Revisiting the Total Ion Yield X-ray Absorption Spectra of Liquid Water Microjets

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Abstract

Measurements of the total ion yield (TIY) X-ray absorption spectrum (XAS) of liquid water by Wilson et al. [*J. Phys. Condens. Matter.*, 14 (2002) L221-L226 and *J. Phys. Chem. B* 105, (2001) 3346-3349] have been revisited in light of new experimental and theoretical efforts in our group. Previously, the TIY spectrum was interpreted as a distinct measure of the electronic structure of the liquid water surface. However, our new results indicate that the previously obtained spectrum may have suffered from, as yet unidentified, experimental artifacts. Although computational results indicate that the liquid water surface should exhibit a TIY XAS that is fundamentally distinguishable from the bulk liquid XAS, the new experimental results suggest that the *observable* TIY XAS is actually nearly identical in appearance to the total electron yield (TEY) XAS, which is a bulk probe. This surprising similarity between the observed TIY and TEY XAS likely results from large contributions from X-ray induced electron stimulated desorption of ions, and does not necessarily indicate that the electronic structure of the bulk liquid and liquid surface are identical.

Introduction

Previously, some of the authors presented total ion yield (TIY) and total electron yield (TEY) X-ray absorption spectroscopy (XAS) measurements and calculations of liquid and gas-

phase water, from which it was deduced that the liquid water surface is comprised of water molecules "with acceptor-only hydrogen bonding configurations [which] constitute an important and previously unidentified component of the liquid/vapor interface."[1] However, new results from experimental and theoretical efforts in our group no longer support this conclusion. Herein, we discuss the new evidence and provide some discussion of what may have led to the previous conclusions.

In contrast to TEY-XAS, which is a bulk probe, TIY-XAS is generally thought to provide a measure of the electronic structure of the *surface* of a sample because of the shallow escape depth (< 5 Å) of ions from the condensed phases [2, 3]. In fact, comparative studies of the EXAFS spectra of liquid jets of water and methanol had shown the TIY to be quite different from the TEY in both cases [4]. Differences between the TEY and TIY XA spectra for ice also demonstrated that the bulk and surface of ice are spectroscopically distinct [5]. Standard EXAFS analyses yielded different O-O distances from the respective TIY than from the TEY, with water exhibiting a lengthening and methanol a contraction. Subsequent theoretical calculations supported this observation of surface relaxation of these fundamental liquids [6-8]. The total ion yield X-ray absorption spectrum of liquid water was previously measured [1, 9]. It was observed that the TIY-XAS spectrum of liquid water strongly resembled the gas-phase water spectrum (see Figure 1), with three sharp features observed at the gas phase positions (corresponding to transitions from the core level 1s orbital to the 4a1, 2b2 and 3a1/3b1 unoccupied water molecular orbitals [10, 11]) that were broadened by ~ 10% [1, 9]. Additionally, two discrete features observed at higher energies in the gas-phase spectrum (corresponding to transitions to multiple Rydberg states [10, 11]) were absent in the TIY liquid spectrum. The absence of these two features was considered as evidence that the observed TIY spectrum originated from the

condensed phase, because the extended nature of Rydberg features should make them particularly sensitive to condensation. Because of this evidence, in addition to the observed broadening of the first three features relative to the gas phase, the experimentally observed TIY spectrum was interpreted, via comparison to a calculated XA spectrum, as indicating that the liquid water surface comprises a substantial fraction of "acceptor-only" molecules [1].

Since the publication of these initial results, a new end-station was designed and built to facilitate measurement of X-ray spectra of highly volatile liquids, such as water. Much effort has subsequently been made to reproduce the previously observed liquid water TIY-XA spectrum using this new end-station, but without success. We have tested and eliminated nearly all possible experimental differences between the old system and the new system that could lead to the observation of a fundamentally different TIY-XA spectrum.

Results

Before discussing the merits of the previously reported TIY-XAS, we begin with a discussion of our more recent observations. The current TIY- XAS generally more strongly resembles the *bulk* liquid XAS spectrum than the gas-phase spectrum. A comparison between the "old" TIY spectrum and a representative "new" TIY spectrum is shown in Figure 1. It is to be noted that the new TIY-XAS (and the gas-phase TIY and liquid TEY) were collected with a step-size of 0.1 eV, whereas the "old" spectrum was collected with a 0.2 eV step-size. All measurements were made at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory.

