

Ab Initio Calculation of Isotopic Fractionation in $\text{B(OH)}_3(\text{aq})$ and $\text{BOH}_4^-(\text{aq})$

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Computational methods are becoming increasingly central to understanding the fractionation of stable isotopes in geochemical systems. A prominent application is the fractionation of ^{11}B and ^{10}B between boric acid B(OH)_3 and borate ion B(OH)_4^- in seawater. Boron isotopes are key indicators of the pH and CO_2 content of oceans in the geologic past.¹ In seawater solutions at 25 °C and $[\text{B}]_{\text{total}} = 4.5$ ppm, B(OH)_3 and B(OH)_4^- exist in equal concentrations at pH ~ 8.8 . Since the $^{11}\text{B}/^{10}\text{B}$ ratio differs between B(OH)_3 and B(OH)_4^- , the isotopic composition of each species is a function of pH over the range where both species coexist in appreciable concentrations. If it is assumed that only B(OH)_4^- is incorporated into minerals, then the pH of seawater in equilibrium with the minerals at the time of deposition can be obtained from the $^{11}\text{B}/^{10}\text{B}$ ratio in the mineral phases. The calculation of pH requires knowledge of the isotope fractionation factor α_{34} . In the harmonic limit, $\alpha_{34} = \beta_{\text{B(OH)}_3}/\beta_{\text{B(OH)}_4^-}$ (β_3/β_4) where β is the reduced partition function ratio:

$$\beta = \left(\frac{Q_h}{Q_l}\right) = \prod_i \frac{u_{hi}}{u_{li}} \frac{e^{-u_{hi}/2}}{1 - e^{-u_{hi}}} \frac{1 - e^{-u_{li}}}{e^{-u_{li}/2}} \quad (1)$$

where $u_{(h,l)i} = \hbar c 2\pi\omega_{(h,l)i}/kT$, h and l refer to the heavy isotope and light isotopes, respectively, and the product runs over all frequencies.²

Paleo-ocean pH estimates have until recently relied on semiempirical estimates of α_{34} ,³ in part because of the difficulty of measurements at $[\text{B}]_{\text{total}} = 4.5$ ppm. Several problems have lately been identified in the original work, and improvements have been sought through electronic structure calculations.^{4,5} Recent measurements of the isotope-induced shift in the $\text{p}K_a$ of B(OH)_3 have reported α_{34} values close to 1.028, within 1 per mil of the Hartree–Fock calculations.^{5c–e} This level of agreement is surprising as the Hartree–Fock calculations involve extensive frequency scaling. The approach combines the effects of solvation, inadequacies in the wave function, and anharmonicity into a single factor, making systematic improvement difficult.

Here, we take a new approach to estimating α_{34} for aqueous species, using ab initio molecular dynamics (AIMD).⁶ The AIMD approach is useful because the fractionating species are embedded in real solvent at configurations typical of 300 K. Moreover, the vibrational frequencies obtained through AIMD are not restricted to be harmonic. This study is the first time AIMD has been applied to the calculation of isotopic fractionation. First, we establish whether the AIMD calculations are capable of reproducing the observed frequencies for $\text{B(OH)}_4^-(\text{aq})$ and $\text{B(OH)}_3(\text{aq})$. Second, we explore the utility of eq 1 in reproducing α_{34} . Work on gas-phase systems, for example, indicates that it is better to use harmonic frequencies in eq 1 rather than anharmonic frequencies

