

On the proper use of the Bigeleisen–Mayer equation and corrections to it in the calculation of isotopic fractionation equilibrium constants

Qi Liu^a, John A. Tossell^{b,c}, Yun Liu^{a,*}

^a State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

^b Department of Chemistry and Institute for Basic Energy Science and Technology, George Washington University, Washington, DC 20052, USA

^c Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA

Received 10 March 2010; accepted in revised form 7 September 2010; available online 17 September 2010

Abstract

The Bigeleisen–Mayer equation has been the theoretical corner-stone of stable isotope geochemistry for decades. It is necessary to use harmonic frequencies to justify several of the approximations and the Teller–Redlich product rule employed inside the Bigeleisen–Mayer equation. However, since the publication of the Bigeleisen–Mayer equation in 1947, many researchers have ignored this important requirement. They either directly used experimentally observed fundamental frequencies from vibrational spectra, which include anharmonicity contributions, or used harmonic frequencies from quantum chemical calculations but improperly scaled the frequencies to fit the experimentally observed fundamentals. Such errors have become one of the major error sources in the prediction of equilibrium isotopic fractionation. Moreover, many researchers still use the Bigeleisen–Mayer equation to handle H/D exchange reactions, even though it has been established that the Bigeleisen–Mayer equation is not sufficient for dealing with H/D isotope exchange reactions. This mishandling could easily cause several per mil errors in isotope fractionation factor.

Since quantum chemical calculations now play a central role in understanding stable isotope fractionation, it is necessary to clarify these important issues. Several simple gaseous molecules are used as examples in this study to show how important it is to use pure harmonic frequencies instead of experimental fundamentals within the Bigeleisen–Mayer equation and to use theoretical methods beyond the Bigeleisen–Mayer equation when dealing with the H/D isotope exchange reactions. Adapting the work of Richet et al. (1977), we also discussed a series of modified formalisms to include higher-order corrections to the Bigeleisen–Mayer equation, such as anharmonicity, quantum mechanical rotation, centrifugal distortion, vibration–rotation coupling, hindered internal rotation, etc. The issues and methods discussed in this study can help to improve the accuracy of theoretical prediction of equilibrium stable isotope fractionation in geochemistry.

© 2010 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

Theoretical calculation of isotopic fractionations applying statistical mechanical methods was suggested almost

one century ago (Lindemann, 1919; Lindemann and Aston, 1919; Urey and Rittenberg, 1933; Urey and Greiff, 1935). Urey (1947) and Bigeleisen and Mayer (1947) independently proposed a formalism to estimate the isotopic fractionations without calculating the moments of inertia through employing the Teller–Redlich product rule (Redlich, 1935). In addition, Urey (1947) first brought up the idea of using O isotopes as the paleothermometer which immediately drew much attention of geologists and triggered the formation of stable isotope geochemistry

* Corresponding author. Address: State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, 46 Guanshui Rd., Guiyang 550002, China. Tel.: +86 851 5890798.

E-mail address: liuyun@vip.gyig.ac.cn (Y. Liu).

(Urey et al., 1951). For decades, this method (so-called Bigeleisen–Mayer equation or the Urey model) has been the theoretical corner-stone of stable isotope geochemistry. The advantage of using this method is that it largely simplified the calculation procedure by cancelling out as many identical energy terms as possible before the final numerical calculation, concentrating on the vibrational frequency shifts of the different isotopologues (Bigeleisen, 1965).

Theoretically, the Bigeleisen–Mayer equation needs pure harmonic vibrational frequencies to justify the harmonic oscillator and rigid rotator approximations and the Teller–Redlich product rule used within it. Wilson et al. (1955) have shown how to obtain the exact expression of the Teller–Redlich product rule by employing harmonic oscillator and rigid rotator approximations. However, this requirement of using harmonic frequencies has been largely ignored. One reason is that, except for diatomic molecules, it is very difficult to obtain pure harmonic frequencies from the experimental spectroscopic data, especially for polyatomic molecules with low symmetry. Therefore, many researchers, who did not have any practical means to obtain pure harmonic frequencies, chose to either use the experimental fundamentals to build the harmonic force field or even directly use the experimental fundamentals in the Bigeleisen–Mayer equation, partly because the requirement of accuracy was not as high as it is today.

The development of computational quantum chemistry dramatically changed the scenario because it could easily provide pure harmonic frequencies (e.g., Harris, 1995). There are an increasing number of such studies in stable isotope geochemistry field using quantum chemistry (e.g., Driesner and Seward, 2000; Oi, 2000; Oi and Yanase, 2001; Schauble et al., 2003, 2006; Jarzecki et al., 2004; Schauble, 2004, 2007; Anbar et al., 2005; Liu and Tossell, 2005; Tossell, 2005; Zeebe, 2005; Seo et al., 2007; Rustad and Bylaska, 2007; Domagal-Goldman and Kubicki, 2008; Otake et al., 2008; Rustad and Zarzycki, 2008; Rustad et al., 2008; Domagal-Goldman et al., 2009; Zeebe, 2009; Li et al., 2009). However, some researchers use scale factors to scale the harmonic frequencies in order to match experimental fundamentals. Usually, recommended frequency scale factors include corrections for the inadequacy of the quantum chemistry theoretical method used and the anharmonicity contribution. For example, the scale factor typically used to match Hartree–Fock harmonic vibrational frequencies to experimental fundamentals is about 0.90, while that needed to match harmonic frequencies for highly correlated methods (like QCISD and CCSD) to experimental fundamentals is about 0.95 (Cramer, 2002, see Table 9.3). This suggests that corrections for lower level methods like Hartree–Fock are on the order of 5% and anharmonicity corrections are also about 5%. The scaling for anharmonicity, however, is not necessary for the requirement of using harmonic frequencies in the Bigeleisen–Mayer equation. We note that the method used in Liu and Tossell (2005) to calculate the $^{11}\text{-}^{10}\text{B}$ fractionation factor between $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$, uses a scale factor to match calculated harmonic vibrational frequencies to experimental fundamentals, probably an undesirable procedure.

In addition, Bigeleisen and Mayer (1947) have pointed out that the harmonic approximation and rigid rotation is not sufficient for H/D exchange. However, for a long time, many researchers ignored this point, erroneously using the Bigeleisen–Mayer equation in some H/D isotope exchange reactions.

This study shows the importance of using harmonic frequencies in the Bigeleisen–Mayer equation. Then, by following the work of Richet et al. (1977), we provide a series of modified formalisms to include higher-order corrections to the Bigeleisen–Mayer equation, such as anharmonicity, quantum mechanical rotation, centrifugal distortion, vibration–rotation coupling and hindered internal rotation corrections (other corrections such as nuclear field shift effect, nuclear spin effect and pressure effect are already well addressed and therefore not given in this study, e.g., Bigeleisen (1996) and Polyakov and Kharlashina (1994)). These corrections are important for the H/D isotope exchange reactions. The principles illustrated in this work will help to improve the accuracy of theoretical prediction of stable isotope fractionation, which is a rapidly growing field in geochemistry.

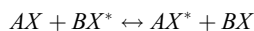
The importance of using harmonic frequencies in the Bigeleisen–Mayer equation has recently been pointed out by Rustad and Bylaska (2007) and Zeebe (2009). For the B isotope fractionation between $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$, Rustad and Bylaska (2007) found that anharmonic frequencies gave a fractionation equilibrium constant of 0.86 while harmonic frequencies gave 1.028, in agreement with the directly measured experimental value (Klochko et al., 2006). Zeebe (2009) performed very demanding anharmonic frequency calculations for CO_3^{2-} ...water clusters and established that anharmonic corrections were no more than 2‰ for O isotope fractionation. However, his approach only corrects the frequencies for anharmonic effects and ignores many other terms (like G_0) which we discuss below.

2. METHODS

2.1. Bigeleisen–Mayer equation

The Bigeleisen–Mayer equation (Bigeleisen and Mayer, 1947; Urey, 1947) is the method mainly used for determining the equilibrium isotope exchange constant K in stable isotope geochemistry. There are several good reviews of this method (e.g., Richet et al., 1977; O’Neil, 1986; Criss, 1991, 1999; Chacko et al., 2001; Schauble, 2004 and others).

For an isotope exchange reaction:



where the “*” denotes the one with the heavier isotope. K can be calculated from the isotope partition function ratios of those two molecules:

$$K = \frac{\left(\frac{Q_{\text{tran}}^* Q_{\text{rot}}^* Q_{\text{vib}}^* Q_{\text{elec}}^* \dots}{Q_{\text{tran}} Q_{\text{rot}} Q_{\text{vib}} Q_{\text{elec}} \dots} \right)_{AX}}{\left(\frac{Q_{\text{tran}}^* Q_{\text{rot}}^* Q_{\text{vib}}^* Q_{\text{elec}}^* \dots}{Q_{\text{tran}} Q_{\text{rot}} Q_{\text{vib}} Q_{\text{elec}} \dots} \right)_{BX}} \quad (1)$$

Here, the partition function (Q) is given by (e.g., McQuarrie and Simon, 1999)

$$Q = \sum_m \exp\left(-\frac{E_m}{kT}\right) \quad (2)$$

where E_m , k and T stand for the energy of state m , the Boltzmann constant and the temperature in Kelvin, respectively.

The Bigeleisen–Mayer equation uses harmonic oscillator and rigid rotator approximations for vibrational and rotational partition functions. The translational, rotational and vibrational partition functions can be written as (e.g., McQuarrie and Simon, 1999)

$$Q_{trans} = V \left(\frac{2\pi MkT}{h^2}\right)^{3/2} \quad (3)$$

$$Q_{rot} = \frac{\pi^{1/2}(8\pi^2 kT)^{3/2}(I_A I_B I_C)^{1/2}}{sh^3} \quad (4)$$

$$Q_{vib} = \prod_i \frac{\exp(-hc\omega_i/2kT)}{1 - \exp(-hc\omega_i/kT)} \quad (5)$$

where V is the volume, M is the mass, I_A is the moment of inertia around axis A of rotation, h is the Planck constant, s is the symmetry number of the molecule and ω_i is the harmonic frequency of normal mode i in the unit of cm^{-1} . Eqs. (3) and (4) are in classical partition function forms while Eq. (5) is in quantum mechanics form (Singh and Wolfsberg, 1975). This choice of partition functions is due to that the translation and the rotation can be described already quite accurately in classical forms at room temperature and above.

If we further employ the Teller–Redlich product rule (Redlich, 1935; Wilson et al., 1955):

$$\left(\frac{I_A^* I_B^* I_C^*}{I_A I_B I_C}\right)^{1/2} \left(\frac{M^*}{M}\right)^{3/2} \left(\frac{m}{m^*}\right)^{3n/2} \prod_i \frac{u_i}{u_i^*} = 1 \quad (6)$$

then, the reduced isotope partition function ratio (RPFR) or “(s*/s) f ” of an isotopologue pair (e.g., AX^*/AX) can be expressed in terms of normal-mode frequencies, ω_i , before and after isotope substitution (Bigeleisen and Mayer, 1947):

$$\text{RPFR}(AX^*/AX) = \frac{s^*}{s} f = \prod_i^{3n-6} \frac{u_i(AX^*) \exp[-u_i(AX^*)/2] \{1 - \exp[-u_i(AX)]\}}{u_i(AX) \exp[-u_i(AX)/2] \{1 - \exp[-u_i(AX^*)]\}} \quad (7)$$

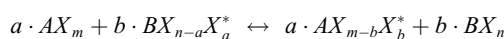
where

$$u_i = \frac{hc\omega_i}{kT} \quad (8)$$

The equilibrium constant for a single-isotope-substitution reaction is:

$$K = \frac{\left(\frac{s}{s^*}\right)_{AX} \text{RPFR}(AX^*/AX)}{\left(\frac{s}{s^*}\right)_{BX} \text{RPFR}(BX^*/BX)} \quad (9)$$

Usually, the isotopic fractionation factor α is used by geochemists instead of K . Consider a multiple-isotopes-exchange equilibrium:



According to the definition of α , we have

$$\begin{aligned} \alpha_{AX_m-BX_n} &= \frac{R_{AX_m}}{R_{BX_n}} \\ &= \frac{[AX_{m-1}X^*] + 2[AX_{m-2}X_2^*] + \cdots + m[AX_m^*]}{[AX_{m-1}X] + 2[AX_{m-2}X_2] + \cdots + m[AX_m]} \\ &\quad \bigg/ \frac{[BX_{n-1}X^*] + 2[BX_{n-2}X_2^*] + \cdots + n[BX_n^*]}{[BX_{n-1}X] + 2[BX_{n-2}X_2] + \cdots + n[BX_n]} \\ &\approx \left(\frac{[AX_m^*]}{[AX_m]}\right)^{1/m} \bigg/ \left(\frac{[BX_n^*]}{[BX_n]}\right)^{1/n} = K^{1/mn} \end{aligned} \quad (10)$$

if all the isotopes of interest are in the equivalent atom positions and fully substituted (i.e., $a = n$ and $b = m$). Note that α is equal to $K^{1/mn}$ only if we ignore the excess factors (Richet et al., 1977). The excess factor results from the deviation from the rule of geometric mean and is only becoming meaningful when the concentrations of related minor isotopologues (e.g., HD^{18}O for water molecule, D_2 for H_2 , etc.) become significant, which are unlikely situations in the majority of geological studies. For the partially isotope substituted reaction (i.e., $a < n$ and $b < m$), then

$$\alpha = \left[\left(\frac{s^*}{s}\right)_{AX}^{1/b} \bigg/ \left(\frac{s^*}{s}\right)_{BX}^{1/a} \right] \times K^{1/ab} \quad (11)$$

When one molecule contains several non-equivalent atoms of an element, more careful mathematic treatment should be applied in the specific cases. Hereafter, we define β factor as (when ignore the excess factor):

$$\begin{aligned} \beta(AX_{m-1}X^*/AX_m) &= \text{RPFR}(AX_{m-1}X^*/AX_m) \\ \beta(AX_{m-b}X_b^*/AX_m) &= \text{RPFR}(AX_{m-b}X_b^*/AX_m)^{1/b} \end{aligned} \quad (12)$$

Note that the ignored excess factors should be different for the different isotopic pairs considered in the isotopic equilibrium.

