

**A Raman Spectroscopic and Ab Initio Investigation of Aqueous  
Boron Speciation under Alkaline Hydrothermal Conditions:  
Evidence for the Structure and Thermodynamic Stability of the  
Diborate Ion**

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**SUPPLEMENTARY INFORMATION**

## Section S1: Typical Experimental Raman Spectra, Computational Gas Phase Results and Charge Balance Results

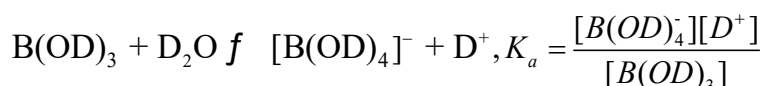
Experimental Raman Spectra corresponding to Figure 2 (Plots showing the experimental polarized Raman spectra and the resulting isotropic and the solvent corrected Raman spectra shown in Figure S1a to S2).

Calculated Raman frequencies for different species in gas phase are tabulated in Table S1a and S1b. Boron concentrations and the charge balance corresponding to the solution composition calculated based on the integrated peak intensity based on Model 2 is given in Table S2.

## Section S2: Heavy Water Sodium Borate Experiments

Solvent subtracted reduced isotropic Raman spectra were recorded at 250 °C and 20 MPa from three solutions (1 molal NaB(OD)<sub>4</sub>, 1 molal NaB(OD)<sub>4</sub> + 1 molal excess NaOD and 1 molal NaB(OD)<sub>4</sub> + 2 molal excess NaOD). We were not able to observe any peaks other than the B(OD)<sub>4</sub><sup>-</sup> symmetric stretching band (~705 cm<sup>-1</sup>) and the B(OD)<sub>3</sub> symmetric stretch which is split by Fermi resonance (~815 cm<sup>-1</sup> and 905 cm<sup>-1</sup>). Even with 2 molal excess of NaOD, no other peaks were observed, and the boric acid peaks persisted.

The persistence of B(OD)<sub>3</sub> in borates solutions even with 2 molal excess NaOD reflects differences in the speciation of borate in H<sub>2</sub>O and D<sub>2</sub>O due to deuterium isotope effects. First, the deuterium isotope effect has been shown to cause the ionization constant of boric acid to be lower in heavy water (Ref 1).



Hence at a given sodium borate molality under the same conditions, there is always a higher concentration of B(OD)<sub>3</sub> relative to B(OD)<sub>4</sub><sup>-</sup> in D<sub>2</sub>O than that of B(OH)<sub>3</sub> relative to B(OH)<sub>4</sub><sup>-</sup> in H<sub>2</sub>O. As a result, a larger excess of NaOD is needed to completely eliminate the B(OD)<sub>3</sub> bands in heavy water when compared to light water systems. This undoubtedly explains why the boric acid peaks persisted even in a 2 molal excess NaOD solution at 250 °C, which was the highest NaOD concentration we could use without damaging the sapphire windows of the titanium-sapphire flow cell.

In addition, the lower relative concentrations of B(OD)<sub>4</sub><sup>-</sup> in the D<sub>2</sub>O undoubtedly suppress the formation of the two diborate species, both because there is a lower molality of borate reactant, and because of the deuterium isotope effect on the diborate formation constants which is unknown.

Finally, the interpretation of the heavy water spectra is complicated by the Fermi resonance which splits the symmetric stretching vibrational band of B(OD)<sub>3</sub>. The Gaussian computational

calculations used here cannot predict the Fermi resonance effect. This complicates the comparison of computationally predicted and experimentally recorded spectra in D<sub>2</sub>O. In addition, the Fermi resonance of the B(OD)<sub>3</sub> symmetric stretch is associated with an overtone mode. As a result, its' scattering coefficient can no longer be assumed to be independent of temperature for speciation calculations based on mass balance.

**Table S1a:** Ab initio Calculated Raman Frequencies ( $\text{cm}^{-1}$ ) and Raman Activity of Perchlorate, Postulated Diborate Species, and Metaborate Ion, in the Gas Phase.

