On the Symmetry of the Hydrogen Bonds in Ice VII

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at present attempting to extend the temperature range of our studies. The limiting factor for this program is of course the considerable computer time required for the molecular-dynamics calculations. We are also beginning to observe the formation rate of Ar_2^* and hope to look more critically at the complex-formation mechanism.

ACKNOWLEDGMENTS

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The interaction of the hydrogen atoms with nearest neighbor oxygen atoms in the hydrogen bonds of ice VII are approximated by two equivalent Morse potentials. With the inclusion of a repulsive oxygen-oxygen interaction, the model predicts a transition to symmetric hydrogen bonding in ice VII at a pressure between 350 and 800 kbar.

INTRODUCTION

Recently, Yean and Riter[1] compared the PV data of ice VII[2] with a model for the hydrogen bonds which is based on two Morse potential functions, one for the hydrogen bridge bond $O \cdots H$ and one for the chemical bond O–H. With the use of the known bond energies and force constants, the model described the PV data of ice VII within the experimental accuracy. The calculation indicated[1] that the OH distance decreases from 0.957 to 0.942 Å, when the pressure increases from 22 to 165 kbars, and the authors[1] concluded that "the protons remain on their original oxygen." This result is, however, only a direct consequence of the *a priori* assumption of two inequivalent Morse potentials.

Different *a priori* assumptions seem to be justified, if one considers the following facts:

(1) the dissociation of water is well known.[3] The relative stability of the ionic species indicates that the interaction of the proton in hydrogen bonds with bond lengths of about 2.8 Å has to be described by a potential with two minima.

(2) The hydrogen bonds in ice favour the proton jumping.[4–6]

(3) A decreasing asymmetry of the hydrogen bonds has been observed in different compounds for decreasing bond lengths.[7]

(4) In general, three potentials are required to describe the interaction of three particles.

With these points in mind, a model is developed which (1) starts from three potentials, (2) assumes *a priori* two equivalent proton potentials, (3) determines the potentials from bond energies and force constants, (4) describes the PV data of ice VII equally as well as does the model of Yean and Riter,[1] (5) represents the known variation of the proton position with the bond length,[7] and (6) allows some conclusions on the structure of ice VII under high pressures.

THE MODEL

The internal energy of ice VII at zero temperature is approximated in the present model by the sum of the potential energies of an equivalent number of idealized hydrogen bridge bonds.

The relative coordinates of the two oxygen atoms and of the hydrogen atom are represented in Fig. 1. The first oxygen atom is bound to the ice lattice by two "bridge bonds" and by one "valence bond," offering one "valence bond" to the hydrogen atom of the bridge. For the second oxygen atom, the situation is inversed.

In the general case, which is represented by Eq. (1), different Morse potentials have to be assumed for the interaction of the proton with the "single bound" and "double bound" oxygen neighbors, and a third potential has to be added for the direct oxygen–oxygen interaction. The constant term V_{OO} represents the sublimation energy of ice VII plus the zero point energies, when the equilibrium state of ice VII at zero pressure and

temperature is taken as zero point for the energy scale. The total potential is given by Eq. (1):

$$V(r_{OH}, r_{H\cdots O}, r_{OO}) = V_{OH}\{1 - \exp[-\alpha_{OH}(r_{OH} - a_{OH})]\}^2$$

$$+ V_{H\cdots O}\{1 - \exp[-\alpha_{H\cdots O}(r_{H\cdots O} - a_{H\cdots O})]\}^2$$

$$+ V_O \exp(-2\alpha_O r_{OO}) + V_{OO} - V_{H\cdots O}. \quad (1)$$

The V's, α's, and a's correspond to the respective bonding energies, force constants, and equilibrium positions.[1]

If one considers only equilibrium properties of ice VII, the bending of the bonds can be neglected,[1] i.e., $r_{H\cdots O} = r_{OO} - r_{OH}$. The well known phenomena of proton jumps in ice[4-6] can be explained only when the sum of the proton potentials gives a nearly symmetric potential with well pronounced minima on both sides. Cooperative reorientations of water molecules in ice, which accompany protonic jumps as well as changes in the equilibrium positions, favor a symmetric potential. Furthermore, no reason can be given for asymmetric hydrogen–oxygen potentials at very short oxygen–oxygen distances $r_{OO} \simeq 2a_{OH}$. The assumption $V_{H\cdots O} = V_{OH}$, $\alpha_{H\cdots O} = \alpha_{OH}$ and $a_{H\cdots O} = a_{OH}$, which gives fully equivalent potentials for the interaction of the proton with either of the neighboring oxygen atoms, is therefore considered to represent a good approximation for the hydrogen bonds in ice. The corresponding *a priori* symmetric potential is given by Eq. (2):

