

# Ice under Pressure: Transition to Symmetrical Hydrogen Bonds

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We have examined at a rudimentary level the quantum-mechanical many-body problem for coupled proton motions along hydrogen bonds in compressed ices. Four cases are considered: ice Ic, ices VII and VIII, and the hypothetical planar "square ice". Soft mode calculations were carried out for each to help identify patterns of long-range proton order that contribute to the ground state. With a two-level description of each hydrogen bond, and the Hartree approximation, a phase transition in the ground state is predicted to occur when the oxygen neighbor spacing has been reduced sufficiently. This transition can be viewed as an "ionization catastrophe", and in fact such is expected to occur at all temperatures in the phase diagram of water at which ices VII and VIII experimentally are encountered.

## 1. Introduction

An interesting structural correlation has been known for many years concerning hydrogen bonds connecting oxygen atoms in crystals at ordinary pressures.<sup>1,2</sup> Specifically this correlation shows that covalent O-H bond lengths stretch as  $r_{OO}$ , the distance between hydrogen-bonded oxygens, decreases. In particular the data indicate that when the participating oxygens are as close, or closer, than about 2.4 Å the hydrogen should be found at the midpoint position. Indeed such symmetrical hydrogen bonds are observed in crystals at 1 atm, though only in ionic groupings (solvated H<sup>+</sup> or OH<sup>-</sup>).

These observations suggest that if pressure were applied to substances containing hydrogen-bonded oxygens so as to vary the relevant oxygen separation, the same correlation should obtain. In particular if the substance were ice, then application of pressure sufficient to reduce the neighbor distance to about 2.4 Å ought to have the effect of converting the asymmetric hydrogen bonds to symmetric form. The pressures required for this transformation are expected to be sufficiently high that it is the ice VII and ice VIII regions of the H<sub>2</sub>O phase diagram that would

require exploration. Walrafen et al. have in fact recently examined ice VII to about 30 GPa (where  $r_{OO} \approx 2.5$  Å) and have observed a remarkable drop in the frequency of O-H stretching vibrations,<sup>3</sup> which likely is symptomatic of substantial increase in the equilibrium O-H bond length toward a midpoint position.

The possibility of a pressure-induced transition in ice to a new form with symmetrical hydrogen bonds has been theoretically considered before. Holzapfel<sup>4</sup> has examined the linear motion of a single proton between two neighboring oxygens, where that proton was subject to the presence of a pair of equivalent Morse potentials. He finds that the critical bond length

$$r_{OO} = 2.41 \text{ \AA} \quad (1.1)$$

separates the two regimes of proton potential characterized respectively by a single minimum at the bond midpoint, and by a pair of equivalent minima displaced from the midpoint.

By treating the proton classically in Holzapfel's one-particle model (i.e., searching for the potential minimum at each  $r_{OO}$ ), it is straightforward to show that the crystal energy will exhibit a singularity in  $r_{OO}$  (or pressure) at the critical lattice spacing (1.1). By itself this might seem to

(1) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond", Freeman, San Francisco, 1960, p 259.

(2) J.-O. Lundgren and I. Olovsson, "The Hydrated Proton in Solids", in "The Hydrogen Bond. II. Structure and Spectroscopy", P. Schuster, G. Zundel, and C. Sandorfy, Ed.; North Holland, New York, 1976, p 497.

(3) G. E. Walrafen, M. Abebe, F. A. Mauer, S. Block, G. J. Piermarini, and R. Munro, *J. Chem. Phys.*, **77**, 2166 (1982).

(4) W. B. Holzapfel, *J. Chem. Soc.*, **56**, 712 (1972).

indicate existence of a symmetry-changing phase transition to a new form of ice. But the fact remains that protons are quantum mechanical, and the eigenfunctions and eigenvalues for one-dimensional motion along the bond will be nonsingular functions of  $r_{00}$  even at the critical spacing (1.1).

It seems clear that the problem of proton motions in ice under pressure requires a detailed quantum-mechanical study. Furthermore, it is surely insufficient to consider just one-body motion; protons are strongly coupled in a way which gives rise at ordinary pressures to ice formed from intact water molecules that are hydrogen bonded according to the so-called Pauling ice rules.<sup>5</sup> Our objective in this paper has been to undertake such a quantum-mechanical many-body analysis, and to see if indeed a legitimate phase transition should be expected from asymmetric-bond ice VII or ice VIII to a new symmetric-bond form.

The appropriate many-proton Hamiltonian is discussed in section 2. This Hamiltonian forms the basis for a set of soft-mode calculations described in section 3 that are directed toward discovering the natural low-energy arrangements of protons in expanded lattices. Knowledge of these low-energy proton patterns then is used in section 4 to investigate the Hartree approximation to the protonic ground state, with the conclusion that indeed a phase transition can emerge from the quantum-mechanical many-body theory. Section 5 discusses experimental implications of our results and indicates how a more accurate quantum theory might be constructed.

## 2. Many-Proton Hamiltonian

The ices to be considered are the closely related ice VII and ice VIII, as well as the cubic ice Ic. In each of these forms every oxygen is connected to four near neighbors by hydrogen bonds. While ice Ic is known to form only at low pressure it is natural to include it in the present study since the high-pressure forms VII and VIII consist structurally of two interpenetrating ice Ic lattices.<sup>6</sup> Furthermore, it is possible that ice Ic, if first cooled to very low temperature, could be compressed to the regime of interest ( $r_{00} \approx 2.4 \text{ \AA}$ ) without undergoing oxygen-lattice restructuring; and because nonbonded neighbors are absent it should require far less pressure than with ices VII and VIII to achieve this goal.

