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Infrared spectra of molecular B(OH)₃ and HOBO in solid argon

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Anhydrous $B(OH)_3$ was pressed into a pellet and sublimed at room temperature under vacuum to give molecular $B(OH)_3$ for argon matrix infrared study. The spectrum showed sharp fundamentals without the effect of hydrogen bonding observed in the solid. Fermi resonances were characterized for two fundamentals. The observed frequencies for $B(OH)_3$ and the three deuterium substituted molecules are in agreement with values from self-consistent field/ double zeta plus polarization (SCF/DZP) calculations allowing for appropriate scale factors. The major thermal decomposition products from pulsed laser evaporation of $B(OH)_3$ were H_2O , B_2O_3 , and HOBO. Molecular HOBO was characterized by a strong 2020 cm⁻¹ fundamental, which was confirmed by SCF/DZP calculations.

INTRODUCTION

The oxidation of boron is important for the investigation of potential rocket fuels¹ and interesting intermediates in the oxidation process from boron to the stable B_2O_3 product.² Unfortunately the presence of water intercepts BO₂ as HOBO in route to B_2O_3 . Hence, the characterization of the HOBO intermediate is an important chemical problem.³ There is, however, relatively little information on the HOBO intermediate. In 1960 infrared emission from the B₂O₃-H₂O system in the 1000-1200 °C temperature range was assigned to HOBO.⁴ Concurrent mass spectroscopic studies of this equilibrium have identified HOBO as a major vapor species.^{5,6} A matrix isolation study of the B₂O₃-H₂O equilibrium at 1200 °C has also reported provisional assignments to HOBO fundamental vibrations.⁷ Finally, the vapor in equilibrium with solid metaboric acid (HOBO)₃ at 100 °C contained a broad absorption band in the 2000 cm⁻¹ region expected for HOBO.⁸

Following our interest in boron oxides,² we sought the matrix infrared spectrum of HOBO from the pulsed laser decomposition of orthoboric acid $B(OH)_3$. Although B(OH)₃ is a well known hydrogen-bonded solid and Lewis acid in solution, 9^{-12} very little is known about the B(OH)₃ vapor species although $B(OH)_3$ is receiving attention as a potential flame retardant.¹³ Early infrared studies showed features consistent with the presence of molecular B(OH)₃ in the vapor.¹⁴ Ogden and Young have recently shown that molecular B(OH)₃ evaporates from the solid at 35-45 °C by using mass spectroscopy or trapping in solid nitrogen for matrix infrared spectroscopy.¹⁵ Both ortho- and metaboric acids have very recently been studied in the vapor phase by vibrational spectroscopy.¹⁶ In the course of pulsed laser evaporation of solid BN, the B(OH), hydrolysis product was identified in solid argon.¹⁷ We report here an argon matrix isolation study of molecular B(OH)₃ and its thermal decomposition products including H₂O and HOBO.

EXPERIMENT

The pulsed laser evaporation matrix-isolation apparatus has been described.² Orthoboric acid (Sigma 99%) was pressed into a 1 cm diam×4 mm thick pellet and used as a target. The target was rotated at 1 rpm and ablated by 15, 20, or 30 mJ/pulse of Nd-YAG fundamental into a stream of condensing argon. Fourier-transform infrared (FTIR) spectra were recorded at 2 cm^{-1} resolution on a Nicolet 5 DXB spectrometer; frequency accuracy is ± 0.5 cm⁻¹. It was discovered that adequate B(OH)₃ sublimed from the target at room temperature for measurement of the matrix infrared spectrum. Similar experiments were done with a metaboric acid (99.9% Metron) pellet and boron nitride discs (Aesar) reacted with a drop of H_2O , D_2O , or $H_2^{18}O$ for two weeks in a sealed container. Deuterated boric acids were prepared by dissolving B₂O₃ (99.9995% Aesar) in excess D₂O (Aldrich 99.8 atom %D) at 60-70 °C and drying under vacuum. Partially deuterated samples were also prepared using 1/1 and 3/1 D₂O/H₂O mixtures.

RESULTS

Matrix infrared spectra of $B(OH)_3$ and its decomposition products will be presented using different chemical precursors.

 $B(OH)_3$. Figures 1-3 show typical spectra of boric acid vapor trapped in solid argon (a) from room temperature sublimation for 4 h and (b) a different experiment with pulsed laser evaporation of the sample for 2 h using 20 mJ/pulse. Note the strong, sharp 3688.6 cm^{-1} absorption (half-width 2.4 cm⁻¹) and weak broad 3190 ± 5 cm⁻¹ band, sharp new absorptions at 1471.9, 1459.8, 1429.1, and 1414.9 cm^{-1} , sharp new 1028.2 and 992.4 cm⁻¹ bands, the sharp 692.2–666.4 cm^{-1} 1–4 doublet, and the strong, sharp 436.0 cm⁻¹ band with a partially resolved 432.1 cm⁻¹ shoulder, a weak 1–4 doublet at 1208.1 and 1182.4 cm^{-1} and a weak 918.4 cm^{-1} band all labeled B in spectrum (a) and listed in Table I. Laser evaporation produced these absorptions and weak new product bands due to ${}^{11}BO_2$ at 1299 and 1274 cm⁻¹, ${}^{11}BO_2$ at 1931 and 1920 cm⁻¹, ${}^{11}BO$ at 1854.7 cm⁻¹, and stronger bands due to ${}^{11}B_2O_3$ at 2063.2 cm⁻¹ and ${}^{10}B_2O_3$ at 2130.1 cm⁻¹ and markedly increased familiar water^{2,18} absorptions labeled W at 3777, 3756, 3712, 1624, 1608, and 1592 cm^{-1} , and water dimer at 3574 cm⁻¹ as shown in spectrum (b). Laser evaporation