Species	Basis set	HF		B3LYP		MP2		
		$\nu \text{ cm}^{-1}$	Raman activity	$\nu \text{ cm}^{-1}$	Raman activity	$\nu \text{ cm}^{-1}$	Raman activity	
$\text{ClO}_4^-$	6-31G*	975	20.9	852	27.8	971	25.2	
	6-31+G*	958	32	819	50.4	944	48.6	
	6-311+G*	948	30.5	805	48.9	942	47.8	
$[\text{B}_2\text{O}(\text{OH})_5]^-$	6-31G*	760	3.1	682	1.09	691	1.5	
		993	0.8	709	4.44	719	4.57	
				931	2.36	940	1.93	
	6-31+G*	755	3.93	576	1.26	576	1.25	
		968	1.06	684	1.48	689	2.7	
		983	2.03	706	5	713	5.47	
	6-311+G*			919	5.1	928	4.96	
			740	1.13	576	1.39	582	1.4
			754	3.44	686	1.63	693	1.5
			965	1.03	704	4.29	716	6.1
			979	1.99	916	5.28	929	5.09
							1277	11.7
$[\text{B}_2\text{O}(\text{OH})_6]^{2-}$	6-31G*	730	5.38	681	6.55	686	5.69	
						695	2.27	
	6-31+G*	728	6.22	566	1.76	568	1.9	
				679	4.24	685	7.81	
				860	1.39			
				917	1.96			
				921	1.27			
6-311+G*	727	6.3	564	1.94	570	1.99		

[B <sub>2</sub> O(OH) <sub>6</sub> ] <sup>2-</sup>				679	4.56	693	7.9
(Continued)				734	1.23	777	1.26
				850	1.31		
				916	2.96		
		741	4.14	688	4.79	622	1.4
		919	1.6	781	1.65	654	1.17
	6-31G*			861	2.59	699	3.69
						785	1.91
						880	1.84
		736	4.55	583	1.5	600	1.97
		913	3.18	684	5.93	656	1.63
	6-31+G*			851	3.81	699	5.7
[B <sub>2</sub> (OH) <sub>7</sub> ] <sup>-</sup>						742	1.09
						865	3.7
		736	4.48	683	5.55	598	1.86
		908	3.06	727	1.02	662	1.42
	6-311+G*			847	3.54	701	1.22
						706	5.04
						869	3.62
		851	4.21	790	4.91	796	6.47
	6-31G*	1195	1.71	1106	2.23	1117	3.23
				1604	2.47	1616	1.81
		852	4.63	791	3.57	793	7.37
	6-31+G*	1171	1.16	1531	46	1087	1.83
						1521	28.7
		847	4.11	787	2.84	794	6.53
[BO(OH) <sub>2</sub> ] <sup>-</sup>	6-311+G*	1182	1.27	1526	47.6	1094	1.99
(Continued)						1525	30.4

		588	2.32	546	2.36	550	2.43
	6-31G*	652	2.65	591	4.69	597	4.99
		780	1.79	718	2.44	719	2.05
						722	2.9
		581	2.18	538	3.32	540	3.24
	6-31+G*	645	4.67	583	4.03	589	6.22
		778	1.42	632	4.15	670	2.14
						719	1.94
		576	2.44	534	3.69	541	3.66
	6-311+G*	644	4.35	581	4.32	592	6.34
		775	1.3	634	3.79	667	2.09
						722	2.14

**Table S1b:** Ab initio Calculated Raman Frequencies ( $\text{cm}^{-1}$ ) Calculated using Different Levels of Theory for Neutral Diborate Species in the Gas Phase.

Aqueous Species	Symmetry	Basis Set	$\nu / \text{cm}^{-1}$			Experimental
			Calculated			
			HF	B3LYP	MP2	
$[\text{B}_2(\text{OH})_6]^0$	$C_{2v}$ #3	6-31G*	618	577	578	865
			769	711	725	
		6-31+G*	614	571	571	
			765	705	718	
		6-311+G*	613	571	581	
			764	702	730	
$[\text{B}_2\text{O}(\text{OH})_4]^0$	$C_{s/1}$ #6	6-31G*	823	779	779	865
		6-31+G*	819	771	771	
		6-311+G*	821	773	780	

