ARTICLE

Speciation of borate in aqueous solution studied experimentally by potentiometry and Raman spectroscopy and computationally by DFT calculation

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Supporting Information

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The potentiometric titrations experimental conditions

In a typical titration, a solution (5.0 – 20.0 mL) containing the initial concentration of 0.01 - 0.7 M of boric acid and appropriate amount of 0.5 M $NaClO_4$ is titrated with 0.5 M NaOH. The titration cup was always kept in an argon atmosphere with small positive pressure to avoid the effect from the CO_2 in the air. The EMF data were gathered at intervals predetermined by the data collection criterion; for instance, the drift of EMF (Δ E) was less than 0.1 mV for 60 s. With starting solutions containing various concentrations of $B(OH)_3$ and $HClO_4$, several titrations were carried out (See Table S1.). Using the program *Hyperquad* 2014[1], the formation constants of borate ions were determined on a molar scale. The three standard deviations (3σ) calculated by the computer program characterize the degree of uncertainty.

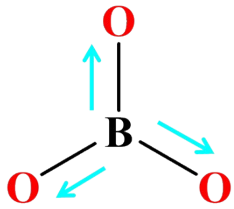
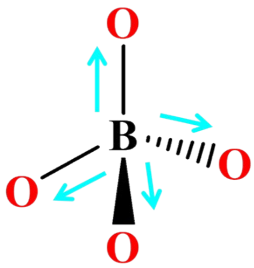
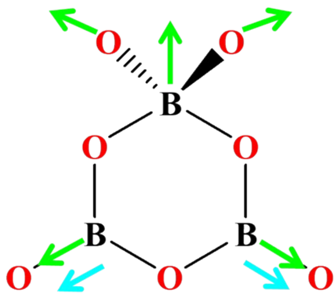
Table S1. The potentiometric titrations experimental conditions, 25 °C

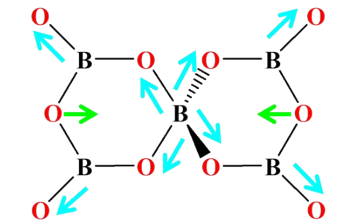
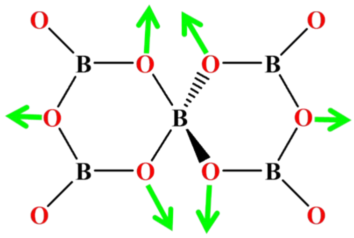
No.	V_0/mL	C^0_B/M	C^0_H/M	C_{tire}/M
1	20.0	0.00998	0.00514	0.504
2	20.0	0.0249	0.00514	0.504
3	10.0	0.0499	0.0103	0.504
4	10.0	0.0998	0.0103	0.504
5	5.0	0.249	0.0205	0.504
6	5.2	0.480	0.0198	0.504
7	5.2	0.661	0.0198	0.504

Where I=0.5 M $NaClO_4$. V_0 denotes initial cup solution in mL. $C_B{}^0$ denotes initial cup Boron concentration in M. $C_H{}^0$ denotes initial cup Hydrogen ions concentration in M. C_{tire} denotes the titrants concentration of NaOH in M.

The calculated vibrational frequencies and the vibrational modes

Table S2 The calculated vibrational frequencies, the vibrational modes and Raman activity coefficient of borate ions. Where ν_1, ν_2, ν_3, ν_4 are the characteristic vibrational modes related to the borate ions (ν_{1a} and ν_{1b} denotes two different symmetric stretching vibration of $B_4O_5(OH)_4{}^{2-}$), while the ν_{as}, ν_b and ν_c denotes asymmetrical stretching, molecular bending, and molecular dangling, respectively. Where B3 and B4 denotes the plane triangle boron and tetrahedron boron. The blue arrow in the diagram of the vibrational modes is the B-O symmetric stretching vibration. The green arrow is the vibration of the boron or oxygen atom in the direction of the arrow.

species	Raman vibrational frequencies/cm^{-1} exp.	Raman vibrational frequencies/cm^{-1} cal.	Raman activity coefficient /(A^4/AMU)	The vibrational modes	Diagram of the vibrational modes
	-	536	3.40	ν_c(O-H)	-
	-	538	3.41	ν_c(O-H)	-
	-	665	0.00	ν_c(B)	-
$B(OH)_3$	874	877	7.47	ν_1	
	-	1037	3.67	ν_c(O-H)	-
	-	1038	3.62	ν_c(O-H)	-
	-	1044	0.16	ν_c(O-H)	-
	-	521	0.60	ν_b(O-B-O)	-
$B(OH)_4^-$	741	728	4.62	ν_1	
	-	866	3.64	ν_c(O-H)	-
	-	1018	0.03	ν_c(B)	-
	-	1026	1.06	ν_c(O-H)	-
	-	1070	10.09	ν_c(O-H)	-
	-	537	0.19	ν_c(O-H)	-
	-	537	6.08	ν_c(O-H)	-
	-	548	0.70	ν_c(O-H)	-
$B_3O_3(OH)_4^-$	610	593	5.34	ν_1	
	-	674	0.81	ν_c(B3)	-

