{}^{16}O_3$, 2.6% $DH^{11}B_2{}^{16}O_3$, and <0.6% each of all others. [b] At 15 mm, the 10-cm cell contained 56.9% $H_2{}^{11}B_2{}^{16}O^{18}O_2$, 26.4% $H_2{}^{10}B^{11}B^{16}O^{18}O_2$, 8.1% $H_2{}^{11}B_2{}^{16}O_2{}^{18}O$, 3.8%

assigned as the asymmetric BH stretching mode and can be observed to shift to 1977 cm^{-1} in the deuterated molecule. Band shape, also, supports this choice. The BH bending mode is expected to appear around 1000 cm^{-1} (appears at 990 cm^{-1} in boroxine) and the band at 979 cm^{-1} has the correct band shape and the large deuterium shift necessary to make this assignment appropriate. The intense band at 1375 cm^{-1} is assigned as the in-plane ring stretching mode on the bases of band shape and location (compare with the stretching mode at 1389 cm^{-1} in boroxine). This leaves two ring motions to be assigned. At least two bands are overlapped in the 1150–1200-cm^{-1} region of the spectrum of $H_2{}^nB_2{}^{16}O_3$ and with the help of the spectrum of $H_2{}^{10}B_2{}^{16}O_3$ it was possible to conclude that the lower frequency band at 1169 cm^{-1} has the correct band shape to be a B-type band. This left only a low-frequency ring-bending motion unassigned. Although the band at 741 cm^{-1} seemed to be higher than anticipated, it did show a double Q branch characteristic of the B-type bands at higher resolution. Except for the deuterated species, it was not difficult to follow the isotopic shifts of the aforementioned bands for all of the isotopically labeled molecules. Product rule calculations (Table III) support the assignment of the B_2 species.

The analysis of the deuterated compound was complicated because of the overlapping of at least four different fundamentals in the region around 750 cm^{-1} (see Figure 2). Thus, the assignment of ν_{14} at 759 cm^{-1}

TABLE II (*Continued*)

Freq, cm^{-1}	Intens	Species	Assignment and remarks
	$H_2{}^nB_2{}^{16}O^{18}O_2$[b] (*Continued*)		
1379, 1389, *1390.5*,[d] 1395, 1398	s, sh	$^{10}B^{11}B$	ν_3
1726 b	vw	$^{11}B_2$	$2\nu_9$ (1764)
1755	vw	$^{10}B^{11}B$	$2\nu_{12}$ (1788)
2120	w	$^{11}B_2$	$\nu_6 + \nu_{12}$ (2110)
2140	w	$^{10}B^{11}B$	$\nu_3 + \nu_{10}$ (ν_{10} ~750
2330	vw	$^{11}B_2$	$\nu_{12} + \nu_{14}$ (2337)
2355	vw	$^{10}B^{11}B$	$\nu_3 + \nu_7$ (ν_7 ~975; 2365.5)
2510	w	$^{11}B_2$	$\nu_{12} + \nu_{13}$ (2517.5)
~2540	w, sh	$^{10}B^{11}B$	$\nu_3 + \nu_5$ (2556.5)
2649, *2651*,[d] 2655	vs	$^{11}B_2$	ν_{11} B-type band
	$H_2{}^nB_2{}^{18}O_3$[c]		
404, *409*, 436 PQR	m	$^{11}B_2$	ν_{10}
689, *711*, 729	m	$^{11}B_2$	ν_{15} B-type band center taken as strongest Q branch
715	sh	$^{10}B^{11}B$	ν_{11}
719	w	?	?
742[d] Q	w	$^{11}B_2$	ν_6
821[d] Q	vw	$^{11}B_2$	ν_5
864, *880* PQ	vs	$^{11}B_2$	ν_9 R maximum obscured
871 Q	vw		
874 Q	s	$^{10}B^{11}B$	ν_{13}
876 Q	w		
883 Q	m, sh		
892 Q	vs	$^{10}B^{11}B$	ν_{12}
894 Q	w, sh		
896 Q	w	$^{10}B_2$	ν_9
952 Q	vw, sh	$^{11}B_2$	ν_4
967, *971*,[d] 977	w–m	$^{11}B_2$	ν_{14} B-type band
1095 Q	w	$^{11}B_2$	ν_3
1134, *1139*,[d] 1142	vs	$^{11}B_2$	ν_{13} B-type band
1154.5[d]	m	$^{10}B^{11}B$	ν_5
1179 Q	s, sh	$^{11}B_2$	ν_2
1197 Q	w, sh	$^{10}B^{11}B$	ν_4
1345, 1357, *1359*[d]	vs	$^{11}B_2$	ν_{12} B-type band other maxima obscure
1381, *1384*[d]	s, sh	$^{10}B^{11}B$	ν_3 B-type band other maxima obscure
1965–1990 b	w	?	Broad maximum (?)
~2105	vw	$^{11}B_2$	$\nu_6 + \nu_{12}$ (2101)
2490	w	$^{11}B_2$	$\nu_{12} + \nu_{13}$ (2498)
2530	vw, sh	$^{10}B^{11}B$	$\nu_3 + \nu_5$ (2538.5)
2647, *2651*,[d] 2653	vs	$^{11}B_2$	ν_{11} B-type band

