Characterisation of Ortho- and Meta-boric Acids in the Vapour Phase

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Vibrational spectroscopy in the vapour phase has shown metaboric acid cyclic trimer in equilibrium with monomeric orthoboric acid and water. An approximately equal amount of boron (1:3 mole ratio) is present as $(HBO_2)_3$ and as H_3BO_3, at 350 °C and a few atmospheres total (water and boric acid) pressure; a condensed phase of widely variable composition is also present. Proportionately very much less trimer is present at the lowest temperatures (just over 100 °C for IR work).

The use of copious quantities of boric acid in the emergency core-cooling system of nuclear reactors has prompted interest in the vapour-phase species of wet, oxidised boron. The volatility of boric acid at ambient temperatures has long been remarked, but we need to increase our understanding of the equilibria involving aqueous and vapour-phase boron-containing molecules, particularly in competition with even minimally acidic species such as carbon dioxide.*

Ogden and Young[1] have demonstrated the existence of monomeric orthoboric acid, H_3BO_3 or $B(OH)_3$, in the vapour phase at modest temperatures, and shown that the structure in a nitrogen matrix is spectroscopically consistent with the expected C_{3h} point group. Some incompletely reported vapour-phase infrared work also appears in the literature.[2]

Experimental

Infrared spectroscopy (4000–500 cm^{-1}) and IR data processing were carried out on a Perkin-Elmer 1600 series FT instrument, using cells with silicon windows fused into borosilicate glass. Extended averaging gave spectra of sufficient quality to enable the subtraction of the background due to the silicon windows and the equilibrium concentrations of water, and to separate the spectra of the two forms of boric acid appearing with different relative concentrations at different temperatures. A flat baseline could not be expected under these conditions, if only because the rotational envelopes of vapour species change with temperature; nevertheless the results are impressive.

Intra-cavity Raman spectroscopy was used to enhance the signal from the poorly scattering boric acid species in the vapour phase. A Coherent Radiation 'Innova 90' argon-ion laser was used with a folded cavity, formed by replacing the front mirror with a pair of concave mirrors slightly off axis. This arrangement formed a secondary beam waist between the external mirrors, thus avoiding the loss associated with a focusing lens. Quartz Brewster-angle cells were constructed locally. The Raman signal was focused onto the modified entrance slits of a Cary 81 double monochromator, and detected using a conventional photomultiplier tube and ratemeter.

Temperatures of up to 350 °C were used, with differential heating to keep windows clear of condensed phases.

Results and Discussion

Figs. 1 and 2 show representative IR and Raman spectra for vapour-phase boric acid. The composition of the vapour phase is not much affected by initial sample composition in the range H_3BO_3 to HBO_2, although H_3BO_3 generally gives the best vaporisation ratio; it is not possible, at modest temperatures, simultaneously to volatilise all the boron in a given sample and volume, without adding water to the system and creating a spectroscopically unacceptable concentration of water vapour. Under loading also leads to a water dominated vapour. Consideration of the vapour-phase equilibrium (1) thus gives

$$3\,H_3BO_3 \rightleftharpoons (HBO_2)_3 + 3H_2O \qquad (1)$$

only limited insight, the ratio of boron-containing species to water being decided by vapour pressures over a condensed phase of variable composition. Clearly there is a complex series of interacting condensed and vapour-phase equilibria in the B–O–H system, with the condensed phase accommodating the bulk of the changes in overall composition in the spectroscopically accessible region.

It is not clear whether some degree of humidity is required to mediate the slow (days/weeks) evaporation of boric acid left in an open vessel. The material may be transported about a *closed* evacuated tube by means of a modest temperature differential, but this should probably be regarded as a chemical vapour transport process in which free water from the condensed phase is recycled, buffering the vapour-phase equilibrium.

