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## Stable boron isotope fractionation between dissolved $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$

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**Abstract**—The stable boron isotope ratio ( $^{11}\text{B}/^{10}\text{B}$ ) in marine carbonates is used as a paleo-pH recorder and is one of the most promising paleo-carbonate chemistry proxies. Understanding the thermodynamic basis of the proxy is of fundamental importance, including knowledge on the equilibrium fractionation factor between dissolved boric acid,  $\text{B}(\text{OH})_3$ , and borate ion,  $\text{B}(\text{OH})_4^-$  ( $\alpha_{(\text{B}(\text{OH})_3-\text{B}(\text{OH})_4^-)}$ , hereafter  $\alpha_{(\text{B}_3-\text{B}_4)}$ ). However, this factor has hitherto not been determined experimentally and a theoretically calculated value (Kakihana and Kotaka, 1977, hereafter KK77) has therefore been widely used. I examine the calculations underlying this value. Using the same spectroscopic data and methods as KK77, I calculate the same  $\alpha_{(\text{B}_3-\text{B}_4)} = 1.0193$  at 300 K. Unfortunately, it turns out that in general the result is sensitive to the experimentally determined vibrational frequencies and the theoretical methods used to calculate the molecular forces. Using analytical techniques and *ab initio* molecular orbital theory, the outcome for  $\alpha_{(\text{B}_3-\text{B}_4)}$  varies between  $\sim 1.020$  and  $\sim 1.050$  at 300 K. However, several arguments suggest that  $\alpha_{(\text{B}_3-\text{B}_4)} \geq 1.030$ . Measured isotopic shifts in various  $^{10}\text{B}$ -,  $^2\text{D}$ -, and  $^{18}\text{O}$ -labeled isotopomers do not provide a constraint on stable boron isotope fractionation. I conclude that in order to anchor the fundamentals of the boron pH proxy, experimental work is required. The critics of the boron pH proxy should note, however, that uncertainties in  $\alpha_{(\text{B}_3-\text{B}_4)}$  do not bias pH reconstructions provided that organism-specific calibrations are used. Copyright © 2005 Elsevier Ltd

### 1. INTRODUCTION

The goal of the current work is to establish a value for the equilibrium stable boron isotope fractionation between dissolved  $\text{B}(\text{OH})_3$  and  $\text{B}(\text{OH})_4^-$ ,  $\alpha_{(\text{B}_3-\text{B}_4)}$ . The information sought is of geochemical interest, yet the sole way to retrieve this information — if not by experimental means — is currently through physical theories and mathematical calculations. The latter approach is followed here and therefore this is a mathematical paper. However, since my primary goal is to contribute to a geochemical problem, the current work is not published in a physical chemistry journal because it would remain unrecognized by the geochemical community.

It is interesting to note that because there is yet no experimental value for  $\alpha_{(\text{B}_3-\text{B}_4)}$  (see section 9.2), this is in some respect similar to the determination of the stable oxygen isotope fractionation between water and calcite which Urey first calculated in his theoretical landmark paper (Urey, 1947) but which was experimentally established only 3 years later (McCrea et al., 1950). It is just that the corresponding time lag in the present case already amounts up to 28 years.

The value of  $\alpha_{(\text{B}_3-\text{B}_4)}$  is of fundamental importance for the basis of the stable boron isotope proxy which is one of the most promising tools to reconstructing atmospheric  $\text{CO}_2$  in the past. More specifically, stable boron isotopes from fossil marine carbonates such as foraminifera are used to reconstruct the pH of the paleo-ocean which, combined with additional information, holds the key to paleo- $p\text{CO}_2$  levels (e.g., Hemming and Hanson, 1992; Spivack et al., 1993; Sanyal et al., 1995; Palmer et al., 1998; Pearson and Palmer, 2000; Tyrrell and Zeebe, 2004). This technique may be referred to as ‘paleoacidimetry’

(Fig. 1) and theoretical aspects of this tool are currently investigated by the author of the present paper and co-workers (Zeebe et al., 2001, 2003).

The application of stable boron isotope fractionation to urgent questions such as past atmospheric  $\text{CO}_2$  levels indicates the necessity to comprehend the thermodynamic basis of this tool. This includes the determination of an accurate value of the fractionation factor  $\alpha_{(\text{B}_3-\text{B}_4)}$  between the dominant dissolved boron species in seawater, boric acid and borate ion. As mentioned above, the factor has hitherto not been determined experimentally (see section 9.2). As a result, theoretical values such as  $\alpha_{(\text{B}_3-\text{B}_4)} = 1.0193$  (at 300 K) from KK77 are widely used in the literature (cf. also Christoph et al., 1976, and Oi, 2000). Due to the growing interest in boron isotope systematics, it is timely to investigate how this value was derived, how reliable it is, and how sensitive it is to variations in data and parameter values that go into the calculations. The calculations are not trivial and the mathematical techniques required are not among the tools of primary interest to geochemists or paleo-oceanographers — the results of the calculations, however, are.

In the current paper I will re-examine the calculations of KK77 and Kotaka and Kakihana (1977) (sections 2 and 3). Using the same spectroscopic data and methods as KK77, I also calculate  $\alpha_{(\text{B}_3-\text{B}_4)} = 1.0193$  at 300 K (section 3.3). I will then show that in general, however, the result sensitively depends on the vibrational frequencies of the involved molecules (section 4) and the theoretical methods used to calculate the forces in the molecule (sections 5 and 6). Using the spectroscopic data available in the literature and different theoretical methods, the outcome for  $\alpha_{(\text{B}_3-\text{B}_4)}$  varies between  $\sim 1.020$  and  $\sim 1.050$  at 300 K. However, several lines of reasoning indicate that  $\alpha_{(\text{B}_3-\text{B}_4)} \geq 1.030$ . Unfortunately, measured isotopic shifts in various isotopomers of  $\text{B}(\text{OH})_3$  and  $\text{B}(\text{OH})_4^-$ , labeled with  $^{10}\text{B}$ ,  $^2\text{D}$ , and  $^{18}\text{O}$  do not provide a constraint on stable boron isotope

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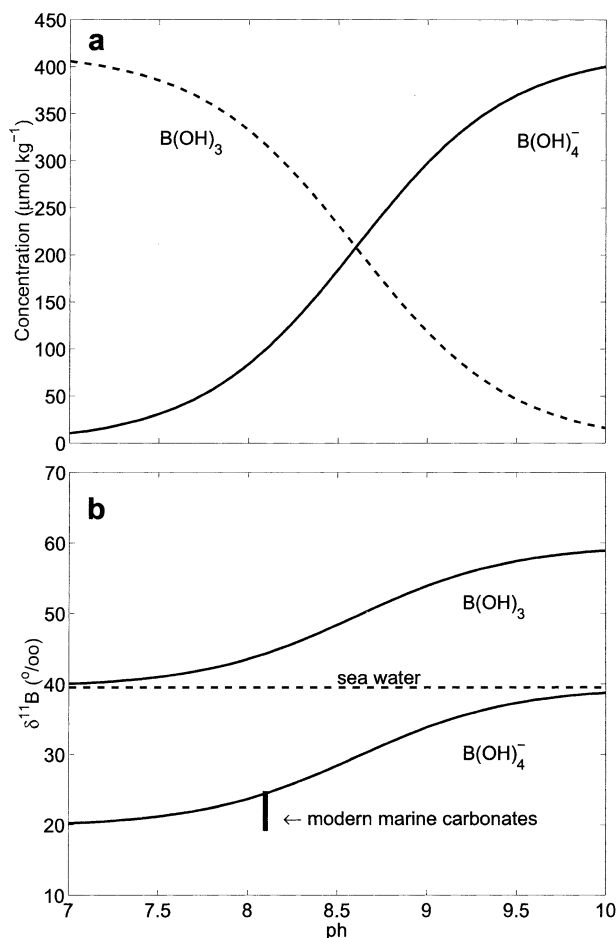


Fig. 1. (a) Concentration of the major dissolved boron species boric acid ( $\text{B(OH)}_3$ ) and borate ion ( $\text{B(OH)}_4^-$ ) in seawater and (b) stable boron isotope fractionation between them as a function of pH, using  $\alpha_{(\text{B3-B4})}$  after KK77. The isotopic composition of  $\text{B(OH)}_4^-$  increases with pH and so does the  $\delta^{11}\text{B}$  of carbonates, provided that  $\text{B(OH)}_4^-$  is preferentially incorporated in the carbonates. As a result, variations of seawater pH in the past should be traceable by variations of  $\delta^{11}\text{B}$  in fossil carbonates. This is the basis of the boron paleo-pH proxy (cf. Hemming and Hanson, 1992).

fractionation (section 7). The temperature dependence of  $\alpha_{(\text{B3-B4})}$  is discussed in section 8. I conclude the paper by encouraging experimental workers to directly determine  $\alpha_{(\text{B3-B4})}$ . This is essential to safely anchor the inorganic basis of paleoacidimetry. To address the critics of paleoacidimetry it is emphasized, however, that lack of an accurate value for  $\alpha_{(\text{B3-B4})}$  does not bias pH reconstructions provided that single species calibrations for foraminifera are used.

## 2. THERMODYNAMIC ISOTOPE FRACTIONATION

In thermodynamic equilibrium, the isotopic fractionation between two molecules depends on the difference in the zero-point energy of molecular vibration of the molecules containing either the light or the heavy isotope. Knowing the frequencies of molecular vibration, one can calculate the energy difference and hence the isotopic fractionation in thermodynamic equilibrium. This is the basis of the theory described in e.g. Urey

(1947). The theory is not recapitulated here and the reader unfamiliar with it is referred to Urey (1947) and more recent reviews and applications (e.g., Bigeleisen, 1965; Richet et al., 1977; Criss, 1999; Schauble et al., 2001; Zeebe and Wolf-Gladrow, 2001).

For the calculation of the isotopic equilibrium constant, the ratio of the reduced partition functions  $(Q'/Q)_r$  of the molecule containing the light and the heavy isotope are required. For polyatomic molecules, this ratio is given by:

$$\left(\frac{Q'}{Q}\right)_r = \frac{s}{s'} \prod_i \frac{u'_i}{u_i} \frac{\exp(-u'_i/2)}{1 - \exp(-u'_i)} \frac{1 - \exp(-u_i)}{\exp(-u_i/2)} \quad (1)$$

where primes denote quantities pertaining to the isotopically substituted molecule,  $s$ 's are symmetry numbers and  $u = hc\omega/kT$ ,  $u' = hc\omega'/kT$  where  $h = 6.62607 \times 10^{-34}$  J s is Planck's constant,  $c = 299,792,458$  m  $\text{s}^{-1}$  is the speed of light,  $\omega = 1/\Lambda$  is the wavenumber of vibration (often given in  $\text{cm}^{-1}$ ), and  $\Lambda$  is the wavelength. (The frequency of vibration is  $\nu = c/\Lambda$ ; the wavenumber  $\omega$  and the frequency  $\nu$  are often used equivalently). Boltzmann's constant is  $k = 1.38065 \times 10^{-23}$  J  $\text{K}^{-1}$  and  $T$  is the absolute temperature in Kelvin. Strictly, application of Eqn. 1 requires molecules in the gas phase and harmonic vibrations (for more details, see references above and Rosenbaum, 1997; Young et al., 2002).

