

Proton Resonance Shift of Water in the Gas and Liquid States*

J. C. HINDMAN

Chemistry Division, Argonne National Laboratory, Argonne, Illinois

(Received 20 January 1965)

Temperature-dependence measurements have been made on the chemical shift of the proton of a water molecule in the liquid state and in the gas state at varying pressure. The problem of relating these experimental data to the intermolecular forces leading to cohesion and to hydrogen-bond formation between water molecules is considered in detail. It is shown that a consistent treatment of the chemical shift, thermal, and dielectric data for water can be given based on a two-state model involving an equilibrium between a hydrogen-bonded "icelike" fraction and a "monomer" fraction whose interaction with the lattice arises entirely from London dispersion forces.

Using semiempirically derived values of the chemical shift and energy associated with the condensation of water vapor to "monomer," the magnitude of the shift associated with the transformation to ice is calculated. It is then shown that, on the assumption that the hydrogen bond is electrostatic in character, the "polar" contribution to this shift can be related through the appropriate shielding equations to the dipole moment of the water molecule in ice. The magnitude of the dipole moment derived from these relationships is found to be in excellent agreement with values derived from dielectric data.

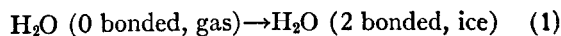
The possibility that the shielding changes may in part be due to processes other than the breaking of hydrogen bonds is considered. It is shown that the model leads to the conclusion that the chemical shift in the transformation of ice to water at 0°C could be entirely accounted for either by a stretching of the hydrogen bonds or a small amount of bending of the bonds. It is noted that if some bond breaking does occur, as required by the fact that water is a liquid, then the amount of stretching and/or bending will be limited.

INTRODUCTION

IN a preceding paper¹ the effect of univalent ions on the proton resonance of water was interpreted in terms of electrostatic interactions of the ions with water of hydration and in terms of structural alterations in the surrounding liquid. Before extending the treatment to the interpretation of the effect of higher-charge-type electrolytes, it appeared desirable to consider refinements in the model and applicability of the approach to the study of molecular interactions in water itself. We have concerned ourselves with two problems; first, the amount of information that can be derived from the chemical shift alone and, second, whether starting with the assumption that the hydrogen bond can be represented by an electrostatic model,^{2,3} more detailed information can be deduced about the nature of the interactions in the liquid state.

With respect to the first question, Schneider, Bernstein, and Pople⁴ measured the resonance position of the water hydrogen in the liquid phase at various temperatures relative to the resonance position in the gas phase and used to derive a value for the "liquid association shift," suggesting that this contribution to the shift was related to the formation of hydrogen bonds. Since in a system in rapid equilibrium the position of the resonance depends on the statistical average of the various species, a value for the "average

number of hydrogen bonds" could be calculated on the basis of their suggestion if it were assumed that the shift per bond broken were independent of the number of bonds and if one knew the total shift in going from the completely bonded to the nonbonded state. Actually, the situation is complicated by (1), the fact that a direct measurement of the total shift for the transformation



is not yet experimentally feasible because of the broadening of the proton resonance linewidth in ice and (2), the fact that there are other interactions that can affect the shielding in a condensed phase,⁵⁻⁷ i.e.,

$$\sigma_i = \sigma_0 + \sigma_d + \sigma_a + \sigma_F, \quad (2)$$

where σ_i is the total shielding constant, σ_0 is the intramolecular shielding constant for the atom in the isolated molecule, σ_d is the bulk diamagnetic susceptibility contribution, σ_a arises if the molecular susceptibility of the neighboring molecules is anisotropic, and σ_F is the contribution to the shielding due to the electric-field effects of the charge distributions in the neighboring molecules on the atom in question. The bulk magnetic-susceptibility contribution can be calculated by conventional methods.⁴ Also, since the susceptibility of ice is isotropic,⁸ the second term has been neglected. On the other hand, σ_F can be a complex quantity. The number of terms to be included in σ_F depends on the nature of the species present in the medium. In our

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

¹ J. C. Hindman, *J. Chem. Phys.* **36**, 1000 (1962).

² J. Lennard-Jones and J. A. Pople, *Proc. Roy. Soc. (London)* **A205**, 155 (1951).

³ J. A. Pople, *Proc. Roy. Soc. (London)* **A205**, 163 (1951).

⁴ W. G. Schneider, H. J. Bernstein, and J. A. Pople, *J. Chem. Phys.* **28**, 601 (1958).

⁵ M. J. Stephen, *Mol. Phys.* **1**, 223 (1958).

⁶ A. A. Bothner-By, *J. Mol. Spectry.* **5**, 52 (1960).

⁷ A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.* **32**, 1227 (1960).

⁸ K. Lonsdale, *Nature* **164**, 101 (1949).

treatment of the shielding we have considered σ_F to be composed of four terms,

$$\sigma_F = \sigma_W + \sigma_R + \sigma_P + \sigma_O. \quad (3)$$

The van der Waals term σ_W arises as a net consequence of the fluctuating electric field produced by a quantal oscillator and whose nonvanishing square leads to the London dispersion forces and the long-range repulsive forces. This is the dominant term affecting the shielding of a nonpolar solute in an isotropic nonpolar solvent.^{6,7} The reaction-field term^{7,9} σ_R is due to the polarization of the solvent by a polar solute. This term is of consequence in solutions of polar solutes in either polar or nonpolar solvents. The polar term σ_P represents the effect of the polarization of the O-H bonding electrons by an external electric field,^{9,10} which arises in the present case from the charge distribution in the other water molecule involved in the hydrogen bond. This is expected to be the dominant term where strong hydrogen bonds are formed as in the case of water. The final term σ_O indicates the effect of repulsive overlap^{11,12} on the shielding. This term is expected to be of significance only when the molecules are hydrogen bonded.

Determination of the magnitude of the various contributions obviously requires more information than can be obtained from an experimental study of the shielding changes in water alone. As a point of departure for our calculations we have therefore made the initial assumption that the properties of water can be treated as though the liquid were a mixture of two species, a hydrogen-bonded "icelike" fraction and a non-hydrogen-bonded monomeric fraction.¹³⁻¹⁷

To provide an experimental basis for deriving the contributions of these species, the previous chemical-shift measurements⁴ on water have been extended. Gas-phase measurements were made at more than a single temperature and pressure to see if there was evidence for appreciable association in the vapor phase. Additional liquid-phase measurements were also made since the reported linear variation of the chemical shift with temperature would not be compatible with the suggested relationship between the shift and the state of hydrogen bonding as estimated by other means. Additional measurements were also made of the chemical shift of water in dilute solution in organic solvents.¹⁸

The shielding parameters for a monomeric water species have been deduced from the experimental observations on the shielding of water in organic solvents together with data on shielding for organic solutes in these solvents and the theoretical treatments for the dispersion^{19,20} and reaction-field^{7,9} contributions.

The shielding parameters for the icelike phase have been derived as follows: It is assumed that all changes involved in the ice-water transition can be represented in terms of the breaking of hydrogen bonds. The fraction of such bonds broken at 0°C is then calculated from thermal data. Considering that the experimental shielding change in going from the gas to the liquid at 0°, after correction for bulk susceptibility, depends on the fraction of the two phases present, the sum of the contributions for the icelike fraction is then calculated. Since theoretical arguments indicate that the sum of the dispersion and overlap-repulsion contributions is close to zero for the hydrogen-bonded species, the polarization term σ_P is then obtained.

