Evaluation of Isotope Effects on Henry's Law Constants by a Molecular Dynamics Technique

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Dedicated to our teacher, colleague, and friend Jacob Bigeleisen on the occasion of his 70th birthday

Solute isotope effects on Henry's law constants of aqueous solutions of argon atoms, of helium atoms, and of nitrogen molecules are considered. A cell model is employed; the translational and rotational motions are treated in the first quantum approximation while the vibrational motion of nitrogen is fully treated (but assumed to be separable and harmonic). The required mean square forces (or equivalent frequency parameters) are evaluated by classical molecular dynamics calculations.

Introduction

Experimental studies of (solute) isotope effects on Henry's law constants have been carried out on aqueous solutions of helium and a number of inert homonuclear diatomic molecules by Benson and coworkers [1 a, b, c] and by Muccitelli and Wen [1 d]. Very simple models [2, 3] have been invoked in order to understand these isotope effects. The classical molecular dynamics studies here of aqueous solutions of argon, of helium, and of molecular nitrogen were undertaken to obtain further information about these isotope effects.

Isotope effects on the Henry's law constant (k) can be regarded as isotope effects on the equilibrium of the solute atoms/molecules (Ar, He, N_2) between the aqueous phase and the gas phase [2]. In their classic work on equilibrium isotope effects, Jacob Bigeleisen and Maria Goepert Mayer [4] (BM) recognized and emphasized that isotope effects on equilibrium constants are quantum effects. Thus, one can write for the isotope effect here

$$\frac{k_1}{k_2} = \frac{(Q_2^a/Q_1^a)_{qm}/(Q_2^a/Q_1^a)_{cl}}{(Q_2^g/Q_1^g)_{qm}/(Q_2^g/Q_1^g)_{cl}} . \tag{1}$$

Subscripts 1 and 2 refer by convention to light and heavy isotopic molecule respectively, Q refers to molecular partition function, qm refers to quantum mechanical, cl to classical, and the superscripts g and a to gas phase and aqueous phase respectively. The quantum effect on the isotopic partition function ratio is called the reduced isotopic partition function ratio – $(s_2/s_1)\, f$, a name and a symbol associated with BM. Thus,

$$\frac{k_1}{k_2} = \frac{(s_2/s_1)\, f_a}{(s_2/s_1)\, f_g} . \tag{2}$$

For gas phase molecules, in the ideal-gas-rigid-rotor-harmonic-oscillator approximation, $(s_2/s_1)\, f_g$ can be simply expressed as shown by BM. Thus,

$$(s_2/s_1)\, f_g(\mathrm{He}) = (s_2/s_1)\, f_g(\mathrm{Ar}) = 1 ,$$
$$(s_2/s_1)\, f_g(\mathrm{N_2}) = \frac{u_2(1-e^{-u_1})}{u_1(1-e^{-u_2})}\, e^{(u_1-u_2)/2} , \tag{3}$$

where $u = h c \nu / kT$ with ν (in cm^{-1}) the vibrational frequency of the relevant nitrogen molecule. Since the harmonic vibrational frequency of N_2 is known experimentally (*vide infra*), the needed $(s_2/s_1)\, f_g$ values may be regarded as knowns. Thus, the only unknown quantities are the reduced isotopic partition function ratios in the aqueous phase. These are calculated here with aid of classical molecular dynamics (MD) calculations on aqueous solutions.

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Evaluation of Reduced Isotopic Partition Function Ratio $(s_2/s_1)\,f_a$

The reduced isotopic partition function ratio for the solute in aqueous solution $(s_2/s_1)\,f_a$ will be calculated on the basis of a cell model in which the N-atomic solute molecule has 3 N degrees of freedom. For an atom (He or Ar), the three degrees of freedom are the three (hindered) translations; for a diatomic molecule (N_2), there are the three (hindered) translations of the center of mass, the two (hindered) rotations, and the internal vibration of the molecule. A cell model of this type was proposed by Bigeleisen [5] to calculate condensed phase reduced isotopic partition function ratios in connection with vapor pressure isotope effects.