### 2.1. Frequencies of Isotopic Molecules

The most important quantities that enter Eqn. 1 are the fundamental vibrational frequencies,  $\omega$ , of a molecule of a given chemical formula and those of the isotopically substituted molecule,  $\omega'$ . The usual way to determine  $\omega$  and  $\omega'$  is to experimentally measure either one of the two frequencies by infrared and/or Raman spectroscopy from which the force constants in the molecule are determined which is then used to calculate the other frequency. The methods to calculate the forces of polyatomic molecules frequently employed are simple central forces, simple valence forces, generalized valence force fields (GVFF) and Urey-Bradley force fields (UBFF) (cf. Herzberg, 1966; Ross, 1972; Nakamoto, 1997). Another tool is *ab initio* molecular orbital theory (e.g., Hehre et al., 1986). In this paper, I will initially employ GVFF which is an advanced method. Other methods, including UBFF are considered in section 5, while *ab initio* molecular orbital theory is the subject of section 6.

From the GF matrix method (Wilson, 1939, 1941) follows the matrix secular equation which relates the frequencies of molecular vibration to the forces in the molecule:

$$|\mathbf{GF} - E\lambda| = 0 \quad (2)$$

where the  $\mathbf{G}$  matrix depends on the atomic masses and geometry of the molecule (see Appendix A),  $\mathbf{F}$  contains the force constants, and  $\lambda = 4\pi^2c^2\omega^2$ . The  $\lambda$ 's are the eigenvalues of  $\mathbf{GF}$  and are not to be confused with the wavelength  $\Lambda$ . If the frequencies for a molecule say, containing the light isotope,  $\omega$ , are known, one has to determine the elements of  $\mathbf{F}$  from the  $\omega$ 's which is often not straightforward. However, once  $\mathbf{F}$  is determined, the masses of the light isotope in  $\mathbf{G}$  are replaced by those of the heavy and the solution of Eqn. 2 for  $\lambda'$  readily gives the frequencies for the molecule containing the heavy

isotope as the forces in the two molecules are the same. In the following, the solution of the secular equations will lead to quadratic equations, which in general have two solutions. Only one of these solutions yields realistic force constants, the other does not.

### 3. APPLICATION TO B(OH)<sub>3</sub> AND B(OH)<sub>4</sub><sup>-</sup>

Since B exchange is considered in the present case, the isotopic equilibrium constant  $K$  is equal to the fractionation factor  $\alpha$  (cf. Urey, 1947):

$$\alpha_{(B_3-B_4)} = K = \left( \frac{Q_{B(OH)_3}}{Q_{B(OH)_4^-}} \right) / \left( \frac{Q_{B(OH)_3}}{Q_{B(OH)_4^-}} \right) = \frac{\beta_{B(OH)_3}}{\beta_{B(OH)_4^-}} \quad (3)$$

where the commonly used  $\beta$  factors have been introduced which replace the reduced partition function ratios. In the following,  $\beta_{B(OH)_3}$  and  $\beta_{B(OH)_4^-}$  are determined where B(OH)<sub>3</sub> and B(OH)<sub>4</sub><sup>-</sup> are treated as a trigonal planar XY<sub>3</sub> molecule and a tetrahedral XY<sub>4</sub> molecule of  $D_{3h}$  and  $T_d$  symmetry, respectively. Finally,  $\alpha_{(B_3-B_4)}$  is calculated from the ratio of the  $\beta$  factors.

One shortcoming of all the analytical calculations presented in the following is that the OH group is treated as a single mass point, i.e. B(OH)<sub>3</sub> and B(OH)<sub>4</sub><sup>-</sup> are assumed to obey  $D_{3h}$  and  $T_d$  symmetry, which in reality is not true. Numerical calculations with more complex symmetries are presented in section 6.

#### 3.1. Boric Acid, B(OH)<sub>3</sub>

The frequencies of BO<sub>3</sub> given in Table 1 were reported by Thirugnanasambandam and Srinivasan (1969), hereafter wisely TS69, and used to calculate the  $\beta$  factor for B(OH)<sub>3</sub> by KK77. From the calculations in TS69 and KK77 it is obvious that the assumed atomic mass of B in BO<sub>3</sub> pertaining to these frequencies was taken as 10.81 amu. It is later discussed that these frequencies do actually pertain to <sup>11</sup>B and not to the natural abundance of boron and, moreover, that they were determined for La<sup>11</sup>BO<sub>3</sub> and not for B(OH)<sub>3</sub>. For the time being, however, we will follow KK77.

The numbering of the frequencies used here is the same as in Herzberg (1966): one nondegenerate ( $A'_1$ ) vibration  $\omega_1$ , one out-of-plane ( $A''_2$ ) vibration  $\omega_2$ , and two doubly degenerate ( $E'$ ) vibrations  $\omega_3$  and  $\omega_4$ . From these four frequencies, five force constants for the  $F$  matrix have to be determined which requires additional information, see TS69. This procedure and the resulting  $F$  and  $G$  matrices can be found in Appendix A. The numerical values of the force constants as given by TS69 are

Table 1. Vibrational frequencies of BO<sub>3</sub> used by KK77 and of B(OH)<sub>3</sub> as calculated (cm<sup>-1</sup>).

Molecule	$\omega_1$ ( $A'_1$ )	$\omega_2$ ( $A''_2$ )	$\omega_3$ ( $E'$ )	$\omega_4$ ( $E'$ )
BO <sub>3</sub> <sup>a</sup>	939.00	712.00	1284.50 (2) <sup>b</sup>	603.75 (2)
<sup>11</sup> B(OH) <sub>3</sub> <sup>c</sup>	911.02	703.27	1265.30 (2)	587.34 (2)
<sup>10</sup> B(OH) <sub>3</sub> <sup>c</sup>	911.02	731.49	1308.80 (2)	590.60 (2)

<sup>a</sup> Taken by KK77 from TS69, assumed B mass was 10.81 amu.

<sup>b</sup> The twofold degeneracy of  $\omega_3$  and  $\omega_4$  is indicated by "(2)."

<sup>c</sup> Calculated following KK77, see text.  $\omega_1$  is smaller for B(OH)<sub>3</sub> than for BO<sub>3</sub> because of larger  $m_y$ .

displayed in Table 2. Once  $F$  is determined, solution of Eqn. 2 for the corresponding  $\lambda$  yields the frequencies for <sup>11</sup>B(OH)<sub>3</sub> and <sup>10</sup>B(OH)<sub>3</sub> which are included in Table 1.

Inserting the frequencies into Eqn. 1 yields the  $\beta$  factor for B(OH)<sub>3</sub>. Before doing so, some practical remarks are useful. First, a good check on numerical errors in the calculated frequencies provides the Redlich-Teller product rule (Redlich, 1935) which relates  $\omega$  and  $\omega'$  to the masses of the molecules. This rule must be obeyed by any frequency calculation in harmonic approximation. The logarithmic form of the product rule reads in this case (cf., e.g., Chacko et al., 1991):

$$\frac{3}{2} \ln \left( \frac{M'}{M} \right) + \frac{3}{2} \ln \left( \frac{m}{m'} \right) = \sum_i g_i \ln \frac{\omega'_i}{\omega_i} \quad (4)$$

where  $M$ 's and  $m$ 's are the masses of the molecules and exchanged isotopes, respectively, and  $g = [1 \ 1 \ 2 \ 2]$  keeps track of the degeneracy. The values of the left- and right-hand side of Eqn. 4 give:

$$\frac{3}{2} \ln \left( \frac{M'}{M} \right) + \frac{3}{2} \ln \left( \frac{m}{m'} \right) = -0.11800922628245129$$

$$\sum_i g_i \ln \frac{\omega'_i}{\omega_i} = -0.11800922628245128$$

as it should be. Second, the ratio of the symmetry numbers in Eqn. 1,  $s/s' = 1$ , because only the central B atom is exchanged. Third, the product in Eqn. 1 runs twice over  $\omega_3$  and  $\omega_4$  as they are doubly degenerated.

The calculated  $\beta$  factor for B(OH)<sub>3</sub> then is

$$\beta_{B(OH)_3} = 1.1987 \quad \text{at } 300 \text{ K.} \quad (5)$$

KK77 give the same value at 300 K.

#### 3.2. Borate ion, B(OH)<sub>4</sub><sup>-</sup>

The frequencies of B(OH)<sub>4</sub><sup>-</sup> given in Table 3 were measured by Edwards et al. (1955) on the borate ion in aqueous solution and were used to calculate the  $\beta$  factor for B(OH)<sub>4</sub><sup>-</sup> by KK77. Because Edwards et al. (1955) studied borate solutions with boron of natural abundance, in this case it is correct to assume an atomic mass for B of 10.81 amu. The numbering of the frequencies again follows Herzberg (1966): one nondegenerate ( $A_1$ ) vibration  $\omega_1$ , one doubly degenerate ( $E$ ) vibration  $\omega_2$ , and two triply degenerate ( $F_2$ ) vibrations  $\omega_3$  and  $\omega_4$ . From these four frequencies, five force constants for the  $F$  matrix have to be determined which requires additional information, see Krebs et al. (1967) and Müller and Krebs (1967). The resulting  $F$  and  $G$  matrices are given in Appendix B, while the numerical

Table 2. GVFF force constants of BO<sub>3</sub> and B(OH)<sub>4</sub><sup>-</sup> (N m<sup>-1</sup>) following KK77.

Molecule	$F_{11}$	$F_{22}$	$F_{33}$	$F_{34}$	$F_{44}$
BO <sub>3</sub>	831.65 <sup>a</sup>	55.84 <sup>a</sup>	580.28 <sup>a</sup>	-111.77 <sup>a</sup>	129.19 <sup>a</sup>
B(OH) <sub>4</sub> <sup>-</sup>	569.00 <sup>b</sup>	48.00 <sup>b</sup>	280.00 <sup>b</sup>	52.00 <sup>b</sup>	72.00 <sup>b</sup>

<sup>a</sup> From measured frequencies for BO<sub>3</sub> given in Table 1 (after TS96).

<sup>b</sup> From measured frequencies for B(OH)<sub>4</sub><sup>-</sup> given in Table 3 (after Krebs et al. 1967).

values of the force constants are given in Table 2. Once  $F$  is determined, solution of Eqn. 2 for the corresponding  $\lambda$  yields the frequencies for  $^{11}\text{B}(\text{OH})_4^-$  and  $^{10}\text{B}(\text{OH})_4^-$  which are included in Table 3.

The Redlich-Teller product rule gives in this case,  $g = [1\ 2\ 3\ 3]$ :

$$\frac{3}{2} \ln \left( \frac{M'}{M} \right) + \frac{3}{2} \ln \left( \frac{m}{m'} \right) = -0.1232691864494167$$

$$\sum_i g_i \ln \frac{\omega_i'}{\omega_i} = -0.1232691864494168.$$

Finally, the calculated  $\beta$  factor for  $\text{B}(\text{OH})_4^-$  is

$$\beta_{\text{B}(\text{OH})_4^-} = 1.1760 \quad \text{at } 300 \text{ K.} \quad (6)$$

KK77 give the same value at 300 K.