To maintain a theoretical tradition of long standing<sup>7-9</sup> we have also included in our study the hypothetical "square-ice" model. As is the case for the real three-dimensional ices this model connects each oxygen vertex to four others by hydrogen bonds, but on account of its square arrangement of oxygens the constituent  $\text{H}_2\text{O}$  "molecules" will display unnatural linear or right-angle shapes.

We invoke two simplifying assumptions. First, the lattice of oxygens will be regarded as static. Second, the proton motions along hydrogen bonds will be treated as strictly one-dimensional. Consequently, the potential energy for a crystal consisting of  $N$  oxygen vertices and  $2N$  bonding protons will be given the following form:

$$V = V^{(0)}(r_{00}) + V^{(1)}(x_1 \dots x_{2N}; r_{00}) \quad (2.1)$$

Here  $V^{(0)}$  is the potential energy associated with the oxygen lattice, and it depends only on the spacing  $r_{00}$ . The co-

ordinates  $x_j$  measure proton positions from bond midpoints. We take  $V^{(1)}$  to consist of a sum of single-particle bond potentials  $u$  and particle-pair interactions  $v_{jl}$ :

$$V^{(1)} = \sum_{j=1}^{2N} u(x_j) + \sum_{j<l=1}^{2N} v_{jl}(x_j, x_l) \quad (2.2)$$

The bond potentials will be identical for all bonds and will be symmetric:

$$u(x) = u(-x) \quad (2.3)$$

The pair interactions will display translational symmetry and any rotational symmetries consistent with the underlying crystal structure. Although  $u$  and the  $v_{jl}$  will all depend on  $r_{00}$ , the focus of previous work<sup>4</sup> has been entirely on the way that the first of these changes from double-minimum to single-minimum character as  $r_{00}$  declines through the critical region around  $2.4 \text{ \AA}$ .

If we can rely on the known structure and dipole moment of the isolated molecule for guidance, the conclusion must be that the constituent atoms in the ice system bear fractional charges (approximately  $+e/3$  for protons,  $-2e/3$  for oxygens), as a result of imperfect shielding of nuclear charge by electron distributions. Consequently the  $v_{jk}$  will have to exhibit forms appropriate for these or similar charges.

It is convenient to suppose that  $V^{(0)}$  is the potential energy for the entire collection of  $3N$  atoms in a static configuration with all protons at bond midpoints. As a consequence we have by definition

$$u(0) = 0$$

$$v_{jl}(0, x_l) = v_{jl}(x_j, 0) = 0 \quad (2.4)$$

for all  $r_{00}$ .

The bond potential  $u$  corresponds to the change in system potential energy when a single proton is displaced from its bond midpoint. Likewise  $v_{jl}$  is to be extracted from the system potential energy change when protons  $j$  and  $l$  are simultaneously displaced, all others being confined to the midpoint positions. If these protons are located on widely separated bonds  $v_{jl}$  must reduce to the simple Coulombic form:

$$v_{jl} \approx q^2[(\epsilon_\infty r_{jl})^{-1} - (\epsilon_\infty R_{jl})^{-1}] \quad (2.5)$$

where  $\epsilon_\infty$  is an appropriate high-frequency dielectric constant,  $r_{jl}$  is the distance between the two protons, and  $R_{jl}$  is the distance between the bond midpoints. The proton partial charge has been denoted by  $q$ . It is valid to expand expression 2.5 in displacements to obtain the following large distance behavior:

$$v_{jl} \approx (q^2 / \epsilon_\infty R_{jl}^3) (\mathbf{b}_j \cdot \mathbf{T}_{jl} \mathbf{b}_l) x_j x_l$$

$$\mathbf{T}_{jl} = 1 - 3\mathbf{R}_{jl} \mathbf{R}_{jl} / R_{jl}^2 \quad (2.6)$$

In this expression the  $\mathbf{b}_j$  and  $\mathbf{b}_l$  are unit vectors parallel to the respective bonds, oriented in the directions of positive  $x_j$  and  $x_l$ .

Our central task is to solve the eigenvalue problem:

$$(\mathbf{H} - \Lambda_n) \psi_n(x_1 \dots x_{2N}) = 0$$

$$\mathbf{H} = T + V^{(1)} \quad (2.7)$$

where  $T$  is the kinetic energy operator

$$T = -(\hbar^2 / 2m) \sum_{j=1}^{2N} \partial^2 / \partial x_j^2 \quad (2.8)$$

It is an experimental fact that the low-pressure hexagonal ice Ih (and by implication cubic ice Ic as well) exhibits

(5) L. Pauling, *J. Am. Chem. Soc.*, **57**, 2680 (1935).

(6) D. Eisenberg and W. Kaufmann, "The Structure and Properties of Water", Oxford University Press, New York, 1969, Chapter 3.

(7) E. A. DiMarzio and F. H. Stillinger, *J. Chem. Phys.*, **40**, 1577 (1964).

(8) J. F. Nagle, *J. Math. Phys.*, **7**, 1484 (1966).

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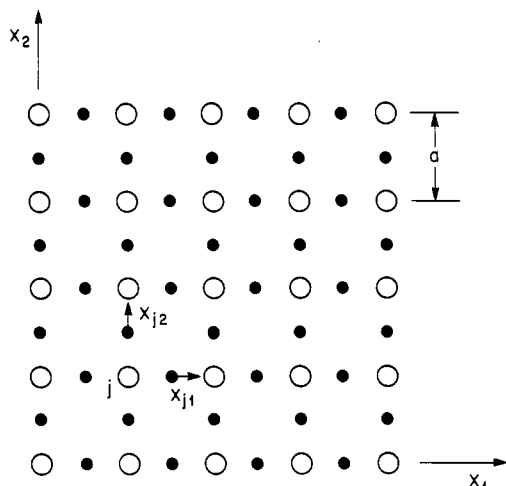


