

**THE STRUCTURE
AND PROPERTIES OF
WATER**

D. EISENBERG

AND

W. KAUZMANN

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Preface

WATER is the most abundant compound on the surface of the Earth and it is the principal constituent of all living organisms. The oceans alone contain 1.4×10^{24} grammes or roughly 320 000 000 cubic miles of water. Another 0.8×10^{24} grammes is held within the rocks of the Earth's crust in the form of water of hydration. The human body is about 65 per cent water by weight, some tissues such as brain and lung being composed of nearly 80 per cent water.

Men of science since Thales have recognized the importance of water in both our internal and external environments, and have studied this substance extensively. Our purpose in writing this book is to summarize from the voluminous literature on water some of the most important and reliable data on this substance and to present the theories that are most effective in correlating these data. We have made no attempt to produce a compendium of data such as that compiled by Dorsey (1940), but we have tried instead to relate the properties of water to its structure. Some important properties of water, such as thermal conductivity and surface tension of the liquid, are not discussed because they have not yet contributed to our understanding of the liquid structure; other properties such as infra-red and Raman spectra are covered in detail because they reveal so much about the structures of ice and liquid water. Though some data on both electrolyte and non-electrolyte solutions are undoubtedly helpful in understanding the structure of water, we have not ventured into the vast literature concerning aqueous solutions.

Realizing that scientists in many fields are interested in water, we have included in the text some background material in physical chemistry which is required in order to follow the discussions of a number of topics. We believe that nearly all material in this book should be accessible to those who have had a first course in physical chemistry.

We have inserted an Addendum at the end of the text; it lists a number of very recent articles on the structure and properties of water, and a few articles overlooked by us during preparation of the

main body of the text. The articles are grouped according to the sections of the text to which they correspond.

During the preparation of this manuscript we have had the pleasure of discussing many interesting questions about water with a large number of friends and colleagues. These people are too numerous to mention individually, but we wish to thank in particular Professor S. I. Chan, Professor C. A. Coulson, Professor R. E. Dickerson, Professor B. Kamb, Dr. J. J. Kozak, Professor R. M. Pitzer, Dr. L. Salem, and Dr. G. E. Walrafen. We also wish to thank Lucy Eisenberg for a great deal of expert editorial advice.

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WALTER KAUFMANN

June 1968

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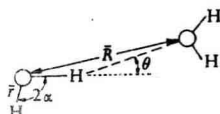
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Glossary of Notation

A	Helmholtz free energy
\AA	Ångstrom unit = 10^{-8} cm
C_p	Heat capacity at constant pressure
C_v	Heat capacity at constant volume
c'	Velocity of light
D	Coefficient of self-diffusion
D	Debye unit = 10^{-18} e.s.u. cm
E	Internal energy
e	Protonic charge
e	Base of natural logarithms = 2.71828
e.s.u.	Electrostatic unit of charge
e.u.	Entropy unit = $\text{cal mol}^{-1} \text{deg}^{-1}$
G	Gibbs free energy
g	Kirkwood correlation parameter
H	Enthalpy
h	Planck's constant
I	Moment of inertia
k	Boltzmann's constant. Various force constants
kbar	Kilobar = 10^9 dyn cm^{-2}
m	Molecular dipole moment in a condensed phase
N	Avogadro's number
N^*	Number of molecules per unit volume
n	Refractive index
P	Pressure
Q	Quadrupole moment
R	Gas constant
S	Entropy
T	Temperature, in $^{\circ}\text{K}$ unless stated otherwise
t	Temperature in $^{\circ}\text{C}$. Time
U	Potential energy
V	Molar volume
v	Vibrational quantum number
ψ	Electrostatic potential
X_A	Mole fraction of component A
α	Molecular polarizability
β	Coefficient of cubical expansion
γ_s	Coefficient of adiabatic compressibility
γ_T	Coefficient of isothermal compressibility

δ	Chemical shift
ϵ	Dielectric constant
ϵ_0	Static dielectric constant
ϵ_∞	High-frequency dielectric constant
η	Coefficient of viscosity
κ	Direct current conductivity
μ	Dipole moment of isolated molecule
ν	Vibrational mode or frequency
ρ_0	Bulk density
$\rho(\bar{R})$	Local density
τ_D	Relaxation times for motions of water molecules; see Section 4.1 (a)
τ_V	
τ_d	Dielectric relaxation time
χ	Magnetic susceptibility
ψ	Molecular orbital
Ψ^*	Molecular wave function

