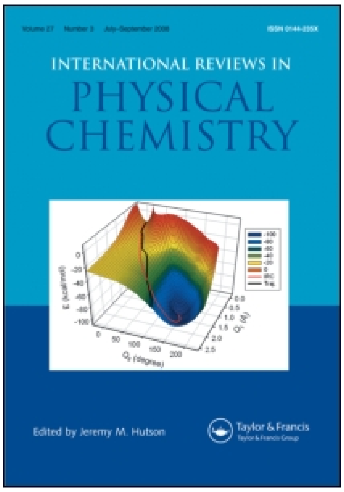

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Differences in the Hydrogen and Deuterium Bonds

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DIFFERENCES IN THE HYDROGEN AND DEUTERIUM BONDS

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ABSTRACT

Differences in equilibrium properties of hydrogen- and deuterium-bonded systems are considered. The potential energy surface is assumed to be independent of the isotopic species and the differences attributed to vibrational motion. A useful understanding of the problem can be gained by considering a hydrogen-bonded species as if it were a linear triatomic molecule AH···B with three significant vibrational modes—the A—H stretching mode and the doubly degenerate H-bond bend. Differences in the stabilities of H- and D-bonded species are related to differences in the zero-point energies of these vibrations.

Three problems are considered in detail: (i) the relative stabilities of dimeric species such as HF···DF and DF···HF; (ii) heats of vaporization of condensed phases such as water and heavy water; and (iii) the molar volumes of H- and D-bonded species.

It is concluded that there can be no short answer to the question: 'Is the hydrogen bond stronger than the deuterium bond?' The equilibrium properties of systems containing hydrogen or deuterium bonds are dependent on vibrational motion of the nuclei and therefore reflect the shape, as well as the depth, of the potential energy surface.

I INTRODUCTION

The hydrogen bond is of interest to physicists, chemists and biologists, and has recently been considered in a three-volume work (Schuster, Zundel and Sandorfy, 1976). This article is concerned with the isotope effect on hydrogen bonds, and in particular with a comparison of the hydrogen and deuterium bonds.

As regards the relative strengths of hydrogen and deuterium bonds, some experiments (for example, Grimison, 1963) have been interpreted in terms of stronger H-bonds; others (for example, Benjamin and Benson, 1963) have been said to indicate stronger D-bonds; it is clear that no general conclusion has been reached. In medium-strong hydrogen bonds, as in hydrogen fluoride, water, etc., differences in the H-bonds and D-bonds are quite sharp, as the following experimental facts indicate (Buckingham, 1980): in isomeric dimers (HF···DF) and (DF···HF), only the D-bonded species (HF···DF) has been observed (Dyke, Howard and Klemperer, 1972), indicating that it is more stable than (DF···HF). One might deduce from this that a D-bond is stronger than the corresponding H-bond; however, the heat of vaporization of liquid HF is 1.07 kJ mol^{-1} *larger* than that of DF. While the molar volume of water at 20°C is smaller by 0.074 cm^3

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mol^{-1} than that of heavy water (implying a tighter binding), the heat of vaporization of liquid D_2O is 1.032 times that of H_2O. Apparently, it is necessary to gain a thorough understanding of the effects of vibrational motion on the hydrogen and deuterium bonds.

In this article the above problems are discussed. The model chosen is one in which we assume that the H-bonded and D-bonded species have the same potential surface. Due to the large difference in mass between H and D, the vibrational behaviour is quite different in the two cases. The bending vibrations of the H-bond are capable of playing an important role and may contribute to binding in the opposite sense to that of the stretching vibrations.

Three problems are considered:

(i) the relative stabilities of dimeric species,
(ii) the heats of vaporization, and
(iii) the molar volumes of H- and D-bonded species.

In reality all the vibrational modes of the hydrogen-bonded species are affected, to a greater or lesser extent, by substitution of the proton by a deuteron. Even for $(H_2O)_2$ there are twelve vibrational modes, so the full problem is apparently very complicated. Fortunately it is possible to gain a useful understanding of the problem by considering the hydrogen-bonded species as if it were a linear triatomic molecule $AH\cdots B$ with just three significant vibrational modes—the A—H stretching mode and the doubly degenerate H-bond bend (which we shall call the libration). We relate differences in the stabilities of H- and D-bonded species to differences in the zero-point energies of the few vibrations which are particularly sensitive to hydrogen bonding.

(i) *The relative stability of isotopically distinct dimers* $HF\cdots DF$, $DF\cdots HF$; $H_2O\cdots DOH$, $H_2O\cdots HOD$; *etc.*

Dyke *et al.* (1972) found that the spectrum of $HF\cdots DF$ but not $DF\cdots HF$ appeared in their molecular-beam studies of the mixed HFDF dimer. Tursi and Nixon (1970) observed, in their infra-red matrix-isolation study of dimeric water in solid nitrogen, the spectrum of $H_2O\cdots DOH$ but not $H_2O\cdots HOD$.

These phenomena affecting isomeric dimers containing hydrogen bonds at low temperature are one of the manifestations of zero-point vibrational energy. We find that the vibrational energy difference between corresponding dimers containing an H-bond and a D-bond is approximately comprised of two terms of opposite sign: one is the difference of bending vibration frequencies of the H-bond and the D-bond, and the other is the difference between the low-frequency shift of the stretching vibrations of the chemical bonds A—H and A—D. The calculated results are that $(HF\cdots DF)$ and $(H_2O\cdots DOH)$ are energetically favoured over $(DF\cdots HF)$ and $(H_2O\cdots HOD)$. The energy differences are large enough to hamper the appearance of the latter in the experiments of Dyke *et al.* (1972) and of Tursi and Nixon (1970) but calculations indicate that $(N{\equiv}C{-}H\cdots N{\equiv}C{-}D)$ is energetically favoured over $(N{\equiv}C{-}D\cdots N{\equiv}C{-}H)$ (*see* Section II).

(ii) *Heats of vaporization of liquid* H_2O *and* D_2O, *and liquid* HF *and* DF

Bigeleisen and Mayer (1947) and Bigeleisen (1961) developed a general statistical-mechanical theory of isotope effects on thermodynamic properties of condensed systems. Whalley (1976) discussed the heats of sublimation of ice and heavy ice, and Frank (1972) analysed the vapour-pressure isotope effect of water and heavy water. In the present paper, the differences in the heats of vaporization of liquid H_2O and D_2O, and of liquid HF and

DF, are calculated using statistical thermodynamics. The facts that the heats of vaporization of liquid D_2O and liquid HF are larger than those of liquid H_2O and liquid DF, respectively, are in part due to zero-point vibrational energies, and cannot be simply interpreted as a difference in H- and D-bond energies.