The reduced isotopic partition function ratio will be calculated by means of the method of quantum corrections for the translational and rotational degrees of freedom. For these degrees of freedom, one expects from the work on vapor pressure isotope effects [5] that the first quantum correction is adequate. In the method of quantum corrections [6]

$$Q_{\mathrm{qm}}=Q_{\mathrm{cl}}(1+\hbar^2\chi_2+\text{terms in higher powers of }\hbar). \quad (4)$$

The first non-vanishing term in the corrections (the first quantum correction) is second order in $\hbar$.

a) Solute Atoms

The classical kinetic energy T for a solute atom in a cell and the corresponding quantum mechanical operator $\hat{H}$ are given respectively by

$$2T=m(\dot{x}^2+\dot{y}^2+\dot{z}^2),$$

$$\hat{H}=-\frac{\hbar^2}{2m}\nabla^2+V, \quad (5)$$

where m is the atomic mass and V is the potential for motion of the atom in the cell. The first quantum correction then has the simple form [6, 7]

$$\hbar^2\chi_2=-\frac{\hbar^2}{24(kT)^3}\frac{1}{m}\langle(\nabla V)^2\rangle \quad (6)$$

$$=-\frac{\hbar^2}{24(kT)^3}\frac{1}{m}\left\langle\left(\frac{\partial V}{\partial x}\right)^2+\left(\frac{\partial V}{\partial y}\right)^2+\left(\frac{\partial V}{\partial z}\right)^2\right\rangle.$$

Brackets signify classical-statistical-mechanical average, and the bracketed quantity here is just the mean square force acting on the particle, taken in Cartesian coordinates. For small quantum correction, one then obtains

$$(s_2/s_1)\,f_a=1+\frac{\hbar^2}{24(kT)^3}\left(\frac{1}{m_1}-\frac{1}{m_2}\right)\langle(\boldsymbol{F})^2\rangle, \quad (7)$$

where m_1 and m_2 refer to mass of light and heavy atom respectively and the last expression in brackets refers to mean square force. The mean square force is independent of isotopic mass and will be evaluated by a classical molecular dynamic calculation.

b) Solute Diatomic Molecules

For a diatomic molecule AB, the kinetic energy can be written as

$$2T=m_A(\dot{x}_A^2+\dot{y}_A^2+\dot{z}_A^2)+m_B(\dot{x}_B^2+\dot{y}_B^2+\dot{z}_B^2) \quad (8)$$

$$=(m_A+m_B)(\dot{X}^2+\dot{Y}^2+\dot{Z}^2)+\mu(\dot{x}^2+\dot{y}^2+\dot{z}^2), \quad (9)$$

and the corresponding quantum mechanical operator $\hat{H}$ is

$$\hat{H}=-\frac{\hbar^2}{2M}\nabla_{\mathrm{cm}}^2-\frac{\hbar^2}{2\mu}\nabla_x^2+V. \quad (10)$$

Here X, Y, Z refer to the coordinates of the center of mass, x, y, z refer to the relative coordinates of the two atoms (i.e. $x=x_A-x_B$, etc.), ∇_{cm}^2 is the Laplacian operator for the center of mass while ∇_x^2 is the Laplacian operator for the relative coordinates of the two atoms, M is the molecular mass, μ the reduced mass of the diatomic molecule, and V the cell potential. The first quantum correction then has the form

$$\hbar^2\chi_2=-\frac{\hbar^2}{24(kT)^3}\left[\frac{1}{M}\langle(\nabla_{\mathrm{cm}}V)^2\right]+\frac{1}{\mu}\langle(\nabla_x V)^2\rangle. \quad (11)$$

The first average term in brackets is the mean square force for translation of the center of mass motion and is similar to the mean square force for the atom in (6); the second averaged term is the generalized mean square force for the relative motion of the two atoms in the molecule. ∇_x can be expressed in terms of polar coordinates r, θ, ϕ, where r then refers to vibrational degree of freedom while θ and ϕ refer to rotational degrees of freedom of the diatomic molecule in the cell.

The $(\nabla V)^2$ contributions for the vibrational and the two rotational degrees of freedom are respectively

$$\left\langle\left(\frac{\partial V}{\partial r}\right)^2\right\rangle, \quad \left\langle\frac{1}{r^2}\left(\frac{\partial V}{\partial\theta}\right)^2\right\rangle,$$

and

$$\left\langle\frac{1}{r^2\sin^2\theta}\left(\frac{\partial V}{\partial\phi}\right)^2\right\rangle. \quad (12)$$