An important point is that, unlike for the liquid TEY or gas-phase TIY, a great deal of variability is found in the *observed* new TIY-XAS from day to day, and even from scan to scan.

This variability in the observed TIY spectrum is related to the magnitude of the gas-phase contribution to the spectrum. Unfortunately, it is not possible to measure TIY or TEY spectra of liquids with large vapor pressures (> ~1 torr) without some contribution from the vapor phase to the condensed phase spectrum. For the TEY, we routinely observe a factor of 10-100 increase in signal as the liquid jet is translated into the X-ray beam focus, i.e. the condensed phase signal dominates. When this condensed phase enhancement is 100x, it is unnecessary to subtract any vapor signal. In contrast, we have observed a maximum condensed phase enhancement of only a factor of 5 for the TIY. More typical values of the recent TIY enhancement are factors of ~2-3. Thus, the vapor phase contributes significantly to the observed TIY spectrum. Moreover, the vapor contribution has been found to be highly dependent on the specific experimental conditions. Consequently, the nature of the observed TIY (and to a much smaller extent the TEY) is extremely sensitive to experimental conditions, although we have been unable to systematically establish which conditions lead to the largest condensed phase enhancement. Given that the relative escape depths of ions and electrons are very different (~5 Å and ~5-50 nm for ions and electrons, respectively), the liquid volume probed by the TEY is ~10-100x larger than that probed by the TIY and, as a consequence, such a difference in the TEY vs. TIY vapor-liquid enhancement factor is to be expected.

In Figure 1, we show TIY spectra from the gas-phase and condensed phase, and a condensed phase TEY spectrum. For this particular TIY condensed phase spectrum, the vapor contribution was relatively small (~20%). For the presented TEY spectrum, we have purposefully selected a scan where the gas-phase contribution was particularly large, although we note that the majority of TEY spectra actually have a negligible gas-phase contribution. For both the TEY and TIY spectra, it is possible to quantitatively account for the gas-phase

contribution by measuring the appropriate gas-phase spectrum just before (or just after) collection of the liquid-phase spectrum. (The gas-phase spectra are measured by translating the liquid-jet ~0.5 mm away from the X-ray focus.) To entirely remove the vapor contribution to the condensed phase TIY spectrum it is typically necessary to scale the observed vapor phase signal by a factor of ~1.2 before subtraction. It is not unreasonable to think that the actual vapor contribution right above the liquid jet surface is somewhat larger than that measured far from the liquid jet, which explains the scaling factor of 1.2. This vapor subtraction procedure has been performed on both the condensed phase TIY and TEY spectra shown in Figure 1. After vapor subtraction, the observed TIY spectrum is very nearly identical to the TEY spectrum (Figure 2). It is unfortunately not possible to directly compare to an old vapor-corrected TIY spectrum because the gas-phase spectra collected during that time period were usually collected with a step-size of 0.1 eV, compared to the 0.2 eV step-size used for the liquid-phase TIY spectrum.

The new TIY spectrum shown in Figure 1 is an extreme example of a TIY observed with very little vapor contribution. In Figure 3, we show three TIY spectra before vapor subtraction that have differing vapor contributions (~20%, 40% and 70%). The magnitude of the vapor contribution correlates inversely with the condensed phase signal enhancement. The two spectra with larger vapor contributions are more representative of what is typically observed. We note that even when the observed TIY spectrum has a vapor contribution as large as ~70% it is still possible to completely subtract the vapor spectrum and obtain a spectrum that is very similar to the TEY spectrum.