### 3.3. Fractionation Factor Between $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$

With the  $\beta$  factors for  $\text{B}(\text{OH})_3$  and  $\text{B}(\text{OH})_4^-$ , Eqn. 3 now yields the fractionation factor at 300 K:

$$\alpha_{(\text{B}_3-\text{B}_4)} = \frac{\beta_{\text{B}(\text{OH})_3}}{\beta_{\text{B}(\text{OH})_4^-}} = \frac{1.1987}{1.1760} = 1.0193.$$

In other words, according to this calculation, boric acid is enriched over borate ion in  $^{11}\text{B}$  by 19.3%; KK77 also give  $1.1987/1.1760 = 1.0193$  or 19.3%. The numerical agreement between the numbers suggest that the methods and calculations used in the current paper and by KK77 were applied correctly. Unfortunately, this does not mean that the number itself is reliable as will be discussed below.

## 4. INFLUENCE OF VIBRATIONAL FREQUENCIES

The most important observational quantities required to determine the fractionation factor using analytical methods are the vibrational frequencies of the molecules. In the following, the measured frequencies for  $\text{B}(\text{OH})_3$  and  $\text{B}(\text{OH})_4^-$  are discussed and their influence on stable boron isotope fractionation is examined.

### 4.1. Vibrational Frequencies of $\text{B}(\text{OH})_3$

As mentioned above, the frequencies used by KK77 for  $\text{B}(\text{OH})_3$  were actually used by TS69 for  $\text{BO}_3$  but measured for

Table 3. Vibrational frequencies of  $\text{B}(\text{OH})_4^-$ ,  $^{11}\text{B}(\text{OH})_4^-$ , and  $^{10}\text{B}(\text{OH})_4^-$  ( $\text{cm}^{-1}$ ).

Molecule	$\omega_1$ ( $A_1$ )	$\omega_2$ ( $E$ )	$\omega_3$ ( $F_2$ )	$\omega_4$ ( $F_2$ )
$\text{B}(\text{OH})_4^-$ <sup>a</sup>	754.00	379.00 (2) <sup>b</sup>	947.00 (3)	533.00 (3)
$^{11}\text{B}(\text{OH})_4^-$ <sup>c</sup>	753.55	379.09 (2)	937.67 (3)	532.83 (3)
$^{10}\text{B}(\text{OH})_4^-$ <sup>c</sup>	753.55	379.09 (2)	975.78 (3)	533.50 (3)
$^{11}\text{B}(\text{OH})_4^-$ <sup>d</sup>	754.00	379.00 (2)	940.37 (3)	532.22 (3)
$^{10}\text{B}(\text{OH})_4^-$ <sup>d</sup>	754.00	379.00 (2)	977.15 (3)	533.67 (3)

<sup>a</sup> Edwards et al. (1955), B mass = 10.81 amu.

<sup>b</sup> Twofold and threefold degeneracy is indicated by "(2)" and "(3)."

<sup>c</sup> Calculated after KK77, see text.

<sup>d</sup> Calculated using UBFF (Urey and Bradley, 1931), see text.

$\text{LaBO}_3$  in crystalline powder and adjusted to  $\text{La}^{11}\text{BO}_3$  (Steele and Decius, 1956). The actual frequencies of  $\text{B}(\text{OH})_3$  were experimentally measured by other authors such as Bethell and Sheppard (1955) in polycrystalline mull and in a single crystal, by Servoss and Clark (1957) as solid in KBr plates and in solution, by Ogden and Young (1988) in low-temperature nitrogen matrix, by Gilson (1991) in the gas phase, and by Andrews and Burkholder (1992) in argon matrix. The measured frequencies of  $\text{B}(\text{OH})_3$  for the skeletal  $\text{BO}_3$  vibration are summarized in Table 4. It is obvious that  $\omega_1$ ,  $\omega_2$ , and  $\omega_4$  are smaller in  $\text{B}(\text{OH})_3$  than in  $\text{LaBO}_3$ , while  $\omega_3$  is larger.

It turns out that the most important change in the  $\beta$  factor due to these frequency differences arises from  $\omega_3$ . The value for  $\omega_1$  is irrelevant as it refers to the totally symmetric stretch which is insensitive to boron mass because the boron atom is fixed in this vibrational mode. Decreasing  $\omega_2$  from 712 to 650  $\text{cm}^{-1}$  changes the  $\beta$  factor by 5%, while decreasing  $\omega_4$  from 603 to 450  $\text{cm}^{-1}$  changes the  $\beta$  factor by 3%. However, increasing  $\omega_3$  from 1284 to 1450  $\text{cm}^{-1}$  changes the  $\beta$  factor by 26% (a five- to ninefold larger effect than for  $\omega_2$  and  $\omega_4$ ). This leads to  $\beta$  factors for  $\text{B}(\text{OH})_3$  that are all larger than that given by KK77, ranging from 1.2205 to 1.2256 (Table 5), almost entirely due to the larger  $\omega_3$  in  $\text{B}(\text{OH})_3$  as compared to  $\text{LaBO}_3$ . As a result, for a given  $\beta_{\text{B}(\text{OH})_4^-} = 1.1760$ , also the fractionation factor  $\alpha_{(\text{B}_3-\text{B}_4)}$  is larger, ranging from  $\sim 36$  to  $\sim 42\%$ .

### 4.2. Vibrational Frequencies of $\text{B}(\text{OH})_4^-$

The frequencies for  $\text{B}(\text{OH})_4^-$  used by KK77 were measured by Edwards et al. (1955) on the borate ion in aqueous solution. Pinchas and Shamir (1972) and Campbell et al. (1985) also measured frequencies of  $\text{B}(\text{OH})_4^-$  in solution by Raman spectroscopy and reported values for  $\omega_1$  and  $\omega_3$  which mainly confirm the results of Edwards et al. (1955) with respect to these two frequencies. Goulden (1959) reported a strong infrared absorption band of  $\text{B}(\text{OH})_4^-$  in aqueous solution near 945  $\text{cm}^{-1}$  but did not make any assignments. Janda and Heller (1980) recorded infrared and Raman vibrational spectra in solid  $\text{Na}(\text{B}[\text{OH}]_4)$  which also support the results of Edwards et al.

Table 4. Measured vibrational frequencies of  $\text{LaBO}_3$  and  $\text{B}(\text{OH})_3$  ( $\text{cm}^{-1}$ ).

Molecule	$\omega_1$ ( $A_1'$ )	$\omega_2$ ( $A_2''$ )	$\omega_3$ ( $E'$ )	$\omega_4$ ( $E'$ )
$\text{La}^{11}\text{BO}_3$ <sup>a</sup>	939.00	712.00	1284.50	603.75
$\text{B}(\text{OH})_3$ <sup>b</sup>	—	648.00	1450.00	540.00
$\text{B}(\text{OH})_3$ <sup>c</sup>	—	639.00	1428.00	544.00
$\text{B}(\text{OH})_3$ <sup>d</sup>	880.00	—	1430.00	500.00
$^{11}\text{B}(\text{OH})_3$ <sup>e</sup>	—	675.00	1426.20	448.90
$^{11}\text{B}(\text{OH})_3$ <sup>f</sup>	866.00	—	1429.00	—
$\text{B}(\text{OH})_3$ <sup>g</sup>	—	667.00	1421.00	432.00

<sup>a</sup> Steele and Decius (1956). Infrared, crystalline powders.  $\omega_1$  was observed because borate group has less than threefold symmetry in  $\text{LaBO}_3$ .

<sup>b</sup> Bethell and Sheppard (1955). Infrared, crystal.

<sup>c</sup> Servoss and Clark (1957). Infrared, solid in KBr plates.

<sup>d</sup> Servoss and Clark (1957). Raman, in solution.

<sup>e</sup> Ogden and Young (1988). Infrared, low-temperature nitrogen matrix.

<sup>f</sup> Gilson (1991). Vapor phase.

<sup>g</sup> Andrews and Burkholder (1992). Infrared, argon matrix.

Table 5.  $\beta$  factor of B(OH)<sub>3</sub> and  $\alpha_{(B3-B4)}$  at 300 K using GVFF, frequencies from different authors, and  $\beta_{B(OH)_4^-} = 1.1760$ .

Author	$\beta_{B(OH)_3}$	$\alpha_{(B3-B4)}$	$[\alpha_{(B3-B4)} - 1]10^3$
TS96	1.1987	1.0193	19.3
Bethell and Sheppard (1955)	1.2256	1.0422	42.2
Servoss and Clark (1957)	1.2205	1.0378	37.8
Ogden and Young (1988)	1.2213	1.0385	38.5
Andrews and Burkholder (1992)	1.2192	1.0367	36.7

(1955). The measured frequencies of B(OH)<sub>4</sub><sup>-</sup> for the skeletal BO<sub>4</sub> vibration are summarized in Table 6.

Regarding stable boron isotope fractionation, only  $\omega_3$  and  $\omega_4$  are relevant as  $\omega_1$  and  $\omega_2$  do not change upon boron isotope substitution. Using the largest reported value of 958 cm<sup>-1</sup> instead of 947 cm<sup>-1</sup> for  $\omega_3$  results in a decrease of  $\alpha_{(B3-B4)}$  by ~3‰ (independent of method used to calculate molecular forces, see below). The measurements by Janda and Heller (1980) of  $\omega_4$  in solid Na[B(OH)<sub>4</sub>] (IR: 528 cm<sup>-1</sup>, Raman: 520 cm<sup>-1</sup>) corroborate the value of 533 cm<sup>-1</sup> given by Edwards et al. (1955). The effect on  $\alpha_{(B3-B4)}$  using either of these frequencies is small.

## 5. INFLUENCE OF DIFFERENT METHODS TO CALCULATE MOLECULAR FORCES

As mentioned in section 2.1, different methods can be applied to calculate the forces in a molecule. The method introduced so far and used by KK77 is based on generalized valence force fields (GVFF). One crucial aspect of this method — when applied to B(OH)<sub>3</sub> and B(OH)<sub>4</sub><sup>-</sup> of assumed  $D_{3h}$  and  $T_d$  symmetry — is that five force constants have to be determined from only four measured fundamental frequencies (see Appendix). Such a system has infinitely many solutions. KK77 used force constants for B(OH)<sub>3</sub> given by TS69 who had tackled this problem by expressing one force constant in terms of another force constant and the masses in the molecule. For B(OH)<sub>4</sub><sup>-</sup>, KK77 used force constants from Krebs et al. (1967) who had applied a technique developed by Fadini (1966) to overcome the problem of infinitely many solutions.

This technique and other methods such as Urey-Bradley

Table 6. Measured vibrational frequencies of B(OH)<sub>4</sub><sup>-</sup> (cm<sup>-1</sup>).