The second and third terms above can be combined to give the rotational contribution, while the first term is the contribution from the diatomic molecule vibration. The vibrational and rotational contributions can be re-expressed in a convenient form by introducing the force vectors acting on the two atoms. Thus

$$\frac{\partial V}{\partial r} = \sum_{q=x,y,z} \left(\frac{\partial V}{\partial q_A} \frac{\partial q_A}{\partial q} \frac{\partial q}{\partial r} + \frac{\partial V}{\partial q_B} \frac{\partial q_B}{\partial q} \frac{\partial q}{\partial r} \right), \tag{13}$$

where q_A refers to a Cartesian coordinate on atom A, q refers to a relative Cartesian coordinate of the two atoms. A similar process is carried out for $\partial V/\partial\theta$ and $\partial V/\partial\phi$. One obtains for the contributions to the mean square forces:

vibrational:

$$\langle F_v^2 \rangle = \left\langle \left\{ \left(\frac{m_B}{m_A+m_B} \boldsymbol{f}_A - \frac{m_A}{m_A+m_B} \boldsymbol{f}_B \right) \cdot \boldsymbol{\eta} \right\}^2 \right\rangle,$$

rotational:

$$\langle F_{rt}^2 \rangle = \left\langle \left\{ \left(\frac{m_B}{m_A+m_B} \boldsymbol{f}_A - \frac{m_A}{m_A+m_B} \boldsymbol{f}_B \right) \times \boldsymbol{\eta} \right\}^2 \right\rangle,$$

translational:

$$\langle F_t^2 \rangle = \langle (\boldsymbol{f}_A + \boldsymbol{f}_B)^2 \rangle. \tag{14}$$

Here $\boldsymbol{\eta}$ is a unit vector along the A–B bond from A to B. The translational term arises from the translational mean square force in (11).

Equation (11) is then transformed into

$$\begin{aligned} \hbar^2 \chi_2 = -\frac{\hbar^2}{24(kT)^3} \Bigg[& \frac{1}{M} \langle (\boldsymbol{f}_A + \boldsymbol{f}_B)^2 \rangle \qquad (15) \\ & + \frac{1}{\mu} \left\langle \left\{ \left(\frac{m_B}{m_A+m_B} \boldsymbol{f}_A - \frac{m_A}{m_A+m_B} \boldsymbol{f}_B \right) \cdot \boldsymbol{\eta} \right\}^2 \right\rangle \\ & + \frac{1}{\mu} \left\langle \left\{ \left(\frac{m_B}{m_A+m_B} \boldsymbol{f}_A - \frac{m_A}{m_A+m_B} \boldsymbol{f}_B \right) \times \boldsymbol{\eta} \right\}^2 \right\rangle \Bigg] \\ = -\frac{\hbar^2}{24(kT)^3} & \left[\frac{\langle F_t^2 \rangle}{M} + \frac{\langle F_v^2 \rangle}{\mu} + \frac{\langle F_{rt}^2 \rangle}{\mu} \right]. \qquad (16) \end{aligned}$$

It may be noted that this equation is equivalent to

$$\begin{aligned} \hbar^2 \chi_2 = -\frac{\hbar^2}{24(kT)^3} \Bigg[& \frac{1}{M} \{ \langle \boldsymbol{f}_A^2 \rangle + \langle \boldsymbol{f}_B^2 \rangle + 2 \langle \boldsymbol{f}_A \cdot \boldsymbol{f}_B \rangle \} \\ & + \frac{1}{\mu} \left\{ \left(\frac{m_B}{m_A+m_B} \right)^2 \langle \boldsymbol{f}_A^2 \rangle + \left(\frac{m_A}{m_A+m_B} \right)^2 \langle \boldsymbol{f}_B^2 \rangle \right. \\ & \left. - 2 \frac{m_A m_B}{(m_A+m_B)^2} \langle \boldsymbol{f}_A \cdot \boldsymbol{f}_B \rangle \right\} \Bigg] \\ = -\frac{\hbar^2}{24(kT)^3} & \left[\frac{\langle \boldsymbol{f}_A^2 \rangle}{m_A} + \frac{\langle \boldsymbol{f}_B^2 \rangle}{m_B} \right]. \qquad (17) \end{aligned}$$

This last form of χ_2 could have been deduced immediately if the Hamiltonian operator had been written as

$$\hat{H} = -\frac{\hbar^2}{2m_A} \nabla_A^2 - \frac{\hbar^2}{2m_B} \nabla_B^2 + V, \tag{18}$$

where ∇_A^2 and ∇_B^2 are the Laplacian operators on nucleus A and nucleus B respectively.