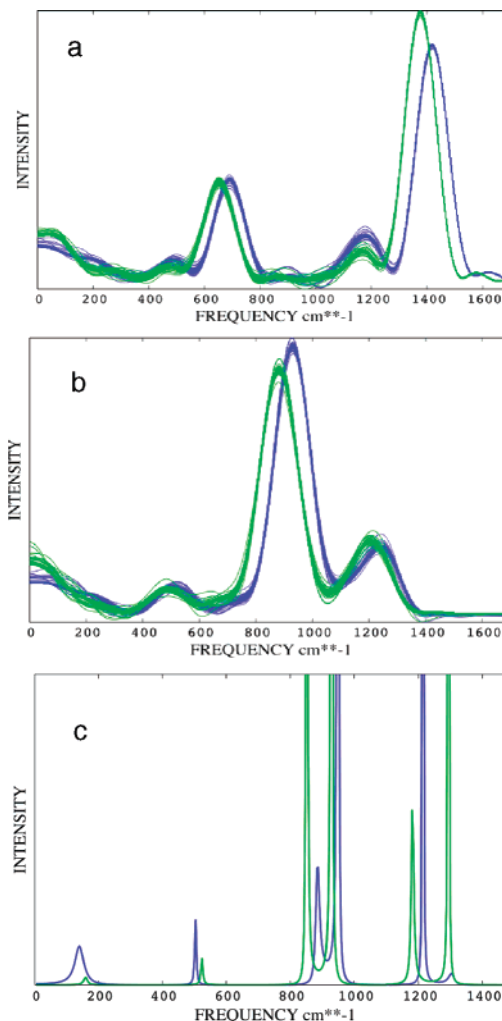


Figure 1. Vibrational density of states for the boron atom in (a) $\text{B(OH)}_3(\text{aq})$, (b) $\text{B(OH)}_4^-(\text{aq})$, and (c) tepleite ($\text{Na}_2\text{ClB(OH)}_4$). Green: ^{11}B ; Blue: ^{10}B . Multiple lines represent spectra calculated from replicas of the VAF within the standard error.

derived from experiment.⁷ It is not clear whether this would remain true in aqueous systems.

B(OH)_4^- and B(OH)_3 are inserted in a small periodic cell of water molecules, and forces are calculated using density functional theory. The forces are used to perform a molecular dynamics simulation. The classical vibrational density of states responsible for boron fractionation can then be obtained by Fourier transformation of the velocity autocorrelation function for the boron atom. All calculations were carried out with NWChem,⁸ employing a plane-wave basis (energy cutoff = 90 au) with Troullier–Martins pseudopotentials⁹ and the PBE96 exchange–correlation functional.¹⁰ We used Car–Parrinello dynamics with the fictitious mass set at 100 au. Electronic and nuclear degrees of freedom were attached

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Table 1. Boron Vibrational Frequencies Calculated for B(OH)₃(aq) and B(OH)₄⁻(aq) from AIMD and B(OH)₄⁻ in Teepleite^a

Boric Acid		Borate	
B(OH) ₃ (aq) C _{3h}	B(OH) ₄ ⁻ (aq) T _d	Na ₂ CIB(OH) ₄ D _{2d}	
		calcd	exptl ¹³
490 ± 6.0 (475 ± 7.6) 2	512 ± 8.4 (488 ± 10.1) 1		
691 ± 1.8 (656 ± 1.8) 1		888	880
[692,666] ^{12a}		(852)	(855)
1180 ± 4.4 (1170 ± 3.8) 2	931 ± 1.0 (882 ± 1.5) 3	948	950
[1150–1156] ^{12b,c}	[945–975] ^{12b,c}	(928)	(928)
1419 ± 0.4 (1377 ± 0.3) 2		1216	1186
[1412,1454] ^{12c}		(1180)	(1167)
	1243 ± 4.4 (1208 ± 4.8) 3	1304	1307
	[1150 (broad)] ^{12b}	(1292)	(1295)

^a The degeneracy of each mode is given in bold numbers associated with the indicated point symmetries. Modes for B(OH)₃(aq) are in the order: H–O–B–O torsion; out-of-plane bend, anharmonic combination band; antisymmetric B–OH stretch. Modes for B(OH)₄⁻(aq) are O–B–O–H torsion, antisymmetric (OH)–B–(OH) bend, and antisymmetric (OH)–B–(OH) stretch. Frequencies given as ¹⁰B (¹¹B) in cm⁻¹. Measured values given in [square brackets] except for teepleite,¹³ which is given in a separate column.

to separate Nose–Hoover thermostats having masses of 250 au.¹¹ In the aqueous systems, the boron species were inserted into a cubic box of 32 water molecules of dimension 18.803 au. The velocity autocorrelation function for boron, C_{VAF}, was computed for 0.5 ps averaged over 5 ps with samples spaced 10 fs apart. Resolution errors were estimated by Monte Carlo simulation involving generation of a series of synthetic replicas within the standard error associated with the C_{VAF}(t). The small mass was chosen to obtain converged vibrational frequencies on the isolated ions. Calculations were performed on Na₂CIB(OH)₄ (teepleite) using a similar protocol. The vibrational density of states for ¹¹B and ¹⁰B in each system is shown in Figure 1, and the peaks are listed in Table 1.

