Comment on “Energetics of Hydrogen Bond Network Rearrangements in Liquid Water”

Smith et al. (1) reported an x-ray absorption spectroscopy (XAS) study of water in a liquid microjet from supercooled to room temperature. From the apparently strong spectral variation with temperature and a subsequent analysis based on fitting sums of Gaussians, they inferred a tetrahedral model for bulk water. Both data and analysis contradict a previous XAS study by Wernet et al. (2) that reported a much smaller temperature dependence for room-temperature water versus 90°C water and, based on a series of experimental and analytical methods, suggested that a dominating fraction of molecules have asymmetrically donating hydrogen bonds (H bonds). We argue here that the Smith et al. (1) study contains fundamental shortcomings, with respect both to the experimental spectra and the data analysis, that need to be addressed, and conclude that the energetics of different species in liquid water cannot be reliably derived from that study.

Closer inspection of both figures presented by Smith et al. (1) brings into question the quality of the temperature-dependent spectra. Figure 2 in (1) shows three different sets of measurements displaying energy differences of approximately 1.2, 1.5, and 1.8 kcal/mol between two different species (as derived from the slopes of the curves). The large variation in the determined energies indicates that some other variable affects the measurements. The lack of reproducibility of the spectral shapes, even at a fixed temperature, is seen in the spread of the measured ratios of post-edge to pre-edge intensities (I_{post}/I_{pre}) for the three different curves: The variation at 5°C, for example, is 21% between the two extreme curves—of the same order of magnitude as the claimed measured temperature effect. Had the measurements been conducted correctly, all the data points depicted in figure 2 in (1) should fall within the error bars of a single line. It has been well established for many years that x-ray absorption spectra can be fully reproduced by careful normalization to the intensity of the incoming beam (3). The question is, What causes the lack of reproducibility of the measurements in (1)?

Because of energy-dependent nonlinear effects, often denoted “saturation effects” [supporting online material (4)], the temperature-dependent spectra reported by Smith et al. (1) are affected by experimental artifacts. When the effective detection and absorption depths are of a similar magnitude, saturation effects occur and, as a consequence, the intensities of the spectrum’s strongest features are reduced. This affects, for example, the value of I_{post}/I_{pre} (4, 5). Contrary to the assumption of Smith et al., XAS measured through detection of low-energy electrons of a bulk water sample results in such saturation effects (4).

Figure 1 compares the spectra presented by Smith et al. (figure 1 in (1)) with spectra for bulk liquid water measured with small-momentum transfer x-ray Raman scattering (XRS) (2), which, as a nonresonant inelastic scattering process, yields the absorption cross section free from saturation effects (6, 7). Temperature-dependent XRS spectra measured at 3.5°C, 25°C, 59°C, and 90°C are shown (Fig. 1, curve b). The water spectra have pre-edge (535 eV), main-edge (537 to 538 eV), and post-edge (540 to 541 eV) features (4). We observe, in accordance with Wernet et al. (2), that with increasing temperature the pre-edge and main-edge increase while the post-edge decreases, corresponding to changes of the populations of different species in the liquid. An isosbestic point at 538.8 eV in the difference spectra (Fig. 1, curve d)—a prerequisite for an interpretation in terms of interconversion between different species—is present here. Furthermore, the spectral change with temperature in water is nearly identical to the change in the spectra upon melting ice, albeit of smaller magnitude (Fig. 1, curve e); the same isosbestic point is observed (2). In the spectra of Smith et al. (Fig. 1, curve a), by contrast, we observe a small increase in the pre-edge intensity and a large decrease in both the main- and post-edge intensities with increasing temperature (Fig. 1, curves a and c), contrary to the temperature dependence in the XRS spectra (Fig. 1, curves b and d) and to the difference between the spectra of ice and water (Fig. 1, curve e). The

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Fig. 1. (a) XAS spectra from Smith et al. (1) for 15°C (solid) and −19°C (dashed). The data were shifted by −0.8 eV to match the energies of the pre-edge peaks with the energy-calibrated spectra in (b). (b) Oxygen K-edge spectra measured with XRS for various temperatures: 3.5°C (dash-dotted), 25°C (solid), 59°C (dotted), and 90°C (dashed). The spectra for 25°C and 90°C are taken from (2). The arrows indicate the intensity variations with increasing temperature. The 25°C spectrum has been normalized in intensity at the main edge (537.5 eV) to 1. All spectra have been normalized to the same area in the energy range displayed. (c) Differences of the spectra in (a), 15°C minus −19°C. (d) Differences between the XAS spectra at 3.5°C, 59°C, and 90°C and the room-temperature spectrum in (a) (symbols denote the raw data, solid lines are smoothed curves): 3.5°C minus 25°C (squares), 59°C minus 25°C (open circles), 90°C minus 256°C (closed circles). Isosbestic point indicated by arrow. (e) Comparison of the 59°C minus 25°C difference (open circles with error bars) to a scaled 25°C water minus ice difference [see (2)]. To best match the intensities of the three peaks, the 25°C water minus ice difference was divided by a factor of 16. A similar analysis was presented in (2) with the 90°C to 25°C difference, where a smaller scaling factor of 10 was required to match the intensities (error bars for the scaling factors are ±4). Isosbestic point is indicated by arrow.
observed large decrease in (I) of the main- and post-edge spectral features follows exactly the expected dependence for a variation of saturation effects in the spectra (4).

A sum rule for XAS relates the integrated spectral intensity to the electron occupation of the probed atomic subshell (8, 9). Because weakening or breaking an H bond does not result in large changes in the O2p electron population and, consequently, also does not cause large changes in the integrated pre-, main-, and post-edge intensity, any difference spectrum should integrate to zero, as is confirmed by the XRS data (Fig. 1, curve d). A difference spectrum obtained from the spectra of Smith et al. (Fig. 1, curve c) indicates severe normalization problems, because the spectrum does not integrate to zero and difference intensity remains at the onset of the continuum. More important, even if the data were area-normalized, they would not confirm the isosbestic point at 538.8 eV (4), which would make them inconsistent with the interpretation in terms of an interconversion between different species and with earlier measurements (2). Indeed, it is often difficult or impossible to properly normalize spectra that have different degrees of saturation.

The analysis of the x-ray absorption spectra in (1) is performed by peak fitting, which assumes incorrectly that the spectrum for each species consists of single peaks and that species contributing to pre-edge do not contribute to post-edge intensities. It is well known, however, that an x-ray absorption spectrum exhibits intensity from the edge to infinite photon energies, including spectral features in the near-edge region (3). The fact that pre-edge–related species contribute also to the post-edge thus makes it incorrect to interpret the slope in the Boltzmann plot [figure 2 in (1)] as a direct measure of the energy difference between the different species. A mathematical analysis reveals (4) that a linear fit within the assumptions of Smith et al. gives an energy difference that is too small by a factor of ~2 to 3. The temperature interval is furthermore too small to observe significant nonlinearity.

We note in passing that Smith et al. (1) also remeasured the temperature-dependent infrared Raman spectra and reported a confirming value of 1.5 kcal/mol; this is in sharp contradiction to the recent value of 2.8 kcal/mol obtained by Walrafen using a similar approach (10).

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References
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Editor's Summary

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