Equation (16) enables us to write Q_{qm}/Q_{cl} in the first quantum correction. As already noted, the first quantum correction is expected to be applicable to the translational and rotational motions in the cell but not to the vibrational motion of the N_2 molecule at 295 (with a fundamental frequency $\nu \sim 2300\ \mathrm{cm}^{-1}$). Therefore, the quantum correction for vibration is separated by 1) omitting the term in $\langle F_v^2 \rangle$ from χ_2 and calling the resulting expression χ_2', and 2) rewriting (4) for the solute diatomic molecule

$$Q_{qm} = Q_{cl}(1 + \hbar^2 \chi_2') \left(1 - \frac{\hbar^2}{24(kT)^3} \frac{\langle F_v^2 \rangle}{\mu} \right). \tag{19}$$

The term in $\langle F_v^2 \rangle$ is just the first quantum correction for a harmonic oscillator with frequency $\nu = (1/2\pi c)(f/\mu)^{1/2}$, where f is the harmonic force constant, and corresponding $\langle F_v^2 \rangle = kTf$. This term is now replaced by Q_{qm}/Q_{cl} for a harmonic oscillator to yield

$$Q_{qm} = Q_{cl}(1 + \hbar^2 \chi_2') \, u(1 - e^{-u})^{-1} e^{-u/2} \tag{20}$$

with $u = hc\nu/kT$. Equation (19) is valid, of course, when the quantum corrections are sufficiently small. However, since large vibrational quantum effects are being considered here, the validity of (19) must rest on the assumption that the vibrational degree of freedom is separable; for the N_2/water system, to which application is made here, this assumption appears justified since energy transfer involving the N_2 vibrational degree of freedom is found to be very slow in the MD calculations (*vide infra*).

The last bracket on the right hand side of (15), which is multiplied by μ^{-1}, can be rewritten as follows, for a homo-atomic diatomic molecule (either $^{14}N_2$ or $^{14}N^{15}N$),

$$\begin{aligned} \Bigg\{ & \frac{1}{2} \left[1 + \left(\frac{m_A - m_B}{m_A + m_B} \right)^2 \right] \langle (\boldsymbol{f}_A \times \boldsymbol{\eta})^2 \rangle \\ & - \frac{1}{2} \left[1 - \left(\frac{m_A - m_B}{m_A + m_B} \right)^2 \right] \langle (\boldsymbol{f}_A \times \boldsymbol{\eta}) \cdot (\boldsymbol{f}_B \times \boldsymbol{\eta}) \rangle \Bigg\}. \end{aligned} \tag{21}$$

Use has been made here of the fact that, within the Born-Oppenheimer approximation, the classical statistical averages of force functions are independent of isotopic mass for homo-atomic molecules so that, for instance,

$$\langle (\boldsymbol{f}_A \times \boldsymbol{\eta})^2 \rangle = \langle (\boldsymbol{f}_B \times \boldsymbol{\eta})^2 \rangle . \tag{22}$$

For homonuclear molecules, the term in $(m_A - m_B)$ above is zero. In the homo-atomic diatomic molecule $^{15}N^{14}N$ which we will consider here, the term $(m_A - m_B)^2/(m_A + m_B)^2$ has the magnitude 0.001. An analysis shows that the neglect of such a term with respect to unity is likely to have a negligible effect on the result. Thus, (21) will be replaced by

$$\langle \{\tfrac{1}{2}(\boldsymbol{f}_A - \boldsymbol{f}_B) \times \boldsymbol{\eta}\}^2 \rangle , \tag{23}$$

an expression which is strictly correct only for a homonuclear molecule.

Thus, on the assumptions of 1) a cell model for solute motion to separate that motion from solvent motion, 2) separability of (harmonic) vibrational motion of solute from translational and rotational motions, and 3) adequacy of first quantum corrections for translational and rotational motions, the following formula has been derived,

$$\begin{aligned}(s_2/s_1)\,f_a = \Biggl[1 + \frac{\hbar^2}{24\,(kT)^3} \Biggl\{ & \left(\frac{1}{M_1} - \frac{1}{M_2}\right) \langle (\boldsymbol{f}_A + \boldsymbol{f}_B)^2 \rangle \\ & + \left(\frac{1}{\mu_1} - \frac{1}{\mu_2}\right) \langle \{(\boldsymbol{f}_A - \boldsymbol{f}_B) \times \boldsymbol{\eta}\}^2 \rangle \Biggr] \\ & \cdot \frac{u_2}{u_1} \left(\frac{1 - e^{-u_1}}{1 - e^{-u_2}}\right) e^{(u_1 - u_2)/2} ,\end{aligned} \tag{24}$$

where $u = h\,c\,\nu/kT$, ν refers to vibrational frequency (cm^{-1}) in aqueous phase and 1 and 2 refer to light and heavy molecule, respectively. Note again that, within the Born-Oppenheimer approximation, the $\langle\ \rangle$ values are independent of the isotopic masses of the atoms. The classically averaged quantities involving forces on the atoms are evaluated here by the molecular dynamics technique.