$H_2{}^{10}B^{11}B^{16}O_2{}^{18}O$, 3.1% $H_2{}^{10}B_2{}^{16}O^{18}O_2$, and a 1.7% total of other species. [c] At 13 mm, the 10-cm cell contained 52.8% $H_2{}^{11}B_2{}^{18}O_3$, 24.5% $H_2{}^{10}B^{11}B^{18}O_3$, and 7.5% $H_2{}^{11}B_2{}^{18}O_2{}^{16}O$. [d] These frequencies are minima and were taken as centers of bands.

TABLE III

PRODUCT RULE CALCULATIONS[a]

Ratio	Vibrational symmetry species B_1		B_2	
	Obsd	Calcd	Obsd	Calcd
$H_2{}^{11}B_2{}^{18}O_3/H_2{}^{11}B_2{}^{16}O_3$	0.981	0.975	0.913	0.904
$H_2{}^{11}B_2{}^{16}O_3/H_2{}^{10}B_2{}^{16}O_3$	0.970	0.971	0.932	0.936
$H_2{}^{11}B_2{}^{16}O^{18}O_2/H_2{}^{11}B_2{}^{16}O_3$	0.998	0.994	0.932	0.933
$D_2{}^{11}B_2{}^{16}O_3/H_2{}^{11}B_2{}^{16}O_3$	0.731	0.723	0.539	0.531

[a] Moments of inertia used in the calculations were obtained from ref 3.

for $D_2{}^{11}B_2{}^{16}O_3$ can be only tentative and has been based upon the product rule and predicted band shape. The assignment of the other B_2 species for $D_2{}^{11}B_2{}^{16}O_3$ presented no obvious difficulty.

A_1 Species.—Not all six of the symmetric vibrations could be assigned, although they are all allowed in the infrared spectrum. The assignment of these fundamentals must be tentative because no quantitative calculations could be used in their assignment. Still a number of them were obvious and, therefore, a discussion of the A_1 fundamentals is in order. As in the case of the B_2 species, two vibrations should involve predominantly BH motions and would be expected to appear near the corresponding B_2 fundamentals. A shoulder is observed on the band at 979 cm^{-1} (B_2) in the $H_2{}^nB_2{}^{16}O_3$ spectrum (Figure 2) and could be followed in the other isotopic species. It shows a large deuterium shift indicating the symmetric BH in-plane bending mode. The other BH motion should be near

TABLE IV

FUNDAMENTAL FREQUENCIES FOR ISOTOPIC SPECIES OF C_{2v} SYMMETRY (CM^{-1})

Assignment		Isotopic species $H_2{}^{10}B_2{}^{16}O_3$	$H_2{}^{11}B_2{}^{16}O_3$	$H_2{}^{11}B_2{}^{16}O{}^{18}O_2$	$H_2{}^{11}B_2{}^{18}O_3$	$D_2{}^{10}B_2{}^{16}O_3$	$D_2{}^{11}B_2{}^{16}O_3$
A_1	ν_1	....	....	....	....	....	....
	ν_2	1237.5	1201	1197	1179	....	1193
	ν_3	1145.5	1114	1101	1095	....	1069
	ν_4	968	961	954	952	....	750
	ν_5	842	833	....	821	....	816
	ν_6	781	776	744	742	....	735[a]
A_2	ν_7	....	....	....	....	....	....
	ν_8	....	....	....	....	....	....
B_1	ν_9	899	883	882	880	785	765
	ν_{10}	431	425.5	425	419	....	359
B_2	ν_{11}	2680	2653	2651	2651	....	1977
	ν_{12}	1419	1375	1366	1359	1395	1350
	ν_{13}	1192	1169	1151.5	1139	1145	1127
	ν_{14}	982	979	971	971	....	759
	ν_{15}	748	741	714	711	....	733

[a] Frequency estimated from the combination band $\nu_2 + \nu_{12}$.

