

## Anharmonic Raman Spectra in High-Pressure Ice from *Ab Initio* Simulations

Anna Putrino\*

*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*

Michele Parrinello

*CSCS Swiss Center for Scientific Computing, Via Cantonale, CH-6928 Manno, Switzerland  
and Physical Chemistry ETH Hönggerberg HCI, CH-8093 Zurich, Switzerland*

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We calculate from *ab initio* molecular dynamics the Raman scattering of high-pressure ice. To this effect we apply a new method based on the Berry phase theory of polarization. Our results are in agreement with recent and difficult experiments and are compatible with a picture in which ice VII is a proton-disordered system and in ice X the hydrogen bond is symmetric.

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Ice under pressure has received much attention in recent years, for a variety of reasons. On the one hand, ice plays a very important role in the physics of the Earth and of the planets, such as Saturn, Uranus, and Neptune [1]. On the other hand, it offers the possibility of studying in a controlled way one of the most important interactions in nature, namely, the hydrogen bond. In particular, using pressure the O-O distance can be continuously modified and brought into a regime in which the double-well barrier that hinders the transfer of a proton to its neighboring water molecule is reduced so greatly that proton transfer is possible. This latter regime is known as the low-energy barrier hydrogen bond [2]. This form of hydrogen bond has great relevance for chemistry and biochemistry [3]. The onset of the low-energy barrier hydrogen bond regime takes place at  $\approx 50$  GPa where ice VIII transforms into proton-disordered ice VII. It has now been established by a combination of *ab initio* simulations and experiments that at least at low temperature the proton disorder is due to translational defects and the proton can jump between two different positions [4]. Further increasing the pressure leads to the total collapse of the double-well barrier and to the emergence of a new phase, ice X, where the proton sits in the middle of the bond, leading to a symmetric hydrogen bond. The arrangement of ice X is isomorphic to the  $\text{Cu}_2\text{O}$  structure [5–8]. While the boundaries between ice VIII and ice VII are well established and are signaled by the disappearance of a small tetragonal distortion of the ice VIII structure [4,9], the transition to ice X and the nature of ice VII are still not fully understood [10]. One of the reasons for this state of affairs is that it is very difficult to perform experiments at these high pressures. In particular, protons, the key actors in this transition, are invisible to x rays [11], and neutron scattering, which would be able to locate the H positions, is not possible at such high pressure [12]. Information on these most important phases has to be inferred from optical experiments. While IR spectra have been presented [13] and interpreted [14] for some time, only very recently has it been possible to obtain Raman data overcoming a series of experimental

difficulties. These data have been analyzed on the basis of an empirical model [15], but a more basic understanding is still lacking. On the other hand, it is not possible to apply to the calculations of the Raman spectrum in ice VII and X the standard *ab initio* techniques because the assumption of harmonic behavior fails for these extremely anharmonic crystals.

In this Letter we present a novel method to evaluate the Raman spectrum of disordered and anharmonic systems in a fully *ab initio* way, from a first-principles simulation run. Our results are in good agreement with experiments and contribute to the understanding of high-pressure ice. In order to calculate the Raman spectrum we make the approximation, appropriate in this case, of working in the zero frequency limit; namely, the incoming radiation cannot induce electronic excitations.

In this case the Raman scattering cross section can be related to the dynamical autocorrelation functions of the polarizability tensor [16]:

$$\alpha_{\mu\nu}(t) = -\frac{\partial \mathbf{P}_\mu}{\partial \mathbf{E}_\nu} \equiv \frac{\partial^2 E}{\partial \mathbf{E}_\mu \partial \mathbf{E}_\nu}, \quad (1)$$

where  $\mathbf{P}$  is the polarization vector,  $E$  is the energy, and  $\mathbf{E}$  is the electric field. In a cubic system, as with ice VII and X, and to a good approximation with ice VIII, we can divide the tensor  $\alpha$  into

$$\alpha(t) = \alpha(t)\mathbf{I} + \beta(t), \quad (2)$$

where  $\alpha(t) = \frac{1}{3} \text{Tr} \alpha(t)$ . Then one has for the two different polarization scattering geometries

$$\mathbf{I}_{\text{VV}}(\omega_f) = \mathbf{I}_{\text{ISO}}(\omega_f) + \frac{4}{3} \mathbf{I}_{\text{VH}}(\omega_f), \quad (3)$$