Molecular Dynamics Calculations

Classical molecular dynamics (MD) studies were carried out on three different microcanonical systems corresponding to 295 K and constant volume using standard techniques [8]: 1) a 2.2 molal solution of argon atoms in water (8 argon atoms and 200 water molecules, basic cubic box length 18.1 Å) with use of an argon-water potential deduced by Kolos et al. [9] by quantum mechanical calculation and fitted here in terms of atom-atom pair potentials Ar–H and Ar–O; 2) a 2.2 molal solution of helium atoms in water in which the helium-water potential is constructed by scaling the argon-water potential, taking into consideration the differences in "sizes" of a helium atom and of an argon atom (basic cubic box length 18.1 Å); 3) a 2.3 molal solution of nitrogen molecules in water (8 nitrogen molecules and 192 water molecules, basic cubic box length 18.0 Å) with use of a nitrogen-water potential deduced by Curtiss and Eisgruber [10] by quantum mechanical calculation and fitted here in terms of atom-atom pair potentials N–O, N–H, and N–N (the latter taken to be the Morse potential corresponding to experimental [11] data for a gas phase N_2 molecule). The force field used for water is the central force model of Stillinger and Rahman [12a], originally developed by Lemberg and Stillinger [12b]. Each system was equilibrated at the desired temperature. Subsequently, the system is propagated for 5000 timesteps without correcting the temperature, equivalent to 1.25 picoseconds; the average temperature of the systems was 295 ± 7 K. Details of the various force fields as well as many further details of the calculations will be reported elsewhere. The effect of solute concentration on the calculated mean square forces was not considered.

Calculation of the Mean Square Forces

The required mean square forces $\langle \boldsymbol{F}_t^2 \rangle$, $\langle \boldsymbol{F}_v^2 \rangle$, $\langle \boldsymbol{F}_{rt}^2 \rangle$ for the atomic solutes and also for homonuclear N_2 solute molecules are calculated from the MD trajectories. Several methods are available; we discuss these for the three types of motions: translational, vibrational and rotational.

a) Translational Motion

1. The translational mean square force $\langle \boldsymbol{F}_t^2 \rangle$ for either the atomic or distomic molecule system can be determined from the MD trajectories through (6) and (14).

2. The mean square forces may also be determined from the form of the autocorrelation function for the velocity ($\boldsymbol{V}$) of the center of mass. The normalized autocorrelation function is given by [13]

$$c(t) = \frac{\langle \boldsymbol{V}(t) \cdot \boldsymbol{V}(0) \rangle}{\langle \boldsymbol{V}^2(0) \rangle} . \tag{25}$$

The autocorrelation function is an even function of the time, and it is straightforward to show that, to second order in t, Taylor's expansion can be written [13],

$$c(t)=1+(t^2/2)\,\langle \dot{V}^2(0)\rangle/\langle V^2(0)\rangle . \tag{26}$$

Writing $\langle \dot{V}^2(0)\rangle$ in terms of the mean square force on the center of mass, $\langle \boldsymbol{F}_\mathrm{t}^2\rangle$, and using the equipartition theorem for $\langle V^2(0)\rangle$ leads to

$$c(t)=1-(t^2/2)\,\langle \boldsymbol{F}_\mathrm{t}^2\rangle/(3\,MkT) . \tag{27}$$

Thus $\langle \boldsymbol{F}_\mathrm{t}^2\rangle$ can be obtained from the second derivative of $c(t)$ at $t=0$; $c(t)$ is evaluated from the atomic velocities obtained during the simulation.