(iii) *Molar volumes of liquid* H_2O *and* D_2O

London (1958) developed a statistical-thermodynamic formula to compute the difference in the molar volumes of metallic ^6Li and ^7Li, and of crystalline ^6LiF and ^7LiF. His calculations are in reasonable agreement with experimental results. Bigeleisen (1961) extended London's methods to a molecular lattice and successfully related the molar volumes of liquid H_2, HD, D_2, T_2 with vapour pressures. However, these theories invariably predict that the molar volume of the heavy isotope should be smaller than that of the lighter one, and they therefore cannot explain why the molar volume of liquid D_2O is larger than that of liquid H_2O. In this article the origin of the fact that the molar volume of liquid D_2O is larger than that of H_2O is attributed to the different behaviour of the bending vibrations of the H- and D-bonds and of the stretching vibrations of the chemical bonds A—H··· and A—D···, which weaken or break down the open structure of water, reducing the molar volume. The amplitudes of the vibrations of the H-bond are larger than that of the D-bond, causing the decrease of the molar volume of liquid H_2O to be larger than that of D_2O.

II THE RELATIVE STABILITY OF ISOMERIC DIMERS HF···DF, DF···HF; H_2O···DOH, H_2O···HOD; ETC.

In this section, the Schrödinger equation for the vibration of the H- and D-bonds is set up by means of a linear triatomic model and it is shown that the total vibrational energy of the H-bond is approximately equal to the sum of the stretching and bending vibrations of the H-bond and the stretching vibration of the chemical bond A—H. Then, the formula for the vibrational energy difference of isomeric dimers may be deduced. Finally, as illustrative examples, the relative stability of the isomeric dimers (HF···DF), (DF···HF); (H_2O···DOH), (H_2O···HOD); and (H—C≡N···D—C≡N), (D—C≡N···H—C≡N) is discussed.

It is well known that, excluding intramolecular hydrogen-bonded systems, most H-bonds are linear or nearly linear; for example, the dimers $(HF)_2$ and $(H_2O)_2$ have H-bonds that are nearly linear (Dyke *et al.*, 1972; Dyke, Mack and Muenter, 1977). A theory of the broadening of the infrared absorption spectra of hydrogen-bonded species,

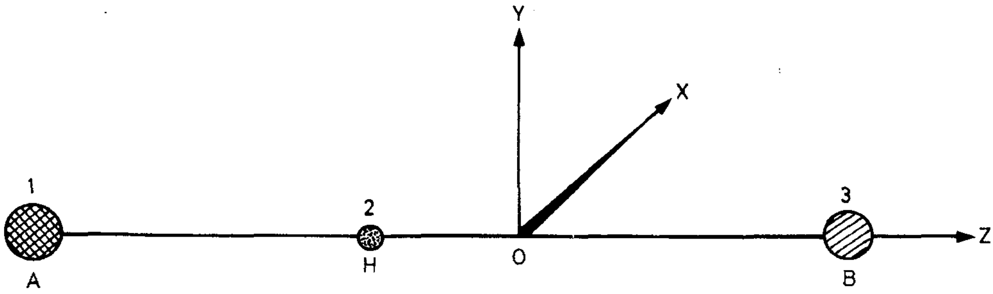

FIG. 1. The co-ordinate system of the triatomic H-bonded molecule A—H···B.

using a linear triatomic model of the type considered in this article, met with success (Coulson and Robertson, 1974, 1975).

For the kinetic term of the Hamiltonian of the system, Nielsen's result (1943) for a linear molecule containing three atoms is adduced as follows. *Figure 1* is a diagram of the H-bond (A—H···B). The co-ordinate system is fixed in the system with the origin O at the centre of mass. The particles are numbered from left to right. The kinetic energy is

$$2T = \sum_{i=1}^{3} m_i(\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) \tag{1}$$

In the new co-ordinates x, y, z, q,

$$\left.\begin{aligned} 3mx/2M &= x_2 - (m_1 x_1 + m_3 x_3)/2m_2 \\ 3my/2M &= y_2 - (m_1 y_1 + m_3 y_3)/2m_2 \\ 3mz/2M &= z_2 - (m_1 z_1 + m_3 z_3)/2m_2 \end{aligned}\right\} \tag{2}$$

$$q = z_1 - z_3$$

where

$$m = m_1 + m_2,\ M = m_1 + m_2 + m_3 \tag{3}$$

q describes the stretching vibration of the H-bond, z describes the stretching vibration of the chemical bond A—H, and (x,y) the in-plane and out-of-plane bending vibrations of the H-bond. The kinetic energy may be written in the new co-ordinates as

$$2T = \mu_1 \dot{q}^2 + \mu_2(\dot{x}^2 + \dot{y}^2) + \mu_3 \dot{z}^2 \tag{4}$$

where

$$\begin{aligned} \mu_1 &= \frac{m_1 m_3}{m} \\ \mu_2 &= \frac{m_2 m^2 I_{xx}^e}{m_1 m_3 M (z_3^e - z_1^e)} \\ \mu_3 &= m_2 m/M \end{aligned} \tag{5}$$

I_{xx}^e is the moment of inertia about the x-axis at equilibrium. z_1^e, z_3^e are equilibrium values of z_1 and z_3. The corresponding kinetic operator in quantum mechanics is

$$T = -\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial q^2} - \frac{\hbar^2}{2\mu_2}\left(\frac{\partial_2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) - \frac{\hbar^2}{2\mu_3}\frac{\partial^2}{\partial z^2} \tag{6}$$

Now consider the potential energy of A—H···B, $U = U(q,z,x,y)$. Due to the linearity of the system, the potential energy can approximately be divided into two parts, one of which is connected with the bending vibration of the H-bond, $U(x,y)$, and the other with the stretching vibrations of the H-bond and of the chemical bond A—H (Wilson *et al.*, 1955):

$$U = U(x,y) + U(q,z) + O(z,x^2) \tag{7}$$

Here $O(z,x^2)$ represents quantities that are of the third and higher order in the nuclear displacements from equilibrium. Because the co-ordinates q, z may be considered as Jacobi co-ordinates, $U(q,z)$ can approximately be divided into two parts (Janoschek, 1976) which are concerned with the stretching vibrations of the H-bond and of the chemical bond A–H:

$$U(q,z) = U(q) + U(z) + U'(q,z) \tag{8}$$

Here $U'(q,z)$ is a quantity describing the interaction between the stretching vibrations of the H-bond and of A–H. Expanding $U'(q,z)$ into a power series in q,z, the cross terms $q^n z^m$ are small and may be omitted (Janoschek, 1976):

$$U'(q,z) \approx U'(q_e,z) + U'(z_e,q) \tag{9}$$

$U'(q_e,z)$ represents the effect of the stretching vibration of the H-bond on the stretching vibration of A–H when the former are at equilibrium positions. In a similar way, the meaning of $U'(z_e,q)$ is the effect of the stretching vibration of A–H on that of the H-bond when the former is at equilibrium. Thus

$$U \approx U(q) + U'(z_e,q) + U(z) + U'(q_e,z) + U(x,y) \tag{10}$$

From equations (6) and (10), the Schrödinger equation for vibration of the H-bond is

$$\left\{\left[-\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial q^2} - \frac{\hbar^2}{2\mu_2}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) - \frac{\hbar^2}{2\mu_3}\frac{\partial^2}{\partial z^2}\right] + U(q) + U'(z_e,q) + U(z) + U'(q_e,z) + U(x,y)\right\}\Psi(q,z,x,y) = E\Psi(q,z,x,y) \tag{11}$$