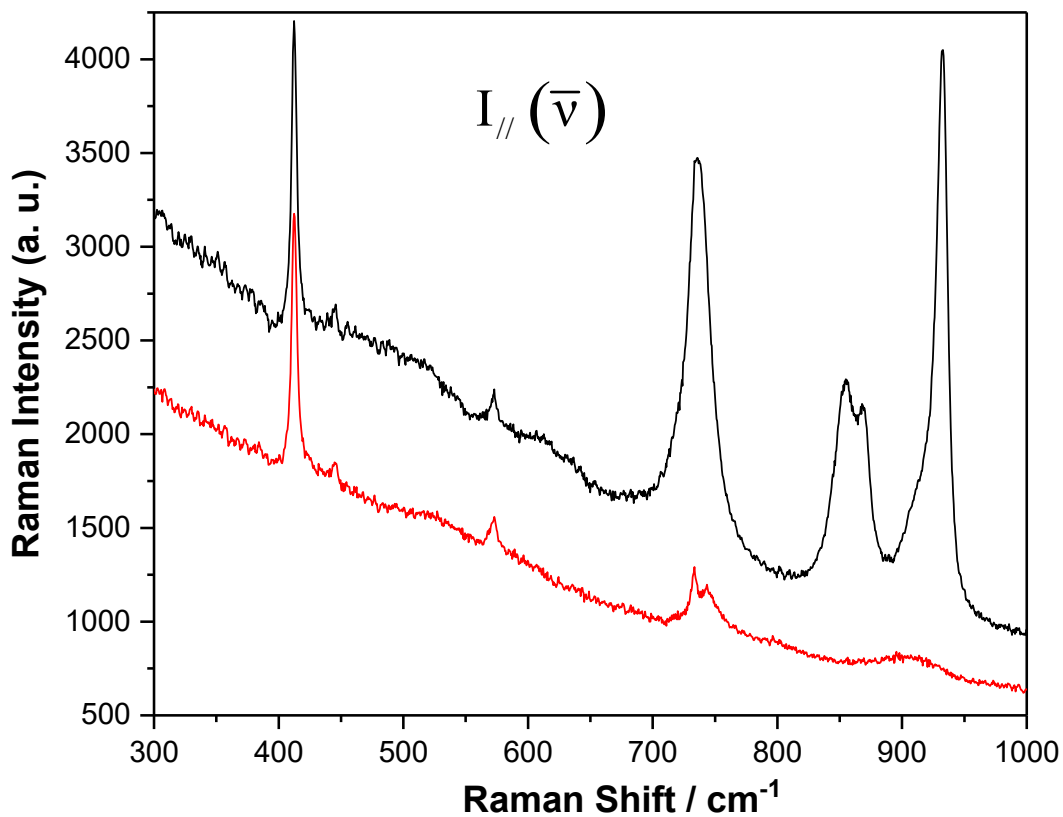
**Table S2:** Charge Balance for Solutions 1, 2, 3, 4, 5 and 6 using Model 2, Assuming Boron Mass Balance

$t / ^\circ\text{C}$	$m^{\text{STB}}(\text{OH})_3$	$\Sigma m_{\text{cations}} - \Sigma m_{\text{anions}}$
	/ $\text{mol}\cdot\text{kg}^{-1}$	
Solution 1 (Run 1), $R_{\text{Buffer}} = 0.980$ , $m_{\text{B}} = 1.0188 \text{ mol}\cdot\text{kg}^{-1}$		
150	1.0188	0.14
200	1.0188	0.19
250	1.0188	0.31
275	1.0188	0.38
300	1.0188	0.35
Solution 1 (Run 2), $R_{\text{Buffer}} = 0.980$ , $m_{\text{B}} = 1.0188 \text{ mol}\cdot\text{kg}^{-1}$		
150	1.0188	0.15
200	1.0188	0.20
250	1.0188	0.32
Solution 2, $R_{\text{Buffer}} = 0.984$ , $m_{\text{B}} = 1.0391 \text{ mol}\cdot\text{kg}^{-1}$		
150	1.0391	0.14
200	1.0391	0.24
250	1.0391	0.34
Solution 3, $R_{\text{Buffer}} = 1.716$ , $m_{\text{B}} = 0.96404 \text{ mol}\cdot\text{kg}^{-1}$		
150	0.96404	0.00
200	0.96404	0.00
250	0.96404	0.00
Solution 4, $R_{\text{Buffer}} = 3.542$ , $m_{\text{B}} = 0.90062 \text{ mol}\cdot\text{kg}^{-1}$		
150	0.90062	0.00
200	0.90062	0.00
250	0.90062	0.00

