



Resonant inelastic X-ray scattering of liquid water

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ABSTRACT

We review recent studies using resonant inelastic X-ray scattering (RIXS) or also here denoted X-ray emission spectroscopy (XES) on liquid water and the assignment of the two sharp peaks in the lone-pair region. Using the excitation energy dependence we connect the two peaks to specific features in the X-ray absorption (XAS) spectrum which have independently been assigned to molecules in tetrahedral or distorted configurations. The polarization dependence shows that both peaks are of $1b_1$ origin supporting an interpretation in terms of two structural species, tetrahedral or disordered, which is furthermore consistent with the temperature-dependence of the two peaks. We discuss effects of life-time vibrational interference and how this affects the two components differently and also leads to differences in the relative peak heights for H_2O and D_2O . We show furthermore that the inherent structure in molecular dynamics simulations contain the structural bimodality suggested by XES, but this is smeared out in the real structure when temperature is included. We present a discussion around alternative interpretations suggesting that the origin of the two peaks is related to ultrafast dissociation and show evidence that such a model is inconsistent with several experimental observations and theoretical concepts. We conclude that the peaks reflect a temperature-dependent balance in fluctuations between tetrahedral and disordered structures in the liquid. This is well-aligned with theories of water under supercooled conditions and higher pressures where water might exist as high- or low-density liquid with different possibilities for a transition between them. With the present work we provide a link between established models for supercooled water, where water's anomalies become extreme, and ambient water, where the anomalous contributions are weaker but still important.

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1. Introduction

The basic understanding of the structure and dynamics of bulk liquid water is central for many areas of natural sciences ranging from condensed matter physics to biology. It is essential that we have tools that can characterize the hydrogen-bonding (H-bonding) network in water. Spectroscopic techniques can provide fingerprints of local H-bonding configurations if there is sufficient spectral contrast. The most popular spectroscopy to probe water has been vibrational spectroscopy but it is hampered by the lack of significant features in the infrared and Raman spectra in the OH stretch region (Fig. 1). This makes decompositions

of the broad feature associated with the internal OH stretch vibrations rather arbitrary. The presence of an isosbestic point in the temperature-dependent Raman spectrum has been interpreted in terms of interconversion of species [1], but the uniqueness of this interpretation has been questioned [2]. In contrast, core-level spectra show distinct peaks and features which depend on aggregation state and temperature and allow a more detailed analysis.

In Figs. 1 and 2, we compare the room temperature IR and Raman spectra of the OH stretch region in liquid water with the X-ray absorption (XAS) and X-ray emission (XES) spectra of the liquid at two different temperatures. In XAS (Fig. 2a) there are three main features: the pre-edge at 535 eV, main edge at 537–538 eV and the broad post-edge at 540–541 eV [5–7]; the spectrum may equivalently be generated through X-ray Raman scattering (XRS), which is an energy-loss technique where a high-energy (keV) photon is inelastically scattered with an energy loss corresponding to the core-excitation energy [8]. With increasing temperature

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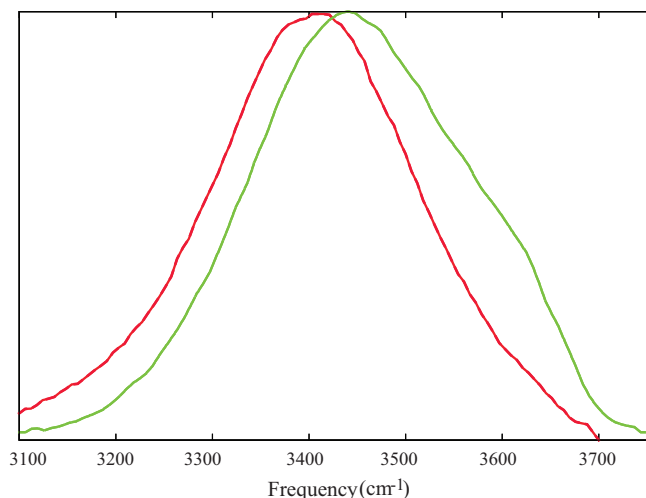


Fig. 1. O—H stretch region of IR (red, dashed) and Raman (green, full) of HDO water in D₂O at room temperature [3,4]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

the post-edge, which is dominating in ice, loses intensity while the main-edge and pre-edge become enhanced and shift to lower energy; clearly then, the post-edge may be assigned to molecules with intact hydrogen (H-) bonds while the pre-edge and main-edge are associated with weakened or broken H-bonds. This assignment is further supported by studies of water at increasing coverage on a Ru(0001) surface, from isolated molecules to small clusters, with one intact and one broken donating H-bond, and larger islands where the ratio of intact to dangling H-bonds increases with increasing coverage [9].

