Supporting Information

Density of Phonon States in Cubic Ice Ic

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Sample Preparation

The H_2O cubic ice sample for the present INS experiment was obtained starting from a hydrogen filled ice in the C_0 phase, i.e. a H_2-H_2O binary compound synthesized in a powder form at high pressure (above 4 kbar) and at temperature $T = 250$ K, that can be recovered at ambient pressure by quenching it at 77 K. Further details about the high-pressure synthesis procedure, performed in the IFAC-CNR laboratories (Italy), are reported in Ref. [1]. The sample was then transferred in an optical vacuum tight cell, inserted in a cryostat and equipped with a gas handling system, that allowed, first, by means of Raman scattering to check the quality of the starting sample, and second to apply the necessary annealing treatment to obtain an empty ice XVII.[2] The recovered ice XVII sample was then shipped to ISIS Neutron and Muon Source (RAL, STFC, UK) in a Dewar cooled by a liquid nitrogen bath. The ice XVII powder was then transferred in a standard flat aluminium cell (1 mm thick) equipped with two temperature sensors placed at the opposite sides of the cell body to ensure a good thermal control, and placed into the TOSCA cryostat through a standard center stick. All the handling procedures of the recovered samples, both C_0 filled ice and ice XVII, were always performed in a dry nitrogen atmosphere keeping a good thermal contact with a liquid nitrogen bath to preserve the sample phase.

Neutron Experiment

The measurements have been performed on TOSCA,[3] a neutron spectrometer devoted to the study of the vibrational dynamics through the INS technique. TOSCA is a crystal-analyzer inverse-geometry spectrometer with final energy, E_1, fixed at about 3.3 meV, selected via two sets of pyrolytic graphite crystals placed at two fixed scattering angles. High-order Bragg reflections are eliminated through a beryllium filter kept at low temperature. The excellent energy resolution ($\Delta\hbar\omega/E_0 \simeq 1.5\% \div 3\%$) and the wide region of the accessible energy transfer ($\hbar\omega = E_0 - E_1$, from -3 to 500 meV, where E_0 is the incident energy) make the

TOSCA spectrometer particularly useful to study the vibrational dynamics of polycrystalline ice samples.

In the actual experiment, the neutron spectrum of the recovered H_2O ice XVII sample was measured at $T = 20$ K for about 1 h (integrated proton current, IPC = 168.4 μAh), verifying that no deterioration of the ice XVII sample during its shipping to ISIS, the filling of the TOSCA cell, and its insertion in the cryostat had occurred. After this check, the sample was heated to 150 K and kept at this temperature for about 1 h, so to induce the transition from ice XVII to ice Ic. Then the sample was cooled again to 20 K and the spectrum of ice Ic was measured for about 3 h (IPC = 583.6 μAh). Afterward, the sample was heated to 268 K and maintained at this temperature for about 1 h to induce the transition from ice Ic to ice Ih. Finally, the sample was cooled down to 20 K and the spectra of ice Ih was measured for about 10 h (IPC = 1811.1 μAh). The collected time-of-flight data[4] were automatically transformed into energy transfer spectra by a dedicated routine present in the MANTID software.[5] Owing to the fully hydrogenated nature of the sample, a 3 h-acquisition time was sufficient to collect an INS spectrum with a extremely small statistical errors, crucial to pinpoint the differences between the ice Ic and Ih.

A similar experimental procedure has been followed for the study of the deuterated ice Ic, whose INS spectra were measured by back-scattering banks of TOSCA spectrometer during a second experiment.[6]

H-DOPS Extraction

The first two steps of the INS data analysis consisted in the subtraction of the empty-cell scattering contributions, and the correction for the well-known self-shielding attenuation, both performed through the analytical approach proposed by Sears.[7] Then multiple scattering contributions made of two (or more) inelastic scattering events have been approximately estimated and found rather small in the $\hbar\omega$ interval of interest (namely, below 130 meV).

For this reasons no multiple scattering corrections were operated on the two INS spectra. Finally, in order to calculate and subtract the multiphonon terms in our data, we set up a self-consistent procedure[8] already successfully used on a number of ice samples.[9] Such an approach, which fully exploits the incoherent approximation,[10] was completely justified for a polycrystalline material formed by H_2O, leading almost directly to the desired H-DOPS. This is due to the much larger neutron cross section, and lower mass, of the proton with respect to oxygen ones. In spite of the approximate character of the multiphonon self-consistent procedure, which assumes a purely incoherent, harmonic, and isotropic treatment of the multiphonon contributions, its practical implementation showed a rapid convergence of the method, and made possible a reliable extraction of the one-phonon component of the self scattering law,[10] from which the H-DOPS, $Z_H(\omega)$, of both Ic and Ih could be extracted up to $\hbar\omega = 130$ meV, that is the region where the librational bands end. Bending and stretching bands of H_2O have been clearly left out of the analysis since the neutron spectrometer used was not optimized for their accurate detection as the Q values corresponding to their typical $\hbar\omega$ ranges were by far too high. It is worth noticing that a very accurate result would require the subtraction of the tiny O contributions from the experimental estimates of $Z_H(\omega)$. The magnitude of these contributions was estimated with the help of the molecular dynamics (MD) simulations and found to be totally negligible in the librational part of the phonon spectra, while quite small, but still visible, in the lattice one. However, since lattice phonons always correspond to collective motions of the H_2O molecules seen as single rigid units, then the H and O contributions to the density of phonon states in this spectral zone show a very similar spectral shape. For this reason, the O scattering corrections to $Z_H(\omega)$ could be reasonably performed by scaling the overall intensity of the lattice part of $Z_H(\omega)$ (i.e., that in the $\hbar\omega$ range from 0 to 50 meV) by an appropriate factor, and then normalizing the corrected $Z_H(\omega)$ to the requested area.

Computational Methods

We took a $3 \times 3 \times 3$ supercell of ice Ic[11] as well as $5 \times 3 \times 3$ supercell of ice Ih from Hayward-Reimers[12] and simulated these two samples at 170 K and 50 K, with lattice constants $a = 6.37451$ Å and $a = 6.36434$ Å, respectively.[11] We carried out centroid molecular dynamics with 64 beads in the i-PI software package[13] using the many-body water potential MB-pol[14] as part of the MBX software package,[15] in conjunction with a Nosé-Hoover thermostat,[16,17] Ewald summation,[18] and a time-step of 0.1 fs for 100 ps, including 10 ps for system equilibration.

The MB-pol interaction model, used together with CMD, has been noted to perform very well for simulating thermodynamic and dynamical properties of ice.[19–21] We obtained the lattice phonon DOS from the Fourier cosine transformation of the averaged velocity autocorrelation function of the oxygen atoms.[18] In addition, the phonon dispersion curves were also extracted from the CMD data.[22]

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