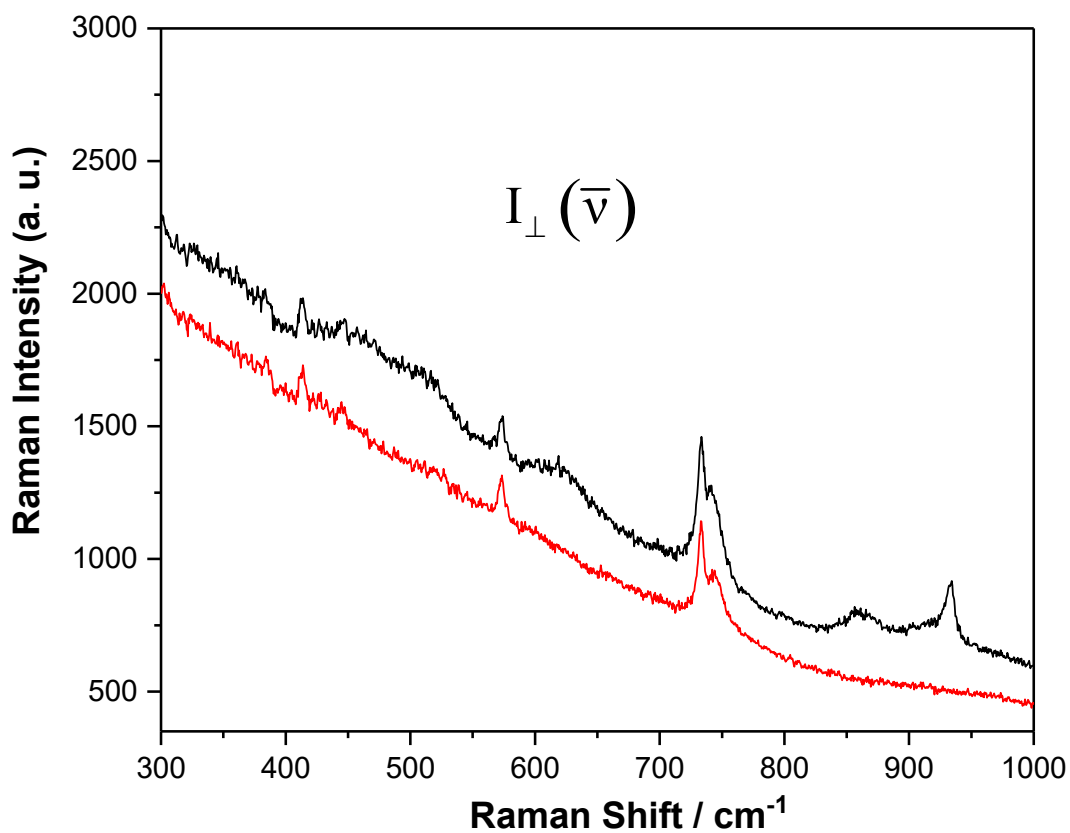


Table S2 (Continued)