The IR and Raman spectra (Table 1) of vapour samples held at approximately 150 °C show peaks attributed to $B(OH)_3$. Small or moderate shifts from the matrix frequencies (expected for nitrogen matrices[3]) and a clearly similar spectral pattern confirm the identity of the species responsible for the IR absorption. Similarly, the observed Raman bands correlate well with expectations based[1] on the IR spectra of unsymmetrical isotopomers and on the Raman-active skeletal vibrations of solid H_3BO_3. The absence of a boron isotope shift for the totally symmetric modes confirms that the boron lies in a special position. Since this molecule exists in the vapour phase only in equilibrium with water at these temperatures, part of the Raman

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* Boron is not a measurable constituent of most fresh waters, despite the use of large quantities overall of perborate bleach in detergents, but sea-water is often quoted at 26 ppm. Since the behaviour of the ocean is a major unknown in computer models of atmospheric chemistry, this comment may be pertinent *e.g.* to the 'greenhouse' effect. At pH 8.2 most of the non-biological boron in sea-water might be expected to speciate as undissociated H_3BO_3, but metal and polysaccharide interactions complicate this simple picture.

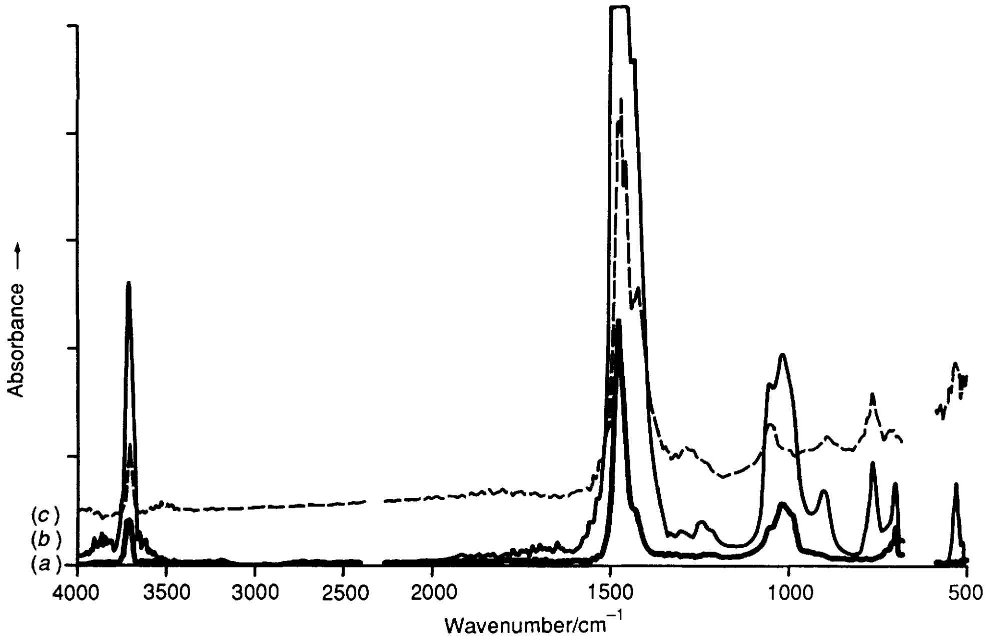

Fig. 1 Infrared absorbance spectra for ^{10}B boric acid: (*a*) at 150 °C, (*b*) at 250 °C and (*c*) difference spectrum, *ca.* (*b*) -4(*a*), to show high-temperature species in isolation. All spectra have been processed to remove D_2O and Si (cell windows), but note that Si obscures a small region of the spectrum in the vicinity of 600 cm^{-1}