FIG. 1. Infrared spectra for boric acid samples in the $4000-3000 \text{ cm}^{-1}$ region: (a) sample sublimed into argon stream and condensed at 12 K for 4 h, and (b) sample evaporated by pulsed laser (20 mJ/pulse at sample) for 1.5 h into argon stream condensed at 12 K. W denotes water, B identifies molecular boric acid, and H indicates molecular HOBO.

also produced a new partially resolved shoulder at 3681 $\rm cm^{-1}$ on the strong, sharp 3688.6 $\rm cm^{-1}$ precursor band in the O-H stretching region, new bands at 2106 and 2023 $\rm cm^{-1}$ with 2033 and 2011 $\rm cm^{-1}$ satellites in the terminal B-O stretching region, and a weak new band at 904 $\rm cm^{-1}$ all labeled H and listed in Table II. Other product features were observed at 3489, 3444, 1383, 1018, 743, and 456 $\rm cm^{-1}$, and weak broad bands were observed at 1210 and 560 $\rm cm^{-1}$.

Additional experiments were done with $B(OH)_3$ and laser evaporation with 15 and 30 mJ/pulse (up to 2 h). The spectra are the same as reported in Figs. 1–3 with different product absorbances. One of these samples was annealed to 25, 35, and 42 K. Annealing to 25 K decreased the *B* bands by 20%, annealing to 35 K decreased the *B* bands by 60% and increased broad absorption at 3200– 3400 cm⁻¹ and 1440 cm⁻¹ and weak 3489 and 3444 cm⁻¹ bands; 42 K annealing continued this trend. The new bands labeled H were also substantially diminished on an-



FIG. 2. Infrared spectra in 2200-1200 cm⁻¹ region for samples in Fig. 1.



FIG. 3. Infrared spectra in 1300–300 cm^{-1} region for samples in Fig. 1.

nealing; however, the 1383, 1018, and 456 cm^{-1} product bands were little affected.

Two similar experiments were done with a $B(OD)_3$ sample; spectra are shown in Figs. 4-6. Very weak sharp bands at 3689.3, 1015.3, 491.9, and 333.6 cm^{-1} provided evidence for trace hydrogen contamination in the sample. Precursor bands present on initial sample sublimation shown in spectrum (a) include the sharp 2719.8 cm^{-1} band (2.4 cm⁻¹ half-width), the 1444.4–1396.6 cm⁻¹ 1–3 doublet, the sharp 807.9 cm^{-1} band, the sharp 691.0-665.5 cm^{-1} 1–4 doublet, and sharp 385.9 and 317.6 cm^{-1} bands. Pulsed laser evaporation increased these absorptions and produced a shoulder at 2713 cm^{-1} , a 1-4 doublet at 2130.5-2063.4 cm⁻¹ for B_2O_3 , new absorptions at 2100 and 2013 cm⁻¹ labeled D, a broad band at 2380 ± 5 cm⁻¹ with sharp side bands at 2575 and 2551 cm⁻¹, D_2O at 2782, 1196, and 1175 cm⁻¹, and $(D_2O)_2$ at 2616 cm⁻¹, and broad bands at 930 and 525 cm⁻¹. Additional new absorptions were observed at 1368, 766, and 337 cm⁻¹.



FIG. 4. Infrared spectra for boric acid- d_3 samples in the 2800–1800 cm⁻¹ spectral region: (a) sample sublimed into argon stream for 2 h, and (b) sample evaporated by pulsed laser (20 mJ/pulse at sample) for 1.5 h into argon stream and condensed at 12 K. B denotes boric acid and D indicates DOBO.

TABLE I. Major infrared absorptions (cm^{-1}) from sublimation of boric acid into condensing argon at 12 K.

Mode ^a	B(OH) ₃	B(OH) ₂ (OD)	B(OH)(OD) ₂	B(OD) ₃
$v_{b}(e')$	3688.6		3689.3	2719.8
$v_7(e')$	1414.9, 1471.9	1401.2	1409.5, 1459.1	1396.6, 1444.4
$v_8 + v_9(e')$	1429.1, 1459.8 ^b	1420.7	1399.6, 1447.9	
$v_4 + v_{10}(e')$	1182.4, 1208.1			1053.4
$2v_{10}(e')$	1028.2	1011.7, 980.8	1015.3	
$v_8(e')$	992.4 b	879.0, 770.8	804.4	807.9
$v_5 + v_{10}(e')$	918.4			
$v_4(a'')$	666.4, 692.2	666, 691	666, 691	665.5, 691.0
$v_{10}(e'')$	$(520 \pm 5)^{\circ}$	470.7	491.5	$(390 \pm 10)^{\circ}$
$v_{s}(a')$	436.0	353.6	333.6	317.6
vo(e')	432.1	431.4, 400.6	414.0, 386.5	385.9

*Mode symmetry in C_{3h} point group.