2.2. Anharmonic correction

Bigeleisen and Mayer (1947) noticed that the frequency shifts for hydrogen isotope substitution were large and the rotation of hydrogen-containing molecules did not quite follow classical rotation. Later studies (e.g., Benedict et al., 1956; Khachkuruzov, 1959) realized that these large shifts of frequencies contain large contributions from anharmonicity. At the harmonic level, the energy of vibration can be expressed as

$$E_n/hc = \sum_i \omega_i \left(n_i + \frac{1}{2}\right) \quad (13)$$

where n_i is the quantum state of vibration (or vibrational quantum number) of normal mode i . On the basis of Eq. (2), the harmonic partition functions of vibrational ground state and excited states are:

$$Q_{hZPE} = \prod_i \exp(-u_i/2) \quad (14)$$

$$Q_{hEXC} = \prod_i \frac{1}{1 - \exp(-u_i)} \quad (15)$$

If including anharmonic corrections, the vibrational energy can be expressed as (e.g., [Nielsen, 1951](#); [Barone, 2004](#)):

$$E_n/hc = G_0 + \sum_i \omega_i \left(n_i + \frac{1}{2} \right) + \sum_{i < j} x_{ij} \left(n_i + \frac{1}{2} \right) \left(n_j + \frac{1}{2} \right) \quad (16)$$

where G_0 and x_{ij} are constants, both in units of cm^{-1} . The expression for G_0 is very complicated and may not be completely identical in different publications ([Shaffer and Schuman, 1944](#); [Wolfsberg, 1969](#); [Wolfsberg et al., 1970](#); [Zhang et al., 1993](#); [Barone, 2005](#)). We will use the expression of G_0 suggested by [Barone \(2005\)](#) (as ξ_0 in his paper) because it has been used in the popular Gaussian 03 software package ([Frisch et al., 2004](#)). It is given by:

$$G_0 = \frac{\hbar}{128\pi c} \left\{ \sum_i \frac{F_{iii}}{\lambda_i} - \frac{7}{9} \sum_i \frac{F_{iii}^2}{\lambda_i^2} + 3 \sum_{i \neq j} \frac{F_{ijj}^2}{\lambda_j(4\lambda_j - \lambda_i)} - 16 \sum_{i > j > k} \frac{F_{ijk}^2}{\Delta_{ijk}} - 16 \sum_{\alpha=x,y,z} \mu_{\alpha\alpha}^0 \left[1 + 2 \sum_{i > j} (\zeta_{ij}^\alpha)^2 \right] \right\} \quad (17)$$

where $\hbar = h/2\pi$, λ_i , F_{ijk} , F_{iii} are the second, third and fourth order normal coordinate force constants, $\mu_{\alpha\alpha}^0$ is the element of the modified inverse inertia tensor, ζ_{ij}^α is a Coriolis coupling constant. The relationship between harmonic frequency (ω_i) and quadratic force constant (λ_i) at mode i is

$$\omega_i = \lambda_i^{1/2}/2\pi c \quad (18)$$

and

$$\Delta_{ijk} = \lambda_i^2 + \lambda_j^2 + \lambda_k^2 - 2[\lambda_i\lambda_j + \lambda_i\lambda_k + \lambda_j\lambda_k] \quad (19)$$

When n (quantum state of vibration) is zero, Eq. (16) gives the energy of vibrational ground state as

$$E_0/hc = G_0 + \frac{1}{2} \sum_i \omega_i + \frac{1}{4} \sum_{i < j} x_{ij} \quad (20)$$

where x_{ij} is the anharmonic constant of coupling between normal mode i and j , which also can be expressed in terms of quadratic, cubic and quadric normal mode force constants introduced above. According to Eqs. (16) and (20), the partition functions corrected for harmonic vibrational ground state and excited states can be given by the following forms ([Vojta, 1961](#); [Wolfsberg, 1969](#)):

$$Q_{AnZPE} = \exp(-hcG_0/kT) \prod_{i < j} \exp(-hc x_{ij}/4kT) \quad (21)$$

$$Q_{AnEXC} = 1 - \frac{2hc}{kT} \sum_i \frac{x_{ii} \exp(u_i)}{[\exp(u_i) - 1]^2} - \frac{hc}{2kT} \sum_{i < j} \frac{x_{ij} [\exp(u_i) + \exp(u_j)]}{[\exp(u_i) - 1][\exp(u_j) - 1]} \quad (22)$$

The counterpart of Eq. (22), which is using fundamental frequencies instead of harmonic ones, is shown in Eq. (26). Eq. (22) was further approximated by [Richet et al. \(1977\)](#) into the Eq. (49) in their paper.

The fundamental frequency ν_i which is the main absorption line in IR or Raman spectrograph can be expressed as a function of harmonic frequency (ω_i) and anharmonic constant (x_{ij}) in theory (e.g., [Barone, 2004](#)):

$$\nu_i = \omega_i + 2x_{ii} + \frac{1}{2} \sum_{i \neq j} x_{ij} \quad (23)$$

If we represent the vibrational energy with fundamental frequencies ν_i and anharmonic constants x_{ij} , the formula of vibrational energy for excited state n will be ([Pennington and Kobe, 1954](#)):

$$(E_n - E_0)/hc = \sum_i \nu_i n_i + \sum_i x_{ii} n_i (n_i - 1) + \sum_{i < j} x_{ij} n_i n_j \quad (24)$$

Likewise, the partition function of vibrational excited states can be expressed as the product of two parts similar to Eqs. (15) and (22) ([Stockmayer et al., 1944](#); [Pennington and Kobe, 1954](#); [Bron et al., 1973](#)):

$$Q'_{hEXC} = \prod_i \frac{1}{1 - \exp(-u'_i)} \quad (25)$$

$$Q'_{AnEXC} = 1 - \frac{2hc}{kT} \sum_i \frac{x_{ii}}{[\exp(u'_i) - 1]^2} - \frac{hc}{kT} \sum_{i < j} \frac{x_{ij}}{[\exp(u'_i) - 1][\exp(u'_j) - 1]} \quad (26)$$

where $u'_i = hc\nu_i/kT$ by using fundamental frequencies. Therefore, we can adopt the Q' forms and rewrite the partition function corrected for harmonic vibrational excited states as

$$Q_{AnEXC} = \frac{Q'_{hEXC} Q'_{AnEXC}}{Q_{hEXC}} \quad (27)$$

This equation was used by [Wolfsberg and co-workers \(e.g., Bron et al., 1973; Goodson et al., 1982\)](#) and is considered as a more accurate choice than Eq. (22) at low temperature. Both Eqs. (22) and (26) are the results of mathematical approximations (see [Appendix A](#) or [Pennington and Kobe \(1954\)](#) and [Vojta \(1961\)](#) for details). [Table A1](#) shows Eq. (26) produces less numerical error than Eq. (22) at low temperature. However, at extremely high temperatures, Eq. (27) will occasionally produce weird results (see the $\text{NH}_2\text{D-NH}_3$ case in [Table A2](#) and [Fig. 2](#)).

2.3. Vibration–rotation coupling correction

In the [Bigeleisen–Mayer](#) equation, the rotational partition function arises as a result of classical rigid rotator approximation. In this paper, we add three correction factors to reduce errors from this approximation. First, we consider the coupling between vibration and rotation. The rotational constant around axis B in the vibrational state n is given by (e.g., [Pennington and Kobe, 1954](#); [Barone, 2005](#))

$$B_n = B_e - \sum_i \alpha_{B,i} (n_i + 1/2) \quad (28)$$

where B_e is equilibrium rotational constant around axis B , $\alpha_{B,i}$ is vibration–rotation coupling constant between axis B

and normal mode i . The expressions of rotational constants at state n around axis A and C are similar to that for B axis. When $n = 0$, we have the rotational constant around axis B in vibrational ground state as

$$B_0 = B_e - \sum_i \alpha_{B,i}/2 \quad (29)$$

Thus, the partition functions of vibration–rotation coupling corrected for ZPE and vibrational excited states (e.g., Pennington and Kobe, 1954; Vojta, 1960; Bron et al., 1973; Richet et al., 1977) are given by

$$Q_{VZPE} = \prod_{\sigma} \left(\frac{\sigma_e}{\sigma_0} \right)^{1/2} = \left(\frac{A_e B_e C_e}{A_0 B_0 C_0} \right)^{1/2} \quad (30)$$

$$Q_{VEXC} = 1 + \frac{1}{2} \sum_i \frac{\delta_i}{\exp(u'_i) - 1} \quad (31)$$

where σ means the rotation axis A , B and C , and

$$\delta_i = \sum_{\sigma} \alpha_{\sigma,i}/\sigma_0 \quad (32)$$

2.4. Quantum mechanical correction to rotation

Second, the quantum mechanical correction to the classical partition function of rotation is taken into consideration by using this factor (e.g., Stripp and Kirkwood, 1951; Richet et al., 1977):

$$Q_{QmCorr} = 1 + \frac{1}{12} \times \frac{hc}{kT} \left(2A_0 + 2B_0 + 2C_0 - \frac{B_0 C_0}{A_0} - \frac{A_0 C_0}{B_0} - \frac{A_0 B_0}{C_0} \right) \quad (33)$$

where A_0 , B_0 , C_0 are defined as rotational constants around axes A , B and C at vibrational ground state.

2.5. Centrifugal distortion correction

Third, the effect due to the centrifugal distortion during rotation can be included (Wilson, 1936; Kivelson and Wilson, 1952; Barone, 2005):

$$Q_{CenDist} = 1 - \frac{hckT}{4\hbar^4} (3\tau_{aaaa}I_A^2 + 3\tau_{bbbb}I_B^2 + 3\tau_{cccc}I_C^2 + 2\tau_{bbaa}I_B I_A + 2\tau_{cbbb}I_C I_B + 2\tau_{ccaa}I_C I_A) \quad (34)$$

in which τ is the quartic centrifugal distortion constant in units of cm^{-1} , I_{σ} is the principal moment of inertia around axis σ (i.e., A , B or C axis). Note that here $hc\tau_{aaaa}$ is equal to the τ'_{aaaa} defined in Kivelson and Wilson (1952).

2.6. Hindered internal rotation correction

Hindered internal rotation (torsion) is one of the major sources of errors for the harmonic approximation. It is actually a type of vibrational mode which is inherent in many molecules when there is one part of a molecule which rotates with respect to another. At low temperature and/or when the potential barrier height for the hindered rotation is large compared to the energy, the torsion mode behaves more har-

monically; at high temperature and/or when the barrier height is small, it rotates more freely. At present, the theory of hindered internal rotation has been fully developed but the calculation procedure is still cumbersome.