	-	722	1.47	ν_b(O-B4-O)	-
	-	723	0.16	ν_c(B3)	-
	-	787	0.32	ν_c(B4)	-
	-	860	4.43	ν_{as}	-
	-	937	4.67	ν_c(B4)	-
	-	986	0.01	ν_{as}	-
	-	1040	0.59	ν_c(O-H)	-
	-	1095	0.16	ν_c(O-H)	-
	-	1098	4.13	ν_c(O-H)	-
	-	1189	4.84	ν_c(O-H)	-
	525	513	7.31	ν_1	
	-	533	0.00	ν_c(O-H)	-
	-	537	10.32	ν_c(O-H)	-
	-	540	0.03	ν_c(O-H)	-
	-	550	1.03	ν_c(O-H)	-
$B_5O_6(OH)_4^-$	-	668	0.00	ν_c(B3)	-
	-	671	0.93	ν_c(B3)	-
	-	718	0.11	ν_c(B3)	-
	-	723	0.53	ν_b(O-B-O)	-
	760	758	4.22	ν_2	
	-	789	2.21	ν_{as}	-

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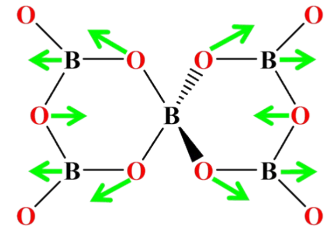
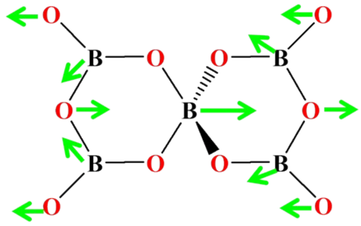
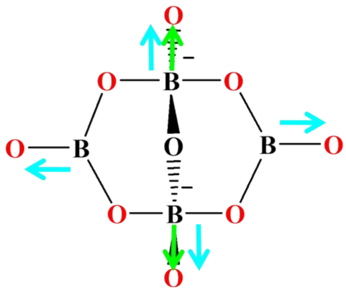
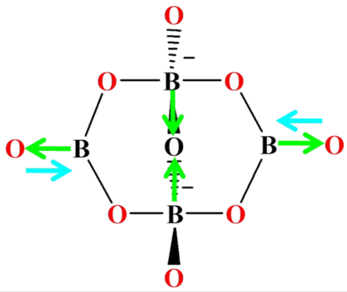
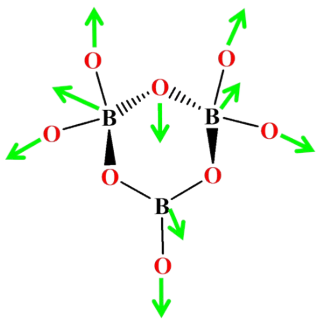
	915	891	8.40	ν_4	
	-	925	0.24	ν_c(B4)	-
	994	1005	1.22	ν_3	
	-	1032	0.00	ν_c(B4)	-
	-	1101	0.25	ν_c(O-H)	-
	-	1111	12.66	ν_c(O-H)	-
	-	1160	0.86	ν_c(B4)	-
	-	510	3.87	ν_c(O-H)	-
	-	516	4.88	ν_c(O-H)	-
	563	547	7.92	ν_{1a}	
	-	550	0.20	ν_c(B4)	-
$B_4O_5(OH)_4^{2-}$	-	564	0.38	ν_c(B4)	-
	-	666	0.03	ν_c(B3)	-
	-	702	0.46	ν_c(B3)	-
	-	714	1.46	ν_c(B3)	-
	-	755	2.66	ν_b(O-B3-O)	-
	-	758	0.65	ν_c(B4)	-
	-	820	0.84	ν_c(B4)	-
	-	836	2.14	ν_c(B4)	-
	-	889	2.42	ν_c(B4)	-
	-	907	0.71	ν_c(B4)	-

	938	937	3.91	ν_{1b}	
	-	1004	0.40	ν_c(B4)	-
	-	1080	0.56	ν_c(O-H)	-
	-	1090	3.89	ν_c(O-H)	-
	-	1123	2.49	ν_c(O-H)	-
	-	1138	0.46	ν_c(O-H)	-
	-	1147	1.21	ν_c(B4)	-
	-	502	2.55	ν_b(O-B4-O)	-
	-	510	3.80	ν_c(O-H)	-
	-	537	2.66	ν_c(O-H)	-
	-	557	0.49	ν_c(B4)	-
$B_3O_3(OH)_5^{2-}$	612	589	5.34	ν_1	
	-	678	2.07	ν_c(O-H)	-
	-	698	1.21	ν_c(B3)	-
	-	721	1.37	ν_c(B3)	-
	-	732	2.24	ν_{as}	-
	-	758	1.86	ν_c(B4)	-
	-	818	3.77	ν_c(B4)	-
	-	882	1.82	ν_c(O-H)	-
	-	929	0.84	ν_1(B3-O)	-
	-	967	2.50	ν_c(B4)	-
	-	1032	2.36	ν_c(O-H)	-

-	1071	2.84	ν_c(O-H)	-
-	1093	3.22	ν_c(O-H)	-
-	1147	1.33	ν_c(O-H)	-
-	1185	1.55	ν_c(O-H)	-

Notes and references

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