

***Ab Initio* Studies on High Pressure Phases of Ice**Changyol Lee,<sup>(1)</sup> David Vanderbilt,<sup>(2)</sup> Kari Laasonen,<sup>(3),(5)</sup> R. Car,<sup>(3),(4)</sup> and M. Parrinello<sup>(5)</sup><sup>(1)</sup>*Department of Physics, Harvard University, Cambridge, Massachusetts 02138*<sup>(2)</sup>*Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08855-0849*<sup>(3)</sup>*Institut Romand de Recherche Numérique en Physique des Matériaux, PHB-Ecublens, CH-1015 Lausanne, Switzerland*<sup>(4)</sup>*Department of Condensed Matter Physics, University of Geneva, Geneva, CH-1211, Switzerland*<sup>(5)</sup>*IBM Research Division, Zürich Research Laboratory, CH-8803 Rüschlikon, Switzerland*

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The pressure-induced transition of H<sub>2</sub>O into the ice X phase, characterized by symmetric hydrogen bonding, is studied using *ab initio* molecular dynamics combined with ultrasoft pseudopotentials. A good description of the hydrogen bond is obtained only after gradient corrections to the local-density approximation are included. The transition into ice X is predicted at 49 GPa, in good agreement with experiment, when proton quantum fluctuations are treated within mean-field theory. Molecular-dynamics simulations show that a mode-softening description of the transition is appropriate.

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H<sub>2</sub>O ice has an unusually rich phase diagram [1]. The dominant hydrogen-bonding interactions give rise to a sequence of rather open structures which become more close packed with increasing pressure. Nevertheless, the phases ice I through ice IX, which occur at pressures up to a few tens of GPa, all still have intact water molecules as their basic building blocks. At a sufficiently high pressure, the molecular picture is expected to break down entirely. For the moderately high pressure ice VII and VIII phases, it is found that the H atoms become more symmetrically bonded with increasing pressure; in fact the covalently bonded O-H distance *increases* while the hydrogen-bonded O-O distance decreases with increasing pressure [2,3]. Thus, in the simplest picture, the transition would occur by having H atoms shift to the fully symmetric positions midway between the two neighboring O atoms, leaving the oxygen lattice intact. Such a speculative phase, in which the distinction between the covalent and hydrogen bonds has been eliminated, is called ice X.

Despite considerable discussion in the literature [4-9], there is to date no compelling direct evidence for the existence of ice X. Experimentally, Raman spectra of ice VIII up to 50 GPa at 100 K demonstrate the appearance of a new band above 40 GPa [4] which could reflect such a transition; and Brillouin scattering studies up to 67 GPa at 300 K also give an indication of a transition at 44 GPa from an anomaly in the behavior of the longitudinal sound velocity [5]. Earlier work based on extrapolation of Raman spectra from lower pressures at room temperature also suggested that a symmetric hydrogen-bond structure might form in ice VII at pressures of about  $75 \pm 20$  GPa [6]. However, little is experimentally known about the positions of the protons in the high pressure phase, because direct measurements like neutron or electron diffraction are difficult. Theoretically, studies based on empirical interatomic potentials have supported the notion of a transition to the ice X structure. An early theoretical calculation by Holzappel [7] predicted a transition to symmetric hydrogen bonding in ice VII at pres-

ures between 35 and 80 GPa. The interaction of the hydrogen atoms with the two nearest-neighbor oxygen atoms was approximated by equivalent Morse potentials. Later, a calculation by Stillinger and Schweizer [8] predicted a transition at roughly 60 GPa. This work included a treatment of the quantum-mechanical many-body problem for coupled proton motions along hydrogen bonds. A more recent estimate by the same authors [9] puts the transition at about 45 GPa. However, to our knowledge there have been no previous *ab initio* quantum-chemical or density-functional calculations on this system.

In this Letter, we describe first-principles calculations of the structural properties of H<sub>2</sub>O ice in the high pressure region relevant to the ice X transition. We employ the Car-Parrinello *ab initio* molecular-dynamics approach [10] to density-functional theory. The treatment of the oxygen atoms, which is usually problematic within plane-wave pseudopotential approaches, is rendered tractable by adopting the ultrasoft pseudopotentials proposed by Vanderbilt [11]. Perhaps surprisingly, we find that the local-density approximation (LDA) must be augmented with gradient corrections for a proper description of the hydrogen bonding. Then, we confirm the existence of a transition into the ice X structure, and predict the transition pressure to be about 49 GPa, consistent with experimental indications [4,5]. Our estimate of the transition pressure includes a mean-field treatment of the quantum fluctuations of the proton positions. Finally, we study the nature of the transition by carrying out molecular-dynamics simulations of the dynamics of the constituent atoms, and verify a mode-softening picture of the transition.