Letting $\Psi(q,z,x,y) = Q(q)Z(z)\Phi(x,y)$ and separating the variables gives

$$\left[-\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial q^2} + U(q) + U'(z_e,q)\right]Q(q) = E_\sigma^{n_q}Q(q) \tag{12}$$

$$\left[-\frac{\hbar^2}{2\mu_2}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + U(x,y)\right]\Phi(x,y) = E_{\nu,\delta}^{n_x,n_y}\Phi(x,y) \tag{12'}$$

$$\left[-\frac{\hbar^2}{2\mu_3}\frac{\partial^2}{\partial z^2} + U(z) + U'(q_e,z)\right]Z(z) = E_\nu^{n_z}Z(z) \tag{12''}$$

and

$$E = E_\sigma^{n_q} + E_\nu^{n_z} + E_{\nu,\delta}^{n_x,n_y} \tag{13}$$

Where $E_\nu^{n_z}$ is the stretching vibrational energy of the chemical bond A–H, $E_\sigma^{n_q}$ is the stretching vibrational energy of the H-bond, $E_{\nu,\delta}^{n_x,n_y}$ is the bending vibrational energy of the H-bond. These are intermolecular vibrations and can be considered as libration. The total vibrational energy of the H-bonded system (A–H···B) is approximately equal to the sum of the energy of the various vibrational modes of the H-bonded system. It may be noted from (12) that the energy $E_\sigma^{n_q}$ of the stretching vibration of the H-bond is dependent on the mass μ_1; from (3) and (5)

$$\frac{1}{\mu_1} = \frac{m_1 + m_2}{m_1 m_3} = \frac{m_A + m_H}{m_A m_B} = \frac{1}{m_B} + \frac{m_H}{m_A m_B} \approx \frac{1}{m_B}$$

which is independent of m_2 (m_H), so

$$E_\sigma^{n_q}(\text{A–H}\cdots\text{B}) \approx E_\sigma^{n_q}(\text{A–D}\cdots\text{B}) \tag{14}$$

Now we can deduce the difference of the vibrational energy between isomeric dimers such as $(\mathrm{H_2O\cdots DOH})$ and $(\mathrm{H_2O\cdots HOD})$ by using the above model. In this case, the H- and D-bonded systems are

$$\begin{array}{l}\mathrm{X{-}H\cdots B}\\ \,|\\ \mathrm{D}\end{array} \quad \text{and} \quad \begin{array}{l}\mathrm{X{-}D\cdots B,}\\ \,|\\ \mathrm{H}\end{array}$$

where X is an atom or a group of atoms. At low temperature, only ground vibrational states need be considered. The total zero-point vibrational energy of the H-bonded system $\begin{array}{l}\mathrm{X{-}H\cdots B}\\ |\\ \mathrm{D}\end{array}$ is

$$E\left(\begin{array}{l}\mathrm{X{-}H\cdots B}\\ |\\ \mathrm{D}\end{array}\right)=E_v^0(\mathrm{X{-}H\cdots})+E_{\nu,\delta}^{0,0}\left(\begin{array}{l}\mathrm{X{-}H\cdots B}\\ |\\ \mathrm{D}\end{array}\right)+E_\sigma^0\left(\begin{array}{l}\mathrm{X{-}H\cdots B}\\ |\\ \mathrm{D}\end{array}\right)+E_{\mathrm{B}}^{\mathrm{int.}}+E_{\mathrm{X}}^{\mathrm{int.}}$$
$$+E_v^0(\mathrm{X{-}D}) \qquad (15)$$

where $E_v^0(\mathrm{X{-}H\cdots})$ is the ground-state stretching vibrational energy of the chemical bond $\mathrm{X{-}H\cdots}$ which is hydrogen-bonded to B, $E_v^0(\mathrm{X{-}D})$ is the ground-state stretching vibrational energy of the chemical bond X–D (which is not deuterium-bonded to another atom), $E_{\mathrm{B}}^{\mathrm{int}}$, $E_{\mathrm{X}}^{\mathrm{int}}$ are the internal vibrational energies of groups B and X

$$E_{\nu,\delta}^{0,0}\left(\begin{array}{l}\mathrm{X{-}H\cdots B}\\ |\\ \mathrm{D}\end{array}\right) \quad \text{and} \quad E_\sigma^0\left(\begin{array}{l}\mathrm{X{-}H\cdots B}\\ |\\ \mathrm{D}\end{array}\right)$$

are the bending and stretching vibrational energies of the H-bond. In the same way, the total vibrational energy of the D-bonded system $\left(\begin{array}{l}\mathrm{X{-}D\cdots B}\\ |\\ \mathrm{H}\end{array}\right)$ is

$$E\left(\begin{array}{l}\mathrm{X{-}D\cdots B}\\ |\\ \mathrm{H}\end{array}\right)=E_v^0(\mathrm{X{-}D\cdots})+E_{\nu,\delta}^{0,0}\left(\begin{array}{l}\mathrm{X{-}D\cdots B}\\ |\\ \mathrm{H}\end{array}\right)+E_\sigma^0\left(\begin{array}{l}\mathrm{X{-}D\cdots B}\\ |\\ \mathrm{H}\end{array}\right)+E_{\mathrm{B}}^{\mathrm{int}}+E_{\mathrm{X}}^{\mathrm{int}}$$
$$+E_v^0(\mathrm{X{-}H}) \qquad (15')$$