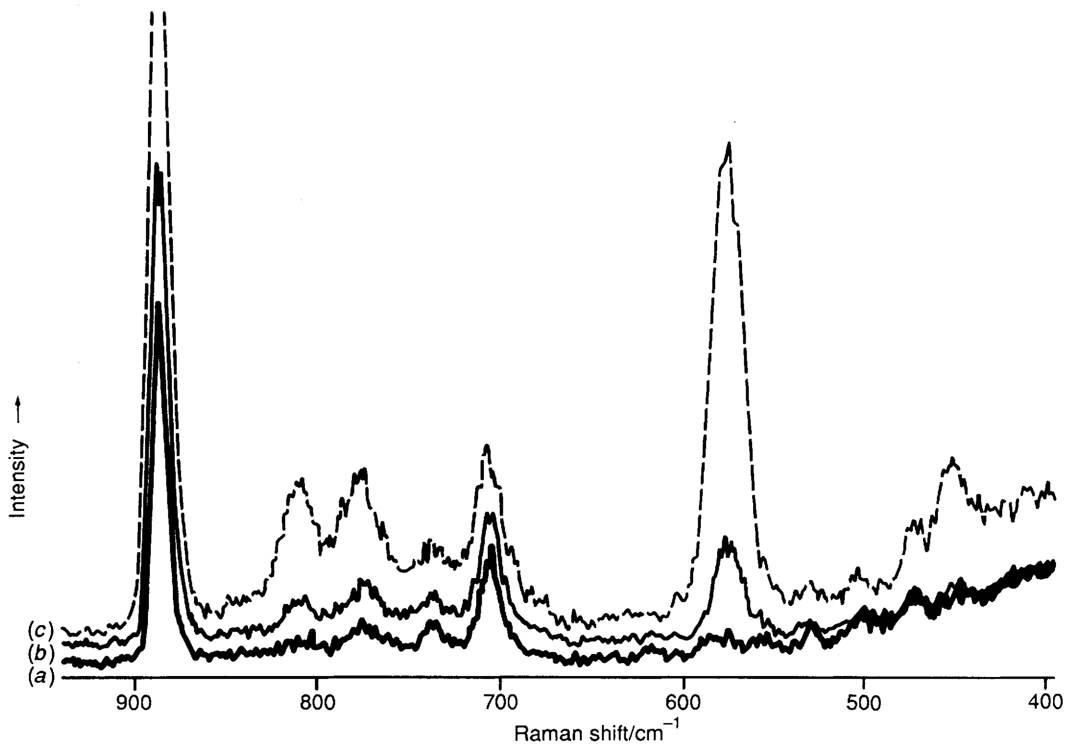

Fig. 2 Intracavity Raman spectra of vapour-phase deuteriated boric acid at (*a*) 150, (*b*) 200 and (*c*) 300 °C (approximately). Boron of natural isotopic composition. All bands are polarised

spectrum is obscured, particularly for weak peaks (by the pure rotational bands of water below 500 cm^{-1}, and to a lesser extent by the deformational mode, extending from 1200 to 2000 cm^{-1}). It is nevertheless surprising that, apart from water bands, only polarised bands are observed at any temperature, and for any set of isotopomers.

The symmetric BO stretch shifts to *higher* frequencies on deuteriation, confirming previous measurements[4] on the IR spectra of unsymmetrical isotopomers, while the intensity and polarisation of the BOD symmetric deformation at 706 cm^{-1} in the Raman spectrum supports the presumed source of this shift, and indicates that the point symmetry is no higher than C_{3h}. The corresponding mode in the proton isotopomers (occurring at *ca.* 1020 cm^{-1}) is much less intense and has a broad envelope, with apparently a double maximum. The separation of these maxima (some 40 cm^{-1} depending on temperature) precludes formulation as normal rotational O and S branches, and it is probable that librational motion of the protons is responsible. The barrier to proton rotation is probably low enough that a full treatment of these putative librational levels would require the use of permutation symmetry under a double group isomorphous with D_{3h}.