Notations pertaining to the water molecule and hydrogen bond



r	O-H bond length
2α	H-O-H bond angle
\bar{R}	Separation of oxygen nuclei of neighbouring water molecules
$180^\circ - \theta$	Hydrogen bond angle

1. The Water Molecule

IN order to interpret the properties of steam, ice, and liquid water, we must understand the water molecule. In this chapter we describe an isolated water molecule in two complementary ways: first in terms of properties that have been deduced from experiments, and second in terms of properties deduced from the electronic theory of chemical valence. The first group of properties is based on measurements made on water vapour at sufficiently low pressures or high temperatures to ensure that interactions between molecules are largely absent. These properties include, for example, the relative positions of the nuclei, and the polarity of the molecule as a whole; but they do not include much information about the disposition of electronic charge within the molecule. Thus for a more detailed picture of the water molecule we must turn to the description given by theory. This provides such details as the shape of the electronic charge cloud of water, and an indication of which parts of the charge contribute most heavily to the total polarity of the molecule. Of course, the separation of these interdependent descriptions is artificial, but it serves to emphasize which portion of our understanding of water is based on observation, and which is based on reasonably accurate models of the molecule.

1.1. The water molecule: description based on experiment

(a) *Composition*

The experiments of Cavendish and Lavoisier in the 1780s established that water is composed of hydrogen and oxygen. Although the careful data of Cavendish were sufficient to prove that two volumes of hydrogen combine with one volume of oxygen, he did not point this out, and it was left to Gay-Lussac and Humboldt to make this discovery in 1805 (Partington 1928). Dumas, in 1842, found that the ratio of the combining weights of hydrogen and oxygen in water is very nearly 2 to 16.

With the discovery of the stable isotopes of oxygen in 1929 and of deuterium in 1932, it was apparent that naturally occurring water is actually a mixture of several species differing in molecular weight.

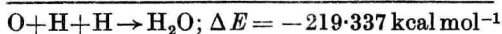
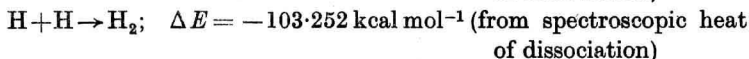
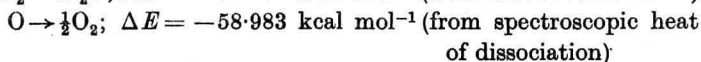
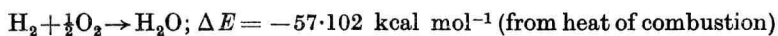
There are at present three known isotopes of hydrogen (^1H , ^2H (deuterium), and ^3H (tritium)), and six of oxygen (^{14}O , ^{15}O , ^{16}O , ^{17}O , ^{18}O , and ^{19}O). Tritium is radioactive with a half-life of 12.5 years. The isotopes ^{14}O , ^{15}O , and ^{19}O are also radioactive, but are short-lived and do not occur significantly in natural water.

The relative abundance of the stable isotopes in water was discussed at length by Shatenshtein *et al.* (1960). The precise isotopic content of natural water depends on the origin of the sample but within the limits of variation, the abundances of H_2^{18}O , H_2^{17}O , and HDO may be stated as 0.20 per cent, 0.04 per cent, and 0.03 per cent respectively. Since preparation of pure H_2^{18}O is exceedingly difficult, virtually all experimental measurements on water have been made on the naturally occurring substance.

A few words should be said about the terminology used in this book. The term *water* refers either to H_2O in all its phases or simply to liquid H_2O , according to the context. *Ice* refers to any of the solid forms of H_2O , not necessarily to ordinary ice I. The terms *steam* and *water vapour* are used interchangeably for gaseous water. Occasionally the term *heavy water* is used for D_2O .