So the difference in the vibrational energies of the isomeric dimers $\begin{array}{l}\mathrm{X{-}H\cdots B}\\ |\\ \mathrm{D}\end{array}$ and $\begin{array}{l}\mathrm{X{-}D\cdots B}\\ |\\ \mathrm{H}\end{array}$ is, from (15) and (15′), using equation (14),

$$\Delta E=E\left(\begin{array}{l}\mathrm{X{-}H\cdots B}\\ |\\ \mathrm{D}\end{array}\right)-E\left(\begin{array}{l}\mathrm{X{-}D\cdots B}\\ |\\ \mathrm{H}\end{array}\right)$$
$$=[E_v^0(\mathrm{X{-}H\cdots})-E_v^0(\mathrm{X{-}H})]-[E_v^0(\mathrm{X{-}D\cdots})-E_v^0(\mathrm{X{-}D})]$$
$$+\left[E_{\nu,\delta}^{0,0}\left(\begin{array}{l}\mathrm{X{-}H\cdots B}\\ |\\ \mathrm{D}\end{array}\right)-E_{\nu,\delta}^{0,0}\left(\begin{array}{l}\mathrm{X{-}D\cdots B}\\ |\\ \mathrm{H}\end{array}\right)\right] \qquad (16)$$

Suppose that for the ground vibrational states

$$E_v^0(\mathrm{X{-}H})/hc\approx\tfrac{1}{2}\omega_v \qquad (17)$$

where ω_v is the fundamental frequency (in wavenumbers) of the corresponding mode of vibration. Then

$$\frac{\Delta E}{hc} \approx \left[\omega_v\begin{pmatrix}\begin{array}{l}\mathrm{X{-}H\cdots B}\\ \,|\\ \mathrm{D}\end{array}\end{pmatrix} - \omega_v\begin{pmatrix}\begin{array}{l}\mathrm{X{-}D\cdots B}\\ \,|\\ \mathrm{H}\end{array}\end{pmatrix}\right] - \tfrac{1}{2}[(\omega_v(\mathrm{X{-}H}) - \omega_v(\mathrm{X{-}H\cdots}))$$

$$- (\omega_v(\mathrm{X{-}D}) - \omega_v(\mathrm{X{-}D\cdots}))] \qquad (18)$$

That is to say, the energy difference between the isomeric dimers $\begin{array}{l}\mathrm{X{-}H\cdots B}\\ \,|\\ \mathrm{D}\end{array}$ and $\begin{array}{l}\mathrm{X{-}D\cdots B}\\ \,|\\ \mathrm{H}\end{array}$ consists of two terms of opposite sign:

(i) the difference of the bending vibration (or libration) frequencies of the H- and D-bonds;
(ii) one-half of the difference of the low-frequency shifts of the AH and AD stretching vibration frequencies due to the effects of the H- and D-bonds.

Three examples of isomeric dimers, namely ($H_2O\cdots DOH$) and ($H_2O\cdots HOD$), ($HF\cdots DF$) and ($DF\cdots HF$), ($H{-}C{\equiv}N\cdots D{-}C{\equiv}N$) and ($D{-}C{\equiv}N\cdots H{-}C{\equiv}N$), are now discussed using equation (18).

Example 1. ($H_2O\cdots DOH$) *and* ($H_2O\cdots HOD$)

The vibrational frequencies of $(H_2O)_2$ and $(D_2O)_2$ are in *Table 1*. From these figures and from equation (18) the vibrational energy differences of the isomeric dimers ($H_2O\cdots HOD$) and ($H_2O\cdots DOH$) are

$$\frac{\Delta E}{hc} = [E(H_2O\cdots HOD) - E(H_2O{-}DOH)]/hc$$

$$= 685 - 505 - \tfrac{1}{2}[(3704 - 3547.5) - (2727 - 2599.1)]$$

$$= 165\ \mathrm{cm}^{-1} \qquad (19)$$

That is to say, $H_2O\cdots DOH$ is energetically favoured over ($H_2O\cdots HOD$) by 165 cm^{-1}. The temperature of the experiment of Tursi and Nixon was 20°K, so

$$\frac{\text{Population of } (H_2O\cdots DOH)}{\text{Population of } (H_2O\cdots HOD)} = \exp(\Delta E/kT) = 1.6 \times 10^5 \qquad (20)$$

TABLE 1. Vibrational frequencies of the dimers $(H_2O)_2$ and $(D_2O)_2$ in cm^{-1}

Vibrational modes	$(H_2O)_2$	$(D_2O)_2$
ω_v (O–H)[a]	3704	2727
ω_v (O–D)		
ω_v (O–H···)[b]	3547.5	2599.1
ω_v (O–D···)		
ω_v (O–H··· B)[c]	685	505

[a] From Wall and Hornig (1965).
[b] From Tursi and Nixon (1970).
[c] For large aggregates from Mann *et al.* (1974) and for the liquids from Eisenberg and Kauzmann (1969b).

So it is not surprising that the spectrum of ($H_2O\cdots HOD$) was not detected in the experiment. In recent molecular beam experiments (Odutola and Dyke, 1980) on the partly deuterated water dimer, the only forms observed for D_3 were deuterium-bonded and both $DOD\cdots OHD$ and $HOD\cdots OD_2$ were detected. The D_2 dimer detected was $DOD\cdots OH_2$. The observations can be explained in a similar way to the distribution of the isomeric dimers ($H_2O\cdots DOH$) and ($H_2O\cdots HOD$).

Example 2. ($HF\cdots DF$) *and* ($DF\cdots HF$)

For the dimer $(HF)_2$, $\omega_v(F{-}H) = 3895$ and $\omega_v(F{-}H\cdots) = 3856\ cm^{-1}$ (Smith, 1959). In order to calculate the energy difference between ($HF\cdots DF$) and ($DF\cdots HF$) by means of equation (18), it is necessary to obtain the bending vibration frequency of the H-bond and the low-frequency shift of the stretching vibration of the chemical bonds F—H and F—D due to the formation of hydrogen and deuterium bonds.

First, let us discuss the in-plane bending vibration of the H-bond. The problem is closely related to that dealing with the hindered rotation of molecules (Pauling, 1930) and the internal rotation of complex molecules (Owen and Cunliffe, 1974). To a first approximation, neglecting the out-of-plane bending and stretching vibrations of the H-bond, the wave equation is

$$\frac{d^2}{d\varphi^2}\Phi(\varphi) + \frac{2I}{\hbar^2}[E_\delta - V(\varphi)]\Phi(\varphi) = 0 \tag{21}$$

where I is the moment of inertia of HF. In the case of a strong H-bonded system, φ is a small quantity and $V(\varphi)$ can be expanded into a series in the angle φ. We retain only the square term, so

$$V(\varphi) = \tfrac{1}{2}V_0\,\varphi^2 \tag{22}$$

Putting (22) into (21) and solving the equation

$$\frac{d^2}{d\varphi^2}\Phi(\varphi) + \frac{2I}{\hbar^2}[E_\delta - \tfrac{1}{2}V_0\,\varphi^2]\Phi(\varphi) = 0 \tag{23}$$

gives

$$E_\delta = (n_\delta + \tfrac{1}{2})\,hc\omega_\delta \tag{24}$$

$$\omega_\delta = \frac{1}{2\pi c}\sqrt{\frac{V_0}{2I}} \tag{25}$$

Using equation (25) and $\omega_\delta(FH\cdots FD) = 600\ cm^{-1}$ (for the liquid, *see* Maybury, Gordon and Katz, 1955), so that

$$\omega_\delta(FH\cdots FD) - \omega_\delta(FD\cdots FH) = \omega_\delta(FH\cdots FD)\left(1 - \frac{1}{\sqrt{2}}\right) = 174\ cm^{-1} \tag{26}$$