Figure 1. Square ice model with bond-centered protons.

virtually the full disorder of the asymmetrically resident protons that is allowed by Pauling ice rules.<sup>5</sup> In terms of the many-body wave equation (2.7) this implies that there is a nearly degenerate grouping of approximately  $(3/2)^N$  eigenstates, including the ground state, at the bottom of the spectrum. Linear combinations of these low-lying states could be found that form wavepackets localizing protons in the canonical ice structures that are typically considered in the classical statistical mechanics of ice models.<sup>7-9</sup>

If indeed there is a phase transition associated with change in symmetry of the hydrogen bonds, then it should appear as a singularity in the limit function

$$f_0(r_{00}) = \lim_{N \rightarrow \infty} \Delta_0(r_{00})/N \quad (2.9)$$

### 3. Soft Modes

It is important to examine the potential energy  $V^{(1)}$  in detail to understand how this function influences the many-proton eigenfunctions. One instructive aspect concerns the quadratic behavior of  $V^{(1)}$  in the neighborhood of the globally centrosymmetric configuration:

$$x_1 = x_2 = \dots = x_{2N} = 0 \quad (3.1)$$

Specifically we can examine the implied phonon spectrum. We will suppose temporarily that the lattice is strongly compressed to assure that harmonic motion about configuration 3.1 involves only real phonon frequencies. Consequently the bond functions  $u$  will for the moment have narrow single minima at the bond midpoints, and so through quadratic order we can write

$$u(x) = \frac{1}{2}u_2x^2 + O(x^4) \quad (3.2)$$

$$u_2 > 0$$

Recalling eq 2.6, we thus consider initially the following quadratic potential hypersurface:

$$V^{(1)} \simeq \frac{1}{2}u_2 \sum_{j=1}^{2N} x_j^2 + (q^2/\epsilon_\infty) \sum_{\langle j,l \rangle} (\mathbf{b}_j \cdot \mathbf{T}_{jl} \cdot \mathbf{b}_l / R_{jl}^3) x_j x_l \quad (3.3)$$

By decompressing the lattice,  $u_2$  will decrease and give rise at some stage to one or more normal modes going to zero frequency. We consider these "soft modes" to be important for the problem in hand since they represent spontaneous patterns of proton dislocation from bond midpoints. These potential-driven deformations play an important role in the full quantum mechanical problem that is analyzed in section 4.

A. *Square Ice*. We examine the simplest case first, namely, the theoretical square ice model. Figure 1 depicts

this model with all protons centered along bonds. As the figure also indicates, it is convenient temporarily to give protons a double index  $(j, \alpha)$

$$1 \leq j \leq N, \quad \alpha = 1, 2 \quad (3.4)$$

because there are two protons per unit cell in this lattice.

As usual the imposition of periodic boundary conditions guarantees that all normal modes will have running wave character. Hence for any given normal mode the time dependence of the displacements has the form

$$x_{j\alpha}(t) = w_\alpha \exp(i\mathbf{k} \cdot \mathbf{R}_{j\alpha} - i\omega t) \quad (3.5)$$

where the amplitude factors  $w_\alpha$  are independent of  $j$  and of  $t$ . The wavevectors  $\mathbf{k} = (k_1, k_2)$  fall within the first Brillouin zone for the square lattice.<sup>10</sup>

$$-\pi/a \leq k_1, k_2 \leq \pi/a \quad (3.6)$$

where the neighbor spacing  $r_{00}$  has for simplicity been denoted by  $a$ .

Substitution of (3.5) into the classical equations of motion leads directly to the phonon dispersion relation:

$$m\omega^2/u_2 = 1 - \frac{1}{2}\lambda\{(C + S) \pm [(C - S)^2 + 4H^2]^{1/2}\} \quad (3.7)$$

The coupling constant  $\lambda$  is

$$\lambda = q^2/\epsilon_\infty a^3 u_2 \quad (3.8)$$

while  $C$ ,  $S$ , and  $H$  are dipolar sums over the protons in a square ice lattice with unit spacing between neighbor oxygens.

$$C(\mathbf{k}) = \sum_{l(\neq j)} R_{j1,l1}^{-3} \cos(\mathbf{k} \cdot \mathbf{R}_{j1,l1}) (3 \cos^2 \theta_{j1,l1} - 1)$$

$$H(\mathbf{k}) = \sum_{l(\neq j)} R_{j2,l1}^{-3} \cos(\mathbf{k} \cdot \mathbf{R}_{j2,l1}) (3 \sin \theta_{j2,l1} \cos \theta_{j2,l1}) \quad (3.9)$$

$$S(\mathbf{k}) = \sum_{l(\neq j)} R_{j2,l2}^{-3} \cos(\mathbf{k} \cdot \mathbf{R}_{j2,l2}) (3 \sin^2 \theta_{j2,l2} - 1)$$

Here the angles  $\theta$  measure the direction of the corresponding vectors  $\mathbf{R}$  connecting bond midpoints with respect to the  $X_1$  axis (see Figure 1).

When  $\lambda = 0$  the  $2N$  protons move independently at a common angular frequency  $(u_2/m)^{1/2}$ . But as  $\lambda$  increases from zero the phonon frequencies spread out across a pair of bands [the two phonon branches correspond to the two signs in eq 3.7].

A detailed numerical study of the phonon spectrum has been carried out wherein lattice sums (3.9) were evaluated over a wide range of finite arrays, and results extrapolated to infinite array size. These results unambiguously show that the lowest phonon frequencies occur at the vertices of the Brillouin zone (3.6). Furthermore such soft modes require that the upper sign be taken in eq 3.7, and thus correspond to maxima with respect to  $\mathbf{k}$  of

$$C + S + [(C - S)^2 + 4H^2]^{1/2} \quad (3.10)$$

When coupling constant  $\lambda$  grows to the critical value

$$\lambda_c(\text{sq}) = 0.069341 \quad (3.11)$$

these zone-vertex modes go to zero frequency. Any further increase in  $\lambda$  would lead to imaginary frequencies, implying proton displacement instability that could only be arrested by anharmonic terms in the bond potentials  $u$ .