The details of our calculations are as follows. The pseudopotential for oxygen has cutoff radii of 1.5 a.u. for the valence wave function and 1.2 a.u. for the local potential; for hydrogen the corresponding values are 0.8 and 0.6 a.u. The charge augmentation functions  $Q_{ij}(\mathbf{r})$  [11] are pseudized using a method similar to that of Rappe *et*

*al.* [12] to insure that Fourier components of the density above twice the cutoff for the electronic wave functions are not needed. The electronic states are expanded in plane waves with kinetic energy up to 20 Ry. Our earlier work has demonstrated that converged results can already be obtained with such a small cutoff when the new pseudopotential approach is used [13]. The calculations are carried out on a 16-molecule supercell, as depicted in Fig. 1. Only the  $\Gamma$  point is used for the Brillouin-zone summations. In ice VII and ice VIII, which are the highest pressure phases with intact water molecules as building blocks, the oxygens take the sites of a bcc lattice as shown in Fig. 1. Equivalently, this structure can be regarded as two interpenetrating diamond-structure sublattices. In ice VII, the protons are disordered within Pauling's ice rules [14] while in ice VIII, the protons show an antiferroelectric order where each diamond sublattice is ferroelectric with the orientation of the polarization vector opposite to that of the other sublattice. Experimentally, a tetragonal distortion along the direction of the polarization vector is observed for ice VIII. However, this distortion is quite small (about 1%), and we therefore expect to capture the essential physics of the transition with our approximation of a precisely cubic supercell.

We have found during this work that the LDA alone is inadequate for the description of hydrogen bonding in H<sub>2</sub>O ice. Compared to the experimental equation of state for ice X (see below), we find that LDA predicts O-O bond distances which are about 10% too short. This is consistent with our group's calculations on the ground-state geometry of water clusters using Vanderbilt and conventional norm-conserving pseudopotentials [15]. Therefore, we have adopted gradient corrections to LDA in the density-functional theory following Becke [16] for the exchange energy part and Perdew [17] for the correlation energy part. This approach has been tested on the

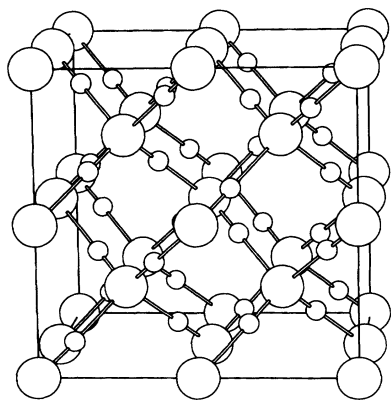


FIG. 1. The structure of ice VIII. The unit cell has sixteen H<sub>2</sub>O molecules with O and H denoted by bigger and smaller circles, respectively. The ice X structure would be obtained by displacing all the H's into O-O bond midpoints.

TABLE I. Comparisons between our theoretical equation of state and experimental equation of state [21].

Lattice constant (a.u.)	Pressure (GPa) from our calculation	Pressure (GPa) from experiment
9.9	103	114
10.0	97	97
10.1	91	87
10.2	85	76
10.3	78	71
10.4	72	68
10.5	65	61

IIA elements and IIB elements by Ortiz and Ballone [18]. The correlation energy per particle of the uniform electron gas is taken from Ceperley and Alder's results [19] for the LDA part.

First, we calculate the equation of state for ice X. The total energies of the unit cell are calculated at lattice constants from 10.0 to 12.0 a.u. in steps of 0.5 a.u., fixing all the protons in the unit cell at the bond midpoints. The data points are fitted by a quadratic function. The hydrostatic pressure is calculated from the derivative of energy with respect to volume [20] using the thermodynamic identity  $p = -\partial E/\partial V$ . The experimental equation of state by Hemley *et al.* [21] shows good agreement with our theoretical one within a few percent error. The equations of state from theory and experiment are compared in Table I. This shows that the gradient-corrected LDA is capable of giving a good description of the structural properties of H<sub>2</sub>O ice.