Finally, we have considered the relationship between the polarization contribution to the shielding and the properties of the water molecules in the hydrogen-bonded state. Use has been made of the Buckingham^{9,21,22} treatment of the electric-field effect to derive the dipole moment for a water molecule in the icelike phase. The value obtained is in good agreement with values for ice derived from model calculations²³ or from dielectric data. As an extension of these calculations, we have considered other possible interpretations of the shielding data. For example, if it were assumed that the intermolecular bond distances were increased to the degree indicated by the change in the maximum of the radial distribution function derived from x-ray data²⁴ in going from ice to water, the heat of fusion of ice could be largely attributed to the stretching of the hydrogen bonds. Alternatively, as indicated by Pople³ in his development of a model for the water structure, very few bonds may be broken but considerable bending of bonds may occur. With the present model, either of these processes will have an effect on the shielding similar to that caused by the breaking of hydrogen bonds. In fact, the calculations indicate that any appreciable stretching and/or bending of bonds in the ice-water transition would severely limit the number of bonds that could be broken.

EXPERIMENTAL

The proton resonance measurements were made with a Varian Associates V-4300B high-resolution spectrom-

⁹ A. D. Buckingham, *Can. J. Chem.* **38**, 300 (1960).

¹⁰ T. W. Marshall and J. A. Pople, *Mol. Phys.* **1**, 199 (1958).

¹¹ A. D. Buckingham and K. P. Lawley, *Mol. Phys.* **3**, 219 (1960).

¹² P. J. Berkeley, Jr., and M. W. Hanna, *J. Chem. Phys.* **41**, 2530, (1964).

¹³ E. Förslind, *Acta Polytech. Chem. Met. Ser.* **3**, 12, 42 (1952).

¹⁴ G. Nemethy and H. A. Scheraga, *J. Chem. Phys.* **36**, 3382 (1962).

¹⁵ R. P. Marchi and H. Eyring, *J. Phys. Chem.* **68**, 221 (1964).

¹⁶ L. Pauling, *Hydrogen Bonding Papers Symp. Ljubljana 1957*, **1** (1959).

¹⁷ H. S. Frank and A. S. Quist, *J. Chem. Phys.* **34**, 604 (1961).

¹⁸ A. D. Cohen and C. Reid, *J. Chem. Phys.* **25**, 791 (1956).

¹⁹ B. B. Howard, B. Linder, and M. T. Emerson, *J. Chem. Phys.* **36**, 485 (1962).

²⁰ W. R. Raynes, A. D. Buckingham, and H. J. Bernstein, *J. Chem. Phys.* **36**, 3481 (1962).

²¹ J. I. Musher, *J. Chem. Phys.* **37**, 34 (1962).

²² P. J. Berkeley, Jr., and M. W. Hanna, *J. Am. Chem. Soc.* **86**, 2990 (1964).

²³ E. J. W. Verwey, *Rec. Trav. Chim.* **60**, 887 (1941).

²⁴ J. Morgan and B. E. Warren, *J. Chem. Phys.* **6**, 666 (1938).

eter operating at 40 or 60 Mc/sec. Samples for the gas-phase measurements were made by introducing a small measured quantity of liquid water into 4-mm-i.d. tubes, centrifuging the water to the bottom, attaching the tube to a vacuum line, freezing the water with an acetone-dry-ice bath, and removing the air by pumping. A given volume of methane gas at known pressure was then condensed into the tube using a liquid-nitrogen bath and the tube sealed. For the measurement of the temperature coefficient of the shift of liquid water a reference sample of methane gas was prepared by sealing a known volume of the gas into a precision 3-mm-o.d. Wilmad glass tube. This tube was inserted into the outer precision 5-mm coaxial tube containing the water and this outer tube then sealed. The frequency separation of the proton signal in the water from that of the methane gas was obtained by the sideband technique.

Samples for measuring the chemical shift of methane gas dissolved in water were made by condensing a given volume of gas at known pressure into tubes containing water and sealing. The "solvent" shift measurements were made using samples of dried and water-saturated solvents sealed in 5-mm tubes containing water-filled capillary tubes. Measurements of the shifts for the methane in water and water in organic solvent samples were made using a C-1024 computer and multiple scans triggered by the water reference peak. Sidebands of the water reference were used to increase the accuracy of the shift measurements.

Temperature control was achieved by use of a glass-flow cryostat. The temperature at the sample location was measured by a substitution technique using a copper-constantan thermocouple enclosed in a glass tube. It is estimated that measurement errors due to temperature fluctuations were reduced by this procedure to ± 0.1 – 0.2 cps.

The chemical shifts δ are reported in the dimensionless units of parts per million, ppm. The convention is used that resonance signals occurring at higher field than the reference have more positive values of the shielding parameter σ and more negative values of the chemical shift parameter δ . The additional convention is used that for the liquid-water shifts, $\delta=0$ at 0°C . The chemical shifts were corrected for bulk-magnetic-susceptibility effects according to the equation

$$\sigma_d = \frac{2}{3}\pi(\chi_{v, \text{reference}} - \chi_{v, \text{sample}}) \quad (4)$$

For the gas-phase measurements the susceptibility corrections are negligible and are neglected. For water, the volume susceptibilities χ_v were calculated using the gram-susceptibility data of Auer²⁵ and density data as tabulated by Dorsey.²⁶ The susceptibility corrections for the organic solvents were calculated using the com-

parison of diamagnetic susceptibilities made by Smith²⁷ and density data from Timmermans.²⁸

RESULTS

The experimental data for the gas-phase shifts are summarized in Table I. It is noted that within the experimental error the $\text{CH}_4(\text{g})$ – $\text{H}_2\text{O}(\text{g})$ shift is independent of temperature and pressure, indicating little or no association of water in the vapor phase. These observations are in accord with calculations from data on the second virial coefficient of water vapor²⁹ and with observations on the Raman spectrum of the vapor.³⁰ Combining the data in Table I with Schneider, Bernstein, and Pople's⁴ value for the $\text{H}_2(\text{g})$ – $\text{CH}_4(\text{g})$ shift ($\Delta\sigma=4.20\times 10^{-6}$) and Newell's³¹ value for the shielding of the hydrogen molecule ($\sigma=26.6\times 10^{-6}$) we obtain for the shielding constant of the isolated water molecule in the gas phase $\sigma=30.2\times 10^{-6}$.

The liquid-phase-shift data are summarized in Fig. 1. Table II gives values of the shifts interpolated for integral temperature intervals. It should be noted that the susceptibility corrections for the supercooled water and for the temperature interval above 70°C are uncertain since they are necessarily obtained by extrapolation.

Using the experimental data in Tables I and II, a minimum value of the "association shift"³⁴ can be calculated to be $\sigma_B = -4.846\times 10^{-6}$ (for water at -15°C). Values of this parameter at other temperatures are given in Table II.

The chemical shift for $\text{CH}_4(\text{g})$ to $\text{CH}_4(\text{H}_2\text{O})$ was measured at 25°C to be $\delta=1.81\times 10^{-6}$, independent of methane pressure between 10 and 100 atm. This yields a calculated value for the solvent shift for CH_4 in water of $\sigma_w = -0.30\times 10^{-6}$. This datum, together with values for the solvent shifts of CH_4 in organic solvents and similar data for water in these solvents (Table

TABLE I. $\text{H}_2\text{O}(\text{g})$ chemical shift from $\text{CH}_4(\text{g})$ reference. $\text{CH}_4(\text{g})\sim 20$ atm at 180° .

Sample No.	t ($^\circ\text{C}$)	$p_{\text{H}_2\text{O}}(\text{g})$ (atm)	$\delta_{\text{H}_2\text{O}-\text{CH}_4}$ (ppm)
1	130	4.5	0.535
	156	4.8	0.607
	165	4.9	0.555
	190	5.1	0.538
2	165	11.4	0.572
	190	12.1	0.568
3	156	4.6	0.535
	190	5.0	0.565
Mean			0.559 ± 0.019

²⁷ G. W. Smith, General Motors Corp. Rept. GMR-317 (1960); GMR-396 (1963).

²⁸ J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds* (Elsevier Publ. Co., Inc., New York, 1950).

²⁹ J. S. Rowlinson, *Trans. Faraday Soc.* **45**, 974 (1949).

³⁰ S. A. Ukholin, *Ref.* 26, p. 56.