Figure 2 shows the pattern of proton displacements involved in the zone-vertex soft modes. We see that the

(10) L. Brillouin, "Wave Propagation in Periodic Structures", Dover, New York, 1953.

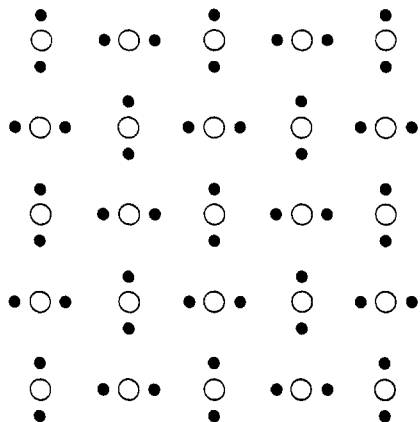


Figure 2. Pattern of proton displacement in square ice that results from zone-vertex soft modes.

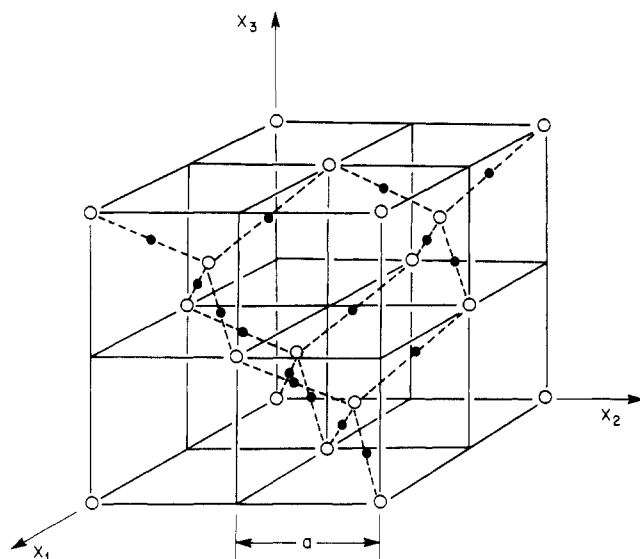


Figure 3. Bonding pattern in cubic ice, with protons at bond midpoints.

lattice now consists of linear "H<sub>2</sub>O" units with alternating orientations.

One of the significant conclusions produced by this two-dimensional model calculation is that the displacement pattern shown in Figure 2 spontaneously arises even while  $u_2$  is positive. Evidently the proton-proton interactions manage to overcome the localizing influence of the still-single-minimum bond potentials at the critical coupling  $\lambda_c$ . This explicitly demonstrates the inappropriateness (even before invoking quantum mechanics) of identifying a bond-symmetrizing phase transition with the vanishing of  $u_2$ .<sup>4</sup> This latter criterion of course corresponds to divergence of  $\lambda$  to infinity.

*B. Cubic Ice.* Figure 3 shows the bonding pattern in cubic ice, with protons located at bond midpoints. The Bravais lattice is face-centered cubic, with two oxygens per unit cell. Consequently there will be four protons per unit cell and thus four phonon branches. Figure 4 illustrates the first Brillouin zone for this structure.<sup>10</sup>

It is straightforward (though somewhat more tedious) to set up the dynamical equations in this case. Once again the phonon spectra are determined by dipolar sums over the unit-spacing lattice, and by coupling constant  $\lambda$  in eq 3.8 wherein distance  $a$  is now defined for ice Ic by Figure 3. The  $\omega^2$  for square ice had the special feature that they were linear in  $\lambda$ ; that is no longer the case.

We shall only summarize results that emerge from the numerical analysis. It is found that the soft modes (i.e., those which first go to zero frequency as  $\lambda$  increases) occur

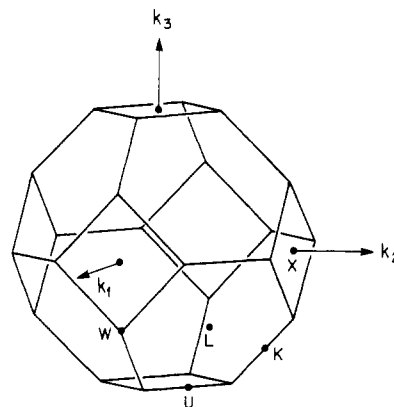


Figure 4. First Brillouin zone for the face-centered cubic Bravais lattice.

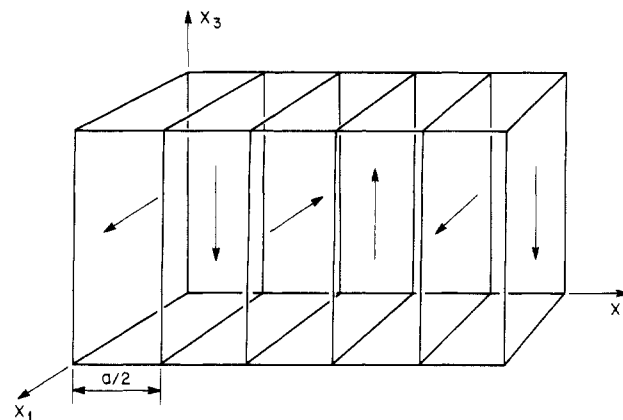


Figure 5. One of the possible polarization patterns produced in ice Ic by spontaneous soft-mode distortion. The planes shown are the successive planes of oxygen atoms (see Figure 3), and the arrows indicate directions of the H<sub>2</sub>O symmetry (dipole) axes.

at the symmetry points X of the Brillouin zone shown in Figure 4, the centers of each of the zone's square faces. The frequencies of these modes in fact go to zero at the critical coupling

$$\lambda_c(\text{Ic}) = 0.0908 \quad (3.12)$$

This result is analogous to that obtained for square ice in that  $u_2$  is still positive at the instability point.