As the temperature is raised, bands due to a second more complex species are detected, with a main Raman band at 593

Table 1 Observed and calculated wavenumbers (cm^{-1}) for some isotopomers of molecular H_3BO_3. The force field matches the vapour-phase frequencies (this work) of the ^{11}B isotopomers, supplemented by matrix data [1] below 700 cm^{-1} (nitrogen matrix). The three a′ modes were observed in the Raman effect; remainder infrared data

$H_3{}^{11}BO_3$		$H_3{}^{10}BO_3$			$D_3{}^{11}BO_3$		$D_3{}^{10}BO_3$			
Vapour	Matrix	Vapour	Calc.	Matrix	Vapour	Matrix	Vapour	Calc.	Matrix	
In Plane										
3705		3705	3705					2722		a′ OH str
866s		866s	866		887s			887		a′ BO str
1020w(br)		1020w(br)	1020		706mw			706		a′ BOH def
3706	3668.5	3706	3706	3668.5	2726	2704.6		2726.1	2704.6	e′ OH str
1429	1426.2	1476.6	1477.8	1478.0	1405	1403.2	1456	1457.7	1452.7	e′ BO str
1017	1009.9	1017	1020.8	1009.9	810	825.5		810.7	825.5	e′ BOH def
	448.9		449.8	450.5		404.7		405.5	405.2	e′ OBO def
Out of plane										
	675.0	700	701.6	700.9		673.7		700.8	699.5	a″ BO_3[a]
	513.8		513.8	513.8		376.0		376.1	376.0	a″ BOH[b]

[a] Out of plane. [b] Torsion.

Table 2 Observed and calculated wavenumbers (cm^{-1}), and approximate intensities in parentheses, for some isotopomers of $(HBO_2)_3$ in the vapour phase [*n* indicates boron of natural isotopic constitution (^{11}B:^{10}B = 4:1)]

$(H^{10}BO_2)_3$		$(H^{n}BO_2)_3$	$(H^{11}BO_2)_3$	$(H^{11}BO_2)_2\cdot H^{10}BO_2$	$(D^{n}BO_2)_3$	$(D^{11}BO_2)_3$	$(D^{11}BO_2)_2\cdot D^{10}BO_2$	
Obs.	Calc.	Obs.[a]	Calc.	Calc.	Obs.	Calc.	Calc.[b]	
Infrared								
3700m	3700 (57)		3700	3700	2730	2721	2721 (68)	e′ OH str
1466s	1466 (70)			1452	1429s	1396	1430 (100)	e′ ^{10}BO str
1417(sh)	1440[c] (18)		1416	1418	1368m		1398 (28)	e′ ^{11}BO str
	1414[c] (3)			1398				
1273mw	1273 (16)	1266m	1238	1244	1276m(br)	1218	1240 (28)	e′ BOH str
				1237			1224	
							1217	
1050m	1050 (50)	1050m	1045	1048		839	840 (25)	e′ BOH def
				1048				
893w	893 (13)		891	892	1085m(br)	920	920 (53)	e′ BO str
766m	766 (10)		745	748	730m	706	710 (67)	a″[d]
530ms	530 (100)		526	527		405	405 (100)	a″ OH[e]
Raman								
3705sp	3700 (100)	3705sp	3700	3700	2733sp	2721	2721 (100)	a′ OH str
(1040wp)[f]	936 (8)	(1040wp)[f]	929	931	776mp	726	726 (45)	a′ BOH def
		892wp		891				
		831wp						
		815mwp						
789mp	789 (31)	772mwp	788	788	810mp	814	814 (20)	a′ BO str
593sp	592 (22)	588sp	589	590	575sp	556	558 (54)	a′ HO–B–O def
480mp[g]	500 (30)	480mp[g]	497	498	452mp	446	447 (40)	a′ OBO def

[a] Survey spectrum only for IR, detail obscured by overlapping isotopomer bands. [b] Intensities for isotopomers combined in 64:48 ratio where appropriate. [c] Frequencies for $(H^{10}BO_2)_2\cdot H^{11}BO_2$ isotopomer, present in 30% abundance. [d] Out of plane. [e] Torsion. [f] Uncertain observation, not included in refinement. [g] Approximate position; partially obscured by water bands.

cm^{-1} ($^{1}H/^{10}B/^{16}O$), comparable in intensity at *ca.* 350 °C to that of H_3BO_3 at 866 cm^{-1}. This indicates that, to a first approximation, the boron is equally distributed between the two forms at this temperature (and pressure).