where

$$\mathbf{I}_{\text{ISO}}(\omega_f) = \frac{N}{2\pi} \int dt e^{-i\omega_f t} \langle \alpha(0) \alpha(t) \rangle \quad (4)$$

and

$$\mathbf{I}_{\text{VH}}(\omega_f) = \frac{N}{2\pi} \int dt e^{-i\omega_f t} \frac{1}{10} \langle \text{Tr}[\beta(0) \cdot \beta(t)] \rangle \quad (5)$$

and  $\omega_f$  is the frequency of the scattered light. In the usual approach  $\alpha$  and  $\beta$  are expanded in the vibrational normal coordinates of the system and from expressions (3)–(5) one can recover the usual expression for the Raman activity. In an anharmonic system and *a fortiori* in a liquid, such an expansion is not valid and one has to evaluate directly the autocorrelations (4) and (5). This can be done by using density functional based *ab initio* molecular dynamics [17] to evaluate the thermal averages in (4) and (5) and evaluating the polarizability tensor fluctuations. An efficient way of evaluating  $\alpha_{\mu\nu}(t)$  can be obtained if one uses the Berry phase formulation of the polarization [18,19] and the recently developed extension of the variational density functional perturbation theory [20]. This leads to a self-consistent *ab initio* scheme where the same type of approximation is used to generate the trajectories and the Raman activity. This is at variance with more empirical approaches where Raman activity requires separate modeling [21]. As in Ref. [14] we generated the trajectories [22] needed to perform the sampling in a cell of water molecules arranged in the ice VIII supercell geometry, where we have neglected the small tetragonal distortion [23]. Without this distortion the ice VIII lattice can be described as composed of two interpenetrating tetrahedrally coordinated sublattices, where the oxygen atoms are arranged in a bcc way and the water dipole moments are antiferroelectrically arranged. As in Ref. [14], when the volume is reduced translational defects are generated such that the protons can jump along the hydrogen bond between two symmetric positions. This leads to proton disorder and to a weakening of the intramolecular bond. At even lower volumes phase X is obtained and the structure of the water molecules is completely lost.

We used the Becke-Lee-Yang-Parr gradient correction [24] to the local density approximation which describes well the hydrogen bonding in water [25], Martins-Troullier norm-conserving pseudopotentials [26], and an integration time step of 0.12 fs. The electronic wave functions and their linear order response to the perturbation were expanded in plane waves up to a cutoff of 70 Ry. The Brillouin zone sampling was restricted to the  $\Gamma$  point. We performed constant volume simulations at different densities, corresponding to pressures from 20 to 125 GPa. The conversion of the simulation cell volume to the pressure is based on the experimental equation of state [11]. Micro-canonical runs up to 7 ps long were performed at the average ionic temperature of  $\sim 300$  K. The correlation function  $\langle \alpha(0)\alpha(t) \rangle$  is computed classically and quantum effect corrections are taken into account by multiplying Eq. (3) by the factor  $[1 - \exp(-\hbar\omega/k_B T)]/2$  [27]. Previous experience [14,28] has shown that quantum effects are only of quantitative significance. In order to eliminate the spurious feature produced by the Fourier transform of a truncated autocorrelation function, we have used the maximum entropy method [29].

The results obtained are shown in Fig. 1 and reproduce the dramatic change observed in the experiments as a func-