$$V_S(r_{OO}, r_{OH}) = V_{OH}\{1 - \exp[-\alpha_{OH}(r_{OH} - a_{OH})]$$

$$- \exp[-\alpha_{OH}(r_{OO} - r_{OH} - a)]\}^2$$

$$+ V_{OO}\{1 - \exp[-\alpha_{OH}(r_{OO} - 2a_{OH}) + \ln(2V_{OH}/V_{OO})]$$

$$+ \exp[-2\alpha_O r_{OO} + \ln(V_O/V_{OO})]\}. \quad (2)$$

The three original potentials are rearranged in Eq. (2) in such a way that the first term corresponds to the potential of the proton at a given oxygen–oxygen distance r_{OO}. The second term represents an effective
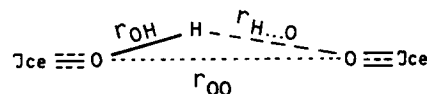

FIG. 1. Relative coordinates for the proton and its neighboring oxygen atoms in the idealized hydrogen bonds.

oxygen–oxygen interaction and includes an indirect attractive and the direct repulsive component. The comparison with experimental data and with the earlier model[1] is facilitated when the effective oxygen–oxygen potential is approximated by an equivalent Morse potential.

The considerations given above support the *a priori* assumption of the symmetric potential (3):

$$V_{SM}(r_{OO}, r_{OH}) = V_{OH}\{1 - \exp[-\alpha_{OH}(r_{OH} - a_{OH})]$$

$$- \exp[-\alpha_{OH}(r_{OO} - r_{OH} - a_{OH})]\}^2$$

$$+ V_{OO}\{1 - \exp[-\alpha_{OO}(r_{OO} - a_{OO})]\}^2. \quad (3)$$

From the potential $V_{SM}(r_{OO}, r_{OH})$, one can derive

(1) the equilibrium position d_{OH} of the proton at a given bond length,

(2) the equilibrium oxygen–oxygen distance d_{OO} at a given pressure P and the corresponding pressure-volume relation,

(3) the pressure dependence of the proton activation or dissociation energy E_D, and

(4) some speculations about the possible phase transition of ice VII to a state with one central hydrogen position only.

The minima d_{OH} of the proton potential at a given O–O distance d_{OO} are derived from the conditions

$$\partial V_{SM}/\partial r_{OH} \big|_{d_{OH}} > 0, \qquad \partial^2 V_{SM}/\partial r_{OH}^2 \big|_{d_{OH}} > 0.$$

The result is

$$d_{OH} = (d_{OO}/2) \pm \{(d_{OO}/2) - a_{OH} + (1/\alpha_{OH})[\ln 2 - \ln(1 + \{1 - 4\exp[-\alpha_{OH}(d_{OO} - 2a_{OH})]\}^{1/2})]\} \qquad \text{if } d_{OO} > d_c,$$

$$d_{OH} = (d_{OO}/2) \qquad \qquad \qquad \qquad \text{if } d_{OO} > d_c. \quad (4)$$

Below the critical distance

$$d_c = 2a_{OH} + (2/\alpha_{OH}) \ln 2, \quad (5)$$

the equilibrium position of the proton is in the center of the hydrogen bond. For $d_{OO} > d_c$, Eq. (4) gives two symmetric minima. The height of the potential well between the two minima is

$$V_D(d_{OO}) = V_{SM}(d_{OO}, d_{OO}/2) - V_{SM}(d_{OO}, d_{OH})$$

$$= V_{OH}(1 - 2\exp\{-\alpha_{OH}[(d_{OO}/2) - a_{OH}]\})^2$$

$$\text{for} \quad d_{OO} > d_c. \quad (6)$$

When zero point energies are neglected, Eq. (3) together with Eq. (4) gives the internal energy of ice VII for unit volume at zero temperature:

$$V_{SM}(d_{OO}) = V_{OO}\{1 - \exp[-\alpha_{OO}(d_{OO} - a_{OO})]\}^2$$

$$\text{if } d_{OO} > d_c,$$

$$V_{SM}(d_{OO}) = V_{OO}\{1 - \exp[-\alpha_{OO}(d_{OO} - a_{OO})]\}^2$$

$$+ V_{OH}\{1 - \exp[-(\alpha_{OH}/2)(d_{OO} - d_c)]\}^2$$

$$\text{if } d_{OO} < d_c. \quad (7)$$

From this relation, the pressure at zero temperature

TABLE I. Values of the potential parameters for ice VII.