There are two common methods for evaluating the effects of hindered internal rotations. The first one is called Pitzer–Gwinn approximation (Pitzer and Gwinn, 1942). The partition function is given by

$$Q_{Tor}^{PG} = \prod_i \frac{(2\pi kT)^{1/2}}{s_i \hbar} I_i^{1/2} \left[\frac{Q_{Quant}^{HO}(\omega_i^{tor})}{Q_{Class}^{HO}(\omega_i^{tor})} \right] \times \exp(-W_i/2kT) I_0(W_i/2kT) \quad (35)$$

where s is the symmetry number of torsional mode which can be ignored in isotope fractionation calculations (see discussion in Section 3.3), I is the moment of inertia for hindered internal rotor, W is the barrier height of the potential, I_0 is a zeroth-order modified Bessel function. Q_{Quant}^{HO} and Q_{Class}^{HO} are harmonic oscillator partition functions of the quantum mechanical and classical form for torsional mode:

$$Q_{Quant}^{HO}(\omega_i^{tor}) = \frac{\exp(-hc\omega_i^{tor}/2kT)}{1 - \exp(-hc\omega_i^{tor}/kT)} \quad (36)$$

$$Q_{Class}^{HO}(\omega_i^{tor}) = \frac{kT}{hc\omega_i^{tor}} \quad (37)$$

where ω_i^{tor} is the harmonic frequency of the i th torsional mode.

The second method was developed by Truhlar (1991) by interpolating a smooth approximation from harmonic oscillator to free rotor, and the partition function of torsional mode can be expressed as

$$Q_{Tor}^T = \prod_i Q_{Quant}^{HO}(\omega_i^{tor}) \tanh \left(\frac{Q^{FR}(I_i)}{Q_{Class}^{HO}(\omega_i^{tor})} \right) \quad (38)$$

with

$$Q^{FR}(I_i) = \frac{(2\pi kT)^{1/2}}{s_i \hbar} I_i^{1/2} \quad (39)$$

Considering that the expression of Pitzer–Gwinn approximation seems to be generally more accurate (McClurg et al., 1997; Knyazev, 1998; Ellingson et al., 2007), we recommend the correction factor from hindered internal rotation to the harmonic partition function of vibration as:

$$Q_{HIR} = \prod_i \frac{(2\pi kT)^{1/2}}{s_i \hbar} I_i^{1/2} \times \exp(-W_i/2kT) I_0(W_i/2kT) / Q_{Class}^{HO}(\omega_i^{tor}) \quad (40)$$

Reader should keep in mind that the above formulas present no consideration of the coupling between different torsional modes which actually exists.

3. RESULTS

3.1. Calculated fundamental frequency vs. experimental fundamental

We use the MP2 method (Møller and Plesset, 1934) with the aug-cc-pVTZ basis set (Schmidt et al., 1993) for

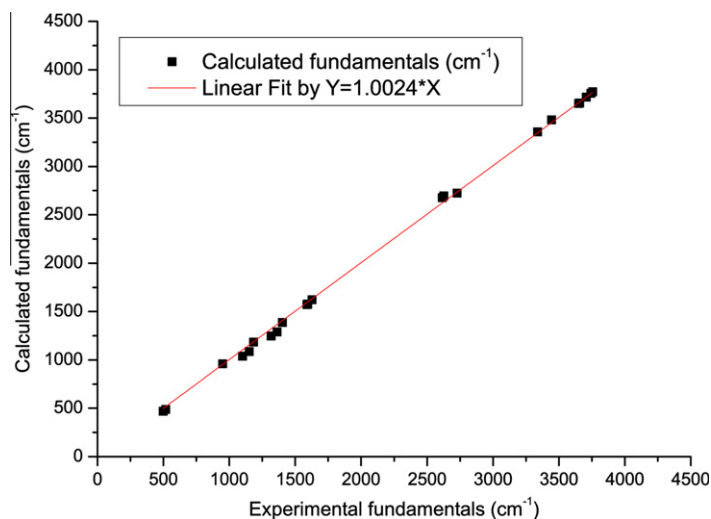


Fig. 1. The least-squares fitting of calculated fundamentals vs. experimental fundamentals. The regression line has a slope of 1.0024.

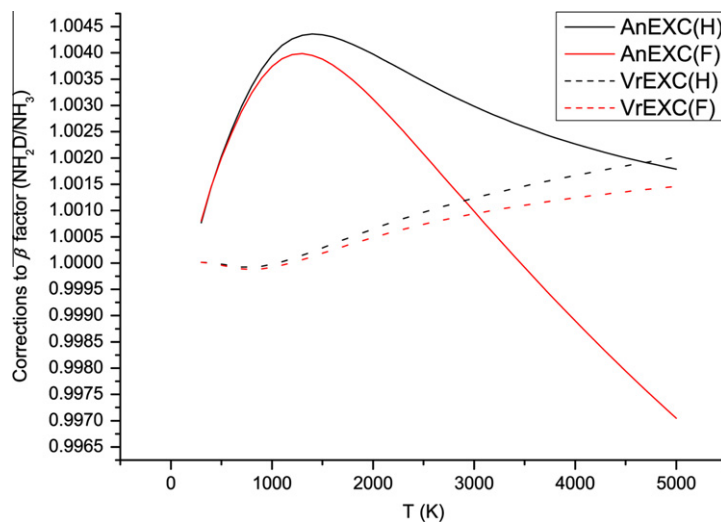


Fig. 2. The temperature dependences of AnEXC and VrEXC corrections of the $\text{NH}_2\text{D}-\text{NH}_3$ exchange reaction. AnEXC(*H*) is using Eq. (22) and AnEXC(*F*) is using Eq. (27). VrEXC(*H*) is using harmonic frequencies and VrEXC(*F*) is using fundamental frequencies.

geometry optimizations, harmonic frequencies and second order perturbation analyses in this study. To check the accuracy of this level of theory, calculated fundamental frequencies from Eq. (23) are compared with the experimental ones (Shimanouchi, 1972, 1977) for a variety of molecules (Table 1). All calculations are performed by using the Gaussian 03 program package (Frisch et al., 2004).

The calculated fundamental frequencies are generally in good agreement with observations (Table 1). However, small differences still exist between all the experimental fundamentals and the calculated ones. They are either caused by the inadequacy of the theoretical level we used or by small perturbations introduced by the experiment study. It is usually difficult to measure a single molecule's IR or Raman spectra without any other experimental aids, such as using a condensed vapor or trapping the molecule

in inert matrices. Such situations are different from the single molecule in vacuum used for the theoretical calculation. Fig. 1 illustrates the linear fitting of calculated fundamentals vs. experimental fundamentals with the slope of 1.0024 and *R*-squared value of 0.9998. We find that MP2/aug-cc-pVTZ level accurately predicts the low frequencies which are often mishandled by many other theoretical methods. We feel our results at the MP2/aug-cc-pVTZ level are quite accurate and that we do not need any frequency scale factor to match experimental frequencies.

3.2. Molecular constants

For the final calculation of various high order corrections to Bigeleisen–Mayer equation, many molecular constants are needed for producing specific partition function

Table 3

The calculated β values and the higher-order corrections to them for a number of polyatomic gas-phase molecules at temperature of 300 K.^a

$T = 300$ K	$\beta(H)$	$\beta(F)$	$\beta(UB)$	CG	AnZPE	AnEXC	VrZPE	VrEXC	QmCorr	CenDist	Total ^b	CPFR ^c	$\Delta(H)$ ^d	$\Delta(F)$	$\Delta(UB)$
H ₂ O*/H ₂ O	1.0657	1.0593	1.0661	0.9998	0.9976	1.0000	1.0000	1.0000	0.9999	1.0000	0.9975	1.0631	0.0026	0.0038	0.0030
HDO/H ₂ O	13.1707	10.8955		1.0421	0.9122	1.0001	0.9961	1.0000	0.9955	1.0009	0.9055	11.9255	1.2452	1.0300	
D ₂ O/H ₂ O	13.4101	10.9057	11.6536	0.9960	0.9161	1.0002	0.9990	1.0000	0.9965	1.0000	0.9121	12.2309	1.1791	1.3253	0.5773
H ₂ S*/H ₂ S	1.0118	1.0109	1.0116	1.0000	0.9997	1.0000	1.0000	1.0000	1.0000	1.0000	0.9997	1.0114	0.0003	0.0005	0.0002
HDS/H ₂ S	6.0110	5.3578		1.0323	0.9447	1.0003	0.9968	0.9999	0.9976	1.0011	0.9407	5.6542	0.3567	0.2964	
D ₂ S/H ₂ S	6.0675	5.4019	5.6186	0.9988	0.9496	1.0004	0.9987	0.9999	0.9982	1.0000	0.9469	5.7455	0.3220	0.3436	0.1269
S*O ₂ /SO ₂	1.0423	1.0409	1.0436	1.0001	0.9994	1.0000	1.0000	1.0000	1.0000	1.0000	0.9994	1.0417	0.0006	0.0008	0.0019
SOO*/SO ₂	1.0827	1.0802		1.0004	0.9990	1.0001	1.0000	1.0000	1.0000	1.0000	0.9989	1.0816	0.0011	0.0014	
SO ⁺ ₂ /SO ₂	1.0827	1.0802	1.0790	1.0002	0.9990	1.0001	1.0000	1.0000	1.0000	1.0000	0.9990	1.0816	0.0011	0.0014	0.0026
N*H ₃ /NH ₃	1.0685	1.0615	1.0736	0.9986	0.9970	1.0001	0.9999	1.0000	1.0000	1.0000	0.9970	1.0653	0.0032	0.0037	0.0083
NH ₂ D/NH ₃	13.8401	11.6910		0.9950	0.9205	1.0008	0.9983	1.0000	0.9977	1.0001	0.9176	12.6997	1.1404	1.0087	
ND ₃ /NH ₃	14.2338	11.4760	12.4695	0.9995	0.9137	1.0010	0.9988	1.0001	0.9984	0.9999	0.9120	12.9817	1.2521	1.5057	0.5122

^a Hereafter, O*, S* and N* denote ¹⁸O, ³⁴S, ¹⁵N, respectively. $\beta(H)$ or $\beta(F)$ means β factor calculated from pure harmonic or fundamental frequencies. $\beta(UB)$ means the β factor calculated from the frequencies generated by Urey–Bradley force field. AnZPE, AnEXC, VrZPE, VrEXC, QmCorr and CenDist are correction factors to partition function ratio. Each correction is expressed as a quotient of corrections of different isotopologues (e.g., $AnZPE = Q_{AnZPE}^*/Q_{AnZPE}$). AnZPE is the anharmonic correction for the zero-point energy, AnEXC is the anharmonic correction for the vibrational excited states, VrZPE is the Vib–Rot coupling correction for the zero-point energy part, VrEXC is the Vib–Rot coupling correction for the vibrational excited states part, QmCorr is a correction for quantum mechanical rotation, and CenDist is the centrifugal distortion correction arising from rotation–vibration interaction. CG means the corrections from the G_0 term which is a part of AnZPE and is used to see how G_0 term affects partition function ratios.

^b TOTAL means the total correction factors to $\beta(H)$ not including CG.

^c CPFR means the corrected partition function ratios which is equal to $\beta(H)$ times the TOTAL factor.

^d $\Delta(H)/\Delta(F)/\Delta(UB)$ means the difference between $\beta(H)/\beta(F)/\beta(UB)$ and CPFR.

$$ZPE(harm) = \frac{1}{2} \sum_i hc\omega_i \quad (42)$$

This treatment is used because the anharmonic constants printed out by standard versions of Gaussian 03 are only to the third digit after the decimal. They are less accurate than the ZPE energies given. For other corrections, we directly use anharmonic constants in the output of Gaussian 03. For corrections for vibrational excited states, we round off the numbers of harmonic and fundamental frequencies to include the third digit after the decimal only (e.g., 111.333 cm⁻¹). For the RPFRR calculation, the harmonic frequencies are given to the fourth digit after the decimal (e.g., 111.4444 cm⁻¹). In Eq. (34) we choose to use the relationship of moments of inertia and rotational constants to obtain the needed moments of inertia around the three rotational axes rather than directly using them in the output of Gaussian 03:

$$I_B = h/8\pi^2 cB_0 \quad (43)$$

We note that there are differences between our theoretically calculated molecular constants and those from experiments (Richet et al., 1977). Most of differences are small and could only bring very small difference of the final corrections to the Bigeleisen–Mayer equation. The largest difference found between our results and those of Richet et al. (1977) is the anharmonic constants of HDS (e.g., x_{13} is -1.787 in this study and -67.96 in Richet et al. (1977)). We notice that the anharmonic constants of HDS in Richet et al. (1977) were calculated by an empirical method (Darling–Dennison rule (Darling and Dennison, 1940), i.e., $x'_{ij} = x_{ij}\omega'_i\omega'_j/\omega_i\omega_j$) rather than using the experimental spectra data because the vibration of HDS was poorly known at that time. Furthermore, HDO and HDS are quite similar cases. The results of HDS and HDO in this study are in accordance with each other. However, the results of HDS and HDO in Richet et al. (1977) are different largely. Therefore, we feel the calculated molecular constants in this study are more reasonable.