Discussion

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It is of interest that the new experimental TIY is nearly identical to the experimental TEY (after vapor subtraction). A unique surface spectrum for the liquid might be expected based on comparison to TIY spectra of the ice surface. The TIY-XA spectrum of the ice surface shows a very strong, polarization dependent, H^+ dominated pre-edge that does not exist in the bulk ice spectrum [5], demonstrating the unique electronic environment of molecules at the ice surface. However, it was concluded that only the pre-edge peak in the ice surface spectrum originated from direct photon stimulated ion desorption (PSID) of molecules in the topmost layer. The majority of the surface spectrum actually arose from X-ray induced electron stimulated desorption (XESD) by secondary electrons, which explains why the main-edge and post-edge of the ice surface spectrum strongly resembled the bulk ice spectrum [5]. We note also that the position of the observed ice surface pre-edge (~534.45 eV) is distinct from both the first gas-phase feature (534.1 eV) and the small bulk ice pre-edge (535.1 eV) [12], in contrast to the old liquid water TIY, wherein the first peak coincides with that of the gas phase, although it was ca. 10% broader.

The lack of a salient difference between TEY and TIY liquid water spectra suggests that the contribution of XESD processes to the observed TIY spectrum overwhelms the signal resulting from direct photo-ionization of the liquid water surface. The spectrum obtained from ions formed via interactions with electrons generated from bulk water molecules will be identical to the electron spectrum itself [13, 14]. Consider, as an example, the observed ion spectrum from ammonia layers on a Ni(110) surface, where it was determined that the XESD contribution to the observed spectrum was 60% of the total signal [13, 14]. If the ammonia system can be considered a reasonable analog of water, we might then expect a *minimum* bulk contribution to the observed TIY spectrum of 60%. However, even this large contribution of ions from XESD in

the ammonia system was observed when there was a negligible vapor signal above the surface, whereas in our system the vapor phase is substantial. Thus, if electrons from the bulk liquid also ionize the vapor phase around the jet, and it is primarily these ions that are detected in our experiment, then the observed TIY spectrum will strongly resemble the TEY spectrum, consistent with our more recent observations. When a vapor phase spectrum is collected, these secondary ions will be of minimal importance (although we point out that there is still some difference between the TEY and TIY spectra of gas-phase water).

Given the up to 100 times increase in the TEY signal from the condensed phase over the vapor phase, the contribution of XESD processes to the formation of ions will increase when the liquid phase spectrum is measured. Thus, any apparent increase in TIY signal from the condensed phase may not actually originate from photo-ions, but rather from the increased number of electrons generated. As such, the TIY spectrum of highly volatile liquids, such as water, may not provide any unique information about the liquid surface. Note, however, that such processes will have a negligible effect on the observed TEY spectrum.

Although we believe our current TIY spectrum to be "correct" (although perhaps not particularly useful, given the potentially large contribution from XESD processes), we are not yet able to explain what experimental difference has engendered the change from the old spectrum to the new spectrum. For now, we believe that it is not unreasonable to think that the old spectrum might actually be the result of some so-far unidentified experimental artifact.

Additionally, when the old spectrum was originally measured, on ALS Beamline 9.3.2, the simultaneously measured TEY reported along with it was incorrect (Figure 4) [9]. Actually, the TEY reported at that time strongly resembles the bulk *ice* spectrum. The old condensed phase TEY does not give a resolved pre-edge feature and the post-edge of the condensed phase TEY

spectrum is larger than the main-edge [9]. Also, a 10x liquid-vapor enhancement factor was observed for both the TIY and TEY, which is inconsistent with the change in relative escape depths of ions and electrons [1]. Later, when the old TIY was collected on ALS Beamline 8.0.1, the simultaneously measured TEY was still in error, although closer to what is now known to be the correct TEY. These observations strongly suggest the presence of some experimental artifact when the original old TIY spectrum was measured. Although the old TIY may have, on occasion, been observed since this original spectrum was obtained, it is possible that the same experimental artifact that caused the TEY to be distorted in the past occurred again, but went unnoticed. One possible explanation is that the liquid jet position fluctuated during the spectrum acquisition, giving rise to the observed old spectrum. We have observed on occasion that the liquid jet can move significantly during a scan, but that the movement can be smooth so that is not always obvious something changed unless it is known a priori what the spectrum should look like, as is the case with the TEY spectrum. Regardless of having knowledge of the specific conditions that lead to observation of the old TIY spectrum, we now conclude that the old TIY spectrum was not a true measure of the electronic structure of the water surface.