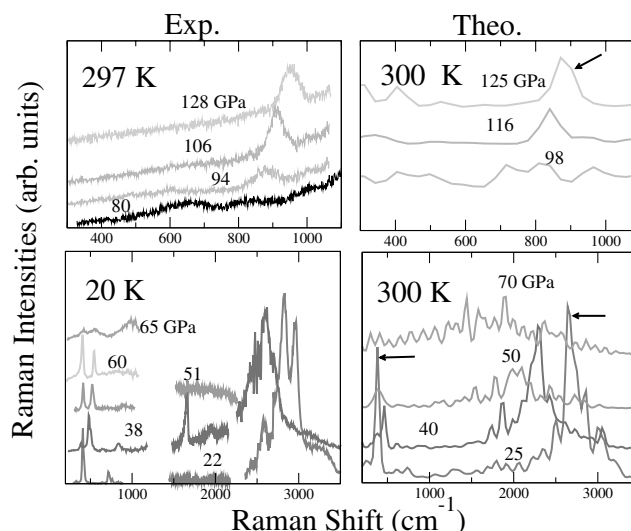


FIG. 1. Raman spectra: comparison with the experiments. Left panels: experimental data from Ref. [15]; right panel: simulated data. The theoretical spectra are obtained using the procedure described in the text. The three arrows indicate (1) the  $\nu_1(A_{1g})$  peak, which can be considered the order parameter of the phase transition, around  $2660 \text{ cm}^{-1}$  in ice VIII at 25 GPa, (2) the unresolved  $\nu_{T_z}(A_{1g}) + \nu_{T_{xy}}(E_g)$  and  $\nu_{T_z}(B_{1g}) + \nu_{T_{xy}}(E_g)$  bands around  $390 \text{ cm}^{-1}$  in ice VIII at 25 GPa, and (3) the  $\nu_T(T_{2g})$  peak, which characterizes the ice X cuprite structure, around  $840 \text{ cm}^{-1}$  in ice X at 125 GPa.

tion of pressure [15]. At the lowest pressure (25 GPa) the behavior of ice VIII is mostly harmonic and one can recognize the peaks which have been assigned by Goncharov *et al.* [15]. Of particular relevance are the three modes

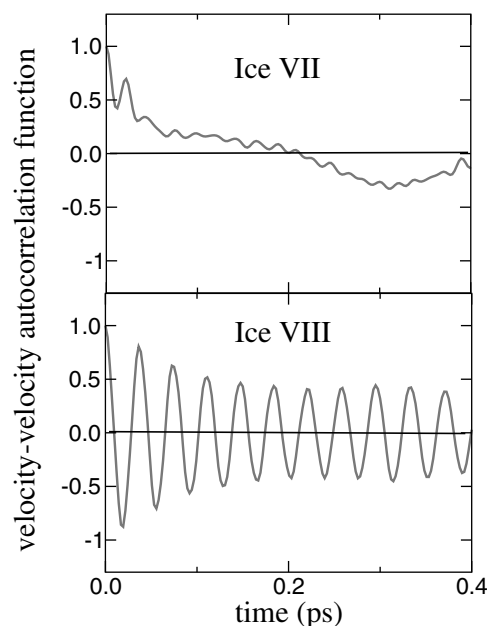


FIG. 2. Velocity-velocity autocorrelation function  $\langle q_{\nu_1(A_{1g})}(t)q_{\nu_1(A_{1g})}(0) \rangle$ ; the autocorrelation function has been normalized to  $\langle q_{\nu_1(A_{1g})}(0)q_{\nu_1(A_{1g})}(0) \rangle$ . The pressure for ice VIII is 25 GPa and for ice VII is 40 GPa.

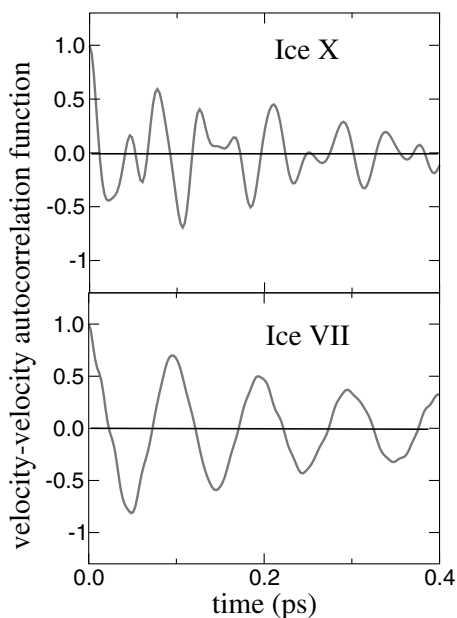


FIG. 3. Velocity-velocity autocorrelation function  $\langle q_{\nu_T(T_{2g})}(t)q_{\nu_T(T_{2g})}(0) \rangle$ ; the autocorrelation function has been normalized to  $\langle q_{\nu_T(T_{2g})}(0)q_{\nu_T(T_{2g})}(0) \rangle$ . The pressure for ice VII is 40 GPa and for ice X is 125 GPa.