In XES (Fig. 2b) of liquid water we have the clearest spectroscopic sign of interconversion between two types of molecular environments or H-bonding situations [10–12]. The non-resonantly excited XES spectrum of the parent gas-phase molecule [13] (Fig. 3) shows the two bonding orbitals, 1b₂ and 3a₁, broadened through vibrational interference effects [11,14], while the non-bonding 1b₁ lone-pair gives a very sharp peak. In the lone-pair region of the liquid we have instead two sharp peaks, 1b₁' and 1b₁'', that do not broaden with increasing temperature, but instead intensity is transferred from the peak at lower emission

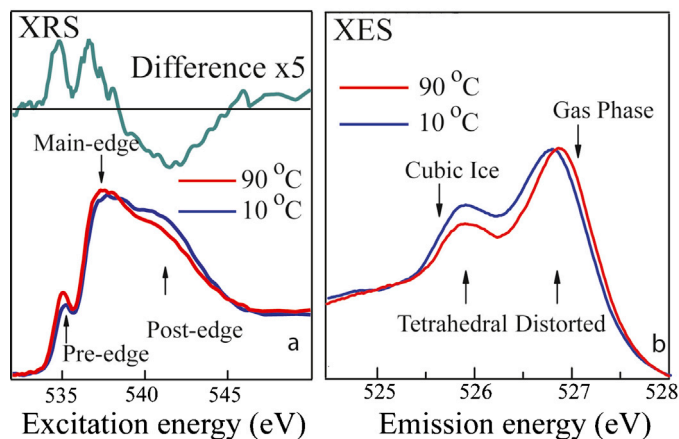


Fig. 2. (a) X-ray Raman scattering spectra of liquid H₂O at 10 and 90 °C normalized to have the same area and the difference between the two spectra magnified by a factor of 5 [10]. (b) The lone-pair 1b₁ region of the O 1s soft X-ray emission spectra of liquid D₂O at 10 and 90 °C using a non-resonant excitation energy of 550 eV. The positions of the corresponding 1b₁ state of crystalline ice and gas phase water are indicated with arrows [11]. The spectra were normalized to give the same peak height of the distorted component.

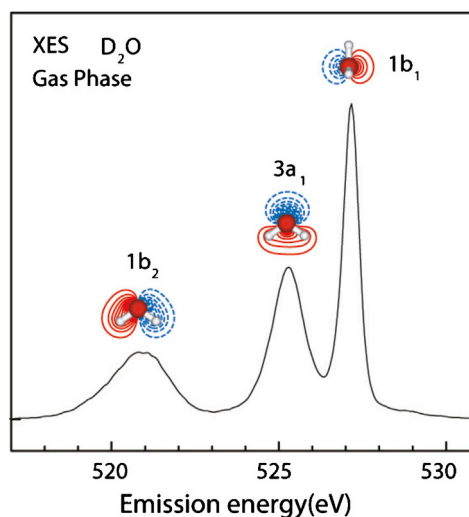


Fig. 3. Non-resonantly excited XES spectrum of gas phase water (from Ref. [13]) showing the bonding 1b₂ and 3a₁ orbitals broadened through vibrational excitations while the 1b₁ lone-pair remains very sharp. The heavier isotope D₂O was chosen to minimize effects of vibrational excitations upon creation of the core-hole.

energy (1b₁'), close to the lone-pair position in crystalline ice, to that at higher emission energy (1b₁''), close to the lone-pair position in non-H-bonded gas phase molecules. The peak close to the lone-pair peak from tetrahedrally coordinated ice lies at fixed energy at all temperatures while the peak at higher emission energy drifts toward the gas phase position as the liquid is heated; the observations are consistent with an assignment of the low emission-energy peak as due to molecules in tetrahedral H-bonding environment and the high emission-energy peak as due to molecules in disordered environments with broken or weakened H-bonds. Furthermore, since XES follows XAS, we can connect the two spectroscopies by tuning the photon energy to the specific pre-, main- and post-edge features in XAS and observe the response in XES. Exciting at the post-edge in XAS leads to an enhancement of the tetrahedral peak in XES, exciting at the main-edge enhances the disordered peak in XES while excitation at the pre-edge in XAS gives only one peak, the disordered, in XES; the pre-edge in XAS on liquid water has been assigned as unique to molecules with disordered environments with broken or weakened H-bonds [5,7,15].

We have over the last decade devoted a major effort to the development of X-ray spectroscopy and scattering measurements of water in its different aggregation forms as well as to developing theoretical techniques to analyze the data; the main results are summarized in several reviews [6,12,16–18] as well as in a recent perspective on the structure of water [19]. In the present contribution we will discuss in some more detail XES on liquid water and specifically relate the spectroscopy to models of the liquid connecting the ambient and deeply supercooled regimes. Of particular interest for many water properties and for the interpretation of XES on water are density fluctuations; here we will discuss how they may be reflected in the XES spectrum of water.

2. Excitation energy dependence

The split 1b₁ peaks can be assigned to specific structural motifs through the connection to XAS results on water [6,7] using selective excitation. As mentioned in the introduction the near-edge region of the XAS spectrum of water (Fig. 2a) has 3 main spectral features: pre-edge (535 eV), main-edge (537–538 eV) and post-edge (540–541 eV) [6,7]. The spectrum of ice has its main intensity in the post-edge region with a shoulder around the main-edge [6,7,20]. In the liquid, the spectral intensity in the post-edge has dropped sub-

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