^bFermi-resonance doublet.

^cDeduced from combination bands.

Similar pulsed laser evaporation experiments were done with boric acid samples prepared from 50/50 and $25/75 H_2O/D_2O$ mixtures and these samples provide useful complementary information. In the O-H and O-D stretching regions, the strong sharp 3688.6 and 2719.8 cm^{-1} bands were unchanged within experimental error; however the broad bands were displaced to 3175 ± 5 and 2390 ± 5 cm⁻¹. Strong new bands were observed in the B-O stretching region (Table I). Figure 7 illustrates the spectrum from $300-1100 \text{ cm}^{-1}$ after laser evaporation for 3 h. The 1-4 doublet at 691.5-666.0 cm^{-1} is intermediate between pure H and pure D values. A new band at 1011.7 cm^{-1} dominates the upper region [Fig. 7(a)]; additional new bands observed at 980.8, 879.0, 770.8 cm^{-1} are marked with 1. The lower region is dominated by 491.5 and 470.7 cm^{-1} bands above the B(OH)₃ band at 436.0 cm^{-1} , and 353.6 and 333.6 cm^{-1} bands above the B(OD)₃ band at 317.6 cm⁻¹. New bands were also observed at 414.0 and 400.6 cm⁻¹ between the 432.1 and 385.9 cm⁻¹ bands for B(OH)₃ and B(OD)₃, respectively. Comparison with the spectrum of a more heavily deuterated sample in Fig. 7(b) identifies new bands labeled 2, which dominate



One experiment was done allowing $B(OH)_3$ to evaporate at room temperature into a flowing nitrogen stream; the spectrum was the same as in Ref. 15 but with less H_2O impurity. A final $B(OH)_3$ experiment was done with 1% N_2 in argon; the spectrum was the same as in Figs. 1–3 with the addition of sharp new satellite features at 3678.6, 1466.8, 1421.2, 1007.0, and 448.7 cm⁻¹ believed to be due to a $B(OH)_3-N_2$ complex.

 $(HOBO)_3$. One experiment was done with metaboric acid. The sublimed sample was indistinguishable from B(OH)₃. Laser evaporation gave the same products with a higher yield in the 2000 cm⁻¹ region, which is contrasted for orthoboric acid and orthoboric acid-d₃ in Fig. 8.

 $BN+H_2O$. In order to complement boron nitride ablation studies and identify impurities in a binary B_xN_y system investigation,¹⁷ a BN disc surface was reacted with water, blotted dry, laser evaporated into an argon stream, and condensed on a 12 K cold window. Strong boron isotopic triplets beginning at 882.3 and 1998.4 cm⁻¹ were



FIG. 5. Infrared spectra in the 1800–1300 cm^{-1} region for samples in Fig. 4.



FIG. 6. Infrared spectra in the 1300–300 cm^{-1} region for samples in Fig. 4.

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FIG. 7. Infrared spectra in the 1100–300 cm⁻¹ region for mixed H/D boric acid samples evaporated by pulsed laser for 3 h into condensing argon stream: (a) sample prepared from 50/50 H₂O/D₂O, and (b) sample prepared from 25/75 H₂O/D₂O. The bands labeled 1 belong to boric acid- d_1 and the bands labeled 2 belong to boric acid- d_2 . Bands due to B(OH)₃ and B(OD)₃ are not labeled.

observed unshifted from the values found using a clean BN substrate.¹⁷ Strong absorptions were observed for $B(OH)_3$ and weak bands for B_2O_3 precisely as reported in Figs. 1-3. Photolysis at 254 nm for 45 min had no effect on the sample. A similar treatment with D_2O , gave the unshifted $B_x N_y$ features and the spectrum reported in Figs. 4-6. These samples contained more water absorptions due to incomplete drying of the wet BN surface. A final experiment with BN reacted with H2¹⁸O gave only water absorptions from room temperature sublimation, but with pulsed laser evaporation the same $B_x N_y$ features and oxygen-18 enrichment in the boric acid and boron oxide product spectrum were observed. A strong sharp absorption was observed at 3677.2 cm^{-1} in addition to the familiar 3688.6 cm^{-1} absorption. One strong new band was observed at 1406.6 cm^{-1} and new features were observed at 1023.9,



FIG. 8. Infrared spectra in the 2160–1920 cm⁻¹ region for pulsed laser evaporated samples: (a) orthoboric acid, (b) metaboric acid, and (c) orthoboric acid- d_3 .



FIG. 9. Structures for $B(OH)_3$ and HOBO calculated at the SCF/DZP level. MBPT(2) dimensions for HOBO in parentheses.

1020.2, 988.2, and 983.1 cm⁻¹. The 692 and 666 cm⁻¹ bands exhibited partially resolved shoulders on the low frequency side.