³¹ G. F. Newell, *Phys. Rev.* **80**, 476 (1950).

²⁵ H. Auer, *Ann. Physik* **18**, 593 (1933).

²⁶ N. E. Dorsey, *Properties of Water Substance* (Reinhold Publ. Corp., New York, 1940).

III), provides a basis for calculation of the shielding effects for "monomeric" water molecules in various environments.

GENERAL THEORY

We start with the assumption that the Bernal and Fowler model³² is essentially correct and that water can be treated as a broken-down ice structure. We also note that if, in addition, the Frank and Wen concept³³ of water as a dynamic system composed of flickering clusters of icelike material and disordered fluid is introduced, we have a two-component model which is adequate as a basis for both qualitative and quantitative treatment of many of the static and dynamic properties of water. We therefore proceed on the assumption that

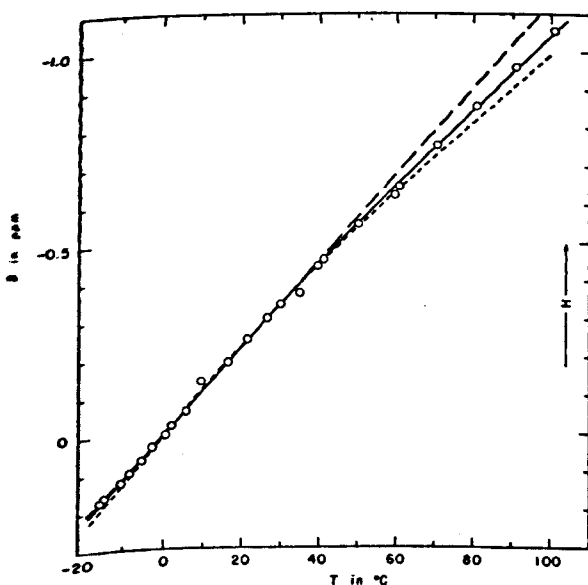


FIG. 1. Chemical shift of water as a function of temperature, δ_{H_2O} at $0^\circ\text{C} = 0$. O, Experimental data; —, straight line; ---, susceptibility corrected shift line.

water can be treated as a two-component system composed, in the first instance, of an icelike fraction and a monomeric "normal" fraction in equilibrium.

We then have two problems: First, to evaluate the shielding parameters associated with each of the components and, second, to determine the magnitude of the various possible contributions to these shielding parameters, in particular to determine the shielding contribution attributable to the formation of hydrogen bonds. To proceed, it is necessary to further define the properties of the two components. We therefore make the following assumptions: (1) That the pertinent properties of the icelike fraction are those of ordinary ice. This assumption is based on the observation that the

³² J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* **1**, 515 (1933).
³³ H. S. Frank and W.-Y. Wen, *Discussions Faraday Soc.* **24**, 133 (1957).

TABLE II. Liquid-phase chemical shifts referred to H_2O at 0°C [$\delta_{\text{H}_2\text{O}}(0^\circ) \rightarrow \delta_{\text{CH}_4}(\text{g}) = -6.720$ ppm].

f°	δ (obs) (ppm)	δ (corr) (ppm)	σ_R (ppm)
-15	0.170	0.190	-4.846
-10	0.115	0.126	-4.782
-5	0.055	0.058	-4.714
0	(0.000)	(0.000)	-4.656
5	-0.058	-0.060	-4.596
10	-0.117	-0.121	-4.535
15	-0.175	-0.179	-4.477
20	-0.231	-0.235	-4.421
25	-0.235	-0.288	-4.368
30	-0.340	-0.341	-4.315
35	-0.394	-0.394	-4.262
40	-0.446	-0.443	-4.213
45	-0.498	-0.492	-4.164
50	-0.549	-0.541	-4.115
55	-0.600	-0.590	-4.066
60	-0.650	-0.636	-4.020
65	-0.700	-0.683	-3.973
70	-0.750	-0.727	-3.929
80	-0.850	-0.820	-3.836
90	-0.948	-0.909	-3.747
100	-1.045	-0.995	-3.661

energy of transformation of ice into any one of the alternate hydrogen-bonded structures suggested as possible species in the liquid phase is probably small.^{32,34} (2) That the hydrogen-bond energy is independent of the number of hydrogen bonds.³⁵ As a corollary we also assume the polarization of hydrogen-bond contribution to the chemical shift to be independent of the number of bonds. (3) That the properties of the water molecules in the monomeric component can be derived on the assumption that in bulk it would be a normal liquid. That is, it is assumed that the molecules are freely rotating and that there is no dipole contribution

TABLE III. Chemical shift of water in CCl_4 and cyclohexane [$\delta_{\text{H}_2\text{O}}(l) = 0$, saturated solutions of H_2O].

Solvent	t ($^\circ\text{C}$)	δ_{expt} (ppm)	δ_{corr} (ppm)	Solvent shift ($\sigma_W + \sigma_R$) (ppm)
CCl_4	0	-3.59	-3.85	-0.81
	25	-3.69	-3.60	-0.77
	50	-3.52	-3.40	-0.72
	75	-3.35	-3.20	-0.68
Cyclohexane- d_{12} ^a	25	-4.05	-3.86	(-0.53)

^a Preliminary measurement, single sample purified by gas chromatography, low solubility of H_2O , and presence of CaH_2 impurity limited accuracy of measurement.

³⁴ R. M. Barrer and W. I. Stuart, *Proc. Roy. Soc. (London)* **A242**, 172 (1957).

³⁵ Some support for this common assumption can be derived from the calculations of R. Grahn [*Arkiv Fysik* **15**, 257 (1959)] which indicate that there is little additional polarization energy per bond contributed by going from the 1-bonded to the 2-bonded state.

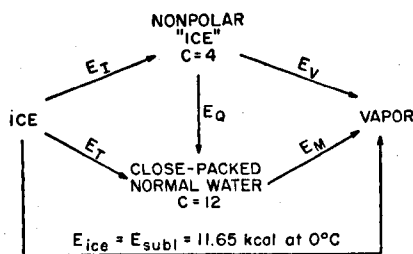
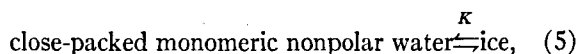


FIG. 2. Schematic representation of processes in converting ice to water vapor.

to the cohesive energy.³⁶ The thermodynamic properties of such a liquid can be derived in a reasonable way by semiempirical calculations.³⁷⁻³⁹ It is similarly possible to estimate the shielding properties of such water molecules from experimental observations on water dissolved in organic solvents.

A schematic representation for hypothetical process involved in the transformation of ice to water vapor used as a basis for deriving the various energy and shielding parameters of interest is shown in Fig. 2. Using this we can write for the equilibrium



with

$$K = f / (1 - f) = \text{ice/monomer},$$

whence

$$f = \frac{E_S - E_M}{E_{ice} - E_M} = \frac{E_S - E_M}{E_T} = \frac{\sigma_E - \sigma_M}{\sigma_P + \sigma_O - \sigma_M} = \frac{\sigma_E - \sigma_M}{\sigma_T}. \quad (6)$$

E_S and σ_E are, respectively, the experimental sublimation energy and shielding constant (Table II) for water at a given temperature, E_M and σ_M the corresponding quantities for the monomeric water, E_{ice} the experimental sublimation energy of ice (Fig. 2), and E_T and σ_T are, respectively, the energy and shielding change for the transformation of ice to water. σ_P is the polarization or hydrogen-bond contribution to the shielding and σ_O the overlap-repulsion contribution. Our first concern is to obtain a value of E_M to be used in calculating f .