Secondly, let us calculate the difference in the red shift of the stretching frequencies of H—F and D—F. Following a perturbation-theory analysis (Buckingham, 1960)

$$\Delta\omega = \omega_v(FH\cdots) - \omega_v(F{-}H) = \frac{B_e}{hc\omega_e}\langle U'' - 3aU'\rangle + O\left(\frac{B_e}{\omega_e}\right)^2 \tag{27}$$

where U' and U'' are first and second derivatives of the intermolecular energy with respect to the internuclear distance in F—H at the equilibrium bond-length r_e, and a is the cubic anharmonic constant in the potential energy of F—H. From equation (27)

$$\frac{\omega_v(\mathrm{FD}\cdots)-\omega_v(\mathrm{F{-}D})}{\omega_v(\mathrm{FH}\cdots)-\omega_v(\mathrm{F{-}H})}\approx\frac{1}{\sqrt{2}}$$

Using $\omega_v(\mathrm{F{-}H}) = 3895$, $\omega_v(\mathrm{F{-}H}\cdots) = 3856\ \mathrm{cm}^{-1}$,

$$[\omega_v(\mathrm{F{-}H})-\omega_v(\mathrm{F{-}H}\cdots)]-[\omega_v(\mathrm{F{-}D})-\omega_v(\mathrm{F{-}D}\cdots)] = 11\ \mathrm{cm}^{-1} \tag{28}$$

Therefore from equations (26) and (28), the difference in the total vibrational energy of the isometric dimers (HF···DF) and (DF···HF) is

$$\frac{E(\mathrm{DF}\cdots\mathrm{HF})-E(\mathrm{HF}\cdots\mathrm{DF})}{hc} = 174-\tfrac{1}{2}\times 11 = 163\ \mathrm{cm}^{-1}$$

(HF···DF) is predicted to be energetically favoured over (DF···HF) by 163 cm^{-1}, and this difference in energy is sufficient to explain why the spectral intensity of (DF···HF) was insignificant in the experiment of Dyke *et al.* (1972).

Curtiss and Pople (1976) used *ab initio* LCAO-SCF computations to obtain a potential surface for the hydrogen fluoride dimer. They calculated a zero-point energy difference of 109 cm^{-1} between HF···DF and DF···HF, with HF···DF having the lower energy.

Rank, Glickman and Wiggins (1965) observed the spectra of the dimeric molecules $\mathrm{H^{35}Cl}$···DCl and $\mathrm{H^{37}Cl}$···DCl but were unable to detect the spectra of $\mathrm{D^{35}Cl}$···HCl and $\mathrm{D^{37}Cl}$···HCl in their infra-red studies of dimeric hydrogen chloride molecules. These experiments were performed at 195°K, and the fact that HCl···DCl is energetically favoured over DCl···HCl may be the reason the spectrum of the dimer DCl···HCl could not be detected.

Example 3. H—C≡N···D—C≡N *and* D—C≡N···H—C≡N

The experimental vibrational frequencies for $(\mathrm{HCN})_2$ and $(\mathrm{DCN})_2$ are shown in *Table 2*. From equation (18) and *Table 2*

$$\begin{aligned}[E(\mathrm{N{\equiv}C{-}H}\cdots\mathrm{N{\equiv}C{-}D})-E(\mathrm{N{\equiv}C{-}D}\cdots\mathrm{N{\equiv}C{-}H})] &= (144-131)-\tfrac{1}{2}[(3282-3205)\\ &\quad -(2616-2574)]\\ &= -5\ \mathrm{cm}^{-1}\end{aligned}$$

In contrast with (HF···DF) and ($\mathrm{H_2O}$···DOH), N≡C—H···N≡C—D is predicted to be energetically favoured over N≡C—D···N≡C—H by approximately 5 cm^{-1}. This figure might not be quantitatively accurate because of the small difference of librational

TABLE 2. Vibrational frequencies in $(\mathrm{HCN})_2$ and $(\mathrm{DCN})_2$ in cm^{-1}*

Vibrational modes	$(\mathrm{HCN})_2$	$(\mathrm{DCN})_2$
ω_ν (—C—H)	3282.0	2616.0
ω_v (—C—H···)	3204.9	2574.4
ω_γ (—C—H···)	144	131

* From King and Nixon (1968).

frequency between the H and D bonds, but apparently D-bonded species are not always energetically favoured over the H-bonded analogues. By considering anharmonic coupling between the AH and AH···B stretching modes, Robertson (1977) found that the deuterium bond in $(CH_3)_2O.DCl$ is weaker by 52 cm^{-1} than the corresponding H bond. And by considering the formic acid dimer, Marechal (1972) deduced that the energy of formation of A—D···B is some 90 cm^{-1} less than that of A—H···B.

III HEATS OF VAPORIZATION OF LIQUID H_2O AND D_2O, AND LIQUID HF AND DF

(*a*) H_2O *and* D_2O

For water vapour, we make two suppositions in this section:

(i) that translation and rotation of the molecules in the vapour may be described by classical statistical mechanics. Spectroscopic studies indicate that hydrogen bonds are rare in water vapour under normal conditions (*see* Eisenberg and Kauzmann, 1969a); Benedict, Classen and Shaw (1952) concluded from experiments that if dimers having resolvable rotational transitions are present in saturated steam at 1 atmosphere, their concentration must be less than 1 per cent of the monomer;

(ii) for the vibrations of water, only the ground state is considered due to the low temperature (about 300°K) relative to the vibrational temperature $h\nu/k$. The partition function for the water vapour can then be written as

$$Z^{(G)}(T) = \left\{ \prod_{i=1}^{3} \exp(-E_i^{0(G)}/kT) \right\}^N \left\{ \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \right\}^N \left\{ \frac{8\pi^2(2\pi kT)^{\frac{3}{2}}(\mathrm{ABC})^{\frac{1}{2}}}{h^3} \right\}^N \Omega^{(G)}(T) \quad (29)$$

where

$$\Omega^{(G)}(T) = (N!)^{-1} \int \cdots \int \exp\{-W^{(G)}(\cdots x_i, y_i, z_i, \theta_i, \varphi_i, \psi_i, \cdots)/kT\} \prod_{i=1}^{N} \mathrm{d}x_i\, \mathrm{d}y_i\, \mathrm{d}z_i \sin\theta_i\, \mathrm{d}\theta_i\, \mathrm{d}\varphi_i \quad (30)$$

where $W^{(G)}$ is the interaction energy of gaseous water molecules.