Calculations. Ab initio geometry and frequency calculations were performed on HOBO and B(OH)₃ with the ACESII computational package.¹⁹ Optimized geometries were obtained at the self-consistent field (SCF) level for HOBO and B(OH)₃ and at second order multibody perturbation theory [MBPT(2)] level for HOBO using a double ζ + polarization (DZP) basis set. The calculated B(OH)₃ geometry [Fig. 9(a)] is very close to the C_{3h} geometry observed for crystalline boric acid, which exhibited a 1.361 Å B-O bond length and 114° B-O-H angle,⁹ and the geometry from earlier ab initio calculations using the DZP basis set.²⁰ Calculations on nonplanar geometries gave higher energies, which is consistent with computational and microwave structures for the similar planar HB(OH)₂ molecule.^{21,22} The SCF geometry for HOBO [Fig. 9(b)] was slightly different from the MBPT(2) geometry, the latter having longer bond lengths and a more acute BOH bond angle.

Frequency calculations were performed on the optimized geometries at the SCF level for HOBO and $B(OH)_3$ and the MBPT(2) level for HOBO. The agreement between the observed and calculated frequencies is reasonable as can be seen by the range of ratios of observed/ calculated frequencies in Table V. Substituted isotopic boron (10/11), oxygen (16/18), and hydrogen (H/D) frequencies were also calculated and tabulated in Tables III and IV. Furthermore, good agreement between observed and calculated isotopic frequency ratios can be dem-

TABLE II. New infrared absorptions (cm^{-1}) produced on pulsed-laser evaporation/decomposition of boric acid and assigned to the HOBO and DOBO molecules.^a

НОВО	DOBO	Assign		
3681	2713	v(OH)		
2106	2100	$v({}^{10}B-O)$		
2033, 2023, 2011	2020, 2013, 2007	$v(^{11}B-O)$		
904	· · · · · · · · · · · · · · · · · · ·	α (H-O-B)		
516, 512?		α (O-B-O)		
447?		δ(H-O-B)		

^aLabeled H and D in figures. Underlined bands are strongest in site split multiplets.

TABLE III. SCF calculated frequencies (cm^{-1}) and intensities (km/mole) for isotopic B(OH)₃ molecules.⁴

10-16-1,1,1	11-16-1,1,1	11-16-1,1,2	11-16-1,2,2	11-16-2,2,2	11-18-1,1,1
466(31)	464(31)	383(154)+	363(192)+	347(209)+	446(27)
466(31)	464(31)	432(32)	416(0) +	416(32)	446(27)
478(387)+	477(379)+	463(31)	417(32)	416(32)	477(381) +
557(0)+	557(0) +	514(167)	445(31)	416(0) +	554(0) +
557(0) +	557(0) +	557(0) +	538(73) +	416(0) +	554(0) +
769(185)+	741(186)+	740(173) +	740(160)+	739(146) +	732(175) +
925(0)	925(0)	839(23)	804(8)	772(0)	878(0)
1109(179)	1108(175)	951(23)	887(72)	886(73)	1091(184)
1109(179)	1108(175)	1107(175)	962(14)	886(73)	1091(184)
1115(0)	1115(0)	1112(63)	1109(121)	969(0)	1104(0)
1608(591)	1555(557)	1539(557)	1529(536)	1528(551)	1537(532)
1608(591)	1555(557)	1553(551)	1545(546)	1528(551)	1537(532)
4205(180)	4205(180)	3062(77)	3061(116)	3061(116)	4191(175)
4205(180)	4205(180)	4205(180)	3063(39)	3061(116)	4191(175)
4207(0)	4207(0)	4207(60)	4206(120)	3062(0)	4194(0)

*10-16-1,1,1 identifies the boron/oxygen/hydrogen isotopes, and + denotes out-of-plane mode.

onstrated by comparison of the values for each fundamental given in the appropriate tables; the observed/calculated frequency ratios range between 0.88 and 0.93 depending on the fundamental involved. The calculated intensities (Table III) are well matched by the observed intensities; the given intensities also identify IR inactive modes, which are allowed but weak in the mixed H/D isotopic molecules. The boron isotopic (10/11) shift for both HOBO and B(OH)₃ was underestimated; the MBPT(2) frequencies show more boron isotopic shift, but the overall agreement with the observed shifts was not as good. The present SCF/

TABLE IV. Frequencies (cm^{-1}) and intensities (km/mol) for isotopic HOBO molecules from SCF and MBPT(2) calculations in DZP basis.

1-16-10-16*	1-16-11-16 ^a	1-18-11-18		Assign	
488(68)	473(63)	469	δ(H-O-B)	
543(96)+	524(90)+	516+	δ(OBO)	
960(260)	955(261)	936	α (H-O-B)		
1048(12)	1045(11)	1001	v("sy	m" O-B-O)	
2299(714)	2223(662)	2186	v("antis	sym" O-B-O)	
4182(327)	4182(326)	4168	ν(O–H)		
2-16-10-16ª	2-16-1	1-16 ^a			
438	4	429	δ(D_O_B)		
543+	524	•+	$\delta(O-B-O)$		
787	776 a(D-O-		(D-O-B)		
1034	1031		ν ("sym" O-B-O)		
2287	22	211	v("antisym" O-B-O		
3051	3050		v(O–D)		
1-16-10-16 ⁶	1-16-11-16	^b 2-16-	10-16 ^b	2-16-11-16 ^b	
479(48)	465(45))	437	427	
539(44)+	520(42)+	53	8+	519+	
1012(43)	1011(57))	820	809	
1029(124)	1023(113)) 1	009	1007	
2163(375)	2089(347)	2	160	2086	
3930(180)	3930(180)	2	862	2862	

^aH–O–B–O isotopes, SCF calculations, + denotes out-of-plane mode. ^bMBPT(2) calculations. DZP frequencies for HOBO are in general agreement with earlier similar unpublished calculations.⁸

DISCUSSION

The new infrared absorptions will be identified and vibrational assignments will be made. Five different groups of bands were observed for different new molecular species from the boric acid system.