	Value from Ref. 1	Determined from		Present choice
V_{OO}	3463 J/cm³	Mean of H-bond energy 4.5–1.5 kcal/mole	Equation of state corresponds to 3.8 kcal/mole	2920 J/cm³
α_{OO}	1.962 Å⁻¹	Corresponding Raman frequency of ice I		1.962 Å⁻¹
a_{OO}	2.858 Å	Bond length in the reference state		2.92 Å
V_{OH}	90 911 J/cm³	Bond energy		90 911 J/cm³
α_{OH}	1.962 Å⁻¹	Stretching frequency	Proton jump energy	2.8±0.2 Å⁻¹
a_{OH}	0.956 Å	OH distance in free water		0.956 Å

$P_0(d_{OO})$ can be derived:

$$P_0 = -(a_{OO}^3/3d_{OO}^2)\{d[V_{SM}(d_{OO})]/d(d_{OO})\}$$

$$P_0 = -\tfrac{2}{3}(a_{OO}^3\alpha_{OO}V_{OO}/d_{OO}^2)\{1-\exp[-\alpha_{OO}(d_{OO}-a_{OO})]\}\exp[-\alpha_{OO}(d_{OO}-a_{OO})] \qquad \text{if } d_{OO}>d_c,$$

$$P_0 = -\tfrac{2}{3}(a_{OO}^3\alpha_{OO}V_{OO}/d_{OO}^2)\{1-\exp[-\alpha_{OO}(d_{OO}-a_{OO})]\}\exp[-\alpha_{OO}(d_{OO}-a_{OO})]$$

$$+ (\alpha_{OH}V_{OH}/\alpha_{OO}V_{OO})\{1-\exp[-\tfrac{1}{2}\alpha_{OH}(d_{OO}-d_c)]\}\exp[-\tfrac{1}{2}\alpha_{OH}(d_{OO}-d_c)] \qquad \text{if } d_{OO}<d_c. \quad (8)$$

This theoretical P_0V relation can be compared with the room temperature PV data,[2] when an additional thermal pressure $P^*(T)$ takes care of the thermal expansion[8]:

$$P = P_0(d_{OO}) + P^*(T) \qquad (9)$$

From the literature values of the bond length at 25 kbar and −50°C[9] and at 0 kbar and −190°C,[10] the thermal pressure at 25°C, $P^*(25°C)=22$ kbar, and the zero pressure–zero temperature bond length $a_{OO}=2.92$ Å are derived. Reasonable values for the parameters V_{OO}, α_{OO}, a_{OO} and V_{OH}, α_{OH}, a_{OH} are summarized in Table I. So far as possible, the values of Yean and Riter[1] were taken also for the present model.

When the value $V_{OO}=2920$ J/cm³ is used in the present model instead of the value of Yean and Riter,[1] the PV data of ice VII[2] are represented within the experimental accuracy by the Eq. (9) with (8). The present value of V_{OO} corresponds to a hydrogen bond energy of 3.8 kcal/mole, which seems to be reasonable[11] for a hydrogen bond with an equilibrium bond length of 2.92 Å.

The parameter α_{OH} of Yean and Riter[1] gives a critical bond length d_c of 2.52 Å. A different estimate of α_{OH} and of d_c results from Eq. (6). In ice I at zero pressure, one knows the bond length $d_{OO}=2.76$ Å,[4] the zero point energy of the proton $E_0=5$ kcal/mole[5] and the activation energy for protonic jumps $E_A=13.0\pm0.8$ kcal/mole.[6] When tunneling is neglected,[5] the sum of zero point and activation energy should be equal to the potential height in appropriate units: $E_A+E_0=V_D(d_{OO})$.

With the numerical values given above, Eq. (6) yields $\alpha_{OH}=2.8\pm0.2$ Å⁻¹. Equation (5) gives the corresponding critical bond length $d_c=2.41$ Å. With the use of these parameters, the variation of the potential minima d_{OH} with respect to the bond length d_{OO} is calculated from Eq. (4) and represented in Fig. 2 together with experimental points of the proton position in O–H···O bonds of different compounds.[7] The pressure scale in Fig. 2 is derived from Eq. (9) and (8). At pressures below 175 kbar, it corresponds to the experimental PV data[2] when the fiducial bond length d_{OO} (22 kbar, 25°C) $=a_{OO}=2.92$ Å is used in the Murnaghan equation.[2] At 800 kbar, the present Eq. (9) and (8) give a bond length of 2.41 Å which compares favorably with the value of 2.44 Å which results from an extrapolation using the Murnaghan equation of Ref. 2. The difference of 0.03 Å is within the present experimental uncertainty of the parameters used in the Murnaghan equation.