The soft modes at each of the six points X are doubly degenerate. The distortion patterns produced by these modes can be formed in any one of six equivalent ways. Each such pattern involves production of H<sub>2</sub>O molecular units whose dipole directions are parallel within successive crystal planes in such a manner as to produce a spiral polarization field. Figure 5 illustrates this type of spontaneous pattern.

When  $\lambda$  has the critical value shown in eq 3.12 there are other modes that have nearly gone to zero frequency, in particular double degenerate pairs at each of the Brillouin zone symmetry points K, L, and W. That the system almost goes unstable in so many ways simultaneously is doubtless related to the Pauling degeneracy of ice, for it suggests that many ways of forming intact H<sub>2</sub>O units will exist with nearly equal energies.

*C. Ices VII and VIII.* Ices VII and VIII geometrically consist of a pair of interpenetrating ice Ic sublattices. Ice VII has the higher symmetry of the two: Each of its oxygen atoms is symmetrically surrounded by eight others, four of which belong to the same sublattice, and the symmetry overall is cubic.<sup>6</sup> The oxygen lattice and hydrogen bond connectivity of ice VIII are similar, resulting in fact from tetragonal distortion of the ice VII structure. Thermodynamically these forms are stable only at high

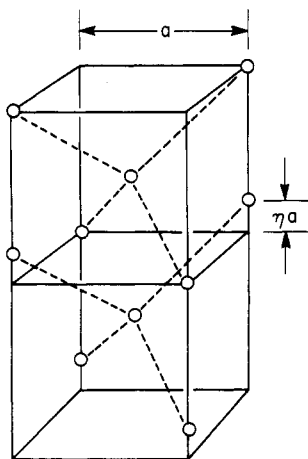


Figure 6. Uniaxial displacement that converts the oxygen framework of ice VII into that of ice VIII.

pressure, above roughly 20 kbar. Ice VII is observed at room temperature, but upon cooling below about 5 °C (nearly independently of pressure), ice VIII spontaneously forms. The former appears to be largely proton disordered over its canonical ice-rule structures; the latter is antiferroelectric with completely polarized sublattices respectively parallel and antiparallel to the tetragonal distortion axis.<sup>11</sup>

We first consider the phonon calculation for ice VII. The Bravais lattice is simple cubic. Each unit cell contains two oxygens and four hydrogens, leading to four phonon branches. The dynamical equations which determine phonon frequencies were set up and solved as in the preceding two cases. The resulting numerical analysis indicates that the relevant soft modes occur at  $\mathbf{k} = 0$  and correspond to ferroelectric polarization along any one of the three cubic axes. Using the same coupling constant definition (3.8) as for ice Ic, we find that the critical coupling constant value is

$$\lambda_c(\text{VII}) \approx 0.080 \quad (3.13)$$

It should be stressed that this conclusion about a ferroelectric instability in ice VII is based on extrapolation. Lattice sums were carried out over a sequence of cubic blocks up to 64 unit cells on a side. At any stage in the sequence the softest modes would appear at a set of symmetry-related points displaced from the origin. But as the summation block increased in size the positions of these softest modes converged smoothly to  $\mathbf{k} = 0$ , and the eigenvectors in that limit corresponded to uniform polarization.

The experimental fact that ice VII is not ferroelectric in its temperature–pressure region of phase stability implies either that its Curie point is below 5 °C or that the potential energy form (3.3) that we have employed is inadequate. In particular one might reasonably question whether use of a constant dielectric shielding factor  $\epsilon_\infty$  at all distances (some of which are indeed small for ice VII) is appropriate.

Figure 6 illustrates the tetragonal displacement between the interpenetrating networks which converts the oxygen framework of ice VII to that of ice VIII. Measurements at the lower stability limit for ice VIII indicate that the fractional displacement  $\eta$  is 0.087.<sup>11</sup> As a result of this displacement the Bravais lattice reverts to that for ice Ic, namely, face-centered cubic. But now four oxygens and eight hydrogens inhabit each unit cell, yielding eight

phonon branches. The first Brillouin zone has already been illustrated in Figure 4.

In order to implement the numerical analysis for ice VIII it was again necessary to carry out lattice sums over finite cubic blocks of ascending size (up to 64 unit cells on a side). Softest modes obtained for finite blocks occur at  $\mathbf{k} \neq 0$ , but in the infinite block limit convergence of these modes to  $\mathbf{k} = 0$  is indicated. Even after effecting the tetragonal distortion from ice VII to ice VIII the pattern of instability continues to be ferroelectric. However, the distortion splits the previous three degenerate soft modes into a lowest frequency subset (polarization perpendicular to the distortion direction) and a very slightly higher frequency subset (polarization parallel to the distortion direction). The former go to zero frequency when the coupling constant increases to the critical value

$$\lambda_c(\text{VIII}) \approx 0.085 \quad (3.14)$$

The failure of our calculations to produce the observed<sup>11</sup> antiferroelectric pattern in ice VIII has led us briefly to examine modifications of the simple potential energy used for the bulk of our calculations. Specifically we have replaced the uniform dielectric screening factor  $\epsilon_\infty^{-1}$  in eq 2.6 by the nonuniform screening function

$$S(R_{jl}) = 1 + (\epsilon_\infty^{-1} - 1)\{1 - \exp[-\alpha(R_{jl} - R_{nn})]\} \quad (3.15)$$

where  $\alpha > 0$ , and  $R_{nn}$  is the distance between nearest-neighbor protons (at bond midpoints). This form smoothly interpolates between no screening at  $R_{nn}$  to the previous uniform screening at large separation. We find that for

$$\alpha = 20, \quad \epsilon_\infty = 10 \quad (3.16)$$

the mode that first goes to zero frequency has the antiferroelectric character that has been observed experimentally. It should also be mentioned that use of the nonuniform screening (3.15) in the undistorted ice VII causes its ferroelectric soft mode to be replaced by zone-vertex modes, even when  $\alpha$  is small and  $\epsilon_\infty$  is close to unity.