3.3. Isotope partition function ratios for corrections beyond harmonic level

Table 3 shows the calculated reduced isotope partition function ratios (or β values) and their higher-order corrections of a number of polyatomic gas-phase molecules at temperature of 300 K for singly or fully isotopic substitutions. The correction of hindered internal rotation to β factor (hereafter, HIR) is not given in tables for following reasons. We tested the HIR of ethane by Gaussian 03 program and found it is equal to the unity (means no correction). The same result was also obtained by many other researchers with similar methods (e.g., Lynch et al., 2005; Ellingson et al., 2006). The general treatment of these methods is to relate the barrier height, the effective moment of inertia and the frequency of torsional mode as

$$W = 8\pi^2 c^2 \omega_{tor}^2 I / s^2 \quad (44)$$

Because the barrier heights of the isotopologues are treated as the same based on Born–Oppenheimer approximation (using the bottom of the well as the reference energy), the

correction of hindered internal rotation of these methods then contributes no effect to the harmonic isotopic partition function ratio:

$$HIR = \prod_i f(W_i)/f(W_i) = 1 \quad (45)$$

where $f(W_i)$ means the function of W_i .

For the case of ethane, including C₂H₆, CH₃-C*H₃, CH₃-CH₂D and CH₃-CD₃ situations, if we consider the torsional mode as a free rotor, it will be temperature-independent for the isotopic partition function ratio. The HIR corrections will be 1 for $\beta(\text{CH}_3\text{-C}^*\text{H}_3/\text{C}_2\text{H}_6)$, 0.989 for $\beta(\text{CH}_3\text{-CH}_2\text{D}/\text{C}_2\text{H}_6)$, 0.992 for $\beta(\text{CH}_3\text{-CD}_3/\text{C}_2\text{H}_6)$ at 300 K, and the corrections will become smaller when the temperature is higher. Because the free rotor is a classical approximation at high-temperature limit, the exact correction should be smaller than the given ones. McClurg et al. (1997) derived an equation to describe the correction of hindered internal rotor to the harmonic partition function for one torsional mode based on the large barrier limit at low temperature:

$$Q_{HIR} = \exp\left(\frac{u^2}{16\frac{W}{kT}}\right) \left[1 + \exp\left(-u + \frac{u^2}{4\frac{W}{kT}}\right) - \exp(-u) \right] \quad (46)$$

when $u \gg 1$

when $u \ll 1$ (i.e., at high temperature), Eq. (40) is recommended instead (McClurg et al., 1997; Knyazev, 1999). According to the Eqs. (46) and (40), the HIR should be 0.9954 to $\beta(\text{CH}_3\text{-CH}_2\text{D}/\text{C}_2\text{H}_6)$ and 0.9951 to $\beta(\text{CH}_3\text{-CD}_3/\text{C}_2\text{H}_6)$ at 300 K and will attenuate to 1 with the increase of temperature.

Ellingson et al. (2006) calculated the torsional partition function ratio for D₂O₂/H₂O₂ by using several approximations. They suggested that the Wigner–Kirkwood approximation (Vojta and Zylka, 1993) best described the studied isotope effects which gave the HIR for $\beta(\text{D}_2\text{O}_2/\text{H}_2\text{O}_2)$ as about 0.990 at 300 K. If this value is correct, then the hindered internal rotation should be much less important than the anharmonicity of ZPE to β factor which is about 0.903 based on our calculation (the shift of total ZPEs in our calculation is very similar to the accurate value from Koput et al. (2001), both are about 1400 cm⁻¹). Unfortunately, there is no good experimental way to precisely determine the isotopic effects of hindered internal rotation. Even with accurate torsional potentials for the simple molecules (e.g., H₂O₂ and ethane), there is no good experimental HIR results of them. Therefore, it is hard right now to compare the calculated HIR results to a “true” value. However, we at least know the “true” value should lie in between 1 and the correction of free rotor to β factor.

From Table 3, except for the anharmonic correction to the zero-point energy (AnZPE), all other high order corrections do not have any noticeable contribution to non-H/D exchange reactions at 300 K (e.g., the O isotope exchange between H₂O* and H₂O). On the contrary, in H/D exchange reactions almost all the corrections are important. Furthermore, AnZPE takes the largest share at the total correction (several percent for H/D exchange reactions). VrZPE and QmCorr could be the second biggest corrections at 300 K. VrZPE gives a correction of about

Table 4

The temperature dependence of corrections to β factors for various studied gas-phase molecules (see more in Supplementary file).

T(°C)	HDO/H ₂ O													
	$\beta(H)$	CG	AnZPE	AnEXC(H) ^a	AnEXC(F) ^b	VrZPE	VrEXC(H) ^c	VrEXC(F) ^d	QmCorr	CenDist	TOTAL(H) ^e	TOTAL(F) ^f	CPFR(H) ^g	CPFR(F) ^h
0	17.7316	1.0464	0.9040	1.0001	1.0001	0.9961	1.0000	1.0000	0.9951	1.0008	0.8968	0.8968	15.9021	15.9021
10	15.7681	1.0447	0.9072	1.0001	1.0001	0.9961	1.0000	1.0000	0.9952	1.0009	0.9002	0.9002	14.1947	14.1947
20	14.1351	1.0432	0.9103	1.0001	1.0001	0.9961	1.0000	1.0000	0.9954	1.0009	0.9034	0.9034	12.7695	12.7696
30	12.7633	1.0417	0.9131	1.0001	1.0001	0.9961	1.0000	1.0000	0.9956	1.0009	0.9064	0.9064	11.5683	11.5683
40	11.6003	1.0403	0.9157	1.0001	1.0001	0.9961	1.0000	1.0000	0.9957	1.0010	0.9092	0.9092	10.5467	10.5467
50	10.6062	1.0391	0.9182	1.0001	1.0002	0.9961	1.0000	0.9999	0.9958	1.0010	0.9118	0.9118	9.6708	9.6709
75	8.6720	1.0362	0.9239	1.0002	1.0002	0.9961	0.9999	0.9999	0.9961	1.0011	0.9178	0.9178	7.9590	7.9590
100	7.2859	1.0337	0.9288	1.0003	1.0003	0.9961	0.9999	0.9999	0.9964	1.0011	0.9230	0.9230	6.7249	6.7249
125	6.2581	1.0316	0.9331	1.0003	1.0003	0.9961	0.9999	0.9999	0.9966	1.0012	0.9276	0.9276	5.8050	5.8050
150	5.4740	1.0297	0.9369	1.0004	1.0004	0.9961	0.9998	0.9998	0.9968	1.0013	0.9317	0.9317	5.1001	5.1001
175	4.8613	1.0280	0.9404	1.0005	1.0005	0.9961	0.9998	0.9998	0.9970	1.0014	0.9353	0.9353	4.5470	4.5470
200	4.3727	1.0265	0.9434	1.0005	1.0006	0.9961	0.9997	0.9997	0.9971	1.0014	0.9386	0.9386	4.1044	4.1044
250	3.6495	1.0240	0.9487	1.0007	1.0007	0.9961	0.9996	0.9996	0.9974	1.0016	0.9443	0.9443	3.4463	3.4464
300	3.1463	1.0218	0.9530	1.0009	1.0009	0.9961	0.9995	0.9995	0.9976	1.0017	0.9491	0.9491	2.9861	2.9861
350	2.7803	1.0201	0.9567	1.0010	1.0010	0.9961	0.9994	0.9994	0.9978	1.0019	0.9531	0.9531	2.6500	2.6500
400	2.5045	1.0186	0.9599	1.0012	1.0012	0.9961	0.9993	0.9993	0.9980	1.0020	0.9566	0.9566	2.3958	2.3959
450	2.2908	1.0173	0.9626	1.0014	1.0014	0.9961	0.9992	0.9992	0.9981	1.0022	0.9597	0.9597	2.1983	2.1984
500	2.1212	1.0161	0.9650	1.0015	1.0016	0.9961	0.9991	0.9991	0.9982	1.0023	0.9623	0.9624	2.0414	2.0414
600	1.8716	1.0143	0.9689	1.0019	1.0019	0.9961	0.9989	0.9989	0.9984	1.0026	0.9669	0.9669	1.8096	1.8097
700	1.6987	1.0128	0.9721	1.0022	1.0023	0.9961	0.9987	0.9987	0.9986	1.0029	0.9706	0.9707	1.6488	1.6489
800	1.5734	1.0116	0.9746	1.0025	1.0026	0.9961	0.9985	0.9985	0.9987	1.0032	0.9737	0.9738	1.5321	1.5322
900	1.4795	1.0106	0.9768	1.0027	1.0028	0.9961	0.9984	0.9984	0.9988	1.0035	0.9763	0.9764	1.4445	1.4446
1000	1.4072	1.0098	0.9786	1.0029	1.0030	0.9961	0.9982	0.9982	0.9989	1.0038	0.9785	0.9786	1.3770	1.3771

^a AnEXC(H) means using Eq. (22) to calculate the correction from anharmonicity of vibrational excited states.^b AnEXC(F) means using Eq. (27) to calculate the correction from anharmonicity of vibrational excited states.^c VrEXC(H) means using Eq. (31) but harmonic frequencies within to calculate the correction from Vib–Rot coupling of vibrational excited states.^d VrEXC(F) means using Eq. (31) but fundamental frequencies within to calculate the correction from Vib–Rot coupling of vibrational excited states.^e TOTAL(H) means the total correction to β factor which is equal to the product of AnZPE, AnEXC(H), VrZPE, VrEXC(H), QmCorr and CenDist.^f TOTAL(F) also means the total correction to β factor but using AnEXC(F) and VrEXC(F) instead of AnEXC(H) and VrEXC(H).^g CPFR(H)/CPFR(F) means the product of $\beta(H)$ and TOTAL(H)/TOTAL(F).

0.2–0.4% and QmCorr gives about 0.2–0.5% to the total partition function ratios for H/D exchange reactions. The contributions from the other three corrections are even smaller.

Generally, at 300 K, partition function ratios calculated at the harmonic level are quite accurate for the non-H/D exchange reactions but very bad for H/D exchange. One strange thing is that reduced partition function ratios calculated from fundamental frequencies are better than those calculated from harmonic frequencies for the H/D exchange reactions (Table 3). For example, for the $\text{NH}_2\text{D}/\text{NH}_3$ case, $\Delta(H)$ is much larger than $\Delta(F)$ (1.1404 vs. 1.0087).

Table 4 shows the temperature dependences of those high order corrections by using water vapor in H/D isotopic exchange reactions as an example (see Supplementary file, for other studied molecules). At low temperature, AnEXC(H) and AnEXC(F) give the same corrections, and so do VrEXC(H) and VrEXC(F); at high temperature up to 1000 °C, there is only slight difference between them. From 0 to 1000 °C, AnZPE and QmCorr contributions decrease with increase of temperature, while AnEXC, VrEXC and CenDist contributions increase with temperature. Because TOTAL is mainly affected by AnZPE, it decreases as temperature increases.

3.4. Equilibrium constant K with corrections beyond harmonic level

By applying the higher-order corrections mentioned above, we calculate several equilibrium constants of H/D exchange reactions with well-known experimental results and compare them with those of previous theoretical calculations (Table 5). The results without the G_0 terms of Richet et al. (1977) are actually calculated by us using the molecular constants listed in their paper. The difference between our work and the previous theoretical calculations is that our molecular constants are from quantum chemistry calculations but theirs were from experiments.

For the water vapor internal equilibrium reaction: $\text{H}_2\text{O} + \text{D}_2\text{O} = 2\text{HDO}$, large deviations were found between theoretical studies and experiments (Pyper et al., 1967; Pyper and Newbury, 1970; Pyper and Christensen,

1975). Wolfsberg (1969) showed that it was not sufficiently accurate to add anharmonic corrections without the contributions of G_0 terms to partition function ratios. This point was reiterated in the same issue of the journal by Hulston (1969). This was partly a response to the surprising result that using more accurate calculations (i.e., adding the anharmonic corrections but without G_0 term) gave poorer agreement with experiment than using the Bigeleisen–Mayer equation for some isotope exchange reactions (Hulston, 1969). Later, it was pointed out that other corrections to partition function ratios (e.g., correction for Vib–Rot coupling) should also be considered (Wolfsberg et al., 1970). Our results with G_0 terms for the water vapor internal equilibrium are in good agreement with experiments. The ones without G_0 are significantly different from experiments. We note that our result for this reaction is somewhat different from the value of Simonson (1990) which is 3.85 for the gas-phase at 298.15 K. However, in Simonson (1990), the equilibrium constant for the liquid water calculated from this gas-phase K value was 3.87 at 298.15 K which did not match their reference value 3.82 for the liquid water. It means either the standard gas-phase equilibrium constant K or the relationship between gas-phase equilibrium constant and the liquid-phase one needs to be refined. If the “true” value of the self-equilibrium constant in liquid water is about 3.82 at 298.15 K, the one for gas-phase should be less. Considering the reported K value for gas-phase is near 3.80 at 298.15 K (see Table 5), our results seem slightly better than those of the previous calculations.