We next investigate the stability of the ice X structure with respect to symmetry-breaking H displacements. For this purpose, the Born-Oppenheimer surfaces are investigated for lattice constants 10.0, 10.5, and 11.0 a.u. The total energies of the unit cell are calculated, moving all the protons away from the bond midpoints by the same amount  $\delta$  in an antiferroelectric pattern, and the data points are fitted by fourth-order polynomials. The data and the fitted functions for the lattice constants 10.0 and 11.0 a.u. are shown in Fig. 2. If the protons were classical particles, the phase transition into an asymmetric proton position would occur when the coefficient of the quadratic term changes sign, since this is the point at which the potential energy surface develops a double minimum. The coefficients of the quadratic terms are found to be approximately linear in lattice constant over the range of interest. With such a linear fit, it is found that the coefficient crosses zero at about 9.9 a.u., which corresponds to about 103 GPa according to our theoretical equation of state. This exceeds the experimental transition pressure by more than a factor of 2.

However, protons are so light that their quantum fluctuations are not negligible. We estimate the size of the effect due to the quantum fluctuations of the H coordi-

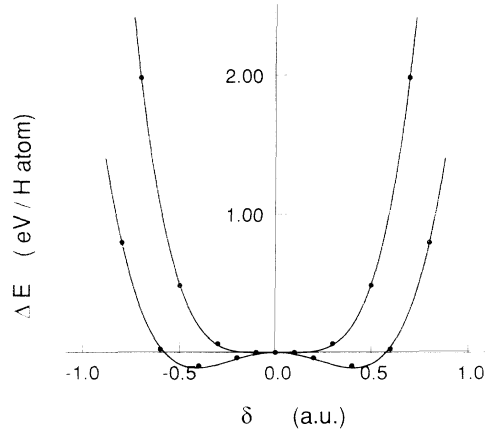


FIG. 2. The Born-Oppenheimer potential energy surfaces of an antiferroelectric collective mode in the ice X structure. The upper and lower curves correspond to lattice constants of 10.0 and 11.0 a.u., respectively.

nates by considering a system of interacting quartic anharmonic oscillators. The analysis is based on the theory of Koehler and Gillis [22]. In this theory, the single-particle Hamiltonian has an on-site term  $H_0$  and an intercell coupling term  $H_1$  which is treated in the mean-field approximation:

$$H_0 = -\frac{1}{2M} \frac{d^2}{du^2} + \frac{1}{2} \alpha u^2 + \varphi u^4, \quad (1)$$

$$H_1 = -\chi u \langle u \rangle, \quad (2)$$

where  $M$  is the mass of the proton,  $u$  is the displacement from the bond midpoint, and atomic units are used. The calculations of Fig. 2 correspond to thinking of  $u$  as an antiferroelectric collective coordinate, in the classical limit, in which case  $H_0 + H_1 = \frac{1}{2} (\alpha - \chi) u^2 + \varphi u^4$ . Thus, the calculations allow us to obtain  $\chi - \alpha$ , which should vanish at the transition to the asymmetric structure. When the kinetic-energy term in  $H_0$  is included, we expect the transition to be shifted so that it will not occur until some positive value of  $\chi - \alpha$ . Following Koehler and Gillis [22], we introduce a trial ground-state wave function of the Gaussian form centered at  $u_0$ ,

$$\Psi(u) = (g/\pi)^{1/4} e^{-g(u-u_0)^2/2}. \quad (3)$$

When the ground-state expectation value of the Hamiltonian is minimized with respect to the two variational parameters  $g$  and  $u_0$ , one finds that

$$u_0^2 > 0, \quad \text{if } \chi^{1/2}(\chi - \alpha) > 6\varphi/\sqrt{M}, \quad (4)$$

and  $u_0 = 0$  otherwise. The transition into an asymmetric position occurs when the equality holds. By calculating the energy as only one proton is displaced from the bond midpoint, keeping the others fixed, the coefficients  $\alpha$  and  $\varphi$  are obtained as a function of lattice constants. We found that  $\chi^{1/2}(\chi - \alpha) - 6\varphi/\sqrt{M}$  vanishes at 10.74 a.u.,

which we identify as the transition lattice constant. This corresponds to 49 GPa in our calculated (classical) equation of state of Table I. (The H quantum fluctuations may also affect the equation of state; we estimate that this effect could increase the transition pressure to as much as 55 GPa. On the other hand, use of the experimental equation of state would give 43 GPa.) The agreement with the experimental estimates of 42 to 47.5 GPa is now quite reasonable, considering the roughness of the mean-field approximation.