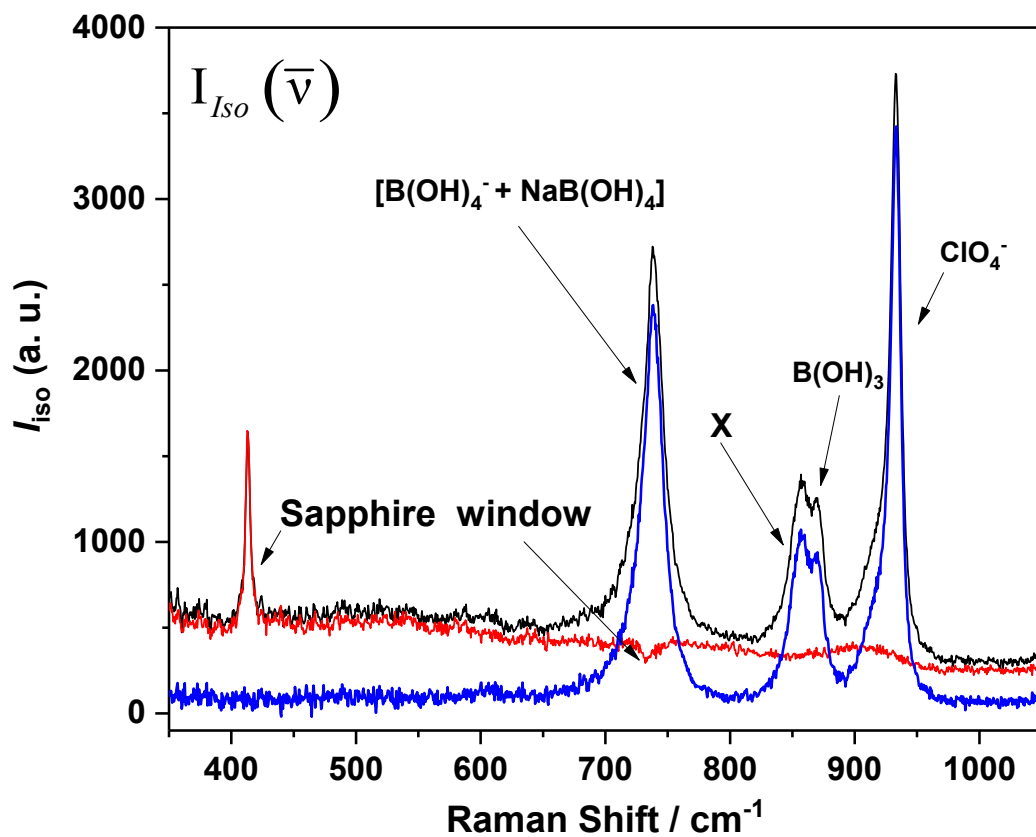
t / °C	$m^{\text{STB}}(\text{OH})_3$	$\Sigma m_{\text{cations}} - \Sigma m_{\text{anions}}$
	/ mol·kg <sup>-1</sup>	
Solution 5, $R_{\text{Buffer}} = 0.980$ , $m_{\text{B}} = 0.32012 \text{ mol}\cdot\text{kg}^{-1}$		
250	0.32011835	0.11
Solution 5, $R_{\text{Buffer}} = 0.980$ , $m_{\text{B}} = 0.32012 \text{ mol}\cdot\text{kg}^{-1} + 0.301 \text{ mol}\cdot\text{kg}^{-1} \text{ NaCl}$		
250	0.32011835	0.11
Solution 6, $R_{\text{Buffer}} = 1.000$ , $m_{\text{B}} = 0.30980 \text{ mol}\cdot\text{kg}^{-1}$		
250	0.3098	0.13
Solution 6, $R_{\text{Buffer}} = 1.000$ , $m_{\text{B}} = 0.30980 \text{ mol}\cdot\text{kg}^{-1} + 0.302 \text{ mol}\cdot\text{kg}^{-1} \text{ LiCl}$		
250	0.3098	0.13