 $B(OH)_3$ The major bands (Table I) were produced by room temperature sublimation of $B(OH)_3$ directly into a condensing argon stream. These bands decreased together on annealing to 35 and 42 K where aggregate absorptions similar to solid¹⁰⁻¹² $B(OH)_3$ appeared in the matrix. Laser ablation slightly increased the growth rate of the major bands and produced four groups of new bands which will be discussed separately below. The major bands are assigned to monomeric molecular $B(OH)_3$ based on comparison to solid,¹⁰⁻¹² nitrogen matrix,¹⁵ and gas phase spectra.^{14,16} Boric acid is extensively hydrogen bonded in the solid, so this comparison must remove the effect of hydrogen bonding.

The present argon matrix spectra show that B(OH)₃ is weakly hydrogen bonded to N₂ in the nitrogen matrix and that the argon matrix environment more nearly approximates the gas phase for modes involving hydrogen. The acids HF and HOF are cases in point: the fundamentals are 3961.5 and 3578.5 cm⁻¹, respectively, in the gas phase,²³ 3919 and 3572 cm⁻¹ in solid argon, and 3880 and 3536 cm^{-1} in solid nitrogen.^{24,25} The 1:1 complexes N₂-HF and N_2 -HOF absorb at 3881 and 3537 cm⁻¹ in solid argon, which shows that hydrogen bonding to one N₂ molecule is the major nitrogen matrix effect for an acid guest molecule.^{24,25} Table V compares B(OH)₃ fundamentals in solid phase, nitrogen matrix, argon matrix, and gas phase. For the fundamentals most sensitive to hydrogen bonding, v_6 (O-H stretch) and v_5 [B-O-H deformation (def)], removing hydrogen bonding increases the former and decreases the latter mode. Doping the argon matrix with 1%

TABLE V. Fundamentals (cm⁻¹) in C_{3k} symmetry for ¹¹B(OH)₃ in different media.

	Solid ^a	N ₂ matrix ^b	Ar matrix ^c	Vapor ^d	SCF ^c	Ratio
$\overline{v_1(a')}$ sym O-H str	3172	•••		3705	4207	0.88 ^h
$v_2(a')$ sym B-O-H bend	1065		$(1015)^{f}$	1020	1115	0.91
$v_3(a')$ sym B–O str	880		• • • •	866	925	0.94 ^h
$v_{4}(a'')$ sym BO ₃ def	648	675	667	•••	741	0.90
$v_s(a'')$ sym B–O–H def	824	514	436		477	0.91
$v_6(e')$ antisym O-H str	3200	3668	3689	3706	4205	0.88
$v_2(e')$ antisym B-O str	1450	1426	(1421) ^g	1429	1555	0.91
$v_{\rm g}(e')$ antisym B-O-H bend	1197	1010	(1012) ⁸	1017	1108	0.91
$v_{q}(e')$ antisym O-B-O bend	540	449	432		464	0.93
$v_{10}(e'')$ antisym B–O–H def		(577)	(520) ^f	•••	557	0.93

^aReference 10; slight differences in Refs. 11 and 13.

^bReference 15.

^cThis work.

^dReference 16.

Ratio argon matrix/SCF frequencies.

^fFundamentals deduced from mixed H/D isotopic bands.

⁸Estimate of unperturbed fundamental without Fermi resonance.

^hRatio vapor/SCF frequencies.

 N_2 gives new v_6 and v_5 bands displaced appropriately for the B(OH)₃-N₂ complex. It is surprising that the effect of hydrogen bonding on the v_9 (O-B-O bend) is as substantial as found.

The present work is in agreement with the vibrational assignments of Ogden and Young¹⁵ when shifts in the fundamentals from solid nitrogen to solid argon are taken into account. In addition, two Fermi-resonance interactions were observed in solid argon. Several fundamentals provide information on $B(OH)_3$ and these will be considered in turn.

The sharp 1–4 relative intensity doublet at 692.2–666.4 cm⁻¹ is indicative of a vibration involving a single boron atom for natural abundance boron. This BO₃ out-of-plane skeletal vibration shows little change from solid to matrix. In the B(OD)₃ experiments the sharp 1–4 doublet at 690.9–665.5 cm⁻¹ revealed a small deuterium shift for this vibration of one boron atom. The presence of oxygen was verified by oxygen-18 substitution although complete enrichment was not possible. The shift in the O–H stretching fundamental from 3688.6–3677.2 cm⁻¹ is appropriate for oxygen-18 substitution.