All of the ice VII and ice VIII results continue to illustrate the earlier point that soft-mode instability appears while the individual bond potentials still have single-minimum character.

#### 4. Hartree Approximation

Soft-mode calculations reported in section 3 indicate that for sufficiently large  $\lambda$  the potential  $V^{(1)}$  leads to a lowest-energy classical structure with intact water molecules that (a) are arranged in a manner consistent with the ice rules, and (b) display long-range proton order. Our next task is to assess the influence of quantization of the short-range and long-range order, and on the ground-state eigenvalue  $\Lambda_0$ . For this purpose we have employed the Hartree approximation to keep the theory manageably simple.

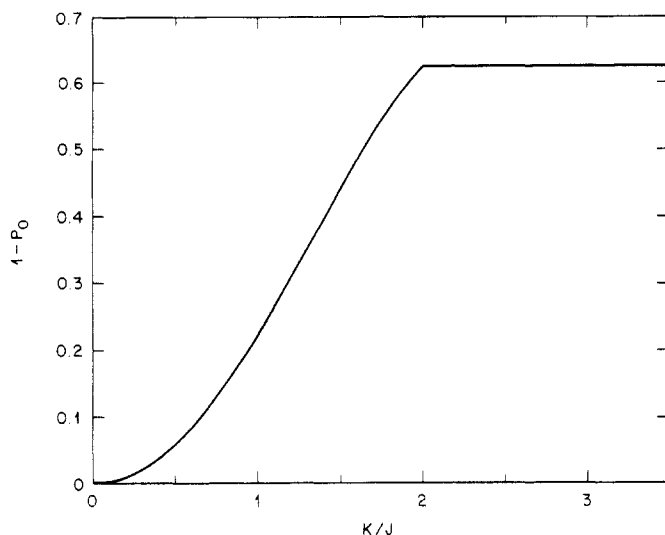
The single particle wave functions  $\phi_n$  for the bond potential  $u(x)$  are solutions of

$$[-(\hbar^2/2m) d^2/dx^2 + u(x) - \epsilon_n]\phi_n(x) = 0 \quad (4.1)$$

We will suppose that they are orthonormal. In principle these  $\phi_n$ , one set for each bond in the ice lattice, constitute a complete set in which the many-proton wave functions  $\psi_n$  can be expanded.

When any of the ices considered is in an expanded state the bond potential  $u$  will have two well-developed minima. The quantum-mechanical ground state will have protons residing near these minima, with correlated residence as dictated by the long-range ferroelectric or antiferroelectric pattern found in section 3. In this circumstance it should

(11) P. T. T. Wong and E. Whalley, *J. Chem. Phys.*, **64**, 2359 (1976).



**Figure 7.** Probability in the Hartree approximation that any given oxygen vertex is an ionic defect.

suffice to employ only the lowest pair of functions  $\phi_0$  and  $\phi_1$  to expand the ground-state wave function  $\psi_0$ , since sums and differences of the two form basis functions localized respectively at the two minima in  $u$ . In this limiting case the single-particle excitation energy

$$2K = \epsilon_1 - \epsilon_0 \quad (4.2)$$

will be just the small tunneling splitting.

In the other extreme of highly compressed ice the excitation energy  $2K$  will be much larger, and protons are now forced to remain localized near the midpoint of the now shorter bond. Once again it should be adequate to use only  $\phi_0$  and  $\phi_1$ , since proton-proton interactions will be relatively weak in comparison with  $2K$ .

These considerations suggest that it should be adequate to use only the two lowest-energy basis functions  $\phi_0$  and  $\phi_1$  per bond over the entire range of lattice spacings. We shall in fact take advantage of this simplification. Some support for this tactic emerges from study of the quartic-oscillator ferroelectric problem by Koehler and Gillis;<sup>12</sup> exact diagonalization of their one-particle Schrödinger equation (with mean field interactions) gave results qualitatively similar to those resulting from a corresponding two-level treatment.

For the restricted basis of  $\phi_0$  and  $\phi_1$ , the Hamiltonian is

$$\mathbf{H} = N(\epsilon_0 + \epsilon_1) + K \sum_{j=1}^{2N} \mathbf{S}_z^{(j)} + \sum_{j<l=1}^{2N} v_{jl} \mathbf{S}_x^{(j)} \mathbf{S}_x^{(l)} \quad (4.3)$$

where we have used the familiar Pauli matrices

$$\mathbf{S}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \mathbf{S}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (4.4)$$

The pair interactions  $v_{jl}$  are given by eq 2.6. Alternatively, we can rotate the basis to the localizing sums and differences of  $\phi_0$  and  $\phi_1$ , in which case

$$\mathbf{H} = N(\epsilon_0 + \epsilon_1) - K \sum_{j=1}^{2N} \mathbf{S}_x^{(j)} + \sum_{j<l=1}^{2N} v_{jl} \mathbf{S}_z^{(j)} \mathbf{S}_z^{(l)} \quad (4.5)$$

The long-range proton orders deduced in section 3 for each of the ices have the property that all bonds are equivalent, and each proton has an unambiguous side of the bond midpoint where it preferentially should reside.