For the internal equilibrium: $\text{H}_2\text{S} + \text{D}_2\text{S} = 2\text{HDS}$, our results with G_0 terms are very close to experiment and again quite different from the ones without G_0 terms. Surprisingly, even without G_0 terms, the results of Richet et al. (1977) match the experiment very well. It is worth to point out that the anharmonic constants (e.g., x_{13}) of the isotopologues of H_2S are produced by the empirical Darling–Dennison rule in Richet et al. (1977), resulting in a large difference between their anharmonic constants and ours. Because there is no G_0 data of HDS provided in Richet et al. (1977), we cannot calculate their result with G_0 term using their molecular constants.

Table 5

The comparison of equilibrium constant K calculated from this study and those from Wolfsberg et al. (1970), Bron et al. (1973), Richet et al. (1977) and experiments.

	Wolfsberg et al. (1970) and Bron et al. (1973)		Richet et al. (1977)		This study		Experiments
	T (K)	With G_0	Without G_0	With G_0	Without G_0	With G_0	
$\text{H}_2\text{O} + \text{D}_2\text{O} \leftrightarrow 2\text{HDO}$	273	3.83	3.23	3.82	3.41	3.77	3.74 ± 0.02^a
	296		3.29		3.47	3.80	3.82 ± 0.06^b
	298	3.85	3.30	3.85	3.47	3.80	3.76 ± 0.02^a
$\text{H}_2\text{S} + \text{D}_2\text{S} \leftrightarrow 2\text{HDS}$	273	3.91	3.86		3.58	3.85	
	298	3.93	3.88		3.62	3.87	3.88 ± 0.03 at 297K ^c
$\text{H}_2\text{O} + \text{HDS} \leftrightarrow \text{HDO} + \text{H}_2\text{S}$	273			2.26	2.25	2.27	$\approx 2.28^d$
	300	2.20		2.10	2.09	2.11	$\approx 2.10^d/2.17^e$

Note. The experimental data are from: (a) Friedman and Shiner (1966); (b) Pyper and Christensen (1975); (c) Pyper and Newbury (1970); (d) Richet et al. (1977); (e) Bron et al. (1973).

For the isotope exchange reaction $\text{H}_2\text{O} + \text{HDS} = \text{HDO} + \text{H}_2\text{S}$, our results show the contribution of G_0 terms is very small (Table 5) but still gives improvement.

Wolfsberg et al. (1970) emphasized the importance of including G_0 for the H/D exchange reactions, which was normally ignored by previous investigators. However, Richet et al. (1977) suggested it was acceptable to ignore G_0 terms for most H/D exchange reactions. Our results show that including G_0 will obviously benefit almost all H/D exchange reactions to different extents. Therefore, we suggest to include G_0 term (e.g., via AnZPE correction discussed in this study) whenever is possible for the H/D exchange reactions.

4. DISCUSSION

4.1. Comparisons of corrections and their temperature dependences

In this study, six corrections to the Bigeleisen–Mayer equation have been investigated. Two of them are caused by anharmonicity of vibration (AnZPE, AnEXC), three of them are caused by vibration–rotation interaction (VrZPE, VrEXC and CenDist), and one is for quantum mechanical rotation (QmCorr). Table 3 and Table 4 show that for the non-H/D exchange reactions, except for the anharmonic correction of zero-point energy (AnZPE), none of these corrections can make noticeable contributions to the final partition function ratios of the molecules studied. Therefore, if we include the AnZPE correction to the Bigeleisen–Mayer equation, we can precisely predict the isotopic fractionation for the non-H/D exchange reactions. On the contrary, for the H/D exchange reactions, almost all the corrections beyond harmonic approximation are important.

Table 4 shows that all corrections to partition function ratios are temperature dependent except VrZPE. The corrections from AnZPE and QmCorr will become smaller as temperature increases. However, the corrections of AnEXC, VrEXC and CenDist will become larger with the increase of temperature. Do they have only monotonous relationships with temperature?

Fig. 2 ($\text{NH}_2\text{D}/\text{NH}_3$ as an example) shows that the anharmonic correction for the vibrational excited states (AnEXC) does not monotonously change with temperature. There is a turning point for AnEXC and it will decrease with temperature after that turning point. The Vib–Rot coupling correction curve for the vibrational excited states (VrEXC) has a very small drop then goes up monotonously with temperature to at least 5000 K. Fig. 2 also shows that the two equations of AnEXC calculation (i.e., Eqs. (22) and (27)) provided in this study will deviate largely from each other at high temperatures. We find that such phenomenon repeats for other isotopic pairs but at even higher temperature. Even for the same $\text{NH}_2\text{D}/\text{NH}_3$ case, its results of VrEXC(H) and VrEXC(F) only have a small deviation from each other at extremely high temperatures. We do not know why this happens but probably due to larger numerical errors at high temperature. It seems AnEXC(H) is more reasonable than AnEXC(F) at extremely high temperatures for the $\text{NH}_2\text{D}/\text{NH}_3$ case.

Readers may note that the Bigeleisen–Mayer equation goes to the unity at the high-temperature limit. However, the corrections we presented here show different trends. It is because these corrections are calculated on the assumption that those molecular constants do not change even at extremely high temperature. It is obviously not true. Those molecular constants will be changed actually if temperature goes high (also with pressure, e.g., Polyakov, 1998). Therefore, these corrections can only describe the accurate isotopic fractionations when the temperature is not extremely high. At the high-temperature limit, molecules will decompose to atoms where no isotope fractionation happens.

4.2. The conditions for employing Teller–Redlich product rule

Table 6 compares the vibrational partition function ratios and products of frequencies by using harmonic frequencies and fundamental frequencies at 300 K. According to the Teller–Redlich product rule, the Q_{t-r} (as shown in Eq. (47)) will exactly equal the product of frequency ratios when using harmonic frequencies:

Table 6

Comparison of vibrational partition function ratios and frequencies products calculated by harmonic frequencies and fundamental frequencies (at 300 K).

	$QR_{vib}(H)$	$QR_{vib}(F)$	QR_{vib}	$\Delta_{vib}(H)$	$\Delta_{vib}(F)$	$\prod \omega^*/\omega$	$\prod \nu^*/\nu$	QR_{t-r}
$\text{H}_2\text{O}^*/\text{H}_2\text{O}$	1.0768	1.0699	1.0742	0.0026	−0.0043	0.9897	0.9901	0.9897
$\text{HDO}/\text{H}_2\text{O}$	20.6726	16.8759	18.7859	1.8867	−1.9100	0.6371	0.6456	0.6371
$\text{H}_2\text{S}^*/\text{H}_2\text{S}$	1.0145	1.0135	1.0142	0.0003	−0.0007	0.9973	0.9974	0.9973
$\text{HDS}/\text{H}_2\text{S}$	9.6187	8.4662	9.0595	0.5592	−0.5933	0.6249	0.6329	0.6250
$\text{SO}_2^*/\text{SO}_2$	1.0714	1.0696	1.0708	0.0006	−0.0012	0.9728	0.9732	0.9728
SOO^*/SO_2	1.1495	1.1460	1.1485	0.0010	−0.0025	0.9419	0.9425	0.9419
$\text{N}^*\text{H}_3/\text{NH}_3$	1.0849	1.0772	1.0816	0.0033	−0.0044	0.9848	0.9854	0.9848
$\text{NH}_2\text{D}/\text{NH}_3$	24.6222	20.4927	22.6443	1.9779	−2.1516	0.5621	0.5705	0.5620

Note. $QR_{vib}(H)$ is vibrational partition function ratio calculated from harmonic frequencies. $QR_{vib}(F)$ is the vibrational partition function ratio calculated from fundamental frequencies. QR_{vib} is the accurate vibrational partition function ratio value which equals to $QR_{vib}(H)$ times AnZPE, AnEXC, VrZPE and VrEXC. $\Delta_{vib}(H) = QR_{vib}(H) - QR_{vib}$, $\Delta_{vib}(F) = QR_{vib}(F) - QR_{vib}$. $\prod \omega^*/\omega$ is the product of ratios of harmonic frequencies. $\prod \nu^*/\nu$ is the product of ratios of fundamental frequencies. Q_{t-r} is calculated by using the following equation and it will be equal to the product of harmonic frequencies ratios according to Teller–Redlich rule: see Eq. (48).

Table 7
The comparison of ZPEs with or without G_0 terms (in the unit of cm^{-1}).

	G_0	ZPE(harm) ^a	ZPE(fund) ^b	ZPE(tot) ^c	$\Delta_{\text{ZPE}}(H)$ ^d	$\Delta_{\text{ZPE}}(F)$ ^e
H ₂ O	−3.8575	4701.5370	4502.6326	4623.9446	77.5923	121.3121
H ₂ O*	−3.8059	4686.1105	4488.5561	4609.0174	77.0932	120.4613
HDO	−12.4655	4070.1353	3913.5652	4011.6997	58.4355	98.1345
H ₂ S	−0.8450	3390.4480	3278.3936	3346.1272	44.3207	67.7336
H ₂ S*	−0.8549	3387.4529	3275.6000	3343.1990	44.2539	67.5990
HDS	−7.4790	2919.1601	2833.7750	2886.7023	32.4579	52.9273
SO ₂	1.0181	1448.8708	1431.8770	1443.4149	5.4560	11.5379
SO ₂ *	1.0061	1434.9815	1418.3487	1429.6404	5.3412	11.2916
SOO*	0.9287	1421.0936	1404.7376	1415.8517	5.2426	11.1135
NH ₃	−5.7926	7584.9123	7261.1563	7462.5229	122.3894	201.3666
N*H ₃	−5.5058	7567.9589	7245.6967	7446.1883	121.7706	200.4916
NH ₂ D	−4.7451	6917.7696	6632.4519	6812.6614	105.1082	180.2095

^a The ZPE as expressed in Eq. (42) using harmonic frequencies.

^b The ZPE as expressed in Eq. (42) but using fundamental frequencies.

^c The “total ZPE” means the ZPE with G_0 term as expressed in Eq. (20).

^d $\Delta_{\text{ZPE}}(H)$ is the difference between ZPE(harm) and ZPE(tot).

^e $\Delta_{\text{ZPE}}(F)$ is the difference between ZPE(fund) and ZPE(tot).

$$Q_{t-r} = \left(\frac{M^*}{M}\right)^{3/2} \left(\frac{I_A^* I_B^* I_C^*}{I_A I_B I_C}\right)^{1/2} \left/\left(\frac{m^*}{m}\right)^{3/2}\right. \quad (47)$$

Table 6 shows $\prod \omega^*/\omega$ (using harmonic frequencies) is the same as Q_{t-r} if ignoring the small numerical errors. $Q_{R_{\text{vib}}}$ is fallen between $Q_{R_{\text{vib}}}(H)$ and $Q_{R_{\text{vib}}}(F)$. In either H/D exchange reactions or non-H/D exchange reactions, $\Delta_{\text{vib}}(F)$ is always larger than $\Delta_{\text{vib}}(H)$ in terms of absolute numbers. These data confirm that using pure harmonic frequencies can always achieve a better vibrational partition function ratio result than using fundamental frequencies. Also, they clearly show that only harmonic frequencies should be used in the Teller–Redlich product rule.

On the other hand, our results show that the errors from using inaccurate frequencies (e.g., fundamental frequencies or harmonic frequencies contain errors) to calculate isotopic fractionations could be reduced by employing the Teller–Redlich product rule (this conclusion can be proved mathematically). The similar conclusion was made by Schaad et al. (1999). They found employing the Teller–Redlich product rule could reduce errors in kinetic isotope effects calculations. It explains why the $\beta(F)$ s are better than the $\beta(H)$ s for the H/D exchange reactions shown in Table 3. Recently, Domagal-Goldman and Kubicki (2008) also suggested to apply the Teller–Redlich product rule to the isotope partition function ratio calculation when uses implicit solvation models (e.g., PCM model).