The strong 1-3 relative intensity doublet at 1444.4-1396.6 cm⁻¹ in B(OD)₃ experiments is due to the v_7 predominantly antisymmetric B-O stretching fundamental based on relative intensities and isotopic shifts. The ¹⁰B-¹¹B isotopic shift for this mode can be approximately calculated for the antisymmetric stretching fundamental of a trigonal BO₃ unit (using only the symmetry coordinate matrix elements). The predicted shift, 46.9 cm⁻¹, is closely matched by the observed shift, 47.8 cm^{-1} . However, in the $B(OH)_3$ experiments, two doublets were observed in this region, a strong doublet at 1471.9-1414.9 cm⁻¹ and a weaker doublet at 1459.7–1428.9 cm^{-1} , the former with a larger (57.0 cm⁻¹) and the latter with a smaller (30.8 cm⁻¹) ${}^{10}B{}^{-11}B$ isotopic shift. Both doublets in B(OH)₃ experiments show approximately 1-2 relative intensities, which reveals more involvement of hydrogen in the normal mode than in the $B(OD)_3$ case. This is indicative of a

Fermi-resonance interaction where the combination band is above the ¹¹B fundamental which forces the ¹¹B fundamental to lower frequency and below the ¹⁰B fundamental which forces the ¹⁰B fundamental to higher frequency. Thus the ${}^{10}B-{}^{11}B$ shift of the v_7 fundamental is increased by the Fermi-resonance interaction and the ¹⁰B-¹¹B separation for the combination band is increased over the combined isotopic shifts of its fundamentals. What fundamentals have the appropriate position, intensity, and symmetry to give a combination band around 1440 cm⁻¹? The $v_8(e')$ and $v_{q}(e')$ fundamentals at approximately 1012 cm⁻¹ (also involved in Fermi-resonance) and 432 cm^{-1} provide the necessary interaction. (These fundamentals have boron isotopic shifts too small to resolve; see Table III.) However, this Fermi resonance was not observed in solid nitrogen, since v_9 is 17 cm⁻¹ higher in solid nitrogen and $v_8 + v_9$ is apparently far enough above v_7 in solid nitrogen to preclude the Fermi-resonance interaction.²⁶

The intense 1028.2–992.4 cm⁻¹ doublet is indicative of a strong Fermi-resonance interaction, which also does not happen in solid nitrogen. The obvious interaction here is with the overtone $2v_{10}$ of the C_{3h} symmetry forbidden $v_{10}(e'')$ fundamental. A 510–520 cm⁻¹ value for v_{10} would give, with anharmonicity, a 1015 ± 5 cm⁻¹ value for $2v_{10}$ and the strong Fermi-resonance interaction observed in the argon matrix infrared spectrum. In solid nitrogen v_{10} is higher and the overtone is too far above v_8 for a Fermiresonance interaction.

On mixed H/D isotopic substitution symmetry lowering and mode mixing occur, which gives additional bands in the spectrum of $B(OH)_2(OD)$ and $B(OH)(OD)_2$. The spectrum in the 1400 cm⁻¹ region involves the lifting of degeneracy and altering the Fermi-resonance interaction. Two fundamentals for each isotopic molecule are given in Table I.

The $v_8(e')$ mode also splits on mixed H/D substitution and the $v_2(a')$ mode shares the same region, so three in-plane H-O-B bending modes and the symmetric B-O stretch $v_3(a')$ are in principle observable for each isotopic molecule. One of these is clearly observed for $B(OH)_2(OD)$ at 1011.7 cm⁻¹, near the position of the unperturbed v_8 mode for $B(OH)_3$. Likewise the analogous band for $B(OH)(OD)_2$ is found at 804.3 cm⁻¹. The observation of $B(OH)(OD)_2$ at 1015.3 cm⁻¹ and $B(OH)_2(OD)$ at 1011.7 cm⁻¹ points to the symmetry forbidden $v_2(a')$ fundamental for $B(OH)_3$ near 1015±5 cm⁻¹.

On symmetry lowering, three out-of-plane hydrogen deformation modes are possible for each mixed isotopic molecule and two of these bands should be intense. New bands appear above the $v_5(a'')$ modes for B(OH)₃ and B(OD)₃ as listed in Table I. The observed B(OH)(OD)₂ and B(OH)₂(OD) bands point to a 520 ± 5 cm⁻¹ value for the unobserved $v_{10}(e'')$ mode of B(OH)₃ and 390 ± 10 cm⁻¹ for B(OD)₃. The $v_9(e')$ mode also splits on mixed H/D substitution, and two new bands were observed for each mixed isotopic molecule.

A 1-4 relative intensity combination band was observed at 1208.1-1182.4 cm⁻¹ with almost the same ¹⁰B-¹¹B separation as v_4 . The frequency difference between each boron isotopic combination band and v_4 fundamental is 516.0±0.1 cm⁻¹, which is the value predicted for $v_{10}(e'')$ of B(OH)₃. Since $(a'') \times (e'')$ is (e') in C_{3h} symmetry, this combination band is fully allowed.

The weaker 918.4 cm⁻¹ band also belongs to B(OH)₃ and it is probably due to the combination band $v_5 + v_{10}$ in weak Fermi resonance with v_8 , which shifts $v_5 + v_{10}$ down somewhat more than the sum of fundamentals and anharmonicity would predict. The strong 1028.2 and 992.4 cm⁻¹ bands and weak 918.4 cm⁻¹ band form a Fermi-resonance triplet with the higher pair in stronger resonance than the lower pair based on intensities and the coincidence of unperturbed bands.