Molecule	$\omega_1 (A_1)$	$\omega_2 (E)$	$\omega_3 (F_2)$	$\omega_4 (F_2)$
B(OH) <sub>4</sub> <sup>-a</sup>	754.00	379.00	947.00	533.00
B(OH) <sub>4</sub> <sup>-b</sup>	744.00	—	958.00	—
B(OH) <sub>4</sub> <sup>-c</sup>	746.00	—	955.00	—
B(OH) <sub>4</sub> <sup>-d</sup>	738.00	—	935.00	528.00
B(OH) <sub>4</sub> <sup>-e</sup>	738.00	—	952.00	520.00
B(OH) <sub>4</sub> <sup>-f</sup>	—	—	945.00	—

<sup>a</sup> Edwards et al. (1955). Raman, in solution. B mass = 10.81 amu.

<sup>b</sup> Pinchas and Shamir (1972). Infrared and Raman, in solution.

<sup>c</sup> Campbell et al. (1985). Infrared and Raman, in solution.

<sup>d</sup> Janda and Heller (1980). Infrared, solid Na[B(OH)<sub>4</sub>].

<sup>e</sup> Janda and Heller (1980). Raman, solid Na[B(OH)<sub>4</sub>].

<sup>f</sup> Goulden (1959). Infrared, in solution. No assignment.

force fields (UBFF) (cf. Herzberg, 1966; Ross, 1973; Nakamoto, 1997) and their effect on  $\alpha_{(B3-B4)}$  are examined in the following.

### 5.1. Urey-Bradley Force Field for B(OH)<sub>3</sub>

Janz and Mikawa (1960) have evaluated Urey-Bradley force constants for planar XY<sub>3</sub> molecules. In this representation, four force constants for the in-plane vibrations have to be determined from three frequencies (the out-of-plane mode is to be treated as in GVFF). Thus again four force constants, here denoted by  $K$ ,  $H$ ,  $F$ , and  $F'$ , have to be determined from only three frequencies which was done by Janz and Mikawa (1960) by using:

$$F' = \gamma F \quad (7)$$

with  $\gamma = -1/10$  or  $-1/13$  (for justification, see Janz and Mikawa, 1960, and references therein). It turned out that variation of  $\gamma$  between  $-1/5$  and  $-1/13$  was irrelevant for the value of  $\alpha_{(B3-B4)}$  calculated. With Eqn. 7, the Urey-Bradley approach leads to a system of three equations with three unknowns which is solvable (Appendix C). With those force constants, the isotopic frequency shift for <sup>11</sup>B(OH)<sub>3</sub> and <sup>10</sup>B(OH)<sub>3</sub>, the  $\beta$  factor, and  $\alpha_{(B3-B4)}$  were calculated.

Following KK77, i.e. using frequencies for B(OH)<sub>3</sub> from TS69, the  $\beta$  factor for B(OH)<sub>3</sub> is then calculated as:

$$\beta_{B(OH)_4^-} = 1.2098 \quad \text{at 300 K}$$

which is larger than 1.1987, the value calculated using GVFF and the same frequencies (Table 7). If the  $\beta$  factor for B(OH)<sub>4</sub><sup>-</sup> is used as given by KK77, then  $\alpha_{(B3-B4)} = 1.0287$  which is ~10‰ larger than the original value given by KK77.

If instead frequencies are used as given by Bethell and Sheppard (1955), the  $\beta$  factor for B(OH)<sub>3</sub> at 300 K is 1.2383. Combining it with the  $\beta$  factor for B(OH)<sub>4</sub><sup>-</sup> given by KK77,  $\alpha_{(B3-B4)} = 1.0530$  which is ~11‰ larger than using GVFF and the same frequencies, and ~34‰ larger than the original value given by KK77 using GVFF and their frequencies (Table 7).

### 5.2. Fadini's "Verfahren der Nächsten Lösung" for B(OH)<sub>4</sub><sup>-</sup>

Using spectroscopic data, Krebs et al. (1967) calculated the force constants in B(OH)<sub>4</sub><sup>-</sup> (see Appendix B) by finding reasonable solutions to the secular equation (Eqn. 2). In this case, the common problem of infinitely many solutions can be reduced to the problem of determining three force constants from two measured frequencies for which Fadini's "Verfahren der

Table 7.  $\beta$  factor of B(OH)<sub>3</sub> and  $\alpha_{(B3-B4)}$  at 300 K using GVFF/UBFF,  $\beta_{B(OH)_4^-} = 1.1760$  and different frequencies.

Method	$\beta_{B(OH)_3}$	$\alpha_{(B3-B4)}$	$[\alpha_{(B3-B4)} - 1]10^3$
GVFF <sup>a</sup>	1.1987	1.0193	19.3
GVFF <sup>b</sup>	1.2256	1.0422	42.2
UBFF <sup>a</sup>	1.2098	1.0287	28.7
UBFF <sup>b</sup>	1.2383	1.0530	53.0

<sup>a</sup> Frequencies from TS69 (after KK77).

<sup>b</sup> Frequencies from Bethell and Sheppard (1955).

nächsten Lösung” was applied (literally translated: “method of closest solution”). Initially, a set of physically reasonable force constants is chosen. From the infinite number of solutions satisfying Eqn. 2, the set of force constants is calculated which is ‘closest’ to the initial set of force constants in a least-square sense (for more details, see Fadini, 1966). Note that the result is in general different from the initial set as the initial set does generally not satisfy Eqn. 2. One possible choice of a set of physically reasonable initial force constants is:

$$\mathbf{F}^i = \mathbf{F}_{\text{diag}} = \mathbf{G}_{\text{diag}}^{-1} \lambda \quad (8)$$

(cf. Krebs et al., 1967). The physical interpretation of Eqn. 8 is a first order approximation that considers the atoms in the molecule to be uncoupled oscillators. For example, in  $\text{B}(\text{OH})_3$ , Eqn. 8 yields  $F_{33}^i = 289$  and  $F_{44}^i = 27 \text{ N m}^{-1}$  from which the ‘closest solution’ is calculated to be  $F_{33} = 280$ ,  $F_{44} = 72$ , and  $F_{34} = 52 \text{ N m}^{-1}$ .

Although it appears physically meaningful to use a model of uncoupled oscillators as a first guess and it also appears likely that the true solution will not be too far away from this guess, it is unclear why the ‘closest solution’ in a mathematical least-square sense should yield values closest to those of the actual physical forces in the molecule. However, Fadini (1966) showed that his method yields good agreement with measured force constants in  $\text{BrCN}$ . Krebs et al. (1967) applied it to molecules of  $T_d$  symmetry including  $\text{B}(\text{OH})_4^-$  and reported that Fadini’s method works well in those molecules. In any case, it is important to evaluate whether or not the precision of this method is sufficient for the current purpose, the calculation of boron isotope fractionation. Since the forces in  $\text{B}(\text{OH})_4^-$  are not accurately known, we cannot evaluate Fadini’s method directly. This leaves us with an examination of the sensitivity of the calculated  $\alpha_{(\text{B3-B4})}$  to variations in the force constants, which is as follows. Increasing  $F_{33}$  or  $F_{34}$  by 30% raises  $\alpha_{(\text{B3-B4})}$  from  $\sim 1.019$  to  $\sim 1.030$ , i.e. an 11% change. Increasing  $F_{44}$  by 30% lowers  $\alpha_{(\text{B3-B4})}$  from  $\sim 1.019$  to  $\sim 1.016$ , i.e. a 3% change. Decreasing the force constants  $F_{33}$  or  $F_{34}$  is equivalent to increasing  $F_{44}$ .

### 5.3. Urey-Bradley Force Field for $\text{B}(\text{OH})_4^-$

Urey and Bradley (1931) proposed a different method to calculate the forces in a molecule which takes into account valence forces and central forces between non-bonded atoms. In particular, they suggested repulsive forces between corner atoms of tetrahedral molecules and introduced a potential energy term proportional to  $1/r_j^n$ , where  $r_j$  is the distance between two corner atoms. I have calculated the force constants of  $\text{B}(\text{OH})_4^-$  according to UBFF (see Appendix D). A good fit to the measured frequencies was obtained using  $n = 10$ . With those force constants, the frequencies of  $^{11}\text{B}(\text{OH})_4^-$  and  $^{10}\text{B}(\text{OH})_4^-$  can be calculated (Table 3), and the  $\beta$  factor for  $\text{B}(\text{OH})_4^-$  is calculated as:

$$\beta_{\text{B}(\text{OH})_4^-} = 1.1722 \quad \text{at } 300 \text{ K}$$

which is close to the value of 1.1760 obtained using GVFF and Fadini’s technique. If the  $\beta$  factor for  $\text{B}(\text{OH})_3$  is used as given by KK77, then  $\alpha_{(\text{B3-B4})} = 1.0226$  which is 3% larger than the value given by KK77 (Table 8).

## 6. AB INITIO MOLECULAR ORBITAL THEORY

In addition to the analytical methods discussed above, also numerical calculations were conducted based on *ab initio* molecular orbital (MO) theory in order to calculate molecular forces, vibrational frequencies, and the fractionation factor. These methods predict electron structure and forces in the molecule using fundamental quantum mechanical theory (e.g., Hehre et al., 1986; Jensen, 1998). The frequencies are then computed based on the calculated, optimized structure of the molecule which only requires information on the atoms, charge, bonds in the molecule, and its symmetry. The full symmetries chosen for  $\text{B}(\text{OH})_3$  and  $\text{B}(\text{OH})_4^-$  are  $C_{3h}$  and  $S_4$  (cf. Ogden and Young, 1988; Hess et al., 1988; Oi, 2000).

Various theories have been used in the realization of *ab initio* MO theory, including Hartree-Fock (HF), Møller-Plesset (MP2), and Density Functional Theory (DFT) which have different strengths and weaknesses (Jensen, 1998). For example, it is well known that HF theory tends to overestimate vibrational frequencies, relative to those observed experimentally because of inadequate dissociation behavior. This is usually accounted for by multiplying the predicted frequencies by a generic frequency scaling factor. The reliability of the method may be evaluated based on the deviations of predicted vs. observed frequencies in a least-square sense. Scott and Radom (1996) evaluated various methods using a total of 1066 experimental frequencies and concluded that the most successful methods are certain types of HF and DFT with specific basis sets. Following their conclusion, I have determined the vibrational frequencies of boric acid and borate ion ( $^{11}\text{B}/^{10}\text{B}$ ) using the following HF and DFT methods and basis sets: HF/6-31G(d), HF/6-31+G(d), HF/STO-3G, B-LYP/6-31+G(d), B-LYP/6-311+G(d,p), and B3-LYP/6-31G(d) as implemented in the GAMESS package (Schmidt et al., 1993). For detailed information on methods and basis sets, see e.g. Hehre et al. (1986), Jensen (1998), and the GAMESS documentation (GAMESS, 2004). MP2 theory was not tested because MP2/6-31G(d), for instance, not appears to offer a significant improvement over HF/6-31G(d) and sometimes shows large errors (Scott and Radom, 1996).