4.3. ZPE and G_0

The total ZPE can be described by G_0 , harmonic frequencies and anharmonic constants (i.e., Eq. (20)). However, due to the complexity of G_0 , many researchers do not include it in their calculation of ZPE. Here, we checked the errors produced by such neglect by comparing the total ZPE (G_0 included) and ZPEs not including G_0 but using harmonic frequencies or fundamental ones in Eq. (42). The energy differences between the total

ZPE and those obtained using harmonic or fundamental frequencies (denoted as $\Delta_{\text{ZPE}}(H)$ or $\Delta_{\text{ZPE}}(F)$) can be expressed as $-(G_0 + \frac{1}{4} \sum_{i \leq j} x_{ij})$ for harmonic frequencies or $G_0 - \frac{3}{4} \sum_i x_{ii} - \frac{1}{4} \sum_{i < j} x_{ij}$ for fundamental frequencies (Grev et al., 1991) (see Table 7).

For cases of H/D exchange, both the G_0 terms and the energy differences deviate significantly from the total ZPE. For non-H/D exchange cases, both the G_0 values and the energy differences from the total ZPE change only a little. These results suggest that G_0 terms shouldn't be ignored for H/D exchange reactions. Importantly, using harmonic frequencies will cause smaller energy difference than using fundamental frequencies for all the cases we tested, which means if one chooses to ignore G_0 for non-H/D exchange reactions, using harmonic frequencies will cause smaller ZPE energy errors.

4.4. Scale factor

In this paper, we did not use any frequency scale factor for the MP2/aug-cc-pVTZ level calculations. However, in isotopic fractionation prediction one often needs to choose an appropriate frequency scale factor when the method used is not of sufficiently high accuracy. This often occurs to isotopic fractionation involving larger molecules.

There are three common types of frequency scale factors. The first type of scale factor is used for scaling harmonic frequencies to match frequencies from experiments (i.e., fundamental frequencies, e.g., Sinha et al. (2004)). The second type is the scale factor for matching an accurate ZPE (i.e., total ZPE mentioned in this paper but generally the G_0 term is ignored, e.g., Scott and Radom (1996)). The third type is the scale factor for matching pure harmonic frequencies (e.g., Zhao and Truhlar, 2008). Generally, the values of these three scale factors are in this order: $sf(\text{fund}) < sf(\text{zpe}) < sf(\text{harm})$, where sf means scale factor for the same quantum chemistry calculation level.

We have shown in this study that pure harmonic frequencies are needed for Bigeleisen–Mayer equation, suggesting the $sf(harm)$ factors have to be used. However, the central idea is to estimate the accurate energy shifts due to isotopic substitution. According to the discussions above, we know an accurate ZPE (i.e., with AnZPE correction) plays a key role in the estimation of isotopic fractionation. By any chance, if we can obtain an accurate ZPE through a very good $sf(zpe)$, we can use this equation to obtain better result:

$$\beta(AX^*/AX)' = \frac{\exp[-ZPE(tot, AX^*)/kT]}{\exp[-ZPE(tot, AX)/kT]} \prod_i^{3n-6} \frac{u_i(AX^*)\{1 - \exp[-u_i(AX)]\}}{u_i(AX)\{1 - \exp[-u_i(AX^*)]\}} \quad (48)$$

It is a modified Bigeleisen–Mayer equation with anharmonic corrections via direct including of zero-point energy, and can provide the enough accuracy for the non-H/D exchanges better than Eq. (7). In quantum chemistry calculations, $sf(harm)$ is only calculated for a few quantum methods, however, $sf(zpe)$ has been derived for many methods (Scott and Radom, 1996; Sinha et al., 2004; Merrick et al., 2007). This makes $sf(zpe)$ easier to be used into isotopic fractionation calculations. For the circumstances that only $sf(fund)$ is known, we recommend using a slightly larger scale factor as $sf(zpe)$ into the calculations (e.g., according to Merrick et al. (2007), $sf(zpe)$ is about 0.02 larger than $sf(fund)$ for numerous quantum methods).

4.5. The practice of using one set of fundamental frequencies

We have showed that one should not directly use the fundamental frequencies in the Bigeleisen–Mayer equation. However, it is often not easy to find fundamental frequencies for both the major isotopologue and the minor one. Therefore, there is another practice used by many researchers when there is only one set of fundamental frequencies in hand. Such practice is to use the fundamental frequencies for the major isotopologue but calculate another set of harmonic frequencies for the minor isotopologue through building a force field from the observed fundamental frequencies. Usually, such force fields are constructed as a harmonic type. The same force constants used for the major isotopologue will be also used for the minor isotopologue. Schauble (2004) explained such vibrational force field modeling in a quite detailed way.

For comparing such “one set of fundamental frequencies” method with the “exact” method with all corrections, we built the Urey–Bradley force field by our calculated fundamental frequencies listed in Table 1. The bond lengths and the bond angles are also obtained from our calculations (e.g., 0.9612 Å and 104.1213° for H₂O, respectively). Because the G and F matrices can only be treated for a specific point group but partly isotopic substitution will lower the symmetry, we only calculate β factors of fully isotopic substitutions and marked as $\beta(UB)$ in Table 3. Our results show that the $\beta(UB)$ factors generally contain larger errors than $\beta(H)$ factors for non-H/D exchanges. For H/D ex-

changes, $\beta(UB)$ s are better than $\beta(H)$ s but it is meaningless to use uncorrected Bigeleisen–Mayer equation (i.e., $\beta(H)$) for H/D exchange reactions.

Goodson et al. (1982) have compared such “one set of fundamental frequencies” practice (referred as [anharm] in their paper) with the one using pure harmonic frequencies (referred as [harm]) for a few diatomic and tri-atomic molecules. We do not know how accurate their harmonic frequencies would be because they used a complicated procedure to obtain those harmonic frequencies from experimental spectra, while the relationship of their results are similar to our $\beta(UB)$ s and $\beta(H)$ s. They found that both ways actually produced similar results for heavy isotopes (non-H/D), but our results show that the $\beta(H)$ s are general better than $\beta(UB)$ s for the non-H/D exchange cases. For the H/D exchanges, they found that the [anharm] way was better than the [harm] way which is confirmed by our results. However the accuracy of $\beta(UB)$ s (or [anharm]) is still not satisfactory to deal with the H/D exchanges, besides as mentioned by Zeebe (2005), the β factor of such practice is very sensitive to the accuracy of the chosen fundamentals. We therefore do not recommend this treatment in the H/D exchanges by using uncorrected Bigeleisen–Mayer equation.

Considering the complexity of constructing the force fields of polyatomic molecules and the further simplifications which often have to be used in building the force fields, we do not recommend using this practice only if one cannot find the aids from quantum chemistry on harmonic frequencies calculation.

5. CONCLUSIONS

Corrections beyond the harmonic level to the Bigeleisen–Mayer equation have been discussed and compared. The hindered internal rotation correction on isotope effects is found to be insignificant for most cases. Anharmonic correction for ZPE, including the G_0 term, has been found to be very important for all kinds of isotope exchange reactions. For the H/D exchange reactions, almost all the high order corrections discussed in this study are important. We have shown through detailed analysis of relevant energy contributions that three improper ways should be avoided when studying equilibrium isotopic fractionations using the Bigeleisen–Mayer equation. First, one should avoid using two sets of fundamental frequencies in any circumstance. Second, one should avoid using the uncorrected Bigeleisen–Mayer equation for the H/D exchange reactions. Third, one should avoid using scale factors for fundamental frequencies to scale calculated harmonic frequencies but rather use the scale factor for accurate ZPE when one has to do so. If all the mistakes mentioned are avoided, the accuracy of theoretical predictions for isotopic equilibrium can be effectively improved.

ACKNOWLEDGMENTS

Y.L. is grateful for funding support from Chinese NSF projects (40773005, 41073015) and Chinese 863 Project (No. 2010AA1222). J.A.T. is grateful for funding support from the U.S. NSF

(EAR-0539109). The authors thank Dr. Veniamin Polyakov and two anonymous reviewers for constructive comments on this paper.

APPENDIX A

A1. Partition function of vibrational excited states

The vibrational energy at excited state n can be expressed as the following form in terms of harmonic frequencies and anharmonic constants:

$$(E_n - E_0)/hc = \sum_i \omega_i n_i + \sum_{i \leq j} x_{ij} \left(n_i n_j + \frac{1}{2} n_i + \frac{1}{2} n_j \right) \quad (\text{A1})$$

Here, we define $y_{ij} = hc x_{ij} / kT$, thus we have the partition function of vibrational excited states:

$$Q_{vibEXC} = \sum_n \left\{ \exp \left[- \sum_i u_i n_i - \sum_{i < j} y_{ij} \left(n_i n_j + \frac{1}{2} n_i + \frac{1}{2} n_j \right) \right] \right\} \quad (\text{A2a})$$

$$= \sum_n \left\{ \exp \left[- \sum_i u_i n_i - \sum_i y_{ii} (n_i^2 + n_i) - \sum_{i < j} y_{ij} \left(n_i n_j + \frac{1}{2} n_i + \frac{1}{2} n_j \right) \right] \right\} \quad (\text{A2b})$$

$$= \sum_n \left\{ \exp \left(- \sum_i u_i n_i \right) \exp \left[- \sum_i y_{ii} (n_i^2 + n_i) - \sum_{i < j} y_{ij} \left(n_i n_j + \frac{1}{2} n_i + \frac{1}{2} n_j \right) \right] \right\} \quad (\text{A2c})$$

$$\approx \sum_n \left\{ \prod_i \exp(-u_i n_i) \prod_i \left[1 - y_{ii} (n_i^2 + n_i) - \sum_{j > i} y_{ij} \left(n_i n_j + \frac{1}{2} n_i + \frac{1}{2} n_j \right) \right] \right\} \quad (\text{A2d})$$

$$\approx \sum_n \left\{ \prod_i \exp(-u_i n_i) \left[1 - \sum_i y_{ii} (n_i^2 + n_i) - \sum_{i < j} y_{ij} \left(n_i n_j + \frac{1}{2} n_i + \frac{1}{2} n_j \right) \right] \right\} \quad (\text{A2e})$$

According to the following relationships:

$$\sum_n \exp(-un) = [1 - \exp(-u)]^{-1} \quad (\text{A3a})$$

$$\sum_n n \exp(-un) = \exp(-u) [1 - \exp(-u)]^{-2} \quad (\text{A3b})$$

$$\sum_n n^2 \exp(-un) = [\exp(-u) + \exp(-2u)] / [1 - \exp(-u)]^{-3} \quad (\text{A3c})$$

$$\sum_n n^m \exp(-un) = (-1)^m \frac{\partial^m}{\partial u^m} \left[\frac{1}{1 - \exp(-u)} \right] \quad (\text{A3d})$$

and the partition function of vibrational excited states to be

$$Q_{vibEXC} = \prod_i \frac{1}{1 - \exp(-u_i)} \left\{ 1 - \frac{2hc}{kT} \sum_i \frac{x_{ii} \exp(-u_i)}{[1 - \exp(-u_i)]^2} - \frac{hc}{2kT} \sum_{i < j} \frac{x_{ij} [\exp(-u_i) + \exp(-u_j)]}{[1 - \exp(-u_i)][1 - \exp(-u_j)]} \right\} \quad (\text{A4a})$$

$$= \prod_i \frac{1}{1 - \exp(-u_i)} \left\{ 1 - \frac{2hc}{kT} \sum_i \frac{x_{ii} \exp(u_i)}{[\exp(u_i) - 1]^2} - \frac{hc}{2kT} \sum_{i < j} \frac{x_{ij} [\exp(u_i) + \exp(u_j)]}{[\exp(u_i) - 1][\exp(u_j) - 1]} \right\} \quad (\text{A4b})$$

Table A1
Comparison of anharmonic corrections to harmonic partition functions of vibrational excited states calculated by harmonic and fundamental frequencies.

T (K)	Q_{AnEXC}										
	H ₂ O	H ₂ O*	HDO	H ₂ S	H ₂ S*	HDS	SO ₂	SO ₂ *	SOO*	SO ₂ *	SOO*
300	1.0001	1.0001	1.0002	1.0004	1.0004	1.0007	1.0025	1.0026	1.0000	1.0000	1.0000
400	1.0005	1.0005	1.0009	1.0013	1.0013	1.0019	1.0046	1.0047	1.0000	1.0000	1.0000
500	1.0014	1.0014	1.0020	1.0027	1.0027	1.0036	1.0069	1.0070	1.0000	1.0000	1.0000
600	1.0026	1.0026	1.0035	1.0044	1.0044	1.0058	1.0094	1.0095	1.0000	1.0001	1.0001
700	1.0041	1.0041	1.0054	1.0065	1.0065	1.0083	1.0119	1.0120	1.0001	1.0002	1.0002
800	1.0059	1.0059	1.0075	1.0089	1.0089	1.0110	1.0144	1.0145	1.0002	1.0003	1.0004
900	1.0079	1.0079	1.0099	1.0115	1.0116	1.0139	1.0169	1.0170	1.0004	1.0005	1.0007
1000	1.0101	1.0101	1.0124	1.0144	1.0144	1.0169	1.0193	1.0194	1.0006	1.0007	1.0010

Table A2
Comparison of corrections of anharmonicity and Vib-Rot coupling of vibrational excited states to partition function ratios calculated by different formulas.