2650 cm^{-1} and is probably masked by the intense B_2 fundamental. The other four fundamentals should involve ring motions and would be expected to be below 1400 cm^{-1}. The intense band at 1201 cm^{-1} is undoubtedly one of the symmetric ring modes. Two other bands are easily assigned as A-type bands on the basis of their band contours. These are the bands at 1114 and 776 cm^{-1}. The band at 776 cm^{-1} appears as a shoulder in the spectrum shown in Figure 2 and its shape is not obviously that of a PQR band, but higher resolution and more intense spectra show up these features better than the reproduction in Figure 2. The remaining fundamental is not so easily placed. In the case of the $D_2{}^nB_2{}^{16}O_3$ spectrum there is an unexplained band at 816 cm^{-1} which is very possibly the other ring fundamental. Very weak bands were observed in this region in some spectra of the other isotopic species and their tentative assignments are included in Table IV.

The exact location of the ν_6 vibration in $D_2{}^{11}B_2{}^{16}O_3$ was impossible to determine from the spectrum, because it is probably masked by other bands found in the same region. However, it was possible to obtain a very good estimate of its frequency (included in Table IV) from the combination band $\nu_6 + \nu_{12}$ found at 2067 cm^{-1}. This combination band appears in all of the spectra. A relatively strong combination band involving the asymmetric stretching mode and a symmetric ring mode is not unusual in boron–oxygen ring compounds.[9]

All of the assigned and estimated fundamental frequencies for the isotopic species of C_{2v} symmetry have been summarized in Table IV.

Vibrational Analysis of Species with C_s Symmetry

In the case of C_s symmetry all the fundamental vibrations are allowed in the infrared. There are only two symmetry species, A′ (in-plane vibrations) and A″ (out-of-plane vibrations), and $\Gamma_{vib} = 11A' + 4A''$.

Isotopic Species Containing $H_2{}^{10}B^{11}B$.—Many of the bands for these isotopic species could be assigned. The assignment of the fundamental vibrations for the $H_2{}^{10}B^{11}BO_3$ species follows readily from those assigned for the $H_2{}^{10}B_2{}^{16}O_3$ and $H_2{}^{11}B_2{}^{16}O_3$ molecules. The assignments are summarized in Table V, using the conventional method of numbering the vibrations. The numbering of ν_2 and ν_{14} is uncertain because of the two missing fundamental frequencies.

TABLE V

FUNDAMENTAL FREQUENCIES FOR ISOTOPIC SPECIES OF C_s SYMMETRY (CM^{-1})

Assignment		Isotopic species $H_2{}^{10}B^{11}B^{16}O_3$	$H_2{}^{10}B^{11}B^{16}O^{18}O_2$	$H_2{}^{10}B^{11}B^{18}O_3$	$D_2{}^{10}B^{11}B^{16}O_3$
A′	ν_1	...	...	...	...
	ν_2	2667	...	...	...
	ν_3	1400	1390.5	1384	1375
	ν_4	1218	1213	1197	1208
	ν_5	1183	1166	1154.5	1139
	ν_6	1127	1110 (?)	...	1083
	ν_7	981	975[a]	...	...
	ν_8	967	...	...	...
	ν_9	...	...	...	...
	ν_{10}	778	...	...	...
	ν_{11}	745	724	715	...
A″	ν_{12}	895	894	892	777
	ν_{13}	875	874	874	...
	ν_{14}	429.5	...	...	...
	ν_{15}	...	...	...	...

[a] Frequencies estimated from combination bands.