At full  $C_{3h}$  and  $S_4$  symmetry,  $\text{B}(\text{OH})_3$  and  $\text{B}(\text{OH})_4^-$  exhibit 10 and 16 fundamentals, respectively. Observed frequencies of these fundamentals and the frequency set determined using B-LYP/6-31+G(d) are given in Tables 9 and 10. (B-LYP/6-31+G(d) was chosen because it is relatively cost-effective, its scaling factor is close to unity and its root mean square error is small, see below). While the data base for  $\text{B}(\text{OH})_3$  is rather extensive, only a few measurements are available for  $\text{B}(\text{OH})_4^-$ .

Table 8.  $\beta$  factor of  $\text{B}(\text{OH})_4^-$  and  $\alpha_{(\text{B3-B4})}$  at 300 K using GVFF/UBFF and  $\beta_{\text{B}(\text{OH})_3} = 1.1987$ .

Method	$\beta_{\text{B}(\text{OH})_4^-}$	$\alpha_{(\text{B3-B4})}$	$[\alpha_{(\text{B3-B4})} - 1]10^3$
GVFF <sup>a</sup>	1.1760	1.0193	19.3
GVFF <sup>b</sup>	1.1797	1.0161	16.1
UBFF <sup>a</sup>	1.1722	1.0226	22.6
UBFF <sup>b</sup>	1.1755	1.0197	19.7

<sup>a</sup> Frequencies from Edwards et al. (1955).

<sup>b</sup>  $\omega_3$  from Pinchas and Shamir (1972).

Table 9. Observed vibrational frequencies (cm<sup>-1</sup>) of B(OH)<sub>3</sub> and calculated using *ab initio* molecular orbital theory (B-LYP/6-31+G(d)).

#	Assignm. <sup>a</sup>	BS55 <sup>b</sup>	SC57	OY88 <sup>11</sup> B	G91 <sup>11</sup> B	AB92	SF <sup>c</sup> <sup>11</sup> B	SF <sup>c</sup> <sup>10</sup> B	B-LYP <sup>11</sup> B	B-LYP <sup>10</sup> B
1(E')	asym OBO bend	540	500	449	—	432	449	451	430	431
2(A'')	sym BOH def	824	—	514	—	436	514	514	432	433
3(E'')	asym BOH def	—	—	—	—	520	—	—	534	534
4(A'')	sym BO <sub>3</sub> def	648	639	675	—	667	675	701	642	667
5(A')	sym BO str	880	880	—	866	—	880	880	845	845
6(E')	asym BOH bend	1197	1140	1010	1017	1012	1010	1010	1022	1024
7(A')	sym BOH bend	1065	1060	—	1020	1015	1020	—	1037	1037
8(E')	asym BO str	1450	1430	1426	1429	1421	1426	1478	1390	1437
9(E')	asym OH str	3200	3180	3669	3706	3689	—	—	3683	3683
10(A')	sym OH str	3172	3250	—	3705	—	—	—	3684	3684

<sup>a</sup> Assignment after Andrews and Burkholder (1992). def = deformation; str = stretch.

<sup>b</sup> BS55 = Bethell and Sheppard (1955); SC57 = Servoss and Clark (1957); OY88 = Ogden and Young (1988); G91 = Gilson (1991); AB92 = Andrews and Burkholder (1992).

<sup>c</sup> Frequencies used for scaling factor (SF) determination. <sup>10</sup>B: Ogden and Young (1988).

The vibrational spectra reported by Devarajan et al. (1974) was assigned to the B(OH)<sub>4</sub><sup>-</sup> unit as measured in teepelite (Na<sub>2</sub>B[OH]<sub>4</sub>Cl). In the low frequency range, it shows large deviations from the results of Edwards et al. (1955) and calculated values and was therefore not used to calculate the scaling factor.

From the frequency sets obtained with the various methods, the  $\beta$  factors and  $\alpha_{(B3-B4)}$  have been determined (Table 11). In addition, based on frequencies measured by various authors, the frequency scaling factor and the root mean square error (RMS, Scott and Radom, 1996) were calculated using least-squares procedure (Tables 9, 10, and 11). Figure 2 shows the observed vs. calculated frequencies using B-LYP/6-31+G(d) for which the scaling factor (slope of the solid line) is 1.0293. In other words, this method underestimates observed frequencies by about 3%. The scaling factor was determined using available observed frequencies for <sup>11</sup>B(OH)<sub>3</sub>, <sup>10</sup>B(OH)<sub>3</sub>, and <sup>11</sup>B(OH)<sub>4</sub><sup>-</sup> up to 1500 cm<sup>-1</sup>. Frequencies of higher wavenumber

are not affected by boron isotope substitution and have no influence on the fractionation factor. Also shown is the scaling factor for HF/STO-3G (dashed line) and the frequency comparison 'observed—measured' for that method (<sup>11</sup>B[OH]<sub>4</sub><sup>-</sup> only). The scaling factor is significantly different (0.8421) from that of B-LYP/6-31+G(d). However, more important is that the calculated frequency corresponding to  $\omega_3$  of B(OH)<sub>4</sub><sup>-</sup> is significantly higher than observed and deviates substantially from the least-square fit line (see arrow).

All methods predict  $\alpha_{(B3-B4)}$  between 25 and 39‰ (Table 11), except for HF/STO-3G which yields  $\alpha_{(B3-B4)} < 1$ . However, the latter method appears inadequate to describe tetrahedral structures, including that of B(OH)<sub>4</sub><sup>-</sup>. HF/STO-3G uses only a minimal basis set and seems to overpredict the higher frequencies of tetrahedral molecules which may be due to the fact that it poorly describes nonspherical anisotropic charge distributions (Hehre et al., 1986). I tested HF/STO-3G on other tetrahedral molecules such as CH<sub>4</sub> and CF<sub>4</sub>, which yielded

Table 10. Observed vibrational frequencies (cm<sup>-1</sup>) of B(OH)<sub>4</sub><sup>-</sup> and calculated using *ab initio* molecular orbital theory (B-LYP/6-31+G(d)).

# <sup>a</sup>	E55 <sup>b</sup>	PS72	D74 <sub>Na<sub>2</sub>B(OH)<sub>4</sub>Cl</sub>	JH80 <sub>Na(B(OH)<sub>4</sub>)</sub>	C85	SF <sup>c</sup> <sup>11</sup> B	B-LYP <sup>11</sup> B	B-LYP <sup>10</sup> B
1(A)	—	—	373	—	—	—	206	206
2(B)	—	—	429	—	—	—	248	248
3(E)	—	—	512	—	—	—	326	326
4(A) <sup>d</sup>	379	—	517	—	—	379	356	356
5(B)	—	—	637	—	—	—	401	401
6(E)	—	—	—	—	—	—	453	455
7(B)	533	—	750	528	—	533	488	489
8(A)	754	744	743	738	746	754	690	690
9(E)	—	—	857	—	—	—	807	821
10(B)	947	958	939	935	955	947	916	947
11(A)	—	—	1178	—	—	—	975	975
12(B)	—	—	1195	—	—	—	1020	1025
13(E)	—	—	1297	—	—	—	1156	1179
14(A)	—	—	3535	—	—	—	3643	3643
15(B)	—	—	3545	—	—	—	3648	3648
16(E)	—	—	3555	—	—	—	3651	3651

<sup>a</sup> Representation in S<sub>4</sub> symmetry after Hess et al. (1988).

<sup>b</sup> E55 = Edwards et al. (1955); PS72 = Pinchas and Shamir (1972); D74 = Devarajan et al. (1974); JH80 = Janda and Heller (1980); C85 = Campbell et al. (1985).

<sup>c</sup> Frequencies used for scaling factor (SF) determination.

<sup>d</sup> Note that frequencies 4, 7, and 10 given by E55, PS72, and C85 refer to T<sub>d</sub> symmetry ( $\omega_2$ ,  $\omega_4$ , and  $\omega_3$ ) and hence do not correspond to a single frequency in S<sub>4</sub> symmetry (Hess et al., 1988).

Table 11.  $\beta$  factors and  $\alpha_{(B3-B4)}$  at 300 K based on *ab initio* molecular orbital theory.

Method	$\beta_{B(OH)_3}$	$\beta_{B(OH)_4^-}$	Scaling factor	RMS <sup>a</sup> (cm <sup>-1</sup> )	$\alpha_{(B3-B4)}$ <sup>b</sup>	$\alpha_{(B3-B4)}^*$ <sup>c</sup>
<i>Hartree-Fock</i>						
HF/6-31G(d)	1.2614	1.2285	0.9240	34	1.0268	1.0251
HF/6-31+G(d)	1.2580	1.2181	0.9356	28	1.0327	1.0309
HF/STO-3G	1.2863	1.2916	0.8421	60	0.9959	0.9985
<i>Density Functional Theory</i>						
B-LYP/6-31+G(d)	1.2166	1.1744	1.0293	34	1.0359	1.0369
B-LYP/6-311+G(d,p)	1.2150	1.1705	1.0265	37	1.0380	1.0390
B3-LYP/6-31G(d)	1.2354	1.2036	0.9792	37	1.0264	1.0259

<sup>a</sup> Root mean square error, see Scott and Radom (1996).

<sup>b</sup> Using uncorrected frequencies.

<sup>c</sup> Using frequencies multiplied by scaling factor.

similar overpredictions. Moreover, the method predicts entirely unrealistic frequencies for  $SO_4^{2-}$ . In summary, the HF/STO-3G overestimation of  $\omega_3$  in  $B(OH)_4^-$  (Figure 2) leads to  $\beta_{B(OH)_4^-}$  being too large and hence  $\alpha_{(B3-B4)}$  being too small (Table 11). The baseline is that HF/STO-3G suffers from an insufficient representation of the orbital structure in  $B(OH)_4^-$  and its predicted  $\alpha_{(B3-B4)}$  value can therefore be discarded.

This is further supported by the fact that the RMS of HF/STO-3G is almost twice as large as for all other methods. It is important that a correlation coefficient ( $R^2$ ) as used by Oi (2000) is not a good criterion for the quality of the method in this case. Indeed, Oi (2000) reported that HF/STO-3G has the largest ('best')  $R^2$  of all methods tested. However, as shown here, it has the worst RMS and prediction of  $\omega_3$  in  $B(OH)_4^-$ , which is crucial for the fractionation factor.