(b) *Energetics of formation*

Suppose we slowly bring together two hydrogen atoms and one oxygen atom, all in their electronic ground states, to form a water molecule in its electronic, vibrational, rotational, and translational ground state (that is, the process takes place at 0 °K). The energy change of this hypothetical reaction, called the *energy of formation at 0 °K*, is obtained by combining thermochemical and spectroscopic data (Wagman *et al.* 1965):



The negative sign indicates, of course, that formation of the molecule is accompanied by a net decrease of energy. In stating a value for the energy of formation, we have been careful to specify that the temperature is 0 °K, because at any higher temperature the energy of formation is somewhat more negative, owing to the difference of the combined

translational energies of the atoms and the combined rotational and translational energies of the molecule. Moreover, heats of formation are usually measured at constant pressure and are, therefore, actually enthalpies of formation. The enthalpy of formation at a given temperature is slightly more negative than the corresponding energy of formation, owing to the pressure-volume term. The enthalpy of formation of water at 25 °C is $-221.54 \text{ kcal mol}^{-1}$ (see Table 1.1).

The *electronic binding energy* of a water molecule is the difference between the energy of the molecule with its nuclei stationary and the sum of the energies of its constituent atoms. It is slightly larger than the energy of formation at 0 °K. This is because even at 0 °K the molecule possesses a residual vibrational energy called the zero-point energy, which is not included in the energy of formation as we have defined it. The zero-point energy is evaluated from spectroscopic data (see Section 1.1 (d)); when it is subtracted from the energy of formation at 0 °K, the electronic binding energy is obtained (Table 1.1).

TABLE 1.1

Energies associated with the formation of a water molecule

(1) Energy of formation from atoms at 0 °K	$-219.34^{\dagger} \text{ kcal mol}^{-1}$
(2) Zero-point vibrational energy	$13.25^{\ddagger} *$
(3) Electronic binding energy = (1) - (2)	-232.59
(4) Enthalpy of formation at 25 °C	-221.54^{\dagger}
(5) Bond energy of O-H bond at 0 °K = $\frac{1}{2} \times (1)$	109.7
(6) Dissociation energy of H-O	101.5^{\S}
(7) Dissociation energy of H-OH = (1) - (6)	117.8

† Wagman *et al.* (1965).

‡ Section 1.1 (d).

§ Cottrell (1958).

The O-H *bond energy* of water is taken as half the energy of formation of the molecule, because water has two O-H bonds; its value is $109.7 \text{ kcal mol}^{-1}$ at 0 °K. A quantity closely related to the bond energy is the *dissociation energy*, which is defined as the energy to break a bond at 0 °K. Curiously enough, neither of the O-H bonds of water has a dissociation energy equal to the O-H bond energy. Cottrell (1958, p. 187) summarized the experimental evidence on this topic and concluded that the most accurate value of the energy for the dissociation of H-O into H and O is $101.5 \pm 0.5 \text{ kcal mol}^{-1}$. Since energy must be conserved, the sum of the dissociation energies of the two bonds of water is equal to the energy of formation, and so the energy for the dissociation of H-OH into H and OH is $117.8 \text{ kcal mol}^{-1}$.

Pauling (1960, p. 622) explained the inequality of the two dissociation

energies as follows: the dissociation of the second O-H bond permits the oxygen atom to undergo an energetically favourable electronic rearrangement, thereby reducing the second dissociation energy. When the second O-H bond is broken, the resulting oxygen atom has a $1s^2 2s^2 2p^4$ electronic configuration. One of the Russell-Saunders states corresponding to this configuration is 3P , and this state is stabilized by resonance of the two unpaired electrons. Pauling estimated that the stabilization energy is about $17.1 \text{ kcal mol}^{-1}$. Thus if the second dissociation produced an oxygen atom in its valence state rather than in the more stable 3P state, the corresponding dissociation energy would be

$$101.5 + 17.1 = 118.6 \text{ kcal mol}^{-1}.$$

This is essentially equal to the energy of the first dissociation.

(c) *Molecular dimensions*

The bond lengths and the bond angle of the water molecule are known with remarkable accuracy from the vibration-rotation spectra of normal and isotopic water vapour. The enormous labour of measuring and assigning the thousands of spectral lines was done by Darling and Dennison (1940), Benedict, Gailar, and Plyler (1956), and a number of others. Dennison (1940) and Herzberg (1950) discuss the procedure for deducing the moments of inertia, and hence the molecular dimensions, from the spectra; here we will be concerned only with the results.