The only assignment of the mixed isotopic species that requires comment is the assignment of the Q branch at 875 cm^{-1} (Figure 2). This band was shown to be exclusively due to the species $H_2{}^{10}B^{11}B^{16}O_3$. A very small shift in frequency (1 cm^{-1}) is observed when the oxygen-16 in the ring is replaced by oxygen-18, and a large deuterium shift is indicated. The only unassigned fundamental which would be predicted to show these characteristics is the out-of-plane vibration ν_{13} (A″). This band is analogous to the infrared-inactive A_2 fundamental ν_7 in the pure isotopic species. Because of the close proximity of the A″ bands at 875 and 895 cm^{-1} in $H_2{}^{10}B^{11}B^{16}O_3$ a Fermi resonance

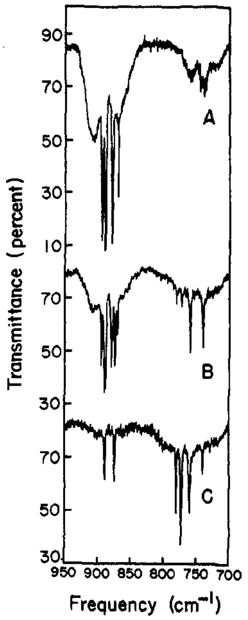

Figure 4.—The 700–950-cm^{-1} region showing the multi-Q *branch structure of the HD species:* (A) *spectrum of the sample* containing 50% $H_2{}^{10}B_{11}B_{16}O_3$ before addition of D_2; (B) spectrum 24 hr after addition of D_2 (major species $H^{11}BD^{10}B^{16}O_3$ and $D^{11}BH^{10}B^{16}O_3$); (C) spectrum 240 hr after addition of D_2 (major species $D_2{}^{10}B^{11}B^{16}O_3$).

between these two fundamentals is possible. This could account for the relatively high intensity of the 875-cm^{-1} band and would explain the shift in the 895-cm^{-1} band toward higher frequency (Figure 2). A similar effect has already been suggested in the case of boroxine for the out-of-plane BH bending vibrations in the $H_3{}^{10}B^{11}B_2{}^{16}O_3$ species.[10]

Isotopic Species Containing HD.—The multi-Q branch structure that one obtains in the 700–900-cm^{-1} region of the spectrum when the partially deuterated species are present is very interesting. The effect is shown in Figure 4. Besides the spectra shown, other spectra were taken which contained other ratios of boron-10 and boron-11. The species present in these spectra and a tentative assignment of the bands are summarized in Table VI. The intensity data available suggested that bands from various isotopic species overlapped. For example, the band at 745 cm^{-1} must be assumed to be a vibration involving the combination D–^{11}B from two isotopic species.

TABLE VI

ASSIGNMENTS FOR THE HD ISOTOPIC SPECIES BETWEEN 700 AND 900 CM^{-1}

Assignment		Isotopic Species			
		$HD^{11}B_2{}^{16}O_3$	$H^{11}BD^{10}B^{16}O_3$	$D^{11}BH^{10}B^{16}O_3$	$HD^{10}B_2{}^{16}O_3$
A″	ν_{12}	878	878	893.4	893.5
	ν_{13}	745	764	745	764

Conclusion

The analysis of the infrared spectrum of $H_2B_2O_3$ is fairly complete and is consistent with the molecule belonging to the C_{2v} symmetry group. Together with the microwave results, the infrared analysis presented here shows that $H_2B_2O_3$ exists in only one configuration. The large residual value of the first-moment equation computed from the microwave results suggested a large anharmonicity in some of the ring-deformation modes. For the out-of-plane vibration ν_9 the first overtone was observed at a frequency indicating a relatively large anharmonicity. Although this motion is termed a BH bending motion, considerable deformation of the ring atoms is involved as indicated by the isotopic shifts. Thus, the suggestion of large anharmonicity is consistent with the infrared results.

Because of the explosive nature of the condensed state of $H_2B_2O_3$ and the low pressures attainable in the gas phase, no attempt was made to obtain a Raman spectrum. Until a Raman spectrum can be obtained, the analysis will have to remain incomplete, although a force constant calculation could lend support to the analysis presented. A more complete understanding of the complex spectra obtained with the partially deuterated species will have to await a mathematical analysis.

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(10) S. K. Wason and R. F. Porter, *J. Phys. Chem.*, **68**, 1443 (1964).