

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

Nilsson *et al.* (1) raise two central issues regarding our recent paper on the energetics of hydrogen bond (H bond) rearrangements in normal and supercooled liquid water (2). The first concerns the quality of our temperature-dependent x-ray absorption (XA) spectra, which Nilsson *et al.* argue exhibit nonlinear saturation effects. The second point concerns the appropriateness of the spectral analysis we employed in (2), wherein it was assumed that specific H-bonding configurations are spectrally resolvable.

Nilsson *et al.* question the quality of the XA data because of the apparent variability in the post-edge/pre-edge component ratios measured at similar temperatures [figure 2 in (2)]. Under constant conditions (e.g., jet size, collection geometry), the XA spectrum is highly reproducible, and therefore each experiment is self-consistent. However, XA spectra taken under different conditions are subject to some variability (Fig. 1). In general, the variability of the pre-edge intensity for the spectra used in figure 2 in (2), taken at approximately the same temperature, is less than 5%, and the variability in the post-edge region is less than 1%. Although there is clearly some inherent variability in the spectral features between data sets as a result of different collection geometries, calibration errors, and normalization, most of the variability shown is a result of the Gaussian deconvolution scheme employed. For each data set, a single spectrum was fit to six Gaussian components, with no constraints placed on any of the fitting parameters. Small differences in, for example, the component positions can affect the degree

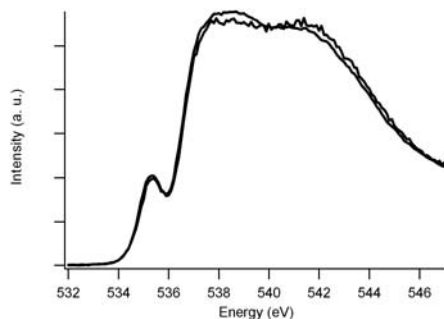


Fig. 1. Two representative spectra used in figure 2 in (2) taken at about the same temperature (-5°C), demonstrating the typical variability in the XAS experiment.

of component overlap, which, in turn, influences the peak area (or the ratio of peak areas). Therefore, it is clear that some uncertainty is inherent in using Gaussian decomposition. However, a systematic exploration of the Gaussian deconvolution scheme shows that the uncertainty stated in (2), ± 0.5 kcal/mol, is appropriate.

Saturation effects result in the reduction in intensity of the strongest spectral features relative to the weaker features (3), as can clearly be seen in figure 1 of the supporting online material accompanying the comment of Nilsson *et al.* (1). Therefore, a simple measure of the degree of spectral saturation is to compare the relative intensity of the pre-edge (weakest XAS feature) to that of the main-edge (strongest XAS feature). For example, in the saturated spectrum shown in (1), the pre-edge is $\sim 80\%$ of the main edge, and in the x-ray Raman scattering (XRS) spectrum, which does not suffer from saturation effects, the pre-edge is $\sim 40\%$ of the main-edge. In the total electron yield near-edge x-ray absorption fine structure (TEY-NEXAFS) spectra shown here (Fig. 1), the pre-edge intensity is 38% of the main edge, which is in very good agreement with the XRS spectrum of Nilsson *et al.* (1, 4). Therefore, based simply on the consistent main-edge intensity relative to the pre-edge, we can conclude that saturation effects are a relatively minor issue.

Indeed, a simple calculation based on the measured condensed phase versus vapor phase signal enhancement reveals that the average electron escape depth is actually somewhat shallow (~ 5 nm), although it is still considered a bulk probe (5). This calculated escape depth is consistent with the commonly accepted average TEY probe depth (6, 7) and is a factor of 80 less than the x-ray penetration depth (400 nm) (8). Furthermore, saturation effects are not temperature dependent, although Nilsson *et al.* argue that changes in the collection geometry resulting from varying the liquid jet tip position with respect to the detector (which changes with temperature) can cause changes in the degree of spectral saturation. The changes in jet geometry that they refer to take place within a few millimeters of the tip, and most of the data in (2) were taken well beyond this region, where the resulting geometry is quite stable. In addition, if there were significant changes in

the degree of spectral saturation resulting from changes in the measurement position with respect to the jet nozzle, one would not expect to find the experimentally observed van't Hoff temperature dependence.