3. The spectral density $f(\omega)$ for a given $c(t)$ is

$$f(\omega)=\frac{1}{\pi}\int_{-\infty}^{\infty} e^{i\omega t}\,c(t)\,\mathrm{d}t = \frac{2}{\pi}\int_{0}^{\infty}(\cos\omega t)\,c(t)\,\mathrm{d}t\,, \tag{28}$$

where the second equality follows because $c(t)$ is even. From the inverse relationship

$$c(t)=\int_0^\infty (\cos\omega t)\,f(\omega)\,\mathrm{d}t, \tag{29}$$

one can obtain by expanding the cosine,

$$c(t)=1-(1/2)\,\omega_\mathrm{et}^2\,t^2+\ldots\,. \tag{30}$$

Here, use has been made of the fact that $f(\omega)$ is normalized and the translational Einstein frequency has been defined,

$$\omega_\mathrm{et}^2=\int_0^\infty \omega^2 f(\omega)\,\mathrm{d}\omega\,. \tag{31}$$

From the comparison of (27) and (30), it follows that

$$\omega_\mathrm{et}^2=\langle \boldsymbol{F}_\mathrm{t}^2\rangle/(3\,M\,kT). \tag{32}$$

Thus, $\langle \boldsymbol{F}_\mathrm{t}^2\rangle$ can be evaluated through the Einstein frequency obtained from the Fourier transform of the autocorrelation function.

b) Vibrational Motion

$\langle \boldsymbol{F}_\mathrm{v}^2\rangle$ can be determined by methods similar to those for the determination of $\langle \boldsymbol{F}_\mathrm{t}^2\rangle$.

1. The vibrational mean square force $\langle \boldsymbol{F}_\mathrm{v}^2\rangle$ can be determined from the forces $\boldsymbol{f}_\mathrm{A}$ and $\boldsymbol{f}_\mathrm{B}$ acting on the atoms of the diatomic molecule during the simulation [Eq. (14)].

2. One finds for the normalized autocorrelation function for the time derivative of the internuclear separation ($\dot{r}$) to second order in t,

$$c(t)=1-(t^2/2)\,\langle \boldsymbol{F}_\mathrm{v}^2\rangle/(\mu\,kT). \tag{33}$$

The factor of 3 in the denominator of the last term in (27), which arises from 3 translational degrees of freedom, has been replaced here by a factor of 1. In the derivation of (33), the equation of motion for r was taken to be

$$\mu\ddot{r}=-\frac{\partial V}{\partial r}\,. \tag{34}$$

Thus, the centrifugal contribution, which is negligible in the calculations carried out here, was omitted. This method for obtaining $\langle \boldsymbol{F}_\mathrm{v}^2\rangle$ from the second derivative of the autocorrelation function at $t=0$ was not employed in the present application.

3. The vibrational Einstein frequency ω_ev arising from the vibrational spectral density obtained from the Fourier transform of the $\dot{r}$ autocorrelation function is related to $\langle \boldsymbol{F}_\mathrm{v}^2\rangle$ by

$$\omega_\mathrm{ev}^2=\langle \boldsymbol{F}_\mathrm{v}^2\rangle/(\mu\,kT). \tag{35}$$

Thus, $\langle \boldsymbol{F}_\mathrm{v}^2\rangle$ can be obtained from the Fourier transform of the autocorrelation function.

c) Rotational Motion

1. The rotational mean square force $\langle \boldsymbol{F}_\mathrm{rt}^2\rangle$ can be determined from the forces $\boldsymbol{f}_\mathrm{A}$ and $\boldsymbol{f}_\mathrm{B}$ acting on the atoms during the simulation [Eq. (14)].

2. The rotational mean square force may also be determined from the form of an autocorrelation function. If one recognizes that the rotational force $\boldsymbol{F}_\mathrm{rt}$ multiplied by the internuclear separation r,

$$r\,\boldsymbol{F}_\mathrm{rt}=[\tfrac{1}{2}(\boldsymbol{f}_\mathrm{A}-\boldsymbol{f}_\mathrm{B})\times\boldsymbol{\eta}]\,r\,, \tag{36}$$

is just the torque with respect to the center of mass of the homonuclear molecule, then one finds straightforwardly that

$$\frac{\mathrm{d}\boldsymbol{L}}{\mathrm{d}t}=r\,\boldsymbol{F}_\mathrm{rt}\,, \tag{37}$$

where $\boldsymbol{L}$ is the angular momentum with respect to the center of mass. Consequently, the desired autocorrelation function is the one for the angular momentum of the diatomic molecule, which can be determined from the velocities and coordinates calculated during the

Table 1. Translational Einstein frequencies ν_{et} in cm^{-1}, 295 K.