In addition to the experimental difficulties associated with reproducing TIY-XA spectra from volatile liquid jets, as discussed above, the attribution of the old TIY spectrum to acceptor-only molecules was based on comparisons to calculated XA spectra, which we find may have been in error as well. The distinct features in the old spectrum were interpreted, via comparison with density functional theory (DFT) calculations of X-ray spectra obtained using the StoBe-Demon computational package [15], as arising from "acceptor-only" species at the surface [1]. The acceptor-only species identified from these calculations existed in a very specific configuration, with the two hydrogen atoms pointing away from the liquid and a relatively large

O-O distance; in other words, the molecule which yielded this spectrum was essentially a gas-phase molecule in the vicinity of the surface (note the very strong similarity between the calculated acceptor-only spectrum and the calculated gas-phase spectrum [16, 1]). More specifically, the particular "surface" molecule which yielded a calculated spectrum similar to the old TIY spectrum was obtained by first selecting a bulk liquid configuration where the shortest O-O distance was 3 Å and then by eliminating some of the surrounding water molecules. This method of generating "surface" configurations was rationalized because, at the time, the state-of-the-science molecular dynamics simulations (with non-polarizable potentials) of the liquid water surface did not evidence the surface O-O relaxation that was thought to occur [4]. Calculations of molecules at the surface that made even a single hydrogen bond did not yield the gas-phase like sharp features observed in the old spectrum. Undoubtedly, water molecules will exist in a variety of bonding configuration at the surface. The similarity of the observed old TIY to the acceptor-only spectrum was rationalized by assuming that a significant fraction of the ions ejected from the liquid surface arose from molecules in specific acceptor-only configurations, and that all other ionization channels were suppressed. This was not an unreasonable assumption given that, for the water ice surface, H^+ ions dominate the observed TIY spectrum, indicating a sensitivity to a particular ionization channel [5, 12].

To provide a sense of the robustness of the identification of the surface "acceptor-only" species from the calculations, we have performed additional calculations using similar computational methods as in Ref. [1] of six other "acceptor-only" species, using configurations taken from an SPC/E molecular dynamics simulation of the liquid water surface (see Figure 5c) [17]. Surface molecules were identified as those that were within 2 Å of the surface. As expected, these water molecules are found to exist in a variety of bonding configurations where,

in this case, the bonding state (donor, acceptor) of the molecules was specified according to the criteria of *Wernet et al.* (2003) [18]. Here, we have used 17 molecule water clusters, wherein a central water was selected along with the 16 nearest-neighbor waters, based on the oxygen-oxygen distance (R_{OO}). It is evident, even from these few calculations, that the spectra of surface acceptor-only molecules that exist with even slightly different configurations are highly variable. We note that the calculations show that acceptor-only molecules generally exhibit a sharper peak structure at low-energies compared to single-donor or double-donor surface configurations, although some single-donor configurations actually do exhibit the low-energy sharp peaks (Figure 5). Thus, we now find that only calculated spectra for surface acceptor-only molecules with *very specific* (dimer-like) configurations give good agreement with the "old" TIY spectrum.

We have also calculated an effective average surface spectrum from 55 randomly-sampled unique surface water molecules, not all acceptor-only molecules, and an average bulk spectrum from 107 unique bulk water molecules. (Note that the exact nature of the calculated average spectrum depends strongly on the broadening parameters used [19]. Here we have used the same parameters as in Cappa *et al.* (2005) [20]. We have not used the ΔKohn-Sham energy scale correction [21] because this has been demonstrated to be unnecessary in producing average water spectra [22], although is certainly important when comparison of spectra of individual molecules is desired.) The calculated average XA spectra of the bulk and surface water molecules are very different (Figure 6). The calculated pre-edge intensity for the average surface is large compared to that of bulk water, as is the calculated main-edge intensity, suggesting that if the experimental TIY were a true probe of the electronic structure of the liquid surface then we should not observe such similar condensed phase TEY and TIY.