Nilsson *et al.* also argue that there are “severe” normalization problems with the spectra shown in (2), based on the fact that the difference spectrum presented in (2) does not sum to zero over the near-edge region. This statement is misleading. The spectra presented in (2) were area-normalized over a larger region than shown (that is, to 551 eV, not to 547 eV). The two spectra we showed [figure 2 in (2)] have identical areas when considered over this larger energy range and, therefore, the difference spectrum over this larger range does properly sum to zero. Additionally, the XAS sum rule to which Nilsson *et al.* refer more rigorously applies over the entire oxygen K-edge spectrum, not just to the near-edge region (9). We note that clear variations in the continuum region (543 to 555 eV) with temperature have also been observed in the Auger yield NEXAFS spectra of ice, measured by Blum *et al.* (10). This relatively surface-sensitive technique should not be subject to saturation effects. Temperature-dependent changes in the position of the O-O σ^* continuum resonance (~ 562 eV) have previously been used to determine the average O-O distance in amorphous solid water (11). Therefore, we conclude that there is no fundamental reason for the continuum region to be invariant with temperature, and thus the differences observed in figure 1 in (2) are not indicative of saturation effects.

Nilsson *et al.* also point out that an isosbestic point is not observed in our temperature-dependent spectra, which they claim is a prerequisite to a two-state analysis. However, this is not the case—an isosbestic point is not at all necessary for a two-component system (12).

Nilsson *et al.* argue that the spectral analysis presented in (2) is flawed because it is based on an incorrect assumption—that the temperature dependences of the single-donor and double-donor species are spectrally distinguishable. It was clearly stated in (2) that this was a simplifying assumption and that the validity was, in part, based on the linearity observed in the individual plots in figure 2 in (2). Nilsson *et al.* estimate that the energy difference reported in (2) is a factor of 2 to 3 lower than the actual energy, based on cross-section ratios derived from their calculations of single-donor and double-donor-like water molecules. However, their mathematical analysis is a misrepresentation of the fitting procedure carried out in (2). We deconvolved the XA spectra into Gaussian components and

used the Gaussian peak area in our analysis to better represent the actual configurations (2); by contrast, the analysis presented in Nilsson *et al.* (1) is based only on the spectral intensity at specific energies (peak intensities) rather than on the area. Thus, the conclusions in (1) are not directly comparable with the results in (2). Nonetheless, when the data in (2) are analyzed using peak intensities, the van't Hoff slopes are, in general, still very linear, but the observed slope is lower by a factor of ~ 1.8 than the value ($\Delta E = 0.8$ kcal/mol versus 1.5 kcal/mol) that we reported in (2). Thus, if this lower value, derived from consideration of spectral peak intensity, is used, our previously reported value of ΔE is actually in reasonable agreement with the underestimate claimed by Nilsson *et al.* (1)—especially when the accuracy of their estimated cross-section ratios, which are based on calculations using highly ordered model clusters, are considered.

Furthermore, as stated by Nilsson *et al.*, the temperature-dependent change in relative populations of single-donor (SD) and double-donor (DD) species derived by Wernet *et al.* is actually quite small (SD/DD = 80/15 at 25°C and 85/10 at 90°C). For this result to hold true, the difference in energy between these two species must also be relatively small. Indeed, ΔE can easily be calculated using the populations from (4) and assuming

a Boltzmann distribution for the two species, as shown below:

$$\frac{N_{DD}}{N_{SD}} = A * \text{Exp}\left(\frac{\Delta E}{R * T}\right) \quad (1)$$

$$\frac{15}{80} = A * \text{Exp}\left(\frac{\Delta E}{R * 298}\right) \quad (2)$$

$$\frac{10}{85} = A * \text{Exp}\left(\frac{\Delta E}{R * 363}\right) \quad (3)$$

Combining expressions 2 and 3 and rearranging to eliminate A yields

$$\Delta E = \frac{R * [\ln(\frac{15}{80}) - \ln(\frac{10}{85})]}{\frac{1}{298} - \frac{1}{363}} = 1.5 \text{ kcal/mol} \quad (4)$$

Thus, ΔE determined directly from the Wernet *et al.* x-ray data is actually—and, perhaps, surprisingly—in excellent agreement with that presented in (2), as determined from our own NEXAFS data.

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Supporting Online Material

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