DISCUSSION

The present model correlates the equation of state of ice VII through Eq. (8) with an effective interatomic potential. A reasonable set of parameters, Table I, for these potentials reproduces the PV data of ice VII[2] with virtually the same accuracy as does the Murnaghan equation in Ref. 2. Equation (6) indicates a strong decrease of the activation energy for protonic jumps under pressure in agreement with the observed steep increase of the conductivity in pure water under high

FIG. 2. Correlation between O–H$\cdots$O distances d_{OO} and O–H distances d_{OH} in hydrogen bonds. The points represent experimental values of different compounds at zero pressure, Ref. 7; the curve is calculated in the present model for ice VII under pressure. The pressure range, in which one expects the transition to symmetric bonding, is shaded. The pressure range of the x-ray experiments, Ref. 2, is marked on the theoretical curve by a heavier line.
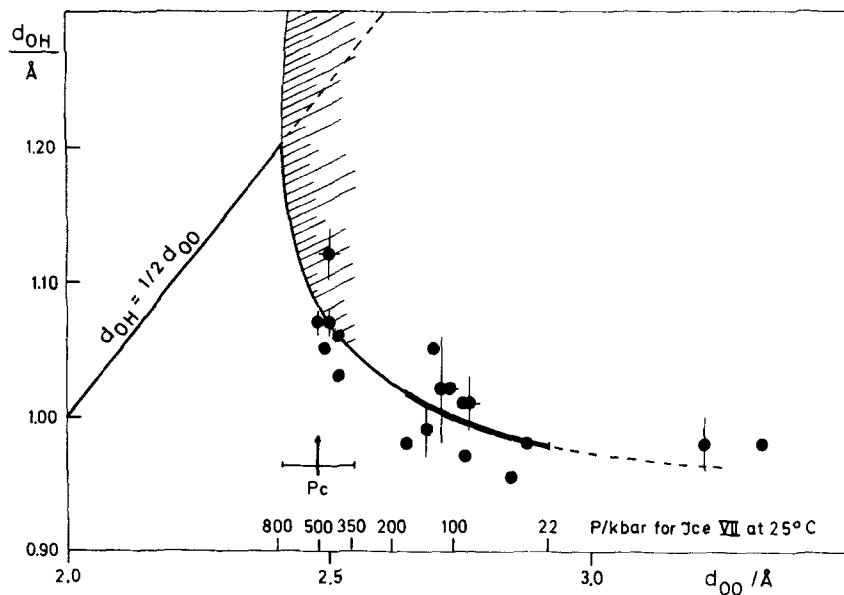
pressures.[3] The calculated variation of the equilibrium proton position, Eq. (4), comes close to a least square fit through the experimental points.[7] Equation (5) determines the critical bond length for the transition of the proton to the center of the bond. According to Eq. (8), the pressure increases steadily with decreasing bond length at the critical value d_c and the compressibility shows a discontinuity when the proton zero point energy is neglected. The finite zero point energy of the proton, finite temperature, and proton tunneling enhance the transition already at lower pressures. The decrease of the zero point energy in the transition could possibly yield a first order phase transition.

If one takes into account that the zero point energy of the protons in hydrogen bonds is about 5 kcal/mole[5] (for deuterons about 3.5 kcal/mole) one expects different transition pressures for H_2O and D_2O ice VII. The finite zero point energy E_0 decreases the critical bond length by $\Delta d_c = -(2/\alpha_{OH}) \ln[1 - (E_0/V_{OO})^{1/2}]$.

A typical value for Δd_c is 0.15 Å. The transition to the symmetric state is, therefore, expected to occur at a pressure P_c of about 500 kbar at zero temperature. At lower pressures, an antiferroelectric ordering[10] of the two sublattices in ice VII[9] seems very likely and responsible for the transition of ice VII into the ordered state ice VIII.[10] Ice VIII can be considered to represent the state with asymmetric hydrogen bonding, where as ice VII at pressures below P_c corresponds to a state with hydrogen bonds which are symmetric in the sense of a long time average. In this picture, P_c represents the pressure at which the transition temperature between ice VIII and ice VII and correspondingly the electric moments of the sublattices approach zero.

A phenomenon which is possibly related to this transition is the unusual bending of the melting curve ice VII,[12] which was discussed recently.[13]

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