The translation of these features into a Hartree approximation to  $\psi_0$  is the following well-known form ( $0 \leq \theta \leq \pi/2$ ):

$$\psi_0 \approx \prod_{j=1}^{2N} [\cos \theta \phi_r^{(j)}(x_j) + \sin \theta \phi_w^{(j)}(x_j)] \quad (4.6)$$

Here  $\phi_r$  and  $\phi_w$  are the localized bond functions respectively at the "right" and at the "wrong" side of the midpoint, and angle  $\theta$  is a variational parameter to be determined by minimizing the energy.

It is straightforward to show that the variational energy implied by the assumed form 4.6 is

$$\Lambda_0/(2N) = (\epsilon_0 + \epsilon_1)/2 - K \sin(2\theta) - J \cos^2(2\theta) \quad (4.7)$$

Here we have introduced  $J$  by letting  $-2NJ$  be the interaction matrix element when all protons are "right":

$$-2NJ = \sum_{j<l=1}^{2N} \int \int [\phi_r^{(j)}(x_j) \phi_r^{(l)}(x_l)]^2 v_{jl}(x_j, x_l) dx_j dx_l \quad (4.8)$$

Finding the angle  $\theta_m$  that minimizes eq 4.7 is elementary

$$\begin{aligned} \theta_m &= \frac{1}{2} \sin^{-1}(K/2J) \quad (0 \leq K/J \leq 2) \\ &= \pi/4 \quad (2 \leq K/J) \end{aligned} \quad (4.9)$$

The corresponding per-proton energies are

$$\begin{aligned} \Lambda_0/2N &= \frac{1}{2}(\epsilon_0 + \epsilon_1) - J(1 + K^2/4J^2) \quad (0 \leq K/J \leq 2) \\ &= \frac{1}{2}(\epsilon_0 + \epsilon_1) - K \quad (2 \leq K/J) \end{aligned} \quad (4.10)$$

Using eq 4.2 to eliminate  $K$ , these expressions become

$$\begin{aligned} \Lambda_0/2N &= \frac{1}{2}(\epsilon_0 + \epsilon_1) - (\epsilon_1 - \epsilon_0)^2/(16J) - J \quad (0 \leq (\epsilon_1 - \epsilon_0)/J \leq 4) \\ &= \epsilon_0 \quad (4 \leq (\epsilon_1 - \epsilon_0)/J) \end{aligned} \quad (4.11)$$

In a decompressed state of the lattice the first part of expression 4.11 gives the protonic energy. The protons are well ordered at this stage, corresponding to angle  $\theta_m$  close to zero. As the lattice is compressed, however, the splitting  $\epsilon_1 - \epsilon_0$  increases toward the critical value  $4J$ , and as a result  $\theta_m$  increases toward  $\pi/4$ , which in turn diminishes the degree of long-range order. All long-range order is lost when  $\theta_m$  reaches  $\pi/4$  ("right" and "wrong" positions for protons become equally likely), and a new form for the energy appears.

Clearly the single-particle eigenvalues  $\epsilon_0$  and  $\epsilon_1$  will be analytic functions of the lattice spacing, as will  $J$ . But the shift from one functional form to another for the energy of the interacting many-proton system constitutes a non-analytic point, i.e., a phase transition. The energy and its first derivative with respect to  $r_{00}$  are continuous across this transition, but the second  $r_{00}$  derivative is discontinuous.

Short-range order is measured by  $P_0$ , the probability that any given oxygen vertex is part of a neutral water molecule. This obtains if two of the four protons along bonds to that oxygen are close while the others reside at the remote ends of bonds. We have already remarked that the classical patterns with long-range order emerging from soft modes in section 3 all have  $P_0 = 1$ . However, it is clear that quantum mechanical fluctuations can cause ionic configurations to occur, with  $P_0 < 1$ .

It is easy to show that within the Hartree approximation

$$P_0 = \cos^8 \theta_m + 4 \cos^4 \theta_m \sin^4 \theta_m + \sin^8 \theta_m \quad (4.12)$$

The quantity  $1 - P_0$  has been plotted against  $K/J$  in Figure 7. This figure shows that the phase transition can be viewed as an ionization catastrophe, with neutral molecules

(12) T. R. Koehler and N. S. Gillis, *Phys. Rev. B*, **7**, 4980 (1973).

only appearing with random expectation ( $P_0 = 3/8$ ) when  $K/J$  exceeds 2.

## 5. Discussion

The displacement distribution  $p^{(j)}$  for proton  $j$  along its bond follows directly from eq 4.6. Specifically one finds

$$p^{(j)}(x_j) = [\cos \theta_m \phi_r^{(j)}(x_j) + \sin \theta_m \phi_w^{(j)}(x_j)]^2 \quad (5.1)$$

This distribution is symmetric about the bond midpoint if and only if  $\theta_m$  is  $\pi/4$ , i.e., the system is disordered. In that event  $p^{(j)}$  is determined entirely by the lowest proton eigenstate:

$$p^{(j)}(x_j) = [\phi_0(x_j)]^2 \quad (5.2)$$

Notice that the question of symmetry of  $p^{(j)}$  about the bond midpoint is logically independent of the following questions:

- (1) Does the bond potential  $u(x)$  exhibit a single or a double minimum?
- (2) Does  $\phi_0$  exhibit a single or a double maximum?
- (3) Does the direction-averaged bond distribution

$$p(x) = \frac{1}{2}[p^{(j)}(x) + p^{(j)}(-x)] \quad (5.3)$$

have a single midpoint maximum or a pair of displaced maxima?

Clearly it is symmetry of  $p^{(j)}$  which has greatest significance in the present study, and when that symmetry exists we believe it is appropriate to call the system "symmetric-bond ice". To the extent that we are able roughly to estimate bond functions and coupling constants in cubic ice, it appears that during compression  $\phi_0$  converts to single maximum character no later (and probably before)  $p^{(j)}$  symmetrizes.