$\nu_1(A_{1g})$ ,  $\nu_3(E_g)$ , and  $\nu_1(B_{1g})$ , which soften with pressure and which appear to go to zero. These are intramolecular modes, which are naturally expected to go to zero in the ice X phase. The mode  $\nu_1(A_{1g})$  has the largest pressure shift and can be considered as the order parameter of the VIII  $\rightarrow$  VII transition, while the VII  $\rightarrow$  X transition from the point of view of the Raman spectra can be related to the emergence in ice X of the  $\nu_1(T_{2g})$  mode from the rather featureless ice VII spectrum. Using our trajectory we can substantiate this picture by looking for instance at the collective coordinates that describe the modes. In particular, we look at the autocorrelation function of the variables:

$$q_n(t) = \sum_{\alpha=1}^{N_i} \sum_{i=1}^3 v_{i\alpha} \epsilon_{i\alpha n}, \quad (6)$$

where  $v_{i\alpha}$  is the  $i$  component of the particle  $\alpha$  velocity and  $\epsilon_n$  is the eigenvector of the  $n$ th normal mode. We contrast in Fig. 2 the behavior of the autocorrelation function  $\langle q_{\nu_1(A_{1g})}(t)q_{\nu_1(A_{1g})}(0) \rangle$  in phases VIII and VII. It can be clearly seen that while in ice VIII this function is highly harmonic with a well-defined period of oscillation and only a very small damping, in ice VII  $\langle q_{\nu_1(A_{1g})}(t)q_{\nu_1(A_{1g})}(0) \rangle$  becomes highly damped and strongly anharmonic. Rather different is the behavior of the  $\nu_1(T_{2g})$  mode (Fig. 3) which by symmetry [5] is related in phase VII to the unresolved  $\nu_{T_z}(A_{1g}) + \nu_{T_{xy}}(E_g)$  and  $\nu_{T_z}(B_{1g}) + \nu_{T_{xy}}(E_g)$  bands. It is seen that in ice VII, as in ice VIII, this mode of vibration is still rather harmonic. In ice X, on the other hand, the behavior is more complex, indicating anharmonicity in line with the observed renormalization and broadening of the mode. Therefore the lack of a visible Raman peak in the ice VII phase must be attributed to the

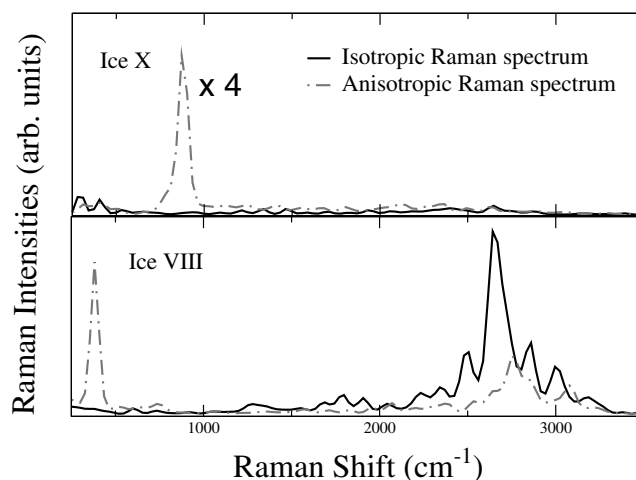


FIG. 4. Isotropic and anisotropic contributions to the Raman spectra: comparison between ice VIII (25 GPa) and ice X (125 GPa).

fact that due to the strong proton disorder very many vibrational modes become active, although with low intensity, leading to a rather featureless spectrum.

It is instructive to look separately at the isotropic and anisotropic contributions to the Raman spectrum.  $\mathbf{I}_{\text{ISO}}$  is expected to be most sensitive to intramolecular modes, while  $\mathbf{I}_{\text{VH}}$  is less discriminating [16]. In Fig. 4 we see that for ice VIII, which is still molecular, this different behavior is apparent. This separation between  $\mathbf{I}_{\text{ISO}}$  and  $\mathbf{I}_{\text{VH}}$  is also apparent in ice X. Here, however, the contribution of  $\mathbf{I}_{\text{ISO}}$  is very small, since the molecular structure has been disrupted. It would be interesting if this prediction could be verified experimentally.

In conclusion, our work adds further support to the point of view that ice X is a symmetric H-bonded cuprite structure; it also validates the complex analysis of the difficult Raman scattering experiment [15]. Last but not least we have developed a new powerful tool to interpret a most important class of experiments, namely, Raman scattering from liquid, disordered, and anharmonic systems.

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\*Present address: Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

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