Metaboric acid, HBO_2, is known in several crystalline modifications, but the low-temperature molecular orthorhombic form 'III' is of most interest. The structure is based on oxygen-bridged $(HOBO)_3$ cyclic trimers, hydrogen bonded into sheets like crystalline orthoboric acid.[5] The vibrational spectra of crystalline metaboric acid (III) have been discussed extensively.[6]

The identification of small amounts of a parent ion $[H_3B_3O_6]^+$ by mass spectroscopy[1] implies that metaboric acid trimer is the most likely candidate for the second spectroscopically observed species in the vapour. This supposition is reinforced by the Raman spectrum; the main polarised Raman band at 575–593 cm^{-1} (depending on the isotopomer) and a second totally symmetric vibration or vibrations in the range 750–820 cm^{-1} very closely match those found for the solid.[6] The magnitudes of the isotope shifts, and the spectral changes accompanying isotopic substitution, follow a similar pattern in vapour and solid. These shifts and changes

Table 3 Infrared and Raman observations (cm^{-1}) of totally symmetric modes (550–1300) of crystalline metaboric acid (III) [*n* indicates boron of natural isotopic constitution (^{11}B:^{10}B = 4:1)]

$(H^nBO_2)_3$	$(H^{10}BO_2)_3$	$(D^nBO_2)_3$
1239[a] IR	1267[a] IR	1226[a] IR
819[a] Raman		805[a] IR
812[b] Raman		
595[a] IR	600[a] IR	577[a] IR
598[a] Raman		
600[b] Raman	602[b] Raman	

[a] Ref. 6. [b] This work.

Table 4 Principal force constants (mdyn Å^{-1} or mdyn Å rad^{-2}; dyn = 10^{-5} N) for boric and formic acids. In the case of formic acid the most closely related terms are listed by entries in the *F* matrix[3]

	H_3BO_3[a]	HCO_2H[b]	$(HBO_2)_3$[a]
f(BO)	5.596	$F_{4,4}$ 6.004	6.067
f(BO_b)[c]			4.492, 4.378
f(OH)	7.602	$F_{1,1}$ 7.188	7.579
δ(OBO)	1.370	($F_{6,6}$) 1.297	1.539, 1.799
δ(BOH)	0.522	$F_{5,5}$ 0.696	0.493
π(BO_3)	0.492	($F_{8,8}$) 0.470	0.402
τ(HOBO)	0.119	$F_{9,9}$ 0.168	0.164

[a] This work. [b] Ref. 3. [c] Bridging oxygen.

are not wholly reproduced by the calculations, but it appears that the potential constants appertaining to the two non-equivalent bonds in the ring are substantially different, despite the similarity in bond lengths[5] within the crystal. Observed frequencies for this molecule are presented in Table 2. Data on some of the totally symmetric modes of crystalline metaboric acid (III) are given in Table 3.

Vibrational analysis using a new symmetrising preprocessor, which will be reported in detail elsewhere, was used to help confirm the identity and structure of the observed species. The principal force constants are summarised and compared with those of formic acid in Table 4. Phenomenological adjustments (not shown) were made to deuteron/proton labelled terms to allow for anharmonicity.

Conclusion

Vapour-phase infrared studies of boric acid at 150 °C have been greatly extended using modern instrumentation, and a second species detected at higher temperatures (above 200 °C). Intracavity Raman spectroscopy has allowed confirmation of the postulated C_{3h} structure for vapour-phase H_3BO_3, and the conclusion that the second species is oxygen-bridged metaboric acid trimer $(HBO_2)_3$ or $(HOBO)_3$, also thought to have C_{3h} point symmetry.

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