For liquid H_2O and D_2O, Einstein's approximation may be used for the molecular hindered rotation or libration. So, the partition function of the assembly is

$$Z^{(L)}(T) = \left\{ \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \right\}^N \left\{ \frac{\exp(-\frac{1}{2}hc\omega_L/kT)}{1 - \exp(-hc\omega_L/kT)} \right\}^{3N} \left\{ \prod_{i=1}^{3} \exp(-E_i^{0(L)}/kT) \right\}^N \Omega^{(L)}(T) \quad (31)$$

where

$$\Omega^{(L)}(T) = (N!)^{-1} \int \cdots \int \exp\{-W^{(L)}(\cdots x_i, y_i, z_i, \cdots)/kT\} \prod_{i=1}^{N} \mathrm{d}x_i\, \mathrm{d}y_i,\, \mathrm{d}z_i \quad (32)$$

where $W^{(L)}$ is the interaction energy of liquid water molecules. Taking the molar volumes of liquid H_2O and D_2O to be the same, the difference between the heats of vaporization of liquid D_2O and H_2O is

$$\begin{aligned}\Delta q &= q(D_2O) - q(H_2O) = (H^{(G)} - H^{(L)})_{D_2O} - (H^{(G)} - H^{(L)})_{H_2O} \\ &\approx N^{-1} kT^2 \left[\frac{\partial}{\partial T} \ln \left\{ \frac{(Z^{(G)}(T)/Z^{(L)}(T))_{D_2O}}{(Z^{(G)}(T)/Z^{(L)}(T))_{H_2O}} \right\} \right]_{N,V} \end{aligned} \tag{33}$$

Putting (29) and (31) into (33), we obtain

$$\begin{aligned}\Delta q = \sum_{i=1}^{3} &[(E_i^{0(G)} - E_i^{0(L)})_{D_2O} - (E_i^{0(G)} - E_i^{0(L)})_{H_2O}] \\ &- \tfrac{3}{2}\{[hc\omega_L \coth(\tfrac{1}{2}hc\omega_L/kT)]_{D_2O} - [hc\omega_L \coth(\tfrac{1}{2}hc\omega_L/kT)]_{H_2O}\}\end{aligned} \tag{34}$$

That is, the difference in the heats of vaporization of liquid D_2O and H_2O consists of two opposed terms: one is due to the difference of libration energy of liquid D_2O and H_2O, and the other to the difference in the red shift of the intramolecular vibrational energy of liquid D_2O and H_2O.

Now let us attempt to calculate the difference Δq for liquid D_2O and H_2O. If the harmonic oscillator model for intramolecular vibration is used.

$$\begin{aligned}\Delta q = \sum_{i=1}^{3} &[(E_i^{0(G)})_{D_2O} - (E_i^{0(G)})_{H_2O}] - \sum_{i=1}^{3} \tfrac{1}{2}[(hc\omega_i^{(L)})_{D_2O} - (hc\omega_i^{(L)})_{H_2O}] \\ &- \tfrac{3}{2}\{[hc\omega_L \coth(\tfrac{1}{2}hc\omega_L/kT)]_{D_2O} - [hc\omega_L \coth(\tfrac{1}{2}hc\omega_L/kT)]_{H_2O}\}\end{aligned} \tag{35}$$

The zero-point energies of H_2O and D_2O vapours are as follows:

$$\frac{1}{hc}\sum_{i=1}^{3} (E_i^{0(G)})_{D_2O} = 3385.74\ \text{cm}^{-1}, \quad \frac{1}{hc}\sum_{i=1}^{3} (E_i^{0(G)})_{H_2O} = 4631.25\ \text{cm}^{-1}$$

(*see* Darling and Dennison, 1940). The vibrational frequencies of the liquid H_2O and D_2O are given in *Table 3*. The shapes of the stretching bands ω_1, ω_3 in pure liquid H_2O and D_2O, have not been adequately explained in terms of all the coupling effects, but proposals have been made to explain the main features, based either on mixture models or on a continuum model of the liquid. Schulz and Hornig (1961) explained the experimental Raman spectrum with the aid of a continuum structure model of liquid H_2O and D_2O.

TABLE 3. Vibrational frequencies of liquid H_2O and D_2O in cm^{-1} (*see* Kauzmann and Eisenberg, 1969b)

Vibrational modes	Liquid H_2O	Liquid D_2O
Libration ω_L	685	505
X–O–X bending ω_2	1645	1215
O–X stretching ω_1	3439	2532
O–X stretching ω_3	3600	2600

Using this data and equation (35), the calculated differences in the heats of vaporization of D_2O and H_2O are compared with experimental results in *Table 4*.

TABLE 4. The difference of heats of vaporization of liquid H_2O and D_2O in kJ mole^{-1}

Temperature (°C)	$\Delta q_{\mathrm{calc}} = q(D_2O) - q(H_2O)$ (kJ mol^{-1})	Δq_{expt}* (kJ mol^{-1})	$\Delta q_{\mathrm{calc}} - \Delta q_{\mathrm{expt}}$ (kJ mol^{-1})
3.82	1.61	1.70	−0.09
10	1.57	1.51	0.06
25	1.52	1.38	0.14
40	1.45	1.21	0.24
60	1.34	1.09	0.25
80	1.25	0.97	0.28
100	1.16	0.87	0.29

* From Kirshenbaum (1951a).