It is of interest to consider whether the difference between the calculated bulk and surface spectra arises purely from sampling statistics (e.g. the surface spectrum has fractionally more no-donor and single-donor configurations than double-donor configurations compared to the bulk spectrum) or if there are spectral differences even within these broad classes. Average no-donor, single-donor and double-donor spectra for the bulk and surface molecules are shown in Figure 7. We find that the average double-donor spectra for the bulk and surface are very similar, whereas both the average single-donor and no-donor spectra exhibit distinct differences between bulk and surface. In particular, the average single-donor surface spectrum has a much more distinct pre-edge and a main-edge that is larger than the post-edge. Thus, we see that the difference in the calculated XAS between the bulk and surface arise not only from statistical sampling differences, but also from differences in the average spectra within the hydrogen-bonding classifications. We suspect this is because, in the case of surface molecules, there is no molecule that resides in the vicinity of the free -OH whereas, for the bulk molecules, there is still a molecule in the general vicinity of the free -OH, even if a hydrogen bond is not technically formed based on the Wernet et al. criterion (Figure 7).

The three peak structure that was characteristic of the "old" TIY spectrum is not observed in the calculated average spectrum, consistent with the idea that only acceptor-only molecules in very specific configurations yield the observed "old" TIY. A sampling of the individual surface XA spectra used to calculate the average spectrum is shown in Figure 5. Assuming that the MD simulation used to obtain the molecular configurations for the XA spectra calculations provides a reasonable representation of the distribution of actual molecular orientations found at the liquid surface, this result suggests that the calculated spectrum used in Ref. [1] does not actually provide a realistic picture of the predominant species existing at the liquid water surface. We

cannot completely rule out the possibility that the observed XA spectrum arises from a specific ion channel (e.g. protons), the signature of which is not captured by these calculations. Given the above discussion, the assignment of the "old" TIY spectrum to very specific acceptor-only hydrogen bond configurations (where the hydrogens point away from the surface) as deduced from a *single* calculation should now be questioned.

In this study we have only addressed the measurement and interpretation of the near-edge X-ray absorption fine structure spectrum (XAS) of liquid water. Measurements of the extended X-ray absorption fine structure spectrum (EXAFS) spectrum were also previously reported for both pure water and liquid methanol in a comparative study [4]. In EXAFS spectroscopy, the absorption spectrum is measured to energies well beyond the K-edge ionization potential, in this case from ~550 – 1000 eV. The slow oscillations in spectral intensity in this region provide quantitative information on the coordination environment of substances (e.g. for water the number of nearest neighbors and R_{OO}) [23]. There were clear differences observed in the EXAFS oscillations between the measured liquid phase TEY and TIY spectra for both water and methanol. These differences were interpreted as indicating the difference in coordination environment between molecules at the surface and in the bulk liquid. Quantitative analysis of the observed TIY and TEY EXAFS indicated that R_{OO} for water molecules at the liquid surface is somewhat longer (ca. 5%) than the bulk phase value. In contrast, for methanol it was determined that the R_{OO} distance decreases at the surface by about the same amount. Although both are reasonable results, and are consistent with several published theoretical calculations (water and methanol) [6-8] and SFG experiments (methanol only) [24, 25], one might question the previous analysis if indeed it is established the TIY does not provide a straightforward probe of the surface electronic structure. In particular, the potential influence of having a significant vapor

phase or XESD contribution to the observed EXAFS spectrum should be considered, but is beyond the scope of the present study. In the end, we cannot presently make any definitive conclusions regarding the veracity of the liquid water and liquid methanol EXAFS measurements. However, given the large differences of the "old" and "new" XA spectra, it would seem that the EXAFS results should likewise be reconsidered [4].

References:

[1]   Wilson K R, Cavalleri M, Rude B S, Schaller R D, Nilsson A, Pettersson L G M, Goldman N, Catalano T, Bozek J D and Saykally R J 2002 Characterization of hydrogen bond acceptor molecules at the water surface using near-edge x-ray absorption fine-structure spectroscopy and density functional theory *J. Phys. Cond. Matt.* **14** L221-L6

[2]   Smith J D, Cappa C D, Messer B M, Cohen R C and Saykally R J 2005 Response to Comment on "Energetics of hydrogen bond network: Rearrangements in liquid water" *Science* **308** -

[3]   Stöhr J 1992 *NEXAFS spectroscopy* (Berlin ; New York: Springer-Verlag)

[4]   Wilson K R, Schaller R D, Co D T, Saykally R J, Rude B