³⁶ One reason for making this assumption is that a number of authors^{14,16,17} have considered that, and there is some support for this assumption from light-scattering experiments [K. J. Mysels, *J. Am. Chem. Soc.* **86**, 3503 (1964)]; at least at low temperatures such monomers, if they exist, are likely to be in cavities in the icelike network. If we consider that the rotation time of such a monomer is likely to be rapid relative to the relaxation time of the lattice then we would expect that any dipole interactions with the lattice would average out. As a consequence we would expect that there would be no contribution to the shielding of the monomer attributable either to the electric field of the lattice dipoles or to a reaction field caused by orientation of the lattice molecules by the rapidly rotating molecules.

³⁷ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, N.Y., 1944), 2nd ed., p. 304.

³⁸ A. W. Searcy, *J. Chem. Phys.* **17**, 210 (1949).

³⁹ R. W. Taft, Jr., and H. H. Sisler, *J. Chem. Educ.* **24**, 175 (1947).

Monomeric State

Because of the uncertainties involved in making theoretical calculations, a semiempirical approach has been adopted for obtaining the properties of the monomeric state. We start by considering that the liquid would resemble the condensed states of H_2S and H_2Se and have a face-centered-cubic lattice with a coordination number c equal to 12.⁴⁰ One estimate of the sublimation energy is obtained by extrapolation from the sublimation energies of other hydrides according to the procedure of Taft and Sisler.³⁹ Their procedure yields a heat of sublimation at the boiling point, 161°K, for a nonpolar water of 3.2 kcal and an energy of sublimation of 2.9 kcal. A second estimate is based on the use of a Lennard-Jones 12-6 potential function to calculate the potential energy U of the nonpolar water⁴¹

$$U = 3 \langle m^2 \rangle \alpha \frac{S_m}{a_0^6} \left[\frac{C' S_n'}{2c S_n} \left(\frac{a_0}{a} \right)^{12} - \frac{C' S_n'}{C S_m} \left(\frac{a_0}{a} \right)^6 \right], \quad (7)$$

where $\langle m^2 \rangle$ is the mean-square dipole moment of the quantum-mechanical oscillator,^{42,43} α is the polarizability, $S_{m,n}$ and c are the appropriate lattice summation constants and coordination number ($c=12$) for our reference state, a_0 is the intermolecular separation at some temperature for our reference liquid, and $S_{m,n}$, α , c' , and a reflect the variation of these parameters with change in lattice configuration and temperature. The parameters for use in Eq. (7) have been obtained as follows: One value for $a=a_0$ of 3.18 Å for water at 0°K was obtained from the equation of Grojtheim and Krogh-Moe⁴⁴ for the volume behavior of a close-packed water structure. Their expression was derived on the basis that the volume behavior of water at high temperatures approximates that of a normal liquid. A similar value is obtained by consideration of the intermolecular separations in the crystal lattices of H_2S and H_2Se . For these two substances the intermolecular separation is approximately the mean of two values, one obtained by summing the X-H distance in the molecule, the van der Waals radius of hydrogen, and the van der Waals radius of X, the second by summing the X-H distance in the molecule, the covalent radius of hydrogen, and the van der Waals radius of X. For water this procedure yields a van der Waals radius of 1.58 Å. These values are in agreement with similar estimates made by others.^{14,38} Three methods for evaluating $\langle m^2 \rangle$ have been considered. The value obtained from the London⁴² relation, where

$$\langle m^2 \rangle = \frac{3}{2} Q \alpha \quad (8)$$

⁴⁰ R. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1963), 2nd ed., Vol. 1, pp. 368-369.

⁴¹ E. A. Moelwyn-Hughes, *Physical Chemistry* (Pergamon Press, Inc., New York, 1961), 2nd ed., Chap. 7. Values of the lattice summation constants, $S_n = S_{12}$ and $S_m = S_6$, are given by this author.

⁴² F. London, *Trans. Faraday Soc.* **33**, 8 (1937).

⁴³ B. Linder, *J. Chem. Phys.* **33**, 668 (1960).

⁴⁴ K. Grojtheim and J. Krogh-Moe, *Acta Chem. Scand.* **8**, 1193 (1954).

TABLE IV. Calculation of sublimation energy of close-packed water.*

	<i>I</i> (eV)	α (cc $\times 10^{24}$)	V_m^b (cc/mole)	<i>b</i> (cm $\times 10^8$)	$-\chi_m$ ($\times 10^6$)	E_M^b			
						<i>c</i>	<i>d</i>	Exptl ^c	<i>f</i>
H ₂ S	10.42	3.642	26.17	3.95	25.5	2.47	4.95	3.74	
H ₂ O	12.56	1.444	15.18	3.29	12.96	1.65	3.99	(2.90)	2.42

* Reference 49.

^b At boiling point, 231.9°K for H₂S; 161°K for H₂O.

^c London approximation.

^d Kirkwood-Müller approximation.

* For H₂S, $E_{\text{exptl}}=4.06$ kcal. The experimental value has been decreased by 0.32 kcal attributable to the dipole contribution. For H₂O, E_{exptl} is an extrapolated value obtained by the method of Taft and Sisler.⁴⁷

^f Calculation from H₂S data with $f=1.5$, see text.

with $Q=I$, is considered to give a lower limit since Q is generally larger than the ionization potential I .⁴⁵ A probable upper limit^{45,46} is obtained from the Kirkwood-Müller approximation,^{47,48} where

$$\langle m^2 \rangle = -(6m_e c^2 \chi_m / N), \quad (9)$$

m_e is the electron mass, c the velocity of light, χ_m is the molar diamagnetic susceptibility, and N is Avogadro's number. The value of interest has been obtained by following a suggestion of Donath⁴⁵ that $f=Q/I$ be calculated empirically. An appropriate value of f for the present case has been obtained by comparing the calculated cohesive energy of H₂S obtained by use of the London approximation with the sublimation energy. The results of these calculations are summarized in Table IV.⁴⁹ The value of $E_M=2.4$ kcal obtained is in reasonable agreement with that calculated by the extrapolation procedure. Relative cohesive energies for the monomeric water as a function of temperature have been calculated from Eq. (7) using molar volumes V_m obtained from the equation of Grojtheim and

Krogh-Moe⁴⁴ to obtain values for the intermolecular separation a (Table V). These data, together with the experimental values for the sublimation energy of ice, $E_{\text{ice}}=11.65$ kcal, and of water, E_S , derived from the heat-of-sublimation data compiled by Dorsey⁵⁶ and the mean value of $E_M=2.7$ kcal (Table IV), provide the necessary information for the calculation of E_T and f [Eq. (6)]. With this choice of parameters we obtain essentially Pauling's³⁷ result with $f=0.845$, corresponding to 15.5% of the hydrogen bonds being broken in water at 0°C. The values for f calculated on the assumption that the monomers are in a clathrate lattice would be somewhat less although perhaps not as much as would be calculated from the E_M data in Table V since the potential well for the molecules in the cavities would probably not be symmetrical.³⁴

Our next concern is with the evaluation of σ_M [Eq. (6)]. Again we adopt a semiempirical approach. We consider first that σ_M reflects the net shielding contributions arising from the dispersion and repulsive forces. We further consider that the observed reduction in

TABLE V. Calculation of dispersion and repulsive contributions to cohesive energy for different water configurations.

Structure	<i>T</i> (°K)	V_m (cc/mole)	<i>a</i> (Å)	$\frac{1}{2}F(a_0/a)^{12}$	$F'(a_0/a)^6$	Relative net attr. energy	Van der Waals energy $-U=E_M$ (kcal)
Close-packed water ^a	0	13.65	3.18 (a_0)	0.500	1.000	0.50	2.8
	161	15.19	3.29	0.333	0.815	0.48	2.7
	273	16.73	3.40	0.224	0.669	0.44	2.4
	373	18.48	3.51	0.153	0.530	0.40	2.2
	0	18.90	2.73	(3.120)	(2.498)	(-0.62)	(-3.5)
Ice ^b	273	19.65	2.76	(2.736)	(2.339)	(-0.40)	(-2.2)
				0.956	0.927	-0.03	-0.2
				0.024	0.312	0.29	1.3
Clathrate ^c	273	21.96	4.33(6)	0.065	0.934	0.37	1.7

^a For close-packed nonpolar water, $c=12$, $S_N=1.0092$, $S_M=1.2198$, $F=(c'S_N/cS_M)=1$, $F'=(c'S_M/cS_M)=1$.