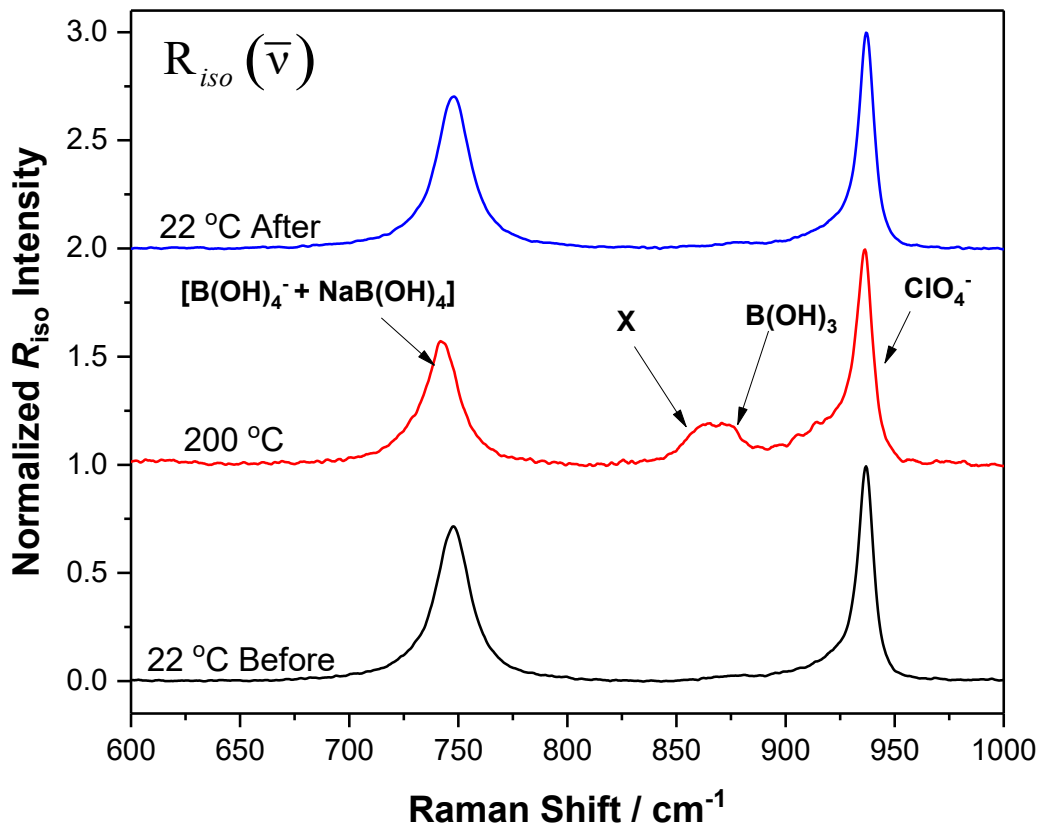
**Figure S1-a:** Raman spectra in vertical polarization,  $I_{//}(\bar{\nu})$  for Solution 1 ( $R_{\text{Buffer}} = 0.980$ ,  $m_{\text{Btotal}} = 1.019 \text{ mol}\cdot\text{kg}^{-1}$ , with  $0.0902 \text{ mol}\cdot\text{kg}^{-1}$  sodium perchlorate) (black) and water (red), at  $250 \text{ }^\circ\text{C}$ , acquired in the sapphire flow cell



**Figure S1-b:** Raman spectra in horizontal polarization,  $I_{\perp}(\bar{\nu})$ , for Solution 1 ( $R_{\text{Buffer}} = 0.980$ ,  $m_{\text{Btotal}} = 1.019 \text{ mol}\cdot\text{kg}^{-1}$  with  $0.0902 \text{ mol}\cdot\text{kg}^{-1}$  sodium perchlorate) (black) and water (red) at 250 °C acquired in the sapphire flow cell.



**Figure S1-c:** Isotropic Raman spectra,  $I_{iso}(\bar{\nu})$ , of Solution 1 ( $R_{\text{Buffer}} = 0.980$ ,  $m_{\text{Btotal}} = 1.019$   $\text{mol}\cdot\text{kg}^{-1}$  with  $0.0902$   $\text{mol}\cdot\text{kg}^{-1}$  sodium perchlorate) (black) and water (red) at  $250$   $^{\circ}\text{C}$  acquired in the sapphire flow cell. The solvent subtracted isotropic spectrum is shown in blue.



**Figure S2:** Normalized reduced isotropic Raman spectra,  $R_{iso}(\bar{\nu})$ , of an aqueous solution ( $R_{\text{Buffer}} = 0.980$ ,  $m_{\text{Btotal}} = 1.019 \text{ mol}\cdot\text{kg}^{-1}$ , with  $0.0902 \text{ mol}\cdot\text{kg}^{-1}$  sodium perchlorate) in stopped flow mode at (a) 22 °C before heating, (b) after heating to 200 °C, and (c) cooled back to 22 °C in stopped flow mode.