System	*A*	*B*	*C*
^{40}Ar in liquid water	71		
^{4}He in liquid water	188		
^{14}N$_2$ in liquid water	95	95	90

A: ν_{et} calculated directly from mean square forces on atoms.
B: ν_{et} calculated from the Fourier transform of autocorrelation function.
C: ν_{et} calculated from second derivative of autocorrelation function.

Table 2. Rotational Einstein frequencies ν_{ert} (cm^{-1}) and vibrational Einstein frequencies ν_{ev} (cm^{-1}), 295 K.

		A [a]	*B* [a]	*C* [a]
ν_{ert}	^{14}N$_2$ in liquid water	78	80	75
ν_{ev}	^{14}N$_2$ in liquid water	2338	2339	
ν_{ev}	^{14}N$_2$ in gas		2349 [b]	

[a] *A*: Calculated directly from mean square forces on atoms.
B: Calculated from the Fourier transform of appropriate autocorrelation function.
C: Calculated from second derivative of autocorrelation function.

[b] This is the value obtained for the vibrational frequency of non-interacting N$_2$ molecules at 295 K. The value is lower than the harmonic frequency of non-interacting N$_2$ molecules because of anharmonicity. This frequency is used to evaluate $(s_2/s_1)\,f_{\text{g}}$ [Eq. (3)] for N$_2$.

MD simulation,

$$\begin{aligned} A_{\text{L}}(t) &= \langle \boldsymbol{L}(t)\cdot \boldsymbol{L}(0)\rangle / \langle \boldsymbol{L}^2(0)\rangle \\ &= 1-(t^2/2)\,\langle \dot{\boldsymbol{L}}^2(0)\rangle / \langle \boldsymbol{L}^2(0)\rangle + \dots \\ &\cong 1-(t^2/2)\,\langle \boldsymbol{F}_{\text{rt}}^2\rangle \Big/ \left\langle \frac{\boldsymbol{L}^2(0)}{r^2}\right\rangle + \dots \qquad (38) \\ &= 1-(t^2/2)\,\langle \boldsymbol{F}_{\text{rt}}^2\rangle/(\mu\, kT) + \dots\,. \end{aligned}$$

Account has been taken that the AB internuclear separation r varies little during the simulation. The equipartition theorem value kT of $\langle \boldsymbol{L}^2/(\mu r^2)\rangle$ has been inserted. Thus, $\langle \boldsymbol{F}_{\text{rt}}^2\rangle$ is obtainable from the second derivative of $A_{\text{L}}(t)$ at $t=0$.

3. The mean square force is also obtainable from the Einstein rotational frequency ω_{ert} obtained from the Fourier transform of $A_{\text{L}}(t)$. Here

$$\omega_{\text{ert}}^2 = \langle \boldsymbol{F}_{\text{rt}}^2\rangle/(2\,\mu\, kT)\,. \qquad (39)$$

In Tables 1 and 2, calculations of the mean square forces for translational, rotational, and vibrational motions, where applicable, are reported. The results are reported in terms of Einstein frequencies ν_{e} (in cm^{-1}) obtained from the corresponding ω_{e}'s of (31), (35), and (39) by

$$\nu_{\text{e}} = \omega_{\text{e}}/(2\,\pi\, c)\,. \qquad (40)$$

These frequencies are, of course, isotope dependent since they depend on total mass (ν_{et}) and reduced mass (ν_{ert} and ν_{ev}) unlike the mean square forces which are isotope independent. The frequencies are reported since they convey more physical insight to those who have employed harmonic cell models in the study of vapor pressure isotope effects; note, however, that no harmonic assumption has been made for translations and rotations in the present calculations. For aqueous N$_2$, various methods of calculating the mean square forces are compared. The agreement between the methods tends to be excellent. It may be noted from (32), (35), and (39) that the relevant mean square force $\langle \boldsymbol{F}_{\text{s}}^2\rangle$ divided by kT may be regarded as the "effective force constant" for the corresponding Einstein frequency. Such a relationship between mean square force and force constant has been mentioned in [7]. It is noteworthy that, when MD calculations for a given system are carried out at different temperatures, $\langle \boldsymbol{F}_{\text{s}}^2\rangle/kT$ tends to be less temperature dependent than $\langle \boldsymbol{F}_{\text{s}}^2\rangle$.