We also calculated the transition lattice constants for other types of proton displacement patterns consistent with the Pauling ice rules, such as a ferroelectric pattern and a disordered pattern. We found no significant difference in the transition lattice constants regardless of the type of the displacement. Moreover, at least within the mean-field theory outlined above, the shift in the transition point due to quantum fluctuations should be roughly the same for each. Therefore, our calculations do not predict which displacement pattern is favored. However, we think the antiferroelectric displacement pattern is likely to require lowest energy when coupling of the proton distortions to the tetragonal strain in the antiferroelectric case is taken into account.

So far we have confirmed that our theory does give a transition near the experimentally observed one. In order to understand better the nature of the transition, we try to find a soft phonon mode at the transition by simulating the atomic vibrational dynamics. While the Car-Parrinello *ab initio* molecular dynamics assumes the validity of classical mechanics [10] and therefore neglects quantum fluctuation effects, this approach should still give important insight into the nature of the transition. We prepare the system in such a way that the ions in the unit cell deviate from the positions in ice X by a small amount in a random fashion and the electrons are in their ground state. We let the system evolve for a duration of about 250 fsec. The phonon density of states is calculated from the Fourier transform of the velocity autocorrelation function, and the total phonon density of states is decomposed into the contributions from different normal modes of the system. In Fig. 3, we show the total phonon density of states and the density of states projected onto the stretching mode of the protons, for several different lattice constants. Note that as the lattice constant approaches the transition from a smaller value, the stretch-mode projected density of states moves toward lower frequency. When we further decompose the stretch modes of the protons into ice-rule preserving (IRP) and ice-rule violating (IRV) ones, we find that the lower-frequency and higher-frequency peaks in the right-hand side of Fig. 3 correspond almost entirely to the IRP and IRV stretch modes, respectively. The center of the IRP peak is clearly shifting to dramatically lower frequency in the first three panels of Fig. 3; a linear fit of  $\omega^2$  versus lattice constant (as expected for a soft mode) indicates that  $\omega \rightarrow 0$

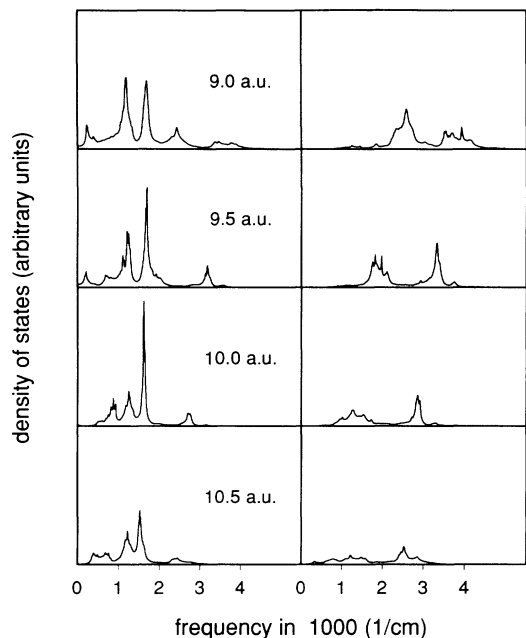


FIG. 3. The total densities of states at several lattice constants (left panels), and the densities of states projected onto the stretching mode of protons (right panels, vertical axis scaled by a factor of 2.4).

at about 10.3 a.u. Meanwhile, the IRV modes shift by only about  $1000 \text{ cm}^{-1}$  over the same range. These results clearly confirm the interpretation of the transition in terms of a mode-softening transition. (The shift of the transition lattice constant from the earlier 9.9 a.u. to the above 10.3 a.u. can be attributed to the thermal fluctuations associated with the 600 K temperature of the simulation; a mean-field estimate predicts a shift of precisely this magnitude.)

In conclusion, we have applied the Car-Parrinello *ab initio* molecular dynamics combined with ultrasoft pseudopotentials to the calculations on high pressure phases of  $\text{H}_2\text{O}$  ice. LDA augmented with gradient corrections in the density-functional theory describes the hydrogen bonding well and the equation of state from the calculation shows a good agreement with experiment. The phase transition between ice X and ice VIII/VII is predicted to occur at 49 GPa when the effect of the quantum fluctuations of the protons is considered in the transition. It is not explained within our theoretical approach why the protons show an antiferroelectric order below the transition pressure at low temperature, which is a possibility of

further study. Finally, the O-H stretch modes which preserve the ice rules are observed to become soft at the transition.

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