Table 11 shows that the difference in  $\alpha_{(B3-B4)}$  due to appli-

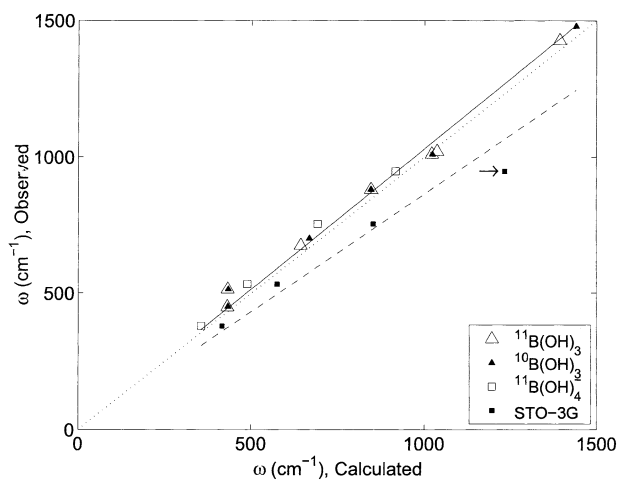


Fig. 2. Observed frequencies of  $B(OH)_3$  and  $B(OH)_4^-$  vs. those calculated by *ab initio* molecular orbital theory (B-LYP/6-31+G(d)), cf. Tables 9 and 10. The solid and dashed lines represent the scaling factor for B-LYP/6-31+G(d) and HF/STO-3G, respectively. The dotted line indicates a slope of unity. For HF/STO-3G, only the 'data-theory' comparison for  $^{11}B(OH)_4^-$  is shown. Note the deviation of the highest  $B(OH)_4^-$  frequency for HF/STO-3G from the dashed line (arrow, see text).

cation of the scaling factor ( $\alpha$  vs.  $\alpha^*$ ) for a given method is significantly smaller than the difference in  $\alpha_{(B3-B4)}$  among the different methods. In other words, the range in  $\alpha_{(B3-B4)}$  as calculated by *ab initio* molecular orbital theory (1.025–1.039) is primarily due to differences in theoretical methods rather than due to uncertainties in the scaling factor. It is worth mentioning that all methods including diffusive functions (which have a '+' sign in their basis set) predict larger  $\alpha_{(B3-B4)}$ . Basis sets without diffusive functions are appropriate for molecules in which electrons are held closely to the nuclear centers. Basis sets including diffusive functions allow a more appropriate description of molecules in which electrons are remote from nuclear centers, including anions. Since  $B(OH)_4^-$  is an anion, it is possible that values of the fractionation factor calculated with +basis sets are more realistic. Those values tend towards the upper end of the spectrum (1.031–1.039).

## 7. FREQUENCY SHIFTS IN VARIOUS ISOTOPOMERS

Another possible constraint on calculated force fields and frequencies is the comparison with observed frequency shifts in isotopomers. For example, Ogden and Young (1988) and Gilson (1991) determined vibrational spectra of  $B(OH)_3$  using extensive isotope labeling including  $^{10}B$ ,  $^2D$ , and  $^{18}O$ . Upon isotope substitution, say  $^1H \rightarrow ^2D$ , the frequencies of certain vibrational modes shift. These shifts can be observed spectroscopically and calculated theoretically, as shown above for  $^{10}B$ . The single most important frequency in  $B(OH)_3$  regarding the fractionation factor is  $\omega_3$ . It would therefore be crucial to better constrain its shift upon isotopic substitution. For this vibrational mode, I have calculated frequency shifts relative to  $^{11}B(OH)_3$  for the isotopomers  $^{10}B(OH)_3$ ,  $^{11}B(O)_3$ ,  $^{10}B(O)_3$ , and  $^{11}B(^{18}OH)_3$ , where  $O = ^{16}O$ . The results obtained using the analytical methods GVFF and UBFF, and *ab initio* MO theory (B-LYP/6-31+G(d)) are compared to observed frequency shifts in Table 12.

The observed increase of  $\omega_3$  for  $^{11}B(OH)_3 \rightarrow ^{10}B(OH)_3$  is 3.63 and 3.33% and hence not provides a constraint on theoretical methods because observations are as equivocal as the calculations (3.41 and 3.69%). Particularly, UBFF cannot be ruled out which predicts the largest  $\alpha_{(B3-B4)} = 1.0530$  of all



Table 12. Observed and calculated frequency shifts of  $\omega_3$  in isotopomers of B(OH)<sub>3</sub>.

Author/ Method <sup>a</sup>	Observed/ Calculated	$\omega_3$ <sup>11</sup> B(OH) <sub>3</sub>	$\omega_3'$ isotopomer	$\Delta\omega_3$ (%) <sup>b</sup>
<sup>10</sup> B(OH) <sub>3</sub>				
OY88	obs.	1426.2	1478.0	+3.63
G91	obs.	1429.0	1476.6	+3.33
GVFF	clc.	1440.8	1490.0	+3.41
UBFF	clc.	1440.0	1493.1	+3.69
BLYP	clc.	1389.7	1437.1	+3.41
<sup>11</sup> B(OD) <sub>3</sub>				
OY88	obs.	1426.2	1403.2	-1.61
G91	obs.	1429.0	1405.0	-1.68
GVFF	clc.	1440.8	1428.6	-0.85
UBFF	clc.	1440.0	1430.1	-0.69
BLYP	clc.	1389.7	1366.2	-1.69
<sup>10</sup> B(OD) <sub>3</sub>				
OY88	obs.	1426.2	1452.7	+1.86
G91	obs.	1429.0	1456.0	+1.89
GVFF	clc.	1440.8	1478.4	+2.61
UBFF	clc.	1440.0	1483.5	+3.02
BLYP	clc.	1389.7	1415.4	+1.85
<sup>11</sup> B( <sup>18</sup> OH) <sub>3</sub>				
OY88	obs.	1426.2	1409.7	-1.16
GVFF	clc.	1440.8	1417.8	-1.60
UBFF	clc.	1440.0	1421.3	-1.30
BLYP	clc.	1389.7	1373.1	-1.19

<sup>a</sup> OY88 = Ogden and Young (1988); G91 = Gilson (1991). GVFF and UBFF with  $\omega_3$  from Bethell and Sheppard (1955). BLYP = B-LYP/6-31+G(d).

$$^b \Delta\omega_3 = (\omega_3'/\omega_3 - 1) \times 100.$$

methods due to the large predicted shift in  $\omega_3$  (+3.69%) upon boron isotope substitution; rather UBFF's predicted shift is consistent with that reported by Ogden and Young (1988). It is important to note that the difference in the predicted shift between GVFF (1440.8 vs. 1490.0 cm<sup>-1</sup>) and UBFF (1440.0 vs. 1493.1 cm<sup>-1</sup>) of only 4 cm<sup>-1</sup> is responsible for a difference in predicted  $\alpha_{(B3-B4)}$  of about 10‰.

Regarding <sup>2</sup>D and <sup>18</sup>O substitution, *ab initio* MO theory predicts values closest to observations throughout. This is not surprising since changes in hydrogen and oxygen mass are certainly better represented in C<sub>3h</sub> symmetry than in D<sub>3h</sub> symmetry of the analytical methods (GVFF and UBFF). In summary, *ab initio* MO theory is likely superior to analytical methods when <sup>2</sup>D and <sup>18</sup>O substitution in B(OH)<sub>3</sub> are considered. However, this statement cannot be made regarding <sup>10</sup>B substitution because it is not supported by the data.

Corresponding results for B(OH)<sub>4</sub><sup>-</sup> are tabulated in Table 13 which summarizes observed and calculated shifts of  $\omega_1$  and  $\omega_3$  in the isotopomers <sup>10</sup>B(OH)<sub>4</sub> and <sup>11</sup>B(<sup>18</sup>OH)<sub>4</sub><sup>-</sup>. The data is sparse and the frequency shifts reported by Janda and Heller (1980) were actually recorded in solid Na(B[OH]<sub>4</sub>). Regarding  $\omega_3$  and <sup>11</sup>B/<sup>10</sup>B exchange, *ab initio* MO theory (B-LYP/6-31 + G(d)) predicts

Table 13. Observed and calculated frequency shifts of  $\omega_3$  and  $\omega_1$  in isotopomers of B(OH)<sub>4</sub><sup>-</sup>.

Author/ Method <sup>a</sup>	Observed/ Calculated	$\omega_i$ <sup>11</sup> B(OH) <sub>3</sub>	$\omega_i'$ isotopomer	$\Delta\omega_i$ (%) <sup>b</sup>
$\omega_3$ <sup>10</sup> B(OH) <sub>4</sub>				
JH85 <sup>c</sup>	obs.	934.0	955.0	+2.25
JH85 <sup>d</sup>	obs.	950.0	978.0	+2.95
GVFF	clc.	937.7	975.8	+4.06
UBFF	clc.	940.4	977.1	+3.90
BLYP	clc.	916.5	947.3	+3.36
$\omega_3$ <sup>11</sup> B( <sup>18</sup> OH) <sub>4</sub> <sup>-</sup>				
C85	obs.	955.0	914.0	-4.29
GVFF	clc.	937.7	929.4	-0.89
UBFF	clc.	940.4	930.5	-1.05
BLYP	clc.	916.5	907.2	-1.01
$\omega_1$ <sup>11</sup> B( <sup>18</sup> OH) <sub>4</sub> <sup>-</sup>				
C85	obs.	746.0	706.0	-5.36
GVFF	clc.	753.6	712.8	-5.41
UBFF	clc.	754.0	713.2	-5.41
BLYP	clc.	690.4	662.2	-4.08

<sup>a</sup> JH80 = Janda and Heller (1980); C85 = Campbell et al. (1985). GVFF and UBFF with  $\omega$ 's from Edwards et al. (1955). BLYP = B-LYP/6-31+G(d).

$$^b \Delta\omega_i = (\omega_i'/\omega_i - 1) \times 100.$$

<sup>c</sup> Infrared, solid Na(B[OH]<sub>4</sub>).

<sup>d</sup> Raman, solid Na(B[OH]<sub>4</sub>).

frequency shifts closest to observations, while analytical methods tend to overestimate this shift. Analytical methods also predict a larger shift for  $\omega_1$  and <sup>18</sup>O/<sup>16</sup>O exchange than B-LYP/6-31+G(d), but in this case the analytical methods are closer to observations. All theoretical methods largely agree on the shift of  $\omega_3$  upon <sup>18</sup>O/<sup>16</sup>O exchange (ca. -1%). The large shift of -4.3% reported by Campbell et al. (1985) is incompatible with the theory for this isotopic substitution and the reason remains unclear.

In summary, taken the Na(B[OH]<sub>4</sub>) data by Janda and Heller (1980) at face value and representative for B(OH)<sub>4</sub><sup>-</sup>, *ab initio* MO theory seems to have an advantage over the analytical methods regarding <sup>10</sup>B exchange. However, this is of little consequence for the calculated reduced partition function ratio and the fractionation factor. The  $\beta$  factor of B(OH)<sub>4</sub><sup>-</sup> calculated by B-LYP/6-31+G(d) (1.1744) is very close to those of GVFF (1.1760) and UBFF (1.1722) at 300 K which translates into a difference in  $\alpha_{(B3-B4)}$  of about 3‰. The big uncertainty in  $\alpha_{(B3-B4)}$  is mostly due to the different results for  $\beta_{B(OH)_3}$  for which, unfortunately, the data is inconclusive.