(*b*) HF *and* DF

The difference in the heats of vaporization of liquid HF and DF may be treated in a similar way to that for H_2O and D_2O. However, there is an important difference. It has been shown (Maybury *et al.*, 1955) that both the liquid and gas phases of hydrogen fluoride are associated to a similar degree; but in water significant association is found only in the liquid. Thus for HF and DF a factor to represent hindered rotation should be included in the partition function of the vapour phase. Because of association of a similar degree in both gas and liquid phases, the contribution of hindered rotation in liquid HF and DF to the difference in the heats of vaporization is approximately cancelled (*see* equation (33)) by that of hindered rotation in the gas. From equation (34), and the above discussion,

$$\Delta q = q(\mathrm{DF}) - q(\mathrm{HF}) = \tfrac{1}{2}hc[(\omega_v^{(G)} - \omega_v^{(L)})_{\mathrm{DF}} - (\omega_v^{(G)} - \omega_v^{(L)})_{\mathrm{HF}}] \tag{36}$$

That is, the difference in the heats of vaporization of HF and DF is due to the difference of the red shift of the stretching vibration of HF and DF in going from the gas to liquid. Using equation (27), equation (36) becomes

$$\Delta q = \tfrac{1}{2}hc(\omega_v^{(G)} - \omega_v^{(L)})_{\mathrm{HF}}\left(\frac{1}{\sqrt{2}} - 1\right) \tag{37}$$

$\omega_v^{(L)}(\mathrm{HF}) = 3450\ \mathrm{cm}^{-1}$ (Maybury *et al.*, 1955) and $\omega_v^{(G)}(\mathrm{HF}) = 3961.42\ \mathrm{cm}^{-1}$ (Talley, Kaylor and Nielsen, 1950). Therefore the difference in the heats of vaporization of liquid DF and HF is

$$q(\mathrm{DF}) - q(\mathrm{HF}) = -0.90\ \mathrm{kJ\ mol}^{-1}$$

The experimental value is −1.07 kJ mol^{-1} (Pascal, 1956).

IV MOLAR VOLUMES OF LIQUID H_2O AND D_2O

It is interesting that both the heat of vaporization and the molar volume of liquid D_2O are larger than the corresponding properties of liquid H_2O. In this section, we attempt to explain why the molar volume of liquid D_2O is larger than that of H_2O.

Interpretations of the temperature dependence of the molar volume of water are usually based on the supposition that two competing effects take place as water is heated (Eisenberg and Kauzmann, 1969c):

(i) The open structure arising from the four-co-ordination of molecules weakens or breaks down, thus reducing the volume. This process corresponds to fusion at the melting temperature, and above the melting point may be regarded as a continuation of fusion.

(ii) The amplitudes of anharmonic intermolecular vibrations increase, as in a normal liquid, thus enlarging the volume.

We shall call these effects *the configurational contribution* (i) and *the vibrational contribution* (ii). In liquid water, the amplitudes of intramolecular vibration are smaller than those of intermolecular vibration and the latter are responsible for the vibrational contribution to the change of volume of water. The stretching vibration of the H-bond is mainly responsible for this, enlarging the molar volume. The bending vibrations of the H-bond and the stretching vibration of the chemical bond —O—H··· weaken or break down the H-bond and the open structure of four-co-ordination (Pople, 1951) thus reducing the volume. They may be considered to be responsible for the configurational contribution. As the temperature increases, the vibrational contribution (ii) through the stretching vibration of the H-bond, enlarges the molar volume. Because the molecules of H_2O and D_2O vibrate as a whole in the stretching vibration, and because the molecular weights of H_2O and D_2O differ by only 10 per cent, the amplitude of the stretching vibration of the H-bond is almost the same as that of the D-bond (*see* equations (12) and (14)). Thus the vibrational contributions to the increase in the molar volumes of H_2O and of D_2O are nearly equal, and the difference of the molar volumes may be attributed to (i) (the configurational contribution). Because the temperature dependence of the molar volume of ice and heavy ice is mainly due to the vibrational contribution (ii), the fact that ice and heavy ice have nearly the same coefficient of thermal expansion ($1.39 \times 10^{-4}\ \mathrm{K}^{-1}$, Dantl, 1962) supports the above analysis.

To elucidate (i), we first discuss the change in the molar volumes of H_2O and D_2O on melting. Due to the difference of a factor of two in the atomic masses of H and D, the amplitudes of the bending vibration of the H-bond and of the stretching vibration of the chemical bond —O—H··· are larger than those of the D-bond and of —O—D···, and the vibration of the H-bond weakens or breaks down the open structure of ice more strongly than that of heavy ice. Therefore, on melting, the decrease in molar volume from ice to liquid H_2O is larger, and the molar volume of liquid H_2O smaller, than for liquid D_2O, since the molar volume of ice is approximately equal to that of heavy ice, D_2O. If $\Delta V^{(0)}_{H_2O}$ and $\Delta V^{(0)}_{D_2O}$ are the changes in molar volume of H_2O and D_2O on melting,

$$\frac{(V^{(L)}_{D_2O} - V^{(\mathrm{ice})}_{D_2O}) - (V^{(L)}_{H_2O} - V^{(\mathrm{ice})}_{H_2O})}{V^{(L)}_{H_2O}} = \frac{\Delta V^{(0)}_{D_2O} - \Delta V^{(0)}_{H_2O}}{V^{(L)}_{H_2O}} = \frac{\Delta V^{(0)}_{D_2O} - \Delta V^{0}_{H_2O:}}{\Delta V^{0}_{H_2O}} \frac{\Delta V^{0}_{H_2O}}{V^{(L)}_{H_2O}} \tag{38}$$

where $V^{(L)}_{H_2O}$, $V^{(L)}_{D_2O}$ are the molar volumes of liquid H_2O and D_2O at the melting-point. It is known from experiment (*see* Kirshenbaum, 1951b) that $(\Delta V^{(0)}_{D_2O} - \Delta V^{(0)}_{H_2O})/\Delta V^{(0)}_{H_2O} = -0.03$, $\Delta V^{(0)}_{H_2O}/V^{(L)}_{H_2O} = -0.10$, so

$$\frac{\Delta V^{(0)}_{D_2O} - \Delta V^{(0)}_{H_2O}}{V^{(L)}_{H_2O}} \approx 0.003. \tag{39}$$

If $V^{(L)}_{H_2O} = 18\ \mathrm{cm^3/mole}$, $\Delta V^{(L)}_{D_2O} - \Delta V^{0}_{H_2O} \approx 0.054\ \mathrm{cm^3/mole}$.

The difference in the molar volumes of liquid H_2O and D_2O changes with temperature; from 0°C to 100°C, $V^{(L)}_{D_2O} - V^{(L)}_{H_2O}$ varies from 0.11 to 0.036 cm^3/mole (*see* Kell, 1979). It is clear that a large part of the difference of the molar volume between liquid H_2O and liquid D_2O above the melting point comes from the difference of the volume changes on fusion at the melting-point.

