



Do X-ray spectroscopies provide evidence for continuous distribution models of water at ambient conditions?

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Ambient water properties have been shown to require heterogeneity (1). Niskanen et al. (2) apply a linear relationship between the intensity of the $4a_1$ excitation in an electron energy loss spectroscopy gas-phase spectrum and the preedge in water and ice from X-ray Raman scattering to extract the number of hydrogen bonds (HBs) and conclude about homogeneity of liquid water. We raise several concerns regarding their analysis and interpretation.

First, an HB number by itself cannot say anything about homogeneity or heterogeneity since one needs to determine the spatial distribution. Second, due to extended X-ray absorption fine structure oscillations (3) and energy-dependent shake-off processes, normalization by the f -sum rule requires measurements extended to 500 eV above the edge, and not only 25 eV as in ref. 2. Third, there exists no strict theoretical foundation for this procedure to derive an HB number, since the orbitals in condensed phase change character and absorption cross-section due to HB formation (4). The authors of ref. 2 rely on spectrum calculations to derive an empirical relationship, but the calculated ambient liquid spectrum (reference 30 in ref. 2) shows major discrepancies with experiment with main- to postedge intensity ratio 2:1. However, the structure used for the calculations corresponds rather to 254 K in terms of the O–O pair-distribution function (5), for which the ratio should instead be almost 1:1 (6). Furthermore, the computed preedge intensities (reference 30 in ref. 2) give a large spread for similar HB situations calling for caution and a precise linear relationship cannot be extracted from these calculations.

It is claimed in ref. 2 that preedge-excited resonant inelastic X-ray scattering (RIXS) probes all bonding

arrangements, but the authors report only one O–H stretch frequency. This single frequency is claimed as consistent with a homogeneous model of water, ignoring that preedge excitation may select a specific class of molecules. Indeed, Harada et al. (7) have scanned the whole X-ray absorption spectroscopy resonance, not only the preedge, demonstrating subensembles with different frequencies.

Higher excitation energies give 2 discrete lone-pair X-ray emission peaks with temperature-dependent relative ratio. Niskanen et al. propose that the A' peak (Figure 4 in ref. 2) originates from core-hole-induced dynamics. The theoretical simulation is problematic by keeping the B' peak at constant energy, independent of scattering duration time. However, the B' peak is at lower energy for H_2O than D_2O (reference 14 in ref. 2), which directly shows that core-hole-induced dynamics shifts this peak down. Thus, keeping the B' peak constant in energy is incorrect and makes instead other peaks move up. With correct energy scale, peak A' should remain in the $3a_1$ region (1.5 to 2 eV from B') and not shift up in energy. Indeed, earlier simulations using this energy calibration (reference 18 in ref. 2 and ref. 8) have assigned peak A' to a_1 symmetry. However, polarization-dependent RIXS measurements show that also this peak is of b_1 symmetry (9).

In Niskanen et al. (2), the 2 peaks seen in ice at low temperature are proposed to support one peak (A') as due to core-hole dynamics. However, for ice measured instead at -10 °C, the B' peak is suppressed and A' dominates, as expected for tetrahedral local structure (reference 46 in ref. 2). Here, rapid equilibrium with the vapor heals beam-induced transformations into high-density amorphous ice (10).

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