TABLE 1.2
Molecular dimensions of D₂O, H₂O, and HDO†

Molecule		D ₂ O	H ₂ O	HDO
Moments of inertia	I_e^{z*}	5.6698	2.9376	4.2715
$\times 10^{40} \text{ g cm}^2 \ddagger$	I_e^{z*}	3.8340	1.9187	3.0654
	I_e^{y*}	1.8384	1.0220	1.2092
Bond length $\times 10^8 \text{ cm}$	\bar{r}_e	0.9575	0.95718	0.9571
Bond angle	$2\alpha_e$	104.474°	104.523°	104.529°

† Determined by Benedict *et al.* (1956).

‡ The z^* -axis passes through the molecular centre of mass and is perpendicular to the plane of the molecule. In H₂O and D₂O, the z^* -axis is the bisector of the bond angle in the plane, and the y^* -axis is perpendicular to the other two. In HDO the z^* and y^* -axes are rotated about the z^* -axis by 21.09° . The subscript e denotes that the corresponding quantity refers to the equilibrium (vibrationless and rotationless) state.

The nuclei of a water molecule form an isosceles triangle, with a slightly obtuse angle at the oxygen nucleus. Table 1.2 shows the molecular dimensions of D₂O, H₂O, and HDO found by Benedict *et al.*

(1956). All entries in this table refer to the *equilibrium state* of the molecule, the hypothetical state in which the molecule is vibrationless as well as rotationless, lacking even zero-point vibrational energy. The fiction of the equilibrium state is adopted because the average molecular dimensions are slightly dependent on the vibrational and rotational states of the molecule. This dependence is small, but is significant when accurate measurements are considered. The superscripts x^* , z^* , and y^* to the moments of inertia in Table 1.2 refer to the axes of the moments: for H_2O and D_2O the x^* -axis is perpendicular to the plane of the molecule, the z^* -axis lies in this plane and is the bisector of the bond angle, and the y^* -axis is perpendicular to the other two. These axes are respectively parallel to the x -, z -, and y -axes of Fig. 1.2 (a) (p. 13), but have their origin at the molecular centre of gravity instead of at the nucleus of the oxygen atom. Note that the largest moment is about the x^* -axis and the smallest is about the y^* -axis.

The equilibrium bond lengths and bond angles of the three isotopic molecules are very nearly equal. This result is consistent with the Born-Oppenheimer approximation, which predicts that the electronic structure of a molecule is independent of the masses of its nuclei. Benedict *et al.* estimated the uncertainty in the values of \bar{r}_e to be $\pm 0.0003 \times 10^{-8}$ cm, and the uncertainty in the values of $2\alpha_e$ to be $\pm 0.05^\circ$. They believe that the best values of the equilibrium dimensions are: $\bar{r}_e = 0.9572 \times 10^{-8}$ cm, and $2\alpha_e = 104.52^\circ$.

As mentioned above, the dimensions of the water molecule depend on the quantum state of the molecule. Their dependence on vibrational states is small. For each vibrational state, the molecular dimensions may be described by three 'effective moments of inertia' (Herzberg 1950, vol. ii, p. 461). Darling and Dennison (1940), using data slightly less accurate than those now available, gave the following expressions for the effective moments of inertia of the water molecule as functions of its vibrational states:

$$I^{x*} \times 10^{40} \text{ g cm}^2 = 2.9436 + 0.0611(v_1 + \tfrac{1}{2}) + 0.0385(v_2 + \tfrac{1}{2}) + 0.0441(v_3 + \tfrac{1}{2}); \quad (1.1 a)$$

$$I^{z*} \times 10^{40} \text{ g cm}^2 = 1.9207 + 0.0398(v_1 + \tfrac{1}{2}) - 0.0249(v_2 + \tfrac{1}{2}) + 0.0077(v_3 + \tfrac{1}{2}); \quad (1.1 b)$$

$$I^{y*} \times 10^{40} \text{ g cm}^2 = 1.0229 + 0.0213(v_1 + \tfrac{1}{2}) - 0.1010(v_2 + \tfrac{1}{2}) + 0.0486(v_3 + \tfrac{1}{2}). \quad (1.1 c)$$

Here v_1 , v_2 , and v_3 are the quantum numbers for the three normal modes of vibration (see the following section).

In the higher rotational levels, the water molecule suffers considerable centrifugal distortion and its dimensions depart significantly from their values in the equilibrium state. For example, in the level corresponding to a rotational quantum number $J = 11$, the bond angle can be decreased by as much as 5.58° , and the bond length may be increased by 0.006×10^{-8} cm (Herzberg 1950, vol. ii, p. 50); these distortions are associated with a sub-level in which the molecule rotates essentially around its y^* -axis.