For B(OH)₃, there is little controversy; as shown in Table 1, the calculations are in reasonably good agreement with observed spectra.¹² There is a lack of consensus on the vibrational spectrum of B(OH)₄⁻. In T_d symmetry (i.e., averaging over the range of O–B–O–H torsions), there should be two triply degenerate B-fractionating modes involving (OH)–B–(OH) ν₁ bending and antisymmetric (OH)–B–(OH) ν₂ stretching motions. These were spuriously assigned in ref 3 at 533.5 (532.82) cm⁻¹ and 975.78 (937.67) cm⁻¹. While nearly all studies agree on the existence of a mode near 950 cm⁻¹, this mode must be the ν₁ bending mode. The measured infrared and Raman spectrum of teepleite¹³ and previous electronic structure calculations on B(OH)₄⁻⁴ show that ν₂ must have a higher frequency, between ~1150 and 1310 cm⁻¹. AIMD predicts that ν₂ = 1243 (1208) cm⁻¹ for B(OH)₄⁻(aq). This prediction can be verified through calculations on teepleite, which exhibits a well-resolved vibrational spectrum.¹³ In this phase, the B(OH)₄⁻ ion has D_{2d} symmetry; the triply degenerate ν₁ and ν₂ modes in T_d symmetry are each split into two contributions with double and single degeneracy. As shown in Figure 1c and Table 1, the AIMD calculations are very close in both position and isotopic shift to the observed modes for both ν₁ and ν₂. More recent measurements in solution show intensity in this region, although the peaks are broad and probably include interference from polyborate species.^{12b,c} The AIMD calculations indicate that the ν₂ frequency in solution should be intermediate between that of the isolated ion (e.g., 1214 cm⁻¹ at the MP2/aug-ccpvdz level) and the ν₂ frequency observed experimentally in the stronger Na⁺–borate environment in teepleite at 1307 cm⁻¹.

Peak positions and isotopic frequency shifts obtained from the AIMD simulations can be used to calculate reduced partition function ratios β_{3,4} and the overall fractionation factor α₃₄. Nearly all previous theoretical estimates have β₃ = 1.22 ± 0.03,^{3–5} close

to the value of 1.27 ± 0.07 derived from AIMD. The calculated value of β₄, 1.47 ± 0.08, differs markedly from previous estimates^{3–5} (1.17–1.23). In ref 3, the discrepancy is due to incorrect mode assignments. Previous quantum-chemical estimates^{4,5} account for neither the large solvent-induced blue shift of ν₂ nor the effective transformation of B(OH)₄⁻ to T_d symmetry in solution; for the gas-phase ion in the harmonic limit, our methods also predict a small value for β₄ = 1.19. Gas-phase calculations from MD simulations of the dynamics of the isolated B(OH)₄⁻ ion give β₄ = 1.16; the large β₄ is due to solvation.

The AIMD calculations give α₃₄ = 0.86, in disagreement with the measured value of 1.028. To explore this discrepancy, configurations were quenched from the AIMD trajectories subjected to normal-mode analysis. From these normal modes (294 for B(OH)₃ and 309 for BOH₄⁻; see Supporting Information), we calculate α₃₄ = 1.2313/1.1972 = 1.028, in agreement with the scaled Hartree–Fock calculations^{5c} and with experiment.^{5de}

Our calculations suggest that eq 1 requires harmonic frequencies. If experimental spectra are used to calculate fractionation factors, harmonic frequencies must be extracted before using eq 1. The AIMD method allows an important connection to be made between the measured anharmonic vibrational spectrum and the measured fractionation factor; because of the large number of normal modes in the solvated harmonic calculation, it is impossible to assess the extent of agreement between the calculated spectra and the measured spectra. Our calculations underscore the importance of further work on incorporating anharmonicity more rigorously in the calculation of isotopic fractionation factors.

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Supporting Information Available: Radial distribution functions and list of harmonic vibrational frequencies for quenched configurations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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