X-ray Raman Spectroscopy at the Oxygen K Edge of Water and Ice

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Introduction

Despite its simple elemental composition, water has a complicated local structure that has puzzled scientists for more than a century [1 and references therein]. X-ray absorption spectroscopy (XAS) and, in particular, the investigation of the near-edge region as a probe of empty electronic states yield unique element-specific information on local structure and chemistry [2]. Conventional XAS studies of the oxygen K edge of bulk water at ambient conditions have been extremely difficult to conduct because of the short attenuation length of x-rays above the O K edge [3], spectral distortions due to the large O concentration (saturation effects) [4, 5], and the surface sensitivity (~nm) of ion/electron yield detection. X-ray Raman scattering (XRS) is a bulk-sensitive (~mm) technique that avoids these difficulties yet still yields XAS information [6-8].

Here we report on the O K-edge spectra of liquid water and ice by using XRS with an energy resolution of ~1 eV. The spectra are compared with conventional XAS data recently obtained by Myneni et al. [9]. The results shed new light on the water puzzle [10] and indicate the power of XRS as a bulk-sensitive probe of local structure and chemistry.

Methods and Materials

In an XRS experiment, the incident photon is inelastically scattered, and a small fraction of its energy is transferred to the sample. Besides vibrational (10-500 meV) and valence band (1-10 eV) excitations, the high energy of hard x-ray photons permits electronic excitations of core levels in the sample (100-1000 eV). Therefore, absorption spectra with edge energies lying in the soft x-ray regime can be measured effectively by using hard x-rays. Its inherent bulk sensitivity and good penetration makes XRS especially valuable for investigating liquids, concentrated complex systems, and samples under ambient and extreme conditions. A recent review shows that high-quality XRS spectra can now be obtained in a matter of minutes to hours for second-row elements [11].

In the present study, we used an array of analyzers to capture a larger solid angle. The corresponding q range of $0.36 < qr < 0.57$ (where q = the momentum transfer and r = the mean orbital radius) is well in the dipole limit.

The experiments were performed at APS undulator beamline 18-ID by using a Si(400) double-crystal monochromator and focusing mode. Raman scattering was analyzed with a high-resolution multicrystal analyzer [12]. The instrument employs eight Si(660) analyzer crystals on intersecting Rowland circles operated close to backscattering at a Bragg angle θ_B of 87° and an energy of 9699 eV. The Raman spectrum was swept by scanning the beamline monochromator energy at a fixed analyzer setting, and the overall energy resolution (convolution of beamline and analyzer resolution) was found to be ~1 eV full width at half maximum (FWHM) by measuring the elastic scattering peak. The scattered intensity was measured with a lead-shielded LN_2-cooled Ge detector. The incident photon flux (I_0) was recorded with a N_2-filled ion chamber, and the spectra were normalized by dividing the detector signal through I_0. The incident beam intensity was on the order of 3×10^{12} photons/s in a 0.1-mm-vertical by 0.2-mm-horizontal focus. Individual scans took 30 min, with 10 s per step. For the liquid water spectrum, 15 scans were added. The Raman spectrum was furthermore corrected for background from Compton scattering by subtracting an extrapolated function fitted to the region well below the absorption edge. Different functions, such as exponential and hyperbolic, were tested; all gave essentially the same result for the corrected spectrum in the near-edge region. To avoid any possible radiation damage, purified water was flown through a tube, and the ice sample assumed to be ice I_h was scanned between individual spectra.

Figure 1 shows the O K-edge spectra as measured by XRS for liquid water and ice. The spectra are displayed as a function of the energy transfer obtained by subtracting the fixed spectrometer energy (9699 eV) from the scanned incident photon energy. A pre-edge feature at 535 eV is clearly discernible, in addition to the main absorption edge (537 eV) and a broad continuum structure (541 eV). The intensity of these three spectral features is clearly different when water is compared in its different condensed phases. This shows that O K-edge spectra as measured by XRS can effectively visualize changes in the hydrogen-bonding (H-bonding) environment of water.

Figure 2 depicts the water and ice spectra by XRS as a function of energy transfer and by XAS as a function of incident photon energy. For easier comparison, the XAS
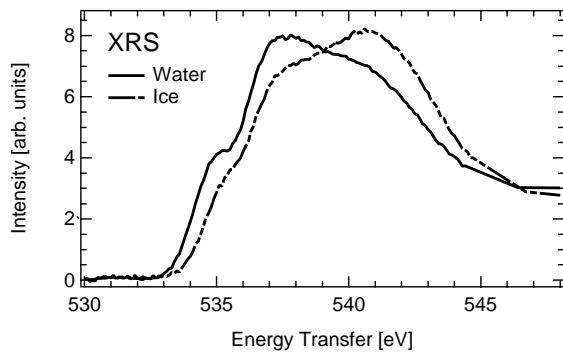
FIG. 1. *X-ray Raman spectra of the oxygen K edge of liquid water (solid line) and ice (dashed line) displayed as a function of energy transfer.*

spectra have been convoluted with a Gaussian function of 1-eV FWHM in order to account for the different energy resolutions (~0.1 eV in the XAS measurement). All features detected by XAS are clearly reproduced with XRS. Discrepancies in the ice spectra can be explained by different sample preparation techniques (polycrystalline ice for XRS vs. a single-crystal ice overlayer for XAS). The prominent difference at higher energies between the XAS and XRS water spectra can be traced back to a saturation of the fluorescence yield XAS measurement. Saturation can be excluded for the XRS measurement, which underscores its importance when relating structural information and the relative intensities of spectral features in a quantitative analysis of bulk-sensitive x-ray absorption spectra. In addition, the absence of saturation for XRS considerably simplifies preparation of the liquid sample.

Acknowledgments

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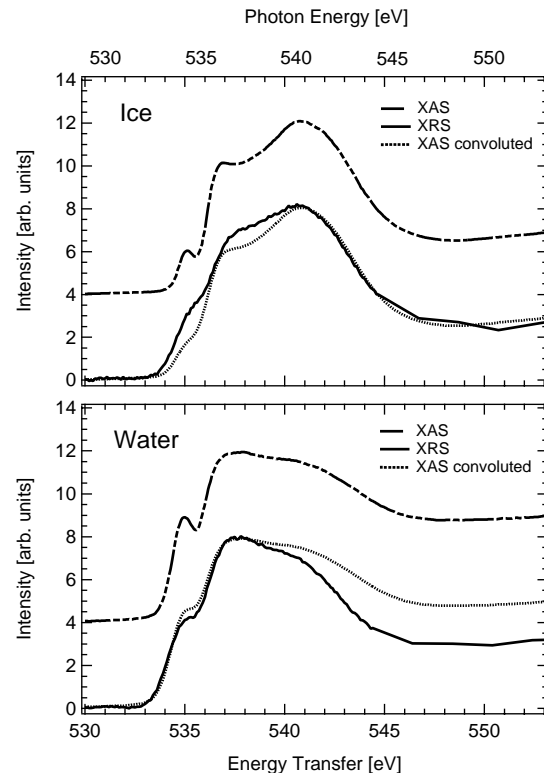[4] S. Eisebitt, T. Boske, and J. E. Rubensson et al., Phys. Rev. B **47**, 14103 (1993).

FIG. 2. *Oxygen K-edge absorption spectra of ice from XRS (solid line, taken from Fig. 1) compared to (top) the XAS spectrum of ice (dashed line) (dotted line is spectrum obtained by convoluting the XAS spectrum with a 1-eV Gaussian function) and (bottom) the same for water. The XAS spectra are taken from Ref. 9.*

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