Though very little is known about the electronically excited states of the water molecule, it is certain that the molecular dimensions in such states differ from those in the ground state. Bell (1965) studied the electronically excited states that are associated with the band origins at 1240 and 1219 Å in the vacuum ultraviolet spectrum of water vapour. He concluded that in the excited state associated with the band origin at 1240 Å, the O-H bond length is increased by 0.065 ± 0.010 Å, and the H-O-H angle is increased by $5.2 \pm 1.8^\circ$. In the other excited state, the O-H bond length is increased by 0.067 ± 0.010 Å, and the H-O-H angle is increased by $8.5 \pm 1.8^\circ$.

Up to this point we have been concerned with the relative positions of the atomic nuclei in a water molecule. Some indication of the mean positions of the electrons relative to the nuclei is also available from experiments. From magnetic and spectroscopic data, one can determine $\langle \Psi^0 | \sum_i r_i^2 | \Psi^0 \rangle$, where Ψ^0 is the electronic wave function for the ground state of the molecule, and r_i^2 is the square of the distance of the i th electron from the molecular centre of mass. The quantity $\langle \Psi^0 | \sum_i r_i^2 | \Psi^0 \rangle$, which can be denoted $\langle r^2 \rangle$ for simplicity, is the mean value of the square of the electronic distance from the molecular centre of mass. For the water molecule $\langle r^2 \rangle$ has the value $5.1 \pm 0.7 \times 10^{-16}$ cm² (Eisenberg *et al.* 1965).

(d) *Molecular vibrations*

The nuclei of molecules, far from occupying fixed positions with respect to each other, are in a continual state of vibration, even at 0° K. An important feature of these vibrations is that they can be described by a limited number of basic vibrations known as the normal modes. A normal mode is a vibration in which all the nuclei oscillate with the same frequency and the same phase. The water molecule has three normal modes and every possible vibration of the molecule can be described as a superposition of these three modes.

The normal modes of vibration of water are shown in Fig. 1.1. Because the motion of the nuclei in the ν_1 and ν_3 vibrations is nearly along the direction of the O-H bonds, these modes are often referred to as O-H stretching vibrations. Similarly, because the H nuclei in ν_2 move in directions almost perpendicular to the bonds, ν_2 is referred to as the

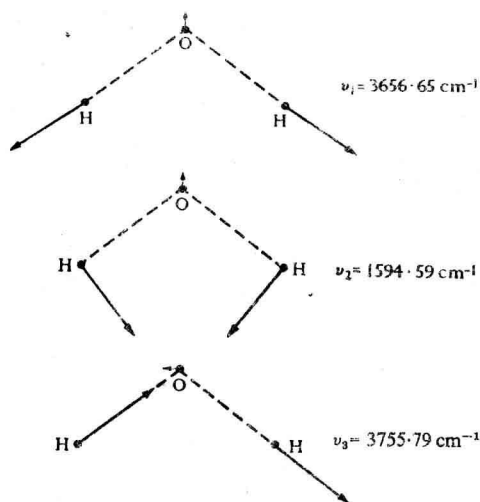


FIG. 1.1. The normal modes of vibration of H_2O . The bonds are represented by dashed lines. The arrows show the relative directions and displacements of the nuclei during a given vibration. If the arrows were drawn to the same scale as the bond lengths they would be only a fraction of the length shown for a molecule in its ground vibrational state. Redrawn from Mills (1963).

H-O-H bending vibration. In fact, ν_1 involves a small amount of H-O-H bending, and ν_2 involves a small amount of O-H stretching. The mode ν_3 is called the asymmetric stretching vibration to distinguish it from the symmetric stretching vibration ν_1 .

The transition of a water molecule from its vibrational ground state to the excited state described by the ν_2 mode is associated with the infra-red absorption band centred at 1594.59 cm^{-1} . During this transition, the quantum number v_2 characterizing the ν_2 mode changes from 0 to 1, while the quantum numbers v_1 and v_3 characterizing the ν_1 and ν_3 modes remain equal to zero. Similarly, the transition from the ground state to the state in which only the first normal mode is excited—the state with quantum numbers $v_1 = 1, v_2 = 0, v_3 = 0$ —is associated with the absorption band centred at 3656.65 cm^{-1} . Table 1.3 lists the frequencies