T (K)	AnEXC(H)			AnEXC(F)			VrEXC(H)			VrEXC(F)		
	HDO/H ₂ O	HDS/H ₂ S	NH ₂ D/NH ₃	HDO/H ₂ O	HDS/H ₂ S	NH ₂ D/NH ₃	HDO/H ₂ O	HDS/H ₂ S	NH ₂ D/NH ₃	HDO/H ₂ O	HDS/H ₂ S	NH ₂ D/NH ₃
300	1.0001	1.0003	1.0008	1.0001	1.0003	1.0008	1.0000	0.9999	1.0000	1.0000	0.9999	1.0000
400	1.0003	1.0006	1.0014	1.0003	1.0006	1.0015	0.9999	0.9998	1.0000	0.9999	0.9998	1.0000
500	1.0006	1.0010	1.0020	1.0006	1.0010	1.0020	0.9997	0.9997	1.0000	0.9997	0.9997	1.0000
600	1.0009	1.0014	1.0025	1.0010	1.0014	1.0025	0.9995	0.9995	1.0000	0.9995	0.9995	0.9999
700	1.0013	1.0017	1.0030	1.0013	1.0018	1.0029	0.9993	0.9994	0.9999	0.9992	0.9994	0.9999
800	1.0016	1.0021	1.0034	1.0017	1.0021	1.0032	0.9990	0.9993	0.9999	0.9990	0.9993	0.9999
900	1.0020	1.0023	1.0037	1.0020	1.0023	1.0035	0.9988	0.9993	0.9999	0.9988	0.9993	0.9999
1000	1.0023	1.0025	1.0040	1.0024	1.0025	1.0037	0.9986	0.9992	1.0000	0.9986	0.9992	0.9999
2000	1.0034	1.0025	1.0040	1.0034	1.0024	1.0031	0.9972	0.9983	1.0006	0.9972	0.9983	1.0005

Likewise, vibrational energy at excited states n can be expanded in fundamental frequencies and anharmonic constants:

$$(E_n - E_0)/hc = \sum_i v_i n_i + \sum_i x_{ii} n_i (n_i - 1) + \sum_{i < j} x_{ij} n_i n_j \quad (\text{A5a})$$

Thus, partition function of vibrational excited states is

$$Q'_{vibEXC} = \sum_n \left\{ \exp \left[- \sum_i v_i n_i - \sum_i x_{ii} n_i (n_i - 1) - \sum_{i < j} x_{ij} n_i n_j \right] \right\} \quad (\text{A6a})$$

$$\approx \sum_n \left\{ \prod_i \exp(-u'_i n_i) \prod_i \left[1 - y_{ii} (n_i^2 - n_i) - \sum_{j > i} y_{ij} n_i n_j \right] \right\} \quad (\text{A6b})$$

$$\approx \sum_n \left\{ \prod_i \exp(-u'_i n_i) \left[1 - \sum_i y_{ii} (n_i^2 - n_i) - \sum_{i < j} y_{ij} n_i n_j \right] \right\} \quad (\text{A6c})$$

$$= \prod_i \frac{1}{1 - \exp(-u'_i)} \left\{ 1 - \frac{2hc}{kT} \sum_i \frac{x_{ii} \exp(-2u'_i)}{[1 - \exp(-u'_i)]^2} - \frac{hc}{kT} \sum_{i < j} \frac{x_{ij} \exp(-u'_i) \exp(-u'_j)}{[1 - \exp(-u'_i)][1 - \exp(-u'_j)]} \right\} \quad (\text{A6d})$$

$$= \prod_i \frac{1}{1 - \exp(-u'_i)} \left\{ 1 - \frac{2hc}{kT} \sum_i \frac{x_{ii}}{[\exp(u'_i) - 1]^2} - \frac{hc}{kT} \sum_{i < j} \frac{x_{ij}}{[\exp(u'_i) - 1][\exp(u'_j) - 1]} \right\} \quad (\text{A6e})$$

Both Eqs. (A4b) and (A6e) are results of approximations. When y is very small, Eq. (A2c) to Eq. (A2d) and Eq. (A6a) to Eq. (A6b) are treated by

$$\exp(y) \approx 1 + y \quad (\text{A7a})$$

and Eq. (A2d) to Eq. (A2e) and Eq. (A6b) to Eq. (A6c) are treated by

$$\prod_i (1 + y_i) = 1 + \sum_i y_i \quad (\text{A7b})$$

The smaller y is, the better approximation will achieve. Table A1 compares Q_{AnEXC} and Q'_{AnEXC} to test the errors by employing the approximations (A7a) and (A7b). Obviously, The error of Q'_{AnEXC} is much smaller than that of Q_{AnEXC} , suggesting Eq. (A6e) is a better choice for calculating partition function of vibrational excited states. Table A2 compares the results of using Eq. (22) (shown as AnEXC(H)) and those using Eq. (27) (shown as AnEXC(F)).

APPENDIX B. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2010.09.014.

REFERENCES

- Anbar A. D., Jarzecki A. A. and Spiro T. G. (2005) Theoretical investigation of iron isotope fractionation between $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}(\text{H}_2\text{O})_6^{2+}$: implications for iron stable isotope geochemistry. *Geochim. Cosmochim. Acta* **69**, 825–837.

- Barone V. (2004) Vibrational zero-point energies and thermodynamic functions beyond the harmonic approximation. *J. Chem. Phys.* **120**, 3059–3065.
- Barone V. (2005) Anharmonic vibrational properties by a fully automated second-order perturbative approach. *J. Chem. Phys.* **122**, 014108.
- Benedict W. S., Gailar N. and Plyler E. K. (1956) Rotation–vibration spectra of deuterated water vapor. *J. Chem. Phys.* **24**, 1139–1165.
- Bigeleisen J. (1965) Chemistry of isotopes. *Science* **147**, 463–471.
- Bigeleisen J. (1996) Nuclear size and shape effects in chemical reactions. Isotope chemistry of the heavy elements. *J. Am. Chem. Soc.* **118**, 3676–3680.
- Bigeleisen J. and Mayer M. G. (1947) Calculation of equilibrium constants for isotopic exchange reactions. *J. Chem. Phys.* **15**, 261–267.
- Bron J., Chang C. F. and Wolfsberg M. (1973) Isotopic partition function ratios involving H₂, H₂O, H₂S, H₂Se, and NH₃. *Z. Naturforsch.* **28a**, 129–136.
- Carbonniere P. and Barone V. (2004) Performances of different density functionals in the computation of vibrational spectra beyond the harmonic approximation. *Chem. Phys. Lett.* **399**, 226–229.
- Chacko T., Cole D. R. and Horita J. (2001) Equilibrium oxygen, hydrogen and carbon isotope fractionation factors applicable to geologic systems. *Rev. Mineral. Geochem.* **43**, 1–81.
- Cramer C. J. (2002) *Essentials of Computational Chemistry: Theories and Models*. Wiley, New York.
- Criss R. E. (1991) Temperature dependence of isotopic fractionation factors. In *Stable Isotope Geochemistry: A Tribute to Samuel Epstein*, vol. 3 (eds. H. P. J. Taylor, J. R. O’Neil and I. R. Kaplan). Geochem. Soc. Spec. Pub., San Antonio, Texas, pp. 11–16.
- Criss R. E. (1999) *Principles of Stable Isotope Distribution*. Oxford University Press, New York.
- Darling B. T. and Dennison D. M. (1940) The water vapor molecule. *Phys. Rev.* **57**, 128–139.
- Domagal-Goldman S. D. and Kubicki J. D. (2008) Density functional theory predictions of equilibrium isotope fractionation of iron due to redox changes and organic complexation. *Geochim. Cosmochim. Acta* **72**, 5201–5216.
- Domagal-Goldman S. D., Paul K. W., Sparks D. L. and Kubicki J. D. (2009) Quantum chemical study of the Fe(III)–desferrioxamine B siderophore complex – electronic structure, vibrational frequencies, and equilibrium Fe-isotope fractionation. *Geochim. Cosmochim. Acta* **73**, 1–12.
- Driesner T. and Seward T. M. (2000) Experimental and simulation study of salt effects and pressure/density effects on oxygen and hydrogen stable isotope liquid–vapor fractionation for 4–5 molal aqueous NaCl and KCl solutions to 400 °C. *Geochim. Cosmochim. Acta* **64**, 1773–1784.
- Ellingson B. A., Lynch V. A., Mielke S. L. and Truhlar D. G. (2006) Statistical thermodynamics of bond torsional modes: tests of separable, almost-separable, and improved Pitzer–Gwinn approximations. *J. Chem. Phys.* **125**, 084305.
- Ellingson B. A., Pu J., Lin H., Zhao Y. and Truhlar D. G. (2007) Multicoefficient Gaussian-3 calculation of the rate constant for the OH + CH₄ reaction and its ¹²C/¹³C kinetic isotope effect with emphasis on the effects of coordinate system and torsional treatment. *J. Phys. Chem. A* **111**, 11706–11717.
- Friedman L. and Shiner V. J. (1966) Experimental determination of disproportionation of hydrogen isotopes in water. *J. Chem. Phys.* **44**, 4639–4640.
- Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., Montgomery, Jr., J. A., Vreven T., Kudin K. N., Burant J. C., Millam J. M., Iyengar S. S., Tomasi J., Barone V., Mennucci B., Cossi M., Scalmani G., Rega N., Petersson G. A., Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Klene M., Li X., Knox J. E., Hratchian H. P., Cross J. B., Adamo C., Jaramillo J., Gomperts R., Stratmann R. E., Yazyev O., Austin A. J., Cammi R., Pomelli C., Ochterski J. W., Ayala P. Y., Morokuma K., Voth G. A., Salvador P., Dannenberg J. J., Zakrzewski V. G., Dapprich S., Daniels A. D., Strain M. C., Farkas O., Malick D. K., Rabuck A. D., Raghavachari K., Foresman J. B., Ortiz J. V., Cui Q., Baboul A. G., Clifford S., Cioslowski J., Stefanov B. B., Liu G., Liashenko A., Piskorz P., Komaromi I., Martin R. L., Fox D. J., Keith T., Al-Laham M. A., Peng C. Y., Nanayakkara A., Challacombe M., Gill P. M. W., Johnson B., Chen W., Wong M. W., Gonzalez C. and Pople J. A. (2004) *Gaussian 03 (Revision E.01)*. Gaussian, Inc., Wallingford, CT.
- Goodson D. Z., Sarpal S. K., Bopp P. and Wolfsberg M. (1982) Influence on isotope effect calculations of the method of obtaining force constants from vibrational data. *J. Phys. Chem.* **86**, 659–663.
- Grev R. S., Janssen C. L. and Schaefer H. F. (1991) Concerning zero-point vibrational energy corrections to electronic energies. *J. Chem. Phys.* **95**, 5128–5132.
- Harris N. J. (1995) A systematic theoretical-study of harmonic vibrational frequencies and deuterium-isotope fractionation factors for small molecules. *J. Phys. Chem.* **99**, 14689–14699.
- Hulston J. R. (1969) Revised zero-point energy calculation for H₂O + D₂O ⇌ 2 HDO isotopic equilibrium. *J. Chem. Phys.* **50**, 1483–1484.
- Jarzecki A. A., Anbar A. D. and Spiro T. G. (2004) DFT analysis of Fe(H₂O)₆³⁺ and Fe(H₂O)₆²⁺ structure and vibrations; implications for isotope fractionation. *J. Phys. Chem. A* **108**, 2726–2732.
- Khachkuruzov G. A. (1959) Vibration constants for isotopic varieties of molecular water. *Trudy Gosudart. Inst. Priklad. Khim.* **42**, 109–130.
- Kivelson D. and Wilson E. B. (1952) Approximate treatment of the effect of centrifugal distortion on the rotational energy levels of asymmetric-rotor molecules. *J. Chem. Phys.* **20**, 1575–1579.
- Klochko K., Kaufman A. J., Yao W. S., Byrne R. H. and Tossell J. A. (2006) Experimental measurement of boron isotope fractionation in seawater. *Earth Planet. Sci. Lett.* **248**, 276–285.
- Knyazev V. D. (1998) Density of states of one-dimensional hindered internal rotors and separability of rotational degrees of freedom. *J. Phys. Chem. A* **102**, 3916–3922.
- Knyazev V. D. (1999) Comment on “Hindered rotor density-of-states interpolation function” [J. Chem. Phys. 106, 6675 (1997)] and “The hindered rotor density-of-states” [J. Chem. Phys. 108, 1748 (1998)]. *J. Chem. Phys.* **111**, 7161–7162.
- Koput J., Carter S. and Handy N. C. (2001) Ab initio prediction of the vibrational-rotational energy levels of hydrogen peroxide and its isotopomers. *J. Chem. Phys.* **115**, 8345–8350.
- Li X., Zhao H., Tang M. and Liu Y. (2009) Theoretical prediction for several important equilibrium Ge isotope fractionation factors and geological implications. *Earth Planet. Sci. Lett.* **287**, 1–11.
- Lindemann F. A. (1919) Note on the vapour pressure and affinity of isotopes. *Philos. Mag.* **38**, 173–181.
- Lindemann F. A. and Aston F. W. (1919) The possibility of separating isotopes. *Philos. Mag.* **37**, 523–534.
- Liu Y. and Tossell J. A. (2005) Ab initio molecular orbital calculations for boron isotope fractionations on boric acids and borates. *Geochim. Cosmochim. Acta* **69**, 3995–4006.
- Lynch V. A., Mielke S. L. and Truhlar D. G. (2005) High-precision quantum thermochemistry on nonquasi-harmonic potentials: converged path-integral free energies and a systematically