The final confirmation of the identification and assignment of molecular B(OH), was obtained with SCF/DZP frequency calculations. Table V also includes the calculated frequencies, which are higher than the observed matrix (and gas phase Raman) fundamentals, as expected. However, the frequency ratios argon matrix/calculated (and gas phase Raman/calculated) are in the range for typical scale factors used to relate SCF frequencies to observed frequencies.²⁷ These calculations predict the forbidden $v_{10}(e'')$ fundamental at 520 ± 20 cm⁻¹ in agreement with the value deduced from combination bands. Furthermore, the SCF/DZP calculations predict the strong $v_5(a'')$ fundamental in the gas phase to be 430 ± 20 cm⁻¹ and cast doubt on a 303 cm⁻¹ value quoted earlier.¹⁴ The ultimate test of agreement between matrix and SCF frequencies is the spectra of $B(OH)_2(OD)$ and $B(OH)(OD)_2$. Using appropriate scale factors from $B(OH)_3$ and $B(OD)_3$, the calculated and matrix fundamentals agree to within 2-3 cm^{-1} for the most part or 5–10 cm^{-1} in the extreme case without any attempt to account for anharmonicity. Agreement for the low frequency bending modes is particularly noteworthy.

HOBO. The group of bands labeled H (Table II) required pulsed laser evaporation from orthoboric and metaboric acid, which also produced B_2O_3 and H_2O . The H bands included an O-H stretching fundamental (3681 cm⁻¹) and a terminal ¹¹B-O stretching mode (2023 cm⁻¹). Natural boron isotopes gave the ¹⁰B-O counterpart (2107 cm⁻¹) and deuterium substitution redshifted the strong B-O vibration 7-10 cm⁻¹ and the O-D stretching fundamental to 2713 cm⁻¹.

The strongest band at 2023 cm⁻¹ is in agreement with a broad gas phase band near 2000 cm⁻¹ in metaboric acid vapor.⁸ Furthermore, the laser decomposition product bands near 2000 cm⁻¹ (Fig. 8) agree with the strongest absorption in solid argon from the major product of the $B_2O_3 + H_2O$ or D_2O reaction at 1200 °C.⁷

Confirmation of the present identification of molecular HOBO is found in the SCF/DZP frequency calculations. The scale factor 0.91, which maps the calculated and observed v_7 modes for B(OH)₃, predicts the strongest fundamental for HO¹¹BO at 2023 cm⁻¹, precisely the observed value. Furthermore, the calculation predicts a 12 cm⁻¹ shift for $DO^{11}BO$ and an 11 cm⁻¹ shift was observed. The SCF calculation predicts HO¹⁰BO at 2092 cm⁻¹, some 15 cm^{-1} below the observed value. Unfortunately the SCF calculation does not adequately describe the mode mixing for ¹¹B and ¹⁰B isotopic molecules and the isotopic frequency ratio is not accurately calculated. In this regard MBPT(2) does slightly better for ${}^{10}B/{}^{11}B$ but not as well for H/D. The scale factor 0.88, which maps the calculated and observed v_6 modes for B(OH)₃, predicts the O-H stretching fundamental for HOBO at 3680 cm⁻¹, in excellent agreement with the 3681 $\rm cm^{-1}$ observed value. The weaker 904, 516, and 447 cm^{-1} bands are tentatively assigned to HOBO with less confidence on the basis of the SCF calculations, where larger scale factors (0.95-0.98) are required to map the frequencies.

On the basis of the present observations and SCF calculations, it is concluded that emission in the 1400 cm⁻¹ region from the B_2O_3 - H_2O system⁴ assigned to HOBO is in fact probably due to $B(OH)_3$. The strong emission bands in the 2000–2100 cm⁻¹ region are probably due to HOBO as assigned.⁴ In the earlier matrix isolation study of the B_2O_3 - H_2O system,⁷ bands in the 1400 cm⁻¹ region must likewise be considered for $B(OH)_3$, which is also evidenced by bands at 3180 and 436 cm⁻¹ in the reported spectrum.

Finally, thermal decomposition of $B(OH)_3$ produced H_2O , HOBO, and B_2O_3 , and decomposition of $B(OD)_3$ gave D_2O , DOBO, and B_2O_3 , as expected from simple stoichiometry.

Other absorptions. Laser evaporation also produced new bands at 3489 and 3444 cm⁻¹ in the O-H stretching region and 2575 and 2551 cm⁻¹ in the O-D stretching region. These bands are intermediate between molecular and solid B(OH)₃ values, and are appropriate for a 1:1 complex between B(OH)₃ and another molecule such as H_2O or B(OH)₃ itself.

The 1383, 1018, and 456 cm⁻¹ product bands decreased only slightly on annealing; deuterium counterparts were observed at 1368, 766, and 337 cm⁻¹. These bands evidence an antisymmetric B–O stretching mode, and B–

O-H bending and deformation modes. Noteworthy is the absence of an out-of-plane BO_3 deformation. These bands provide evidence, but no conclusive proof, for a radical photolysis product like $B(OH)_2$.

The 643.9 cm⁻¹ band in B(OD)₃ laser experiments has a 669.7 cm^{-1 10}B counterpart and no obvious H counterpart. Clearly this band is due to an out-of-plane BO₃ deformation mode. The 643.9 cm⁻¹ band is tentatively identified as the radical BO₃D₂ formed by D atom detachment.