## 8. TEMPERATURE DEPENDENCE

Given the range of outcome for  $\alpha_{(B3-B4)}$  at 300 K calculated in the current paper, no recommendation will be made regarding  $\alpha$ 's temperature dependence, which equally depends on the frequencies/methods chosen. The true temperature sensitivity of the fractionation factor will likely fall somewhere between the smallest and largest temperature sensitivity of the methods

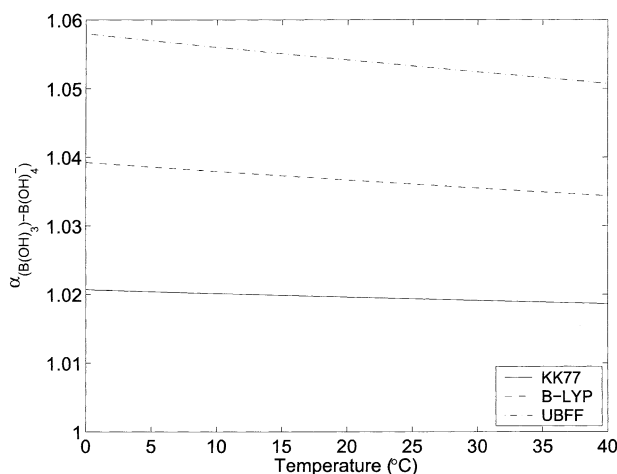


Fig. 3. Temperature dependence of  $\alpha_{(B3-B4)}$  for three different scenarios: after KK77 (solid line), using *ab initio* MO theory (B-LYP/6-31+G(d), dashed line), and UBFF (frequencies of  $B(OH)_3$  from Bethell and Sheppard, 1955,  $\beta_{B(OH)_4} = 1.1760$ , dot-dashed line).

discussed above. In the following, the possible temperature dependence of  $\alpha_{(B3-B4)}$  will therefore be illustrated by presenting two end-member and one intermediate scenario. Figure 3 and Table 14 summarize the temperature dependence of  $\alpha_{(B3-B4)}$  calculated (1) after KK77, (2) using *ab initio* MO theory (B-LYP/6-31+G(d)), and (3) using UBFF (frequencies of  $B(OH)_3$  from Bethell and Sheppard, 1955,  $\beta_{B(OH)_4} = 1.1760$ ). The results obey the following rule: The larger  $\alpha$ 's absolute value, the larger its temperature dependence. Over the temperature range from 0 to 40°C,  $\alpha_{(B3-B4)}$  decreases almost linearly by about 2, 5, and 7‰ for these three scenarios.

## 9. DISCUSSION

The theoretical calculations presented in this paper have resulted in different values for the stable boron isotope fractionation between dissolved boric acid and borate ion,  $\alpha_{(B3-B4)}$ , ranging from 1.0193 to 1.0530 at 300 K — in other words, from about 20 to more than 50‰. Which one is the correct value?

Table 14. Temperature dependence of  $\alpha_{(B3-B4)}$  for three different scenarios.

Temperature (°C)	$\alpha_{(B3-B4)}$		
	KK77 <sup>a</sup>	B-LYP/6-31+G(d) <sup>b</sup>	UBFF <sup>c</sup>
0	1.0207	1.0392	1.0580
5	1.0204	1.0386	1.0570
10	1.0201	1.0379	1.0560
15	1.0199	1.0373	1.0551
20	1.0196	1.0367	1.0542
25	1.0194	1.0361	1.0533
30	1.0191	1.0355	1.0524
35	1.0189	1.0349	1.0516
40	1.0186	1.0344	1.0507

<sup>a</sup> After Kakihana and Kotaka (1977).

<sup>b</sup> Using *ab initio* MO theory (B-LYP/6-31+G(d)).

<sup>c</sup> UBFF, frequencies of  $B(OH)_3$  from Bethell and Sheppard (1955),  $\beta_{B(OH)_4} = 1.1760$ .

My seemingly disappointing answer is that given the data and theoretical means currently available, a solid statement on the precise value of  $\alpha_{(B3-B4)}$  appears untenable. Although this result appears discouraging, it is probably realistic and an advancement over the hitherto credulous use of the value by Kakihana and Kotaka (1977) who used just one set of frequencies and one theoretical method. Moreover, the result of the present paper demonstrates the need for further research and encourages experimental work.

Having stated this, one may speculate about the true value of  $\alpha_{(B3-B4)}$  based on the analytical results obtained in sections 4 and 5. The most important factor affecting the outcome of those calculations is that the frequencies used for  $B(OH)_3$  by KK77 actually pertain to  $LaBO_3$ . All sets of frequencies that were measured on  $B(OH)_3$  show a larger  $\omega_3$  which leads to a larger  $\beta$  factor. If the  $\beta$  factor for  $B(OH)_4^-$  is close to the value given by KK77 and calculated here, then  $\alpha_{(B3-B4)}$  would indeed be larger than ~20‰. However, this requires  $\beta_{B(OH)_4^-}$  to be correct which mainly depends on the reliability of the frequencies measured for  $B(OH)_4^-$ . As mentioned in section 4, the relevant frequencies of  $B(OH)_4^-$  are  $\omega_3$  and  $\omega_4$ . While the value of  $\omega_3$  appears reliable, to my knowledge only one value has been reported for  $\omega_4$  of dissolved  $B(OH)_4^-$  (although supported by data on  $Na[B(OH)_4]$ ). The different theoretical methods lead to approximately the same  $\beta$  factor for  $B(OH)_4^-$ , differing only by about 3‰ for  $B(OH)_4^-$  (section 5.3) but by 11‰ for  $B(OH)_3$  (section 5.1). In summary, if the following presumptions are made: (1) measured  $\omega_4$  in  $B(OH)_4^-$  is reliable, (2)  $\omega_3$  in  $B(OH)_3$  is ~1450  $cm^{-1}$ , and (3) the applied theories introduce an error less than about 10‰, then  $\alpha_{(B3-B4)} > 20‰$ , perhaps 30‰ or larger.

One apparent shortcoming of the analytical calculations is that in reality  $B(OH)_3$  and  $B(OH)_4^-$  do not obey  $D_{3h}$  and  $T_d$  symmetry, respectively. Regarding molecular vibration, these symmetries imply that the OH group behaves as a single mass point which is of course not true because the O–H bond is a usual covalent bond which introduces more degrees of freedom and hence more fundamental frequencies. As a result, the molecules should actually be treated as obeying more complex symmetries in the calculations. Using *ab initio* molecular orbital theory,  $\alpha_{(B3-B4)}$  has been determined using full  $C_{3h}$  and  $S_4$  symmetry for  $B(OH)_3$  and  $B(OH)_4^-$ , respectively. The results for  $\alpha_{(B3-B4)}$  vary between 25 and 39‰, given that HF/STO-3G is inadequate for the description of  $B(OH)_4^-$ . Furthermore, assuming that methods including diffusive functions are more appropriate for the molecular structure of the dissolved boron species,  $\alpha_{(B3-B4)}$  is roughly between 30 and 40‰.

The comparison between measured and calculated frequency shifts in various isotopomers considering  $^{10}B$ ,  $^2D$ , and  $^{18}O$  labeling suggest a certain advantage of *ab initio* MO theory over analytical methods. This is most evident for vibrational modes which require consideration of the full symmetry of the molecules. However, it does not provide a constraint on the outcome for  $\alpha_{(B3-B4)}$ .

### 9.1. Sensitivity of $\alpha_{(B3-B4)}$ to Frequencies and Methods

Based on the evaluation of measured frequencies and methods discussed above, the following estimated sensitivities of  $\alpha_{(B3-B4)}$  to those parameters are given. Frequencies of  $B(OH)_3$ : About 6‰

if TS69's results are discarded (Table 5). Frequencies of B(OH)<sub>4</sub><sup>-</sup>: insufficient data. Analytical methods (GVFF vs. UBFF): About 11‰ (Tables 7 and 8). *Ab initio* molecular orbital theory: About 10‰ if HF/STO-3G is discarded and only basis sets including diffuse functions are considered (Table 11).

## 9.2. Comment on Available Experimental Studies

Several laboratory studies have dealt with  $\alpha_{(B3-B4)}$  and may be misinterpreted to have directly determined  $\alpha_{(B3-B4)}$  experimentally. For example, Kakihana et al. (1977) determined boron isotope fractionation between an ion-exchange resin and an external solution. This fractionation factor is denoted  $^{10}_{11}S$  (their Eqn. 1) which is however not equal to  $\alpha_{(B3-B4)}$ , denoted  $^{10}_{11}K$  (their Table 2). The values for  $\alpha_{(B3-B4)}$  reported in their Table 2 were taken from Kotaka and Kakihana (1977) and Kakihana and Kotaka (1977), determined on a purely theoretical basis. Thus, Kakihana et al. (1977) neither reported a measured  $\alpha_{(B3-B4)}$  value nor an estimate of it based on experimental results. Sonoda et al. (2000) determined boron isotope fractionation due to adsorption of dissolved boron species on a N-methyl-D-glucamine resin phase. This fractionation is denoted  $S$  (their Eqn. 4) which is however not equal to  $\alpha_{(B3-B4)}$ , denoted  $S_0$  (their Eqn. 3). In order to fit the data for  $S$ , they use a value of  $\alpha_{(B3-B4)} = 1.029$ . Thus, based on several assumptions and approximations, a value of 1.029 fits their adsorption data and provides an estimate of  $\alpha_{(B3-B4)}$  but its value has not been directly experimentally determined.

## 10. CONCLUSIONS

In the current paper, stable boron isotope fractionation between dissolved boric acid and borate ion has been investigated. To the best of my knowledge, an experimentally determined value is not available until this day and, as a result, theoretically determined values have been widely applied in the field. The probably most frequently cited value in geochemical applications of  $\alpha_{(B3-B4)} = 1.0193$  at 300 K calculated by Kakihana and Kotaka (1977) is likely to be incorrect, the theoretical evidence derived in this paper suggests it to be larger. Certainly, the implied accuracy of a tenth of a per mil is untenable. Given the data and theoretical means currently available, the full range of values for  $\alpha_{(B3-B4)}$  varies between ~1.020 and ~1.050 at 300 K. However, several arguments suggest that the value is  $\geq 1.030$ .

I conclude that in order to thoroughly anchor the thermodynamic basis of the boron pH proxy, it is inevitable to determine the fractionation factor between dissolved boric acid and borate ion experimentally. For the time being, those opposing the boron pH proxy should keep in mind, however, that lack of an accurate value for this factor does not impair the application of the proxy, provided that calibrations are used that pertain to single species.