- convergent family of generalized Pitzer–Gwinn approximations. *J. Phys. Chem. A* **109**, 10092–10099.
- Møller C. and Plesset M. S. (1934) Note on an approximation treatment for many-electron systems. *Phys. Rev.* **46**, 0618–0622.
- McClurg R. B., Flagan R. C. and Goddard W. A. (1997) The hindered rotor density-of-states interpolation function. *J. Chem. Phys.* **106**, 6675–6680.
- McQuarrie D. A. and Simon J. D. (1999) *Molecular Thermodynamics*. University Science Books Press, Sausalito, California.
- Merrick J. P., Moran D. and Radom L. (2007) An evaluation of harmonic vibrational frequency scale factors. *J. Phys. Chem. A* **111**, 11683–11700.
- Nielsen H. H. (1951) The vibration–rotation energies of molecules. *Rev. Mod. Phys.* **23**, 90–136.
- O’Neil J. R. (1986) Theoretical and experimental aspects of isotopic fractionation. *Rev. Mineral.* **16**, 1–40.
- Oi T. (2000) Ab initio molecular orbital calculations of reduced partition function ratios of polyboric acids and polyborate anions. *Z. Naturforsch.* **55a**, 623–628.
- Oi T. and Yanase S. (2001) Calculations of reduced partition function ratios of hydrated monoborate anion by the ab initio molecular orbital theory. *J. Nucl. Sci. Technol.* **38**, 429–432.
- Otake T., Lasaga A. C. and Ohmoto H. (2008) Ab initio calculations for equilibrium fractionations in multiple sulfur isotope systems. *Chem. Geol.* **249**, 357–376.
- Pennington R. E. and Kobe K. A. (1954) Contributions of vibrational anharmonicity and rotation–vibration interaction to thermodynamic functions. *J. Chem. Phys.* **22**, 1442–1447.
- Pitzer K. S. and Gwinn W. D. (1942) Energy levels and thermodynamic functions for molecules with internal rotation. I: Rigid frame with attached tops. *J. Chem. Phys.* **10**, 428–440.
- Polyakov V. B. (1998) On anharmonic and pressure corrections to the equilibrium isotopic constants for minerals. *Geochim. Cosmochim. Acta* **62**, 3077–3085.
- Polyakov V. B. and Kharlashina N. N. (1994) Effect of pressure on equilibrium isotopic fractionation. *Geochim. Cosmochim. Acta* **58**, 4739–4750.
- Pyper J. W. and Christensen L. D. (1975) Equilibrium constants of hydrogen–deuterium–tritium self-exchange reactions in water vapor as studied with a pulsed molecular-beam quadrupole mass filter. *J. Chem. Phys.* **62**, 2596–2599.
- Pyper J. W. and Newbury R. S. (1970) Hydrogen–deuterium self-exchange in hydrogen sulfide and hydrogen selenide as studied with a pulsed-molecular-beam quadrupole mass filter. *J. Chem. Phys.* **52**, 1966–1971.
- Pyper J. W., Newbury R. S. and Barton G. W. (1967) Study of isotopic disproportionation reaction between light and heavy water using a pulsed-molecular-beam mass spectrometer. *J. Chem. Phys.* **46**, 2253–2257.
- Redlich O. (1935) Eine allgemeine beziehung zwischen den schwingungsfrequenzen isotoper molekeln. *Z. Phys. Chem. B* **28**, 371–382.
- Richert P., Bottinga Y. and Javoy M. (1977) A review of hydrogen, carbon, nitrogen, oxygen, sulphur, and chlorine stable isotope fractionation among gaseous molecules. *Ann. Rev. Earth Planet. Sci.* **5**, 65–110.
- Rustad J. R. and Bylaska E. J. (2007) Ab initio calculation of isotopic fractionation in $B(OH)_3(aq)$ and $B(OH)_4^-(aq)$. *J. Am. Chem. Soc.* **129**, 2222–2223.
- Rustad J. R. and Zarzycki P. (2008) Calculation of site-specific carbon-isotope fractionation in pedogenic oxide minerals. *Proc. Natl. Acad. Sci. USA* **105**, 10297–10301.
- Rustad J. R., Nelmes S. L., Jackson V. E. and Dixon D. A. (2008) Quantum-chemical calculations of carbon-isotope fractionation in $CO_2(g)$, aqueous carbonate species, and carbonate minerals. *J. Phys. Chem. A* **112**, 542–555.
- Schaad L. J., Bytautas L. and Houk K. N. (1999) Ab initio test of the usefulness of the Redlich–Teller product rule in computing kinetic isotope effects. *Can. J. Chem.* **77**, 875–878.
- Schauble E. A. (2004) Applying stable isotope fractionation theory to new systems. *Rev. Mineral. Geochem.* **55**, 65–111.
- Schauble E. A. (2007) Role of nuclear volume in driving equilibrium stable isotope fractionation of mercury, thallium, and other very heavy elements. *Geochim. Cosmochim. Acta* **71**, 2170–2189.
- Schauble E. A., Ghosh P. and Eiler J. M. (2006) Preferential formation of ^{13}C – ^{18}O bonds in carbonate minerals, estimated using first-principles lattice dynamics. *Geochim. Cosmochim. Acta* **70**, 2510–2529.
- Schauble E. A., Rossman G. R. and Taylor H. P. (2003) Theoretical estimates of equilibrium chlorine-isotope fractionations. *Geochim. Cosmochim. Acta* **67**, 3267–3281.
- Schmidt M. W., Baldrige K. K., Boatz J. A., Elbert S. T., Gordon M. S., Jensen J. H., Koseki S., Matsunaga N., Nguyen K. A., Su S. J., Windus T. L., Dupuis M. and Montgomery J. A. (1993) General atomic and molecular electronic-structure system. *J. Comput. Chem.* **14**, 1347–1363.
- Scott A. P. and Radom L. (1996) Harmonic vibrational frequencies: an evaluation of Hartree–Fock, Møller–Plesset, quadratic configuration interaction, density functional theory, and semi-empirical scale factors. *J. Phys. Chem.* **100**, 16502–16513.
- Seo J. H., Lee S. K. and Lee I. (2007) Quantum chemical calculations of equilibrium copper(I) isotope fractions in ore-forming fluids. *Chem. Geol.* **243**, 225–237.
- Shaffer W. H. and Schuman R. P. (1944) The Infra-Red spectra of bent XYZ molecules. Part I: Vibration–rotation energies. *J. Chem. Phys.* **12**, 504–513.
- Shimanouchi T. (1972) *Tables of Molecular Vibrational Frequencies, Consolidated Volume I*. Natl. Stand. Ref. Data Ser., Natl. Bur. Stand Press, Washington, DC. pp. 1–160.
- Shimanouchi T. (1977) *Tables of molecular vibrational frequencies, consolidated volume II*. *J. Phys. Chem. Ref. Data* **6**, 993–1102.
- Simonson J. M. (1990) The enthalpy of the isotope-exchange reaction: $H_2O + D_2O = 2HDO$ at temperatures to 673 K and at pressures to 40 MPa. *J. Chem. Thermodyn.* **22**, 739–749.
- Singh G. and Wolfsberg M. (1975) The calculation of isotopic partition function ratios by a perturbation theory technique. *J. Chem. Phys.* **62**, 4165–4180.
- Sinha P., Boesch S. E., Gu C. M., Wheeler R. A. and Wilson A. K. (2004) Harmonic vibrational frequencies: scaling factors for HF, B3LYP, and MP2 methods in combination with correlation consistent basis sets. *J. Phys. Chem. A* **108**, 9213–9217.
- Stockmayer W. H., Kavanagh G. M. and Mickley H. S. (1944) The thermodynamic properties of gaseous sulfur trioxide. *J. Chem. Phys.* **12**, 408–412.
- Stripp K. F. and Kirkwood J. G. (1951) Asymptotic expansion of the partition function of the asymmetric top. *J. Chem. Phys.* **19**, 1131–1133.
- Tossell J. A. (2005) Calculating the partitioning of the isotopes of Mo between oxidic and sulfidic species in aqueous solution. *Geochim. Cosmochim. Acta* **69**, 2981–2993.
- Truhlar D. G. (1991) A simple approximation for the vibrational partition function of a hindered internal rotation. *J. Comput. Chem.* **12**, 266–270.
- Urey H. C. (1947) The thermodynamic properties of isotopic substances. *J. Chem. Soc. (Lond.)*, 562–581.
- Urey H. C. and Greiff L. J. (1935) Isotopic exchange equilibria. *J. Am. Chem. Soc.* **57**, 321–327.
- Urey H. C. and Rittenberg D. (1933) Some thermodynamic properties of the H^1H^2 , H^2H^2 molecules and compounds containing the H^2 atom. *J. Chem. Phys.* **1**, 137–143.

- Urey H. C., Lowenstam H. A., Epstein S. and McKinney C. R. (1951) Measurement of paleotemperatures and temperatures of the upper cretaceous of England, Denmark, and the South-eastern United-States. *Bull. Geol. Soc. Am.* **62**, 399–416.
- Vojta G. (1960) Grundlagen der statistischen thermodynamik von isotopensystemen mit chemischen reactionen. *Kernenergie* **3**, 917–927.
- Vojta G. (1961) Berechnung der schwingungszustandssumme entarteter anharmonischer oszillatoren mit hilfe der mellinschen integraltransformation. *Ann. Phys.* **462**, 397–402.
- Vojta G. and Zylka C. (1993) Hindered internal rotation in molecular systems: quantum statistics of equilibrium and rate constants in the Wigner function formalism. *Theor. Chim. Acta* **86**, 439–449.
- Wilson E. B. (1936) The effect of rotational distortion on the thermodynamic properties of water and other polyatomic molecules. *J. Chem. Phys.* **4**, 526–528.
- Wilson E. B., Decius J. C. and Cross P. C. (1955) *Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra*. McGraw-Hill Book Co. Press, New York.
- Wolfsberg M. (1969) Correction to the effect of anharmonicity on isotopic exchange equilibria – application to polyatomic molecules. *J. Chem. Phys.* **50**, 1484–1486.
- Wolfsberg M., Massa A. A. and Pyper J. W. (1970) Effect of vibrational anharmonicity on the isotopic self-exchange equilibria $H_2X + D_2X = 2HDX$. *J. Chem. Phys.* **12**, 408–412.
- Zeebe R. E. (2005) Stable boron isotope fractionation between dissolved $B(OH)_3$ and $B(OH)_4^-$. *Geochim. Cosmochim. Acta* **69**, 2753–2766.
- Zeebe R. E. (2009) Hydration in solution is critical for stable oxygen isotope fractionation between carbonate ion and water. *Geochim. Cosmochim. Acta* **73**, 5283–5291.
- Zhang Q., Day P. N. and Truhlar D. G. (1993) The accuracy of second order perturbation theory for multiply excited vibrational energy levels and partition functions for a symmetrical top molecular ion. *J. Chem. Phys.* **98**, 4948–4958.
- Zhao Y. and Truhlar D. G. (2008) The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **120**, 215–241.

Associate editor: Juske Horita