Because our transition is an ionization catastrophe, it is hard to avoid the conclusion that it also occurs at nonzero temperature, i.e., in at least the low-lying excited states which in decompressed ice form the multitude of canonical ice configurations for neutral molecules. A many-body theory which improved on the Hartree approximation in fact should yield ionization catastrophes even for low-lying excited states with no long-range proton order present, but rather with just short-range order. In any case an ionization catastrophe should manifest, and be detectable by, anomalies in the dielectric constant and in the electrical conductivity of the ice vs. pressure.

Our qualitative conclusion is illustrated (in very schematic fashion!) by Figure 8. The figure provides a rough indication of the expected phase diagram in the very high-pressure regime. The bond-symmetrizing transition has been shown as a dotted line. Our calculations with a static oxygen lattice imply that this symmetrizing transition would be of order higher than first; however, it is reasonable that the transition might become first order if coupling of proton motions to lattice phonons were to be included.

There are sure to be yet further transitions encountered in the extremely high-pressure region above the top of Figure 8. Two likely candidates are (a) a crystal structure with close-packed oxygens and (b) a metallic solid phase.

In view of the strong oxygen repulsions<sup>13</sup> that operate between nonbonded neighbors in ices VII and VIII, it seems certain that increasing pressure will cause the distortion parameter  $\eta$  for ice VIII (see Figure 6) to become smaller. In other words, increasing pressure should reduce the tetragonal distortion that distinguishes the ice VIII

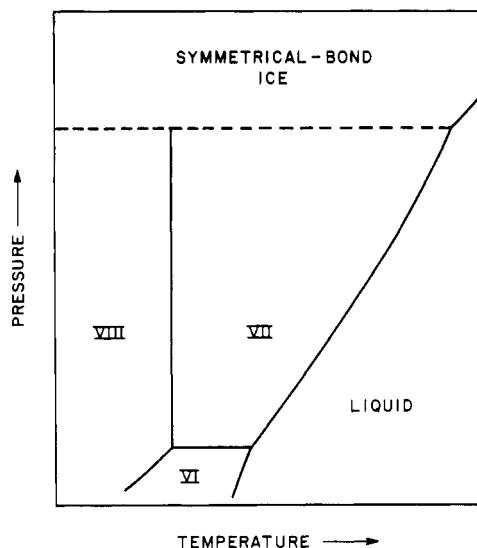


Figure 8. Schematic diagram of the very high-pressure region of the  $H_2O$  phase diagram.

oxygen lattice from that of ice VII. At the transition pressure to symmetrical-bond ice  $\eta$  may have been reduced to practically zero, so at that point the ice VIII to ice VII transition may virtually be only a proton order-disorder transition (a Neel point if ice VIII remains antiferroelectric).

The liquid that coexists with ice VII and symmetrical-bond ice at the triple point shown in Figure 8 is itself likely to be highly ionized.<sup>14</sup> However, there is no compelling reason to believe that an ionization catastrophe phase transition should intrude from the solid state into the liquid region of the phase diagram.

In view of the large number of uncertainties involved it would be foolhardy for us to attempt an absolute prediction of the transition pressure to symmetric bond ice. However one thing is certain: There should be a significant deuterium isotope effect. As a result of its greater mass, the deuteron will have a smaller splitting parameter  $K$  than that for protons. At the same time the interaction parameter  $J$  should proportionately be far less sensitive to isotopic mass. Consequently, the characteristic ratio  $K/J$  will tend to be smaller at a given oxygen lattice spacing  $r_{00}$  in  $D_2O$  ice than in  $H_2O$  ice. In order to have this ratio equal the value necessary to permit a phase change (2 in the Hartree approximation) it is clear that the molar density of  $D_2O$  ice will have to be larger than that for  $H_2O$  ice. In either case if it turns out that 2.4 Å is the approximate range required for  $r_{00}$  to create symmetrical-bond ice in the laboratory, then from the dependence of  $r_{00}$  on pressure determined experimentally by Walrafen et al.<sup>3</sup> the requisite pressure can be estimated very roughly as 600 kbar.

Finally we need to list some ways in which further theoretical effort might continue to increase understanding.

First, there is a clear need for quantitative study of the potential surface for protons moving along compressed hydrogen bonds. The modern methods of quantum chemistry have much to offer here and could succeed in determining the bond function  $u(x)$  accurately over a wide range of oxygen separations. At a somewhat higher level of complexity the pair interactions  $v_{ji}$  should also be amenable to study by quantum-chemical computation, thereby shedding more light on the dielectric shielding and overlap repulsion that are operative in the dense ices. This

(13) B. Kamb, *J. Chem. Phys.*, **43**, 3917 (1965).

(14) K. Tödheide, *Water, Compr. Treat.*, **1**, 502-4 (1972).

should lead to a capability for predicting unambiguously the tetragonal distortion and proton-order pattern in ice VIII.

Second, it is obvious that an improvement over the Hartree approximation is required. This would entail a more realistic description of the configurational correlation of the four protons around each oxygen (even in the absence of long-range proton order). Such an advance is required for ground and excited states to yield an acceptable quantal description of canonical Pauling structures in decompressed ices, specifically in proton-disordered ice VII. The ionization probability shown in Figure

7 would be subject to revision with this more powerful approach to the many-body problem and indeed might then have a rather different type of singularity.

Third, the theory eventually should encompass coupled motions of both oxygens and hydrogens, and the latter should be permitted full three-dimensional motion rather than just the linear freedom imposed in the present work. This final generalization should be helpful to spectroscopists who observe and interpret vibrational bands in the compressed ices.

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