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#### APPENDIX A: GVFF FORCE CONSTANTS FROM VIBRATIONAL FREQUENCIES OF $\text{B}(\text{OH})_3$

The  $G$  and  $F$  matrices for a  $\text{XY}_3$  molecule of  $D_{3h}$  symmetry can be written as:

$$G = \begin{pmatrix} G_{11} & 0 & 0 & 0 \\ 0 & G_{22} & 0 & 0 \\ 0 & 0 & G_{33} & G_{34} \\ 0 & 0 & G_{34} & G_{44} \end{pmatrix};$$

$$F = \begin{pmatrix} F_{11} & 0 & 0 & 0 \\ 0 & F_{22} & 0 & 0 \\ 0 & 0 & F_{33} & F_{34} \\ 0 & 0 & F_{34} & F_{44} \end{pmatrix}$$

with

$$G_{11} = \mu_y$$

$$G_{22} = (3/d^2)(\mu_y + 3\mu_x)$$

$$G_{33} = \mu_y + 3\mu_x/2$$

$$G_{34} = (3\sqrt{3}/2d)\mu_x$$

$$G_{44} = (3/d^2)(\mu_y + 3\mu_x/2).$$

where  $\mu_i$ 's are the reciprocal masses of X and Y and  $d$  is the bond distance; for  $\text{B}(\text{OH})_3$ ,  $d = 1.38 \text{ \AA}$ . Recalling the secular equation

$$|\mathbf{GF} - \mathbf{E}\lambda| = 0,$$

$F_{11}$  and  $F_{22}$  can readily be calculated:

$$F_{11} = \lambda_1/G_{11}$$

$$F_{22} = \lambda_2/G_{22},$$

using  $\lambda_i = 4\pi^2c^2\omega^2$  and  $\omega$  as given in Table 1. Note that in order to yield  $F_i$ 's in units of  $\text{N m}^{-1}$  as given in Table 2, masses have to be expressed in kg and  $d$  in  $\text{\AA}$ . The force constants  $F_{33}$ ,  $F_{34}$  and  $F_{44}$  are to be determined from:

$$F_{33}G_{33} + F_{44}G_{44} + 2F_{34}G_{34} = \lambda_3 + \lambda_4 \quad (\text{A1})$$

$$\begin{vmatrix} G_{33} & G_{34} \\ G_{34} & G_{44} \end{vmatrix} \begin{vmatrix} F_{33} & F_{34} \\ F_{34} & F_{44} \end{vmatrix} = \lambda_3\lambda_4. \quad (\text{A2})$$

But now we are left with three force constants and only two frequencies. TS69 tackled the problem by assuming that the ratio of force constants ( $f$ 's) and kinetic constants ( $K$ 's) is the same (for definitions of  $f$ 's, see TS69):

$$F_{34} = F_{44}d(f'_{\text{da}} - f''_{\text{da}})/d^2(f_{\alpha} - f_{\alpha\alpha}) = F_{44}d(K'_{\text{da}} - K''_{\text{da}})/d^2(K_{\alpha} - K_{\alpha\alpha}) \quad (\text{A3})$$

which relates  $F_{34}$  to  $F_{44}$ , where

$$\begin{aligned}
K'_{\text{d}\alpha} &= -\mu_x/\sqrt{3}\mu_y(\mu_y + 3\mu_x) & G_{11} &= \mu_y \\
K''_{\text{d}\alpha} &= \mu_x/2\sqrt{3}\mu_y(\mu_y + 3\mu_x) & G_{33} &= (3/2)\mu_x + \mu_y \\
K_{\alpha} &= (2\mu_y + 3\mu_x)/9\mu_y/(\mu_y + 3\mu_x) & G_{34} &= \mu_x \\
K_{\alpha\alpha} &= -(2\mu_y + 3\mu_x)/18\mu_y/(\mu_y + 3\mu_x). & G_{44} &= (9/2)\mu_x + 3\mu_y \\
& & GG &= 3\mu_y^2 + 9\mu_x\mu_y
\end{aligned}$$

Substituting Eqn. A3 into Eqns. A1 and A2 and eliminating e.g.  $F_{33}$  from the latter two equations yields a quadratic equation for  $F_{33}$  and all force constants can be obtained (Table 2). Note that the values in Tables 1 and 2 referring to BO<sub>3</sub> were calculated using  $m_x = 10.81$  (average boron mass) and  $m_y = 15.9994$  amu (average oxygen mass) and those referring to <sup>11</sup>B(OH)<sub>3</sub> and <sup>10</sup>B(OH)<sub>3</sub> using  $m'_x = 11.0093$ ,  $m_x = 10.0129$ , and  $m_y = 17.0073$  amu (average oxygen plus hydrogen mass).

### APPENDIX B: GVFF FORCE CONSTANTS FROM VIBRATIONAL FREQUENCIES OF B(OH)<sub>4</sub><sup>-</sup>

The  $G$  and  $F$  matrices for a XY<sub>4</sub> molecule of  $T_d$  symmetry can be written as:

$$\mathbf{G} = \begin{pmatrix} G_{11} & 0 & 0 & 0 \\ 0 & G_{22} & 0 & 0 \\ 0 & 0 & G_{33} & G_{34} \\ 0 & 0 & G_{34} & G_{44} \end{pmatrix};$$

$$\mathbf{F} = \begin{pmatrix} F_{11} & 0 & 0 & 0 \\ 0 & F_{22} & 0 & 0 \\ 0 & 0 & F_{33} & F_{34} \\ 0 & 0 & F_{34} & F_{44} \end{pmatrix}$$

with

$$\begin{aligned}
G_{11} &= \mu_y \\
G_{22} &= 3\mu_y \\
G_{33} &= (3/4)\mu_x + \mu_y \\
G_{34} &= -(8/3)\mu_x \\
G_{44} &= (16/3)\mu_x + 2\mu_y.
\end{aligned}$$

where  $\mu_i$ 's are the reciprocal masses of X and Y. As in the preceding section,  $F_{11}$  and  $F_{22}$  can readily be calculated, see Table 1. The force constants  $F_{33}$ ,  $F_{34}$  and  $F_{44}$  are again to be determined from only two frequencies. Krebs et al. (1967) used the method by Fadini (1966) (see section 5.2) which gives the force constants in Table 2.

### APPENDIX C: UREY-BRADLEY FORCE FIELD FOR B(OH)<sub>3</sub>

The equations for Urey-Bradley force constants for planar XY<sub>3</sub> molecules derived by Janz and Mikawa (1960) are given in the following. The force constants used in UBFF are not be confused with those used in GVFF. In general, force constants have significance only with respect to the potential field in which they appear (Ross, 1972). For the in-plane vibrations, the four force constants  $K$ ,  $H$ ,  $F$ , and  $F'$ , have to be determined from three frequencies using

$$F' = \gamma F \quad (\text{C4})$$

where  $\gamma = -1/10$  or  $-1/13$ . The equations for the normal frequencies are (note that the  $\Phi_{ii}$  used below are different from the  $F_{ii}$  used in GVFF):

$$\begin{aligned}
\lambda_1 &= G_{11}\Phi_{11} \\
\lambda_3 + \lambda_4 &= G_{33}\Phi_{33} - (9/4)G_{34}\Phi_{34} + G_{44}\Phi_{44} = :s \\
\lambda_3\lambda_4 &= [\Phi_{33}\Phi_{44} - (3/16)\Phi_{34}^2]GG = :p
\end{aligned}$$

where

and

$$\begin{aligned}
\Phi_{11} &= K + 3F \\
\Phi_{33} &= K + (3/4)F' + (3/4)F \\
\Phi_{34} &= F' + F \\
\Phi_{44} &= H - (3/4)F' + (1/4)F.
\end{aligned}$$

Using Eqn. C4 and eliminating  $\Phi_{44}$  (essentially  $H$ ), yields a quadratic equation for  $F$ :

$$a_2F^2 + a_1F + a_0 = 0$$

with

$$\begin{aligned}
a_2 &= -\frac{1}{16} [9(\gamma - 3)^2G_{33} + 27(\gamma - 3)(\gamma + 1)G_{34} - 3(\gamma + 1)^2G_{44}] \\
a_1 &= \frac{1}{4} [3(\gamma - 3)s - 6(\gamma - 3)\lambda_1G_{33}/\mu_y + 9(\gamma + 1)\lambda_1G_{34}/\mu_y] \\
a_0 &= s\lambda_1/\mu_y - (\lambda_1/\mu_y)^2G_{33} - pG_{44}/GG.
\end{aligned}$$

Once this equation is solved,  $F'$  is determined from Eqn. C4. Furthermore,

$$\begin{aligned}
\Phi_{33} &= (\lambda_1/\mu_y) + 3F(\gamma - 3)/4 \\
\Phi_{34} &= F(\gamma + 1) \\
\Phi_{44} &= (p/GG + 3\Phi_{34}^2/16)/\Phi_{33}
\end{aligned}$$

and finally:

$$\begin{aligned}
K &= (\lambda_1/\mu_y) - 3F \\
H &= \Phi_{44} + F(3\gamma - 1)/4
\end{aligned}$$

from which all force constants  $K$ ,  $H$ ,  $F$ , and  $F'$  were calculated. Using vibrational frequencies from Bethell and Sheppard (1955), one obtains:

$$[K \ H \ F \ F'] = [551.41 \ 36.68 \ 74.86 \ -7.49] \text{ N m}^{-1}$$

### APPENDIX D: UREY-BRADLEY FORCE FIELD FOR B(OH)<sub>4</sub><sup>-</sup>

Urey and Bradley (1931) suggested repulsive forces between corner atoms of tetrahedral molecules and introduced a potential energy term proportional to  $1/r_j^n$ , where  $r_j$  is the distance between two corner atoms. Their approach leads to three force constants  $k_1$ ,  $k_2$ , and  $\gamma_3$  and the value of  $n$  to be determined from spectroscopic data.

The constants were determined from the following linear equations (Urey and Bradley, 1931):

$$\begin{aligned}
x_1 &= \omega_1^2 = k'_1 + (n + 1)\gamma'_3 \\
x_2 &= \omega_2^2 = k'_2 + \frac{n + 2}{4} \gamma'_3 \\
x_3 &= \omega_3^2 + \omega_4^2 = \frac{1}{3} \left( \frac{3n + 2}{2} \gamma'_3 + 2k'_1 + k'_2 \right) + \frac{m_y}{3\mu} (2\gamma'_3 + k'_1 + 2k'_2)
\end{aligned}$$

where  $k'_1$ ,  $k'_2$ , and  $\gamma'_3$  are equal to  $k_1$ ,  $k_2$ , and  $\gamma_3$  divided by  $4\pi^2c^2m_y$  and  $\mu = m_xm_y/(4m_y + m_x)$ . This can be solved for  $\gamma'_3$ :

$$\gamma'_3 = \frac{2}{3} \cdot \frac{\left( 2 + \frac{m_y}{\mu} \right) x_1 + \left( 1 + 2 \frac{m_y}{\mu} \right) x_2 - 3x_3}{1 + \frac{n}{2} + \frac{m_y n}{\mu}}$$

which readily yields expressions for  $k'_1$ ,  $k'_2$ . Good agreement with the measured  $\omega$ 's for  $\text{B(OH)}_4^-$  given by Edwards et al. (1955) (Table 6), was obtained for  $n = 10$ . The force constants are then calculated as:

$$[k_1 \quad k_2 \quad \gamma_3] = [199.20 \quad 42.90 \quad 33.68] \text{ N m}^{-1}$$

Because of the simple nature of the vibrational modes of  $\omega_1$  and  $\omega_2$ , in this case the following relationship between the force constants of UBFF and GVFF exist:

$$F_{11} = k_1 + (n + 1)\gamma_3$$

$$F_{22} = \frac{1}{3} \left( k_2 + \frac{n + 2}{4} \gamma_3 \right)$$

which gives  $F_{11} = 569.68$  and  $F_{22} = 47.98 \text{ N m}^{-1}$ , being virtually identical to the values given by Krebs et al. (1967) (Table 2).

Finally, with those force constants, the frequencies of  $^{11}\text{B(OH)}_4^-$  and  $^{10}\text{B(OH)}_4^-$  (Table 1) and the  $\beta$  factor can be calculated. The result is  $\beta_{\text{B(OH)}_4^-} = 1.1722$  (Table 8).