The weak 743 cm^{-1} band grows slightly on annealing and it cannot be identified without more information.

CONCLUSIONS

Solid boric acid sublimes at room temperature in vacuum to give molecular $B(OH)_3$. The molecule appears to have C_{3h} symmetry. The vibrational spectrum of molecular $B(OH)_3$ is strongly medium dependent owing to hydrogen bonding interactions. Fermi resonance was observed for two of the (e') fundamentals of $B(OH)_3$ in solid argon. SCF/DZP calculations predicted the vibrational spectrum of molecular $B(OH)_3$, and the d_1 , d_2 , and d_3 species, in excellent agreement with the observed spectra allowing for appropriate scale factors.

The major thermal decomposition products of $B(OH)_3$ were H_2O , B_2O_3 , and HOBO. The latter intermediate was characterized by a strong terminal B–O stretching fundamental near 2020 cm⁻¹, which showed boron and hydrogen isotopic shifts. Again SCF/DZP calculations predicted the HOBO spectrum using scale factors from $B(OH)_3$.

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- ¹R. A. Yetter, H. Rabitz, F. L. Dryer, R. C. Brown, and C. E. Kolb, Combust. Flame **83**, 43 (1991).
- ²T. R. Burkholder and L. Andrews, J. Chem. Phys. 95, 8697 (1991).
- ³N. L. Garland, C. T. Stanton, H. H. Nelson, and M. Page, J. Chem. Phys. **95**, 2511 (1991).
- ⁴D. White, D. E. Mann, P. N. Walsh, and A. Sommer, J. Chem. Phys. **32**, 488 (1960).
- ⁵D. J. Meschi, W. A. Chupka, and J. Berkowitz, J. Chem. Phys. 33, 530 (1960).
- ⁶S. P. Randall and J. L. Margrave, J. Inorg. Nucl. Chem. 16, 29 (1960).
- ⁷ M. J. Linevsky, Technical Report, Defence Technical Information Center, Alexandria, Virginia, 1968.
- ⁸H. H. Nelson, N. L. Garland, C. T. Stanton, and M. Page (unpublished results, 1990).
- ⁹W. H. Zachariasen, Acta Crystallogr. 7, 305 (1954).
- ¹⁰D. E. Bethell and N. Sheppard, Trans. Faraday Soc. 51, 9 (1955).
- ¹¹D. F. Hornig and R. C. Plumb, J. Chem. Phys. 26, 637 (1957).
- ¹²R. R. Servoss and H. M. Clark, J. Chem. Phys. 26, 1179 (1957).
- ¹³J. P. Madacsi and N. P. Knoepfler, Text. Res. J. 49, 176 (1976).
- ¹⁴ J. L. Margrave and S. P. Randall, personal communication quoted by R. Ottinger, S. J. Cyvin, R. W. Mooney, L. A. Kristiansen, and J. Brunvoll, Acta Chem. Scand. 20, 1389 (1966).
- ¹⁵J. S. Ogden and N. A. Young, J. Chem. Soc. Dalton Trans. 1645 (1988).
- ¹⁶T. R. Gilson, J. Chem. Soc. Dalton Trans. 2463 (1991).
- ¹⁷L. Andrews, P. Hassanzadeh, T. R. Burkholder, and J. M. L. Martin, J. Chem. Phys. (in press).
- ¹⁸G. P. Ayers and A. D. E. Pullen, Spectrochim. Acta 32A, 1629 (1976).
- ¹⁹ J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, and R. J. Bartlett, ACES 11, Quantum Theory Project, University of Florida, Gainesville, FL, 1992.
- ²⁰G. Gundersen, Acta Chem. Scand. A 35, 729 (1981).
- ²¹T. Fjeldberg, G. Gundersen, T. Jonvik, H. M. Seip, and S. Saebo, Acta Chem. Scand. A 34, 547 (1980).
- ²²Y. Kawashima, H. Takeo, and C. Matsumusa, Chem. Phys. Lett. 57, 145 (1978).
- ²³ R. M. Talley, H. M. Kaylor, and A. H. Nielson, Phys. Rev. 77, 529 (1950); E. H. Appleman and H. Kim, J. Chem. Phys. 57, 3272 (1972).
- ²⁴L. Andrews and S. R. Davis, J. Chem. Phys. 83, 4983 (1985); L. Andrews, R. T. Arlinghaus, and G. L. Johnson, *ibid.* 78, 6347 (1983);
 L. Andrews and G. L. Johnson, J. Phys. Chem. 88, 425 (1984).
- ²⁵E. H. Appleman and A. J. Downs, J. Phys. Chem. 93, 598 (1989).
- ²⁶ The v_5 fundamental is substantially different in solid argon and nitrogen and the $v_5(a'') + v_8(e')$ combination could provide the Fermiresonance interaction only if the C_{3h} symmetry of B(OH)₃ were lowered. This possibility is not necessary to explain the observed Fermiresonance interaction.
- ²⁷ W. J. Hehre, L. Radom, P. von R. Schleyer, and J. A. Pople, *Ab Initio MO Theory* (Wiley, New York, 1986).

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