The change of molar volume with temperature may be attributed to (i). Above the melting-point, the bending vibration of the H-bond and of the stretching vibration of the chemical bond —O—H··· continue to weaken or break down the H-bonds in liquid H_2O and D_2O as the temperature rises, changing the structure and reducing the molar volume. It may be regarded as a continuation of fusion, and can be interpreted in a similar way to defects in solids. In the theory of point defects, if E_v is the energy required to create a vacancy, then the probability per atom for passage over the barrier is proportional to $e^{-E_v/kT}$. In the process of continuation of fusion due to (i), suppose that the probability with which a molecule is able to change its state from the 'ice state' (open structure) to the 'liquid state' (closely packed structure) is proportional to $e^{-q/kT}$, where q is the energy required to change a molecule from the 'ice state' to the 'liquid state'. The energy E_v required to change an atom from the crystalline state to a hole may be estimated from the heat of vaporization required to change an atom from solid to gas; in a similar way, the energy q is approximately equal to the heat of fusion required to change a molecule from the 'solid' to the 'liquid' form (the change of configuration). The changes in molar volume of H_2O and D_2O due to effect (i) are proportional to $e^{-q_{H_2O}/kT}$ and $e^{-q_{D_2O}/kT}$ respectively, so that

$$\frac{\Delta V^{(i)}_{H_2O}}{\Delta V^{(i)}_{D_2O}} = C \exp[(q_{D_2O} - q_{H_2O})/kT] \tag{40}$$

where C is independent of T and would be expected to be close to unity.

If ΔV_{H_2O} is the change of molar volume from ice at the melting-point to the liquid state at temperature t above the melting-point,

$$\Delta V_{H_2O} = \Delta V^{(0)}_{H_2O} + \Delta V^{(i)}_{H_2O} + \Delta V^{(ii)}_{H_2O} \tag{41}$$

where $\Delta V^{(0)}_{H_2O}$ is the change in molar volume due to the actual fusion from ice to liquid H_2O at the melting point; $\Delta V^{(i)}_{H_2O}$ and $\Delta V^{(ii)}_{H_2O}$ are the changes of molar volume due to effects (i) and (ii) from 0°C to t°C. Since $V^{(ice)}_{D_2O} \approx V^{(ice)}_{H_2O}$

$$\frac{V_{D_2O}}{V_{H_2O}} = 1 + \frac{V_{D_2O} - V_{H_2O}}{V_{H_2O}} \approx 1 + \frac{\Delta V_{D_2O} - \Delta V_{H_2O}}{\Delta V_{H_2O}} \tag{42}$$

And from equation (40)

$$\frac{\Delta V^{(i)}_{D_2O} - \Delta V^{(i)}_{H_2O}}{V_{H_2O}} = \frac{\Delta V^{(i)}_{D_2O}}{V_{H_2O}}\left(1 - \frac{\Delta V^{(i)}_{H_2O}}{\Delta V^{(i)}_{D_2O}}\right) \approx \frac{\Delta V^{(i)}_{D_2O}}{V_{H_2O}}\,(1 - C \exp[(q_{D_2O} - q_{H_2O})/kT)] \tag{43}$$

From equations (41), (42) and (43),

$$\frac{V_{D_2O}}{V_{H_2O}} \approx a + b \exp[(q_{D_2O} - q_{H_2O})/kT] \tag{44}$$

where

$$a = 1 + \frac{\Delta V^{(0)}_{D_2O} - \Delta V^{(0)}_{H_2O}}{V_{H_2O}} + \frac{\Delta V^{(ii)}_{D_2O} - \Delta V^{(ii)}_{H_2O}}{V_{H_2O}} + \frac{\Delta V^{(i)}_{D_2O}}{V_{H_2O}} \tag{44'}$$

$$b = -C\frac{\Delta V^{(i)}_{D_2O}}{V_{H_2O}} \tag{44''}$$

But $(\Delta V^{(ii)}_{D_2O} - \Delta V^{(ii)}_{H_2O})/V_{H_2O}$ is a small quantity (see the discussion of (ii)) and$(\Delta V^{(0)}_{D_2O} - \Delta V^{(0)}_{H_2O})/V_{H_2O} \approx 0.003$ (*see* equation (39)). If the decreased volume of continuation of fusion, $\Delta V^{(i)}_{D_2O}/V_{H_2O}$, is approximately that of real melting, i.e. $\Delta V^{(i)}_{D_2O}/V_{H_2O} \approx -0.1$, then

$$a \approx 0.9, \quad b \approx 0.1C. \tag{45}$$

Using equations (44) and (45), $q_{H_2O} = 6.01$, $q_{D_2O} = 6.28$ kJ mol^{-1} (*see* Nèmethy and Scheraga, 1964) and choosing $C = 0.93$, the results in *Table 5* are obtained; the experimental values are given for comparison.

The above discussion indicates that the origin of the molar volume inequality $V_{D_2O} > V_{H_2O}$ is mainly due to the different behaviour of the bending vibrations of the H- and D-bonds and of the stretching vibrations of the chemical bonds —O—H··· and —O—D···. The amplitude of vibration of the H-bond is larger than that of the D-bond, and the vibrations weaken or break down the open structure of water, reducing its molar volume, and decreasing it more in the case of H_2O than in D_2O.

TABLE 5. The relative molar volumes of liquid H_2O and D_2O

Temperature (°C)	$\frac{V_{D_2O}}{V_{H_2O}}$ (calc.)	$\frac{V_{D_2O}}{V_{H_2O}}$ (expt.*)	Error
0	1.0048	1.0062	−0.0014
10	1.0044	1.0049	−0.0005
20	1.0040	1.0040	0.0000
30	1.0036	1.0033	+0.0003
40	1.0032	1.0028	+0.0004
50	1.0029	1.0025	+0.0004
60	1.0026	1.0022	+0.0004
70	1.0023	1.0021	+0.0002
80	1.0020	1.0020	0.0000
90	1.0018	1.0019	−0.0001
100	1.0015	1.0019	−0.0004

* From Kell (1979).

V CONCLUSION

In Sections II, III and IV, isotope effects on the stability of dimers containing H- and D-bonds, on the heats of vaporization of liquid water and hydrofluoric acid, and on the molar volume of liquid water, have been discussed. The difference in the hydrogen and deuterium bonds depends on the different behaviours of the H- and D-bonds due to the large change in mass from H to D. The bending vibrations of the H- and D-bonds make opposing contributions to those of the stretching vibrations of the chemical bonds A—H··· and A—D··· (as in the stability of the H- and D-bonded dimers and in the heats of vaporization of H_2O, D_2O and HF, DF) or to those of the stretching vibrations of the H- and D-bonds (as in the molar volume). These two opposed factors possess different relative magnitudes in different situations, giving interesting and surprising differences between H- and D-bonded species. Isotope effects on molecular properties are varied, but their origins (within the Born–Oppenheimer approximation) arise from their different vibrational behaviour (Buckingham and Urland, 1975).

To conclude, we return to the original question: is the hydrogen bond stronger or weaker than the deuterium bond? There can be no short answer to this question. The properties of systems containing hydrogen or deuterium bonds are dependent on zero-point motion of the nuclei, and therefore reflect the shape—as well as the depth—of the potential energy surface.

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