The frequencies that have been obtained here for the condensed phase molecules are just the type of quantities that one needs for vapor pressure isotope effect considerations [5]. The MD techniques used here could probably be employed to carry out theoretical studies of vapor pressure isotope effects.

Calculations of the Henry's Law Constants

In terms of the Einstein frequencies ν_{e}, $(s_2/s_1)\,f_{\text{a}}$ can be written

$$\begin{aligned} &(s_2/s_1)\,f_{\text{a}} \\ &= \left\{1+\tfrac{1}{24}\,(h\,c/kT)^2\,[3\,(\nu_{1\,\text{et}}^2-\nu_{2\,\text{et}}^2)+2\,(\nu_{1\,\text{ert}}^2-\nu_{2\,\text{ert}}^2)]\right\} \\ &\quad\cdot \frac{u_{2\,\text{ev}}}{u_{1\,\text{ev}}}\left(\frac{1-e^{-u_{1\text{ev}}}}{1-e^{-u_{2\text{ev}}}}\right) e^{(u_{1\text{ev}}-u_{2\text{ev}})/2} \\ &= (1+\alpha+\beta)\,\gamma\,, \qquad (41) \end{aligned}$$

where $u_{\text{ev}} = h\,c\,\nu_{\text{ev}}/(kT)$. This equation resembles that often used for the reduced isotopic partition ratio in the condensed phase in vapor pressure isotope effect considerations [5]. Table 3 presents $(s_2/s_1)\,f_{\text{a}}$ and $(s_2/s_1)\,f_{\text{g}}$ values evaluated from the frequencies given

Table 3. Isotope effects on Henry's law constant of aqueous solutions k_1/k_2, 295 K.

Quantity	System		
	$^3He/^4He$	$^{14}N_2/^{15}N^{14}N$	$^{36}Ar/^{40}Ar$
k_1/k_2 measured	1.016 [a]	1.00071 [b]	–
$(s_2/s_1)\,f_a$ [Eq. (41)]	1.034	1.08331	1.0017
$(s_2/s_1)\,f_g$ [Eq. (3)]	1.000	1.08230	1.0000
k_1/k_2 calculated [Eq. (2)]	1.034	1.00093	1.0017
γ [c]	–	1.08186	–
α [c] Translational contribution to k_1/k_2	0.034	0.00092	0.0017
β [c] Rotational contribution to k_1/k_2	–	0.00042	–
$\{[\gamma/(s_2/s_1)\,f_g]-1\}$ Vibrational contribution to k_1/k_2	–	−0.00041	–

[a] Ref. [1 a]. [b] Ref. [1 c]. [c] Eq. (41).

in Tables 1 and 2, and from their stated mass dependences. Calculated (k_1/k_2) values are given, as well as experimentally measured ones where available. The deviations from unity of k_1/k_2 are quite small; thus, α and β can be identified as the translational and rotational contributions directly. The small deviation of $[\gamma/(s_2\,s_1)\,f_g]$ from unity is the vibrational contribution. These quantities are also shown in Table 3. For He and Ar there is only a translational contribution. For N_2, all three contributions are non-negligible, although the rotational and vibrational contributions do cancel each other. It appears appropriate to point out that Vogel et al. [14] have found that k_1/k_2 is less than unity for the $^{12}C/^{13}C$ isotope effect for aqueous CO_2; in that case, a negative vibrational contribution must outweigh the translational and rotational contributions.

In the usual theoretical treatments of condensed phase/vapor phase isotope effects [5], experimental observation is used to determine at least some parameter(s) of the condensed phase potential function. However, in the present work, a potential function for water derived to reproduce the observed properties of bulk water in an MD simulation [12] are combined with potential functions of the solute-solvent interaction derived from a priori quantum mechanical calculation, albeit a scaling procedure was employed to derive the helium-water potential from the calculated argon-water potential. The fact that the agreement between calculation and experiment is not better than found here for helium should not be surprising. The agreement between theory and experiment for nitrogen is quite good.

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[7] It can be shown that $\langle(\nabla V)^2\rangle = kT\langle\nabla^2 V\rangle$ (see Ref. [6 b]; this result comes about by using integration by parts with the potential V infinite at the cell boundary). The latter bracket expression is often used in the formulation of quantum corrections, particularly if the potential is harmonic with respect to Cartesian displacements from some "equilibrium value". In such case $\nabla^2 V$ is just the sum of the three diagonal Cartesian force constants.

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