^b For ice, $c'=4$, $S_N'=1.0574$, $S_M'=1.4495$, $F=(c'S_N'/cS_N)$, $F'=(c'S_M'/cS_M)$.

Numbers in parentheses represent values for condensation of nonpolar water to dimensions of ice without change in coordination number. The other values for v_2 correspond to E_0 , Fig. 2.

^c For clathrate, numbers in parentheses represent number of holes of given dimensions. $c=24$ for 6-Å holes (6), $c=20$ for 5-Å holes (2). S_N and S_M assumed the same as for nonpolar water.

* K. S. Pitzer, *Quantum Chemistry* (Prentice-Hall, Inc., New York, 1953), p. 339; *Advan. Chem. Phys.* **2**, 59 (1959).

^b L. Salem, *Mol. Phys.* **3**, 441 (1960).

^c J. G. Kirkwood, *Phys. Z.* **33**, 57 (1932).

^d A. Müller, *Proc. Roy. Soc. (London)* **A154**, 624 (1936).

^e Value of I and α from Ref. 41, density data for calculation of V_m for H₂S from *International Critical Tables* (McGraw-Hill Book Co., Inc., New York, 1928), Vol. 3, p. 22. Molar susceptibility value for H₂S from Ref. 20.

shielding in nonpolar media is brought about by the fluctuating electric field E_D , whose nonvanishing square leads to dispersion forces.^{19,20} The solvent contribution is then

$$\sigma_W = \sigma_L + \sigma_r = -\phi \langle E_d^2 \rangle, \quad (10)$$

where ϕ is a constant¹⁰ and $\langle E_d^2 \rangle$ is the effective mean-square field. This effective mean-square field $\langle E_d^2 \rangle$ will be less than the mean-square field of a fluctuating dipole:

$$\langle E_0^2 \rangle = 2 \langle M^2 \rangle / a^6 = -2U(\text{pair}) / \alpha \quad (11)$$

as a consequence of the repulsive forces. At this point we follow Howard, Linder, and Emerson¹⁹ and assume that $\langle E_d^2 \rangle$ can be calculated by analogy, using the potential-energy relationship for a nonpolar molecule in a static electric field, i.e.,

$$U = -\frac{1}{2} E^2 / \alpha \quad \text{or} \quad E_M = \frac{1}{2} \langle E_d^2 \rangle / \alpha. \quad (12)$$

We then proceeded to calculate $\sigma_M(\text{H}_2\text{O})$ in several ways. First, from Eqs. (10) and (12) we can write

$$\frac{\sigma_{W(M)}(\text{H}_2\text{O})}{\sigma_M(\text{CH}_4)} = \frac{E_M(\text{H}_2\text{O})}{E_M(\text{CH}_4)} \frac{\alpha(\text{CH}_4)}{\alpha(\text{H}_2\text{O})}. \quad (13)$$

Using Gordon and Dailey's⁵⁰ value of -0.20×10^{-6} for $\sigma_W(\text{CH}_4)$, a value of 1.73 kcal for $E_M(\text{CH}_4)$,⁵¹ with $\alpha_{\text{CH}_4} = 2.60 \times 10^{-24}$ ²⁰ and $\alpha_{\text{H}_2\text{O}} = 1.44 \times 10^{-24}$ ⁴¹ and E_M from Table V, we obtain $\sigma_M(\text{H}_2\text{O}) = -0.50 \times 10^{-6}$. An analogous procedure is to use the experimental value for σ_W of CH_4 in CH_4 and H_2O to calculate E_M for CH_4 in H_2O , i.e.,

$$\frac{\sigma_W(\text{CH}_4 \text{ in } \text{H}_2\text{O})}{\sigma_W(\text{CH}_4 \text{ in } \text{CH}_4)} = \frac{E_M(\text{CH}_4 \text{ in } \text{H}_2\text{O})}{E_M(\text{CH}_4 \text{ in } \text{CH}_4)}, \quad (14)$$

and then to calculate σ_M for water from

$$\frac{\sigma_W(\text{H}_2\text{O})}{\sigma_M(\text{CH}_4 \text{ in } \text{H}_2\text{O})} = \frac{E_M(\text{H}_2\text{O})}{E_M(\text{CH}_4 \text{ in } \text{H}_2\text{O})} \frac{\alpha(\text{CH}_4)}{\alpha(\text{H}_2\text{O})}. \quad (15)$$

This gives $\sigma_M(\text{H}_2\text{O}) = -0.43 \times 10^{-6}$. An independent calculation of σ_M can be made using the experimental data for the chemical shift of water in an organic solvent. These experimental values set upper limits for the dispersion contribution since there is also a reaction-field contribution. The magnitude of this reaction-field contribution has been calculated by the procedure of Buckingham,⁹ where

$$\sigma_R = -\phi_a[R] - \phi_b[R^2] \quad (16)$$

and the reaction field R is

$$R = [2(\epsilon_1 - 1)(n_2^2 - 1) / 3(2\epsilon_1 + n_2^2)] [(\mu_2 \cos \theta_2) / \alpha_2]. \quad (17)$$

With $\phi_a = 2.26 \times 10^{-12}$ and $\phi_b = 0.74 \times 10^{-18}$ (see later

text), $\epsilon_{\text{CCl}_4} = 2.273$,²⁸ $n_{\text{H}_2\text{O}}^2 = 1.79$, $\alpha_{\text{H}_2\text{O}} = 1.44 \times 10^{-24}$, $\mu_{\text{H}_2\text{O}} = 1.844 \times 10^{-18}$,⁵² $\cos \theta = \cos \frac{1}{2} \text{HOH} < 0.6115$, $\sigma_R = -0.27 \times 10^{-6}$. This gives $\sigma_{W(M)} = -0.54 \times 10^{-6}$ for H_2O in CCl_4 at 0°C . From the reaction-field model for the dispersion effect¹⁹ we can derive the relation

$$\sigma_M(\text{H}_2\text{O} \text{ in } \text{H}_2\text{O}) = \sigma_W(\text{H}_2\text{O} \text{ in solvent}) (g' \text{H}_2\text{O} / g' \text{ solvent}), \quad (18)$$

where $g' = (2n^2 - 2) / (2n^2 + 1)$. With $n_{\text{H}_2\text{O}}^2 = 1.79$ and $n_{\text{CCl}_4}^2 = 2.13$,²⁸ $\sigma_M(\text{H}_2\text{O} \text{ in } \text{H}_2\text{O}) = -0.43 \times 10^{-6}$. A similar value is obtained from the cyclohexane data. With $\epsilon_{\text{C}_6\text{H}_{12}} = 2.013$,²⁸ $n_{\text{C}_6\text{H}_{12}}^2 = 2.017$,²⁸ $\sigma_R = -0.167 \times 10^{-6}$, and $\sigma_M(\text{H}_2\text{O} \text{ in } \text{H}_2\text{O}) = -0.30 \times 10^{-6}$.

At this point we consider more closely the relationship between the value of the shielding constant derived for the water monomer in the preceding paragraphs and the environment assumed for the molecules in the liquid, i.e., whether the molecules are freely rotating in cavities in a lattice structure²⁶ or are assumed to form a separate liquid phase.¹⁴ We can consider that the properties of such a separate liquid phase would be those of a disordered dipolar liquid, i.e., the molecules would be monomers in free rotational states. For such a molecule in a symmetric solvent structure we might expect cancellation of the dipole forces.⁶ This implies that the solvent shifts of nonpolar solutes in isotropic polar solvents could be accounted for entirely in terms of dispersion forces and of polar solvents in isotropic polar solvents in terms of dispersion and reaction-field interactions. It has already been noted³ that no type of interaction other than dispersion need be invoked to explain the solvent shifts of nonpolar solutes in reasonably isotropic polar solvents. More specifically, we can note that the shielding behavior of methane in water is not significantly different from its behavior in other polar^{7,53} and nonpolar solvents,^{7,53} indicating that in this respect there is nothing abnormal about water as a solvent. Insofar as the water monomers are concerned, we have already indicated that we do not expect a reaction-field contribution if the molecules are in a vacancy in an icelike structure. For these molecules, $\sigma_{W(M)}$ as obtained from the organic-solvent data is used. Where the molecules form a separate phase, a reaction-field contribution is expected. In principle, the reaction-field contribution could be evaluated semiempirically from studies of the shielding changes of water in solvents of varying polarity.⁷ Unfortunately in the solvents thus far examined, chloroform, acetonitrile, nitromethane, etc., the situation has been found to be complicated by the formation of water-solvent complexes. Pending further studies we have, therefore, calculated the reaction-field contribution by the Buckingham⁹ procedure [Eqs. (16)–(17)].

⁵⁰ S. Gordon and B. P. Dailey, *J. Chem. Phys.* **34**, 1084 (1961).
⁵¹ From data in *Selected Values of Physical and Thermodynamic Properties of the Hydrocarbons and Related Compounds* (Carnegie Press, Pittsburgh, Pa., 1953), API Project 44.

⁵² A. A. Maryott and F. Buckley, *Natl. Bur. Std. (U.S.) Circ. No. 537*, 7 (1953).

⁵³ N. Lumbroso, T. K. Wu, and B. P. Dailey, *J. Phys. Chem.* **67**, 2469 (1963).

For monomeric water, with $n^2=1.79$ and $\epsilon=26.5$, $\sigma_R = -0.46 \times 10^{-6}$, and the total solvent shift, $\sigma_M + \sigma_R \cong 0.91 \times 10^{-6}$.

Hydrogen-Bonded State

At this point we could proceed with the calculation of an "average state of hydrogen bonding" for water using the chemical-shift data. However, since processes other than the breaking of hydrogen bonds can lead to shielding changes, we defer this to later and consider first how we might relate configurational alterations in the hydrogen-bonded species to the shielding. To do this we have started with the premise that the hydrogen bond can be represented by an electrostatic model and that the shielding changes associated with dimensional alterations within the complex can be calculated using the Buckingham⁹ treatment for the effect of an electric field on the proton shielding. Our first step is to determine the polarization contribution to the shielding σ_P for the hydrogen-bonded state. To do this we must evaluate the magnitude of the repulsive term σ_0 . We could, of course, assume that Eqs. (10) and (12) are valid regardless of the relative magnitudes of the repulsion and dispersion energies. If the further assumption were made that the calculation of the net cohesive energy for nonpolar ice in Table V were correct, then we would calculate σ_0 to be approximately 0.04×10^{-6} . In view of the questions that can be raised with respect to the validity of both of these assumptions, it appears desirable to consider in more detail the nature of the relationships between the shielding and the dispersion and repulsive forces. First, with respect to the dispersion, the treatment of Marshall and Pople¹⁰ indicates that the bulk of the electric-field effect on the shielding is due to a reduction in the magnitude of the diamagnetic Lamb-type term, corresponding to the partial removal of electrons from the vicinity of the nucleus with consequent reduction in the mean value of $1/r$, i.e.,

$$\sigma_d = \frac{e^2}{3mc^2} \int \frac{\rho(r)}{r} d\bar{r} = \frac{e^2}{3mc^2} \sum \langle r_1 \rangle^{-1}, \quad (19)$$

where $\rho(r) = r\psi_{1s}^2$, and γ is the degree of occupancy of the hydrogen atomic orbital. On the other hand, the effect of the overlap repulsive forces arising from nonbonded electron repulsion has been described in terms of the "cage effect" which results in an increase in $\langle 1/r \rangle$ and an increase in the diamagnetic screening constant.¹¹ The problem is to decide how this contribution is to be determined when the repulsion results from overlap between atomic orbitals rather than from an isotropic compression and, second, the conditions under which we can expect the effect to become significant. To do this we make use of Salem's treatment of short-range repulsive forces.¹⁴ According to Salem, in the region of slight overlap between the electron clouds

of closed-shell polyatomic molecules, the most important contribution to the repulsive forces arises from a reduction of combined electron density in the region of overlap. If localized orbitals are used to describe the electron distribution for the two atoms whose electron clouds overlap, then the total electron population in these orbitals is unchanged when overlap occurs. The effect of the overlap is then to build up negative charge on the two atoms and cause a loss of negative charge between the atoms. The symmetry of the atomic orbitals is unchanged. Maintenance of the spherical symmetry for the hydrogen 1s orbital will then lead to an electron rearrangement resulting in an increase in $\langle 1/r \rangle$ (and an increase in the diamagnetic shielding constant). The amount of charge transferred from the overlap region is proportional to the square of the overlap integral S , i.e., $\rho H_{1s} = 2S^2$. Salem further considers that it is a good approximation to calculate the repulsion effects from the overlap density of the unperturbed wavefunctions for the initial system. This means that as the atoms approach the internuclear separation where the overlap between the unperturbed wavefunctions begins to increase rapidly with decreasing separation, any reduction in $\langle 1/r \rangle$ due to dispersion forces will have been cancelled and we will have a net increase in the shielding proportional to S^2 . Salem has shown that the internuclear separation at which this takes place to be equal to the collision diameter d_0 , i.e., where the dispersion and repulsion energies are equal. From our Lennard-Jones potential function, with $a_0 = 3.18 \text{ \AA}$, d_0 would be 2.83 \AA . We would expect, therefore, that σ_0 should be close to zero. If we take Bader's¹⁵ estimate that, in a hydrogen-bonded O-H...O system at the internuclear distances in ice, S is equal to or less than 0.02, then we could calculate that $\sigma_0 \leq 0.02 \times 10^{-6}$ in agreement with the above discussion.

Considering that σ_0 probably lies within the limits of 0 and 0.1×10^{-6} , σ_M between -0.21×10^{-6} and -0.43×10^{-6} , and with $f = 0.845$ (0°C), σ_P is calculated to lie within the range of -5.43×10^{-6} and 5.57×10^{-6} (Eq. 6).¹⁶

¹⁵ R. F. W. Bader, *Can. J. Chem.* **42**, 1822 (1964).

¹⁶ The value of σ_P obtained would not be significantly altered if we were to make the calculations on the assumption that the monomeric water molecules form a separate phase. Since μ^2/a^3 is considerably greater than kT ($a = 3.18 \text{ \AA}$), the state of minimum potential energy for such a phase would be a rigid dipolar lattice for which the interaction energy would be $E_D = -1.808 \mu^2/a^3$ or about 2.7 kcal [J. M. Luttinger and L. Tisza, *Phys. Rev.* **70**, 954 (1946)]. The next lowest state would be for such a lattice in which the molecules are undergoing impeded rotation or libration [H. Margeneau, *Rev. Mod. Phys.* **11**, 1 (1949)] for which the energy would be reduced by the zero-point kinetic energy of vibration by approximately a factor of 2, or $E_D \cong 1.4$ kcal. For the molecules to be freely rotating monomers they would have to be in a still higher energy state. Considering that a minimum value for E_T [Eq. (6)] would be obtained if we were to take the maximum value of the sublimation energy of the unbonded molecules to be the sum of the contributions for the nonpolar water and the dipole energy of water molecules undergoing impeded rotation, we obtain $E_T \cong 7.9$ kcal. With this value of E_T , $f = 0.82$ for water at 0°C and with the solvent shift, $\sigma_R + \sigma_M = -0.91 \times 10^{-6}$, $\sigma_P = -5.48 \times 10^{-6}$.

¹⁴ L. Salem, *Proc. Roy. Soc. (London)* **A264**, 379 (1961).

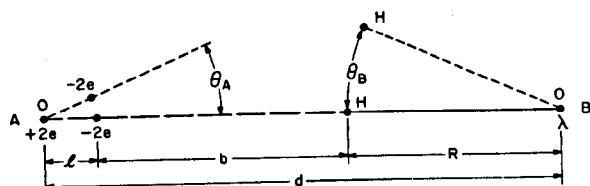


Fig. 3. Model of hydrogen bond. Dotted lines indicate bent bonds. $\theta_A = \theta_B$.

Our next step is to examine the relationship between the polarization contribution to the shielding and the electric-charge distribution in the hydrogen-bonded molecules. We start with a modified representation of the Lennard-Jones and Pople² model for the bond between the lone-pair electrons on one water molecule and the hydrogen of the OH group of the second water molecule (Fig. 3). As in their model, the lone-pair system of Molecule A is represented by a dipole of finite size ($2el = \mu'$). All shielding changes at the proton H are to be related to changes in the magnitude of this dipole μ' . The equation relating the shielding changes at the proton H, due to an external electric field E , can be written⁹

$$\sigma_P = -\phi_a E_x - \phi_b E^2, \quad (20)$$

when $\phi_a = Q_1(\lambda/R^2)$, $\phi_b = 881a^3/108mc^2 = 1.48 \times 10^{-18}$ esu, $\phi_b = 881a^3/216mc^2 = 0.74 \times 10^{-18}$ esu, λ/R^2 is the internal field resulting from the charge distribution within the molecule (B), and E_x is the first power of the component of the external field E along the bond. To obtain λ/R^2 we employ the concept of a "core" comprising the oxygen inner shell and the lone pairs and providing an effective field for the bond pairs⁵⁷ and replace the asymmetric quadrupole representation of the charge distribution in B with an effective charge λ located at the position of the oxygen nucleus. A numerical value for λ/R^2 is then obtained as follows: First, we note that Burnelle and Coulson's⁵⁸ calculations indicate that the net result of all changes in individual moments that occur when the bond angle is increased from that of a water molecule in the gas phase to that of a water molecule in ice is the same as if the OH bond moment were to remain constant and the angle expanded. We therefore calculate a bond moment for the gas molecule using a value of 1.83₄ D for the dipole moment of H₂O (vapor).⁵⁹ Combining this with an R value of 0.99 Å, considered appropriate for ice,^{18,16} we obtain $\lambda/R^2 = 1.53_0 \times 10^6$ for our reference molecule. The multiplying constant ϕ_a is then $2.26_4 \times 10^{-12}$. For any fixed value of the O...O distance d , we can then calculate the electric field corresponding to a given value for the polarization contribution to the shielding and hence

b , l , μ' , and the dipole moment μ of our water molecule A by conventional methods. As a test of our model we have calculated the dipole moment of a water molecule in ice using our derived values for σ_P .

For σ_P per bond equal to -2.72×10^{-8} , $\mu_{\text{H}_2\text{O}}$ (ice) equals 2.41 D. For σ_P per bond equal to -2.78×10^{-8} , $\mu_{\text{H}_2\text{O}}$ (ice) is 2.45 D. A value of the dipole moment for comparison has been calculated from the Auty and Cole⁶⁰ value for the dielectric constant of ice at 0°C using the Kirkwood⁶¹ equation for the dielectric constant ϵ of a polar liquid in the form

$$g\mu^2 = \frac{9kT}{4\pi N} V_M \frac{(\epsilon-1)(2\epsilon+1)}{9\epsilon} \frac{(\epsilon_\infty-1)}{(\epsilon_\infty+2)}. \quad (21)$$

For the ice lattice, the correlation parameter g summed over the first three layers^{3,62} is 2.924. With ϵ_∞ equal to 3.1,⁶² $\mu_{\text{H}_2\text{O}}$ (ice) is 2.44 D. A value of 2.45 D has been calculated by Verwey²³ using a point-charge representation of the water molecule. The fact that the median value of the dipole moment calculated from the polarization shielding factor is within 2% of these values gives us confidence that our treatment of the shielding data is fundamentally satisfactory. In addition this agreement indicates that we could have proceeded with our development in an alternate manner starting with a value for the dipole moment of the water molecule in the ice structure, obtaining the polarization contribution to the shielding without reference to the formation of a liquid phase, and then calculating the fraction of hydrogen bonds broken in the ice-water transformation using the experimental value for the monomer shielding. The results would obviously agree with the calculations based on thermal data. We would therefore consider that the shielding equations provide a suitable framework for the investigation of the effects of structural changes other than the breaking of hydrogen bonds.

"Average" State of Hydrogen Bonding

At this point we consider the results that are obtained if we adhere to our original assumption that the only process occurring in the ice-water transition and in the liquid state at varying temperature is the breaking of hydrogen bonds. In this case the number of hydrogen bonds broken at various temperatures can be calculated from the shielding and thermal data [Eq. (6)]. The results are given in Table VI. We have, for comparison, made similar calculations from dielectric data. The factor $g\mu^2$ [Eq. (21)] is written as $\sum f_i g_i \mu_i$. With μ (monomer) = 1.83₄ D, g (monomer) = 1, μ (ice) = 2.45 D, g (ice) = 2.924, and dielectric-constant data from Harned and Owen,⁶³ we obtain the results

⁵⁷ R. P. McWeeny and K. A. Ohno, Proc. Roy. Soc. (London) **A255**, 367 (1960).

⁵⁸ L. Burnelle and C. A. Coulson, Trans. Faraday Soc. **53**, 403 (1957).

⁵⁹ B. T. Darling and D. M. Dennison, Phys. Rev. **57**, 128 (1940).

⁶⁰ R. P. Auty and R. H. Cole, J. Chem. Phys. **20**, 1309 (1952).

⁶¹ J. G. Kirkwood, Trans. Faraday Soc. **A42**, 7 (1946).

⁶² G. H. Haggis, J. B. Hasted, and T. J. Buchanan, J. Chem. Phys. **20**, 1452 (1952).

⁶³ H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions* (Reinhold Publ. Corp., New York, 1958), 3rd ed., pp. 161ff.

given in Table VI. It should be noted that these latter calculations involve only two assumptions: one, a two-state model and, two, that the cluster size of the hydrogen-bonded aggregates is moderately large, i.e., equal to three layers or 52 molecules. The dielectric calculations do not require that a distinction be made between monomers in lattice cavities or in a separate phase.

The general agreement between the three sets of calculations is satisfactory. The fact that the shielding data indicate a greater fractional change in the average state of hydrogen bonding with temperature may or may not be significant. One way of reconciling this apparent difference would be to assume that at lower temperatures the monomers predominantly enter work network cavities but that at higher temperatures the number of monomers exceeds the number of cavities and a separate phase is formed. Finally, we can note that the average state of hydrogen bonding calculated here is in reasonable agreement with estimates made by some authors^{13,16,17,62} but in marked disagreement with estimates made by others.^{14,44} These differences can, in general, be traced to the properties assumed for the non-hydrogen-bonded species. If a larger fraction of the hydrogen bonds are to be broken in the ice-water transition, it is necessary to assume that the resulting species have interaction energies considerably in excess of those required to form a rigid dipolar lattice and dielectric correlation factors g , much greater than 1, i.e., restricted rotation and molecular association in the non-hydrogen-bonded phase. In addition to the fact that there is no evidence for the existence of such an ordered phase in water, it would be logical to inquire why the properties of the lattice should not be determined by the molecular properties of the water molecules, i.e., why the stable structure would not be a hydrogen-bonded network. An alternative approach is to consider that the hydrogen bonding will persist until the bonds are stretched to a point where the interaction energy falls below that required for dipole orientation.

Alternative Processes

There are a variety of reasons for considering that processes other than the breaking of hydrogen bonds may occur in the ice-water transition and in the liquid. In the first place, we have already noted that there is

TABLE VI. Calculation of the fraction of zero-bonded water from thermal, dielectric, and chemical-shielding data.

t (°C)	Thermal	Shielding ^a	Dielectric
0	(0.155)	(0.155)	0.16
25	0.19	0.21	0.19
50	0.22	0.26	0.22
75	0.25	0.31	0.25
100	0.29	0.35	0.29

^a $\sigma_T = -5.0 \times 10^{-4}$, $\sigma_M = -0.43 \times 10^{-4}$, $\sigma_O = 0$.

no conclusive evidence for the existence of either ice fragments or monomeric water molecules in liquid water. In fact, although x-ray data indicate the existence of short-range order, there is no evidence for any kind of discretely structured regions in the liquid. As a consequence, much of the experimental data can be interpreted equally well on the basis of a continuum model in which few hydrogen bonds are broken but where there is considerable bond stretching and/or bond bending.⁸ (Some breaking of hydrogen bonds must occur since water is a liquid.) The idea that there might be an increase in the intermolecular distance for the hydrogen-bonded species is a direct outgrowth of the observation that the radial distribution curves derived from x-ray studies show an increase in the average near-neighbor distance in melted ice and in water with increasing temperature. Although no unique interpretation of these data can be made, it can be noted that the larger the fraction of an icelike material that is assumed to remain in the liquid the more difficult it is to fit these curves without assuming that the hydrogen bonds have been stretched. The concept of bent bonds is introduced in the continuum model for two reasons: one, the bending of bonds decreases the long-range order and allows the increase in the number of near-neighbor molecules indicated by the x-ray results and, two, the decrease in long-range order is also, necessary to account for the decrease in the correlation parameter g required by the dielectric data. Again, there is no direct experimental evidence for such bent bonds in the liquid.

The effect of assuming the stretching and/or bending of bonds can be related to the experimental shielding data as follows: We start with the assumption that the dipole moment of the water molecule is unchanged from the ice value as the lattice is distorted. Reversing the procedure used in deriving the dipole moment the electric field at the proton of the reference molecule is calculated as a function of angle and O-O distance. The component of this field along the O-H bond is then resolved (for the bent bonds) and the polarization contribution σ_P to the chemical shift calculated [Eq. (20)]. From plots of these σ_P values as a function of angle or distance we can obtain the distance or angle at which the calculated polarization contribution is equal to the experimental value of the shielding at the temperature of interest. Proceeding in this manner we find that the whole of the shielding effect at 0°C could be accounted for either by expansion of the lattice to an O-O distance of 2.85 Å or with an average bend of 13° in the hydrogen-bond angle θ . At 100°C the corresponding O-O distance is 2.96 Å or the angle is 23°. Similarly, one can calculate the amount of monomer that could be formed [Eq. (6)] for an intermediate value of the O-O distance or angle of bend. At 0°C one finds, for example, that for an O-O distance of 2.80 Å the fraction of monomer would be 10% or for an angle of bend of 10°, 6.8%. Two points should be noted with

respect to the above calculations: first, the results should indicate the maximum amount of stretching or bending since the dipole moment of the polarizing water molecules would decrease in either case (we would expect the effect to be partially offset by a decrease in the O-H distance R and an increase in λ/R^2); the second, and more important point, is that the three processes will be mutually limiting. In particular, a very small amount of bond bending would severely restrict the amount of bond stretching or breaking that could occur. Conversely, a limited amount of bond stretching or breaking will impose marked limitations on the amount of bond bending. As an example, we can consider the Pople model.⁸ In this model few (unspecified) bonds are broken but the O-O distance and the angular bend of the bonded species are con-

sidered to be 2.80 Å and 26° at 0°C and 2.95 Å and 30° at 83°C. Our calculations would indicate that excluding the requirement that some bonds must be broken, the amount of bond bending would be limited to ~7° at 0°C and 0° at 83°C.

In summary it is obvious that proton resonance data cannot be interpreted in terms of a unique model for the water structure. On the other hand, it appears that such data can provide information useful in assessing the limitations of various models.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to A. Svirnickas and Mrs. S. Meyer for assistance in the preparation of the samples and obtaining the chemical shift data.

Magneto-Optical Rotatory Dispersion of Porphyrins and Phthalocyanines

P. J. STEPHENS

Institute for the Study of Metals, University of Chicago, Chicago, Illinois
AND

W. SUËTAAK* AND P. N. SCHATZ

Cobb Chemical Laboratory, University of Virginia, Charlottesville, Virginia

(Received 31 January 1966)

Recent MORD data in the region of the visible and near-uv absorption bands of some porphyrins and phthalocyanines are analysed. New computer programs are used to fit general formulas to the experimental data and to extract molecular parameters. Theoretical expressions for the latter are derived, adopting the current interpretation of the observed transitions. The over-all agreement with experiment is good, supporting the assignments. The theory also shows that the magnetic moments of the excited states can be obtained from the data. Values obtained agree with *a priori* calculations in order of magnitude. Further experimental and theoretical work is suggested.

I. INTRODUCTION

IN recent years there has been a great surge of experimental investigations of anomalous magneto-optical rotatory dispersion (MORD) and magnetic circular dichroism (MCD), the compounds so far studied ranging from rare-earth complexes to human oxyhemoglobin.¹⁻⁶ This activity has been largely inspired by the wealth of structural information provided in the

last decade by natural ORD and CD measurements⁷ and has been made possible by the instrumental advances concomitant with that work.

The interpretation of ORD and CD data requires theoretical formulas for the rotation or dichroism as a function of frequency and in terms of molecular parameters. Given such expressions, it is then necessary, first, to fit them to the observed dispersion data and extract values for the parameters, and, second, to relate these quantities to more basic molecular properties.

General treatments of MORD in transparent spectral regions were first given by Kramers,⁸ Rosenfeld,⁹ and Serber¹⁰ (and later extended by Hougen¹¹). Their results

* Permanent address: Research Institute for Iron, Steel and Other Metals, Tôhoku University, Sendai, Japan.

¹ (a) B. Briat, M. Billardon, and J. Badoz, *Compt. Rend.* **256**, 3440 (1963); (b) B. Briat, *ibid.* **258**, 2788 (1964); (c) **259**, 2408 (1964); (d) **260**, 853 (1965); (e) **260**, 3335 (1965).

² (a) V. E. Shashoua, *J. Am. Chem. Soc.* **86**, 2109 (1964); (b) *Nature* **203**, 972 (1964); (c) *J. Am. Chem. Soc.* **87**, 4044 (1965); (d) *Arch. Biochem. Biophys.* **111**, 550 (1965).

³ Y. R. Shen and N. Bloembergen, *Phys. Rev.* **133**, A515 (1964); Y. R. Shen, *ibid.* **134**, A661 (1964).

⁴ D. A. Schooley, E. Bunnenberg, and C. Djerassi, *Proc. Natl. Acad. Sci. (U.S.)* **53**, 579 (1965).

⁵ J. G. Foss and M. E. McCarville, *J. Am. Chem. Soc.* **87**, 228 (1965).

⁶ For a comprehensive review see A. D. Buckingham and P. J. Stephens, *Ann. Rev. Phys. Chem.* (to be published).

⁷ (a) S. F. Mason, *Quart. Rev. Chem. Soc.* **17**, 20 (1963); (b) C. Djerassi, *Optical Rotatory Dispersion* (McGraw-Hill Book Co., Inc., New York, 1960); (c) A. Moscowitz, *Advan. Chem. Phys.* **4**, 67 (1962).

⁸ H. A. Kramers, *Proc. Acad. Sci. Amsterdam* **33**, 959 (1930).

⁹ L. Rosenfeld, *Z. Physik* **57**, 835 (1929).

¹⁰ R. Serber, *Phys. Rev.* **41**, 489 (1932).

¹¹ J. T. Hougen, *J. Chem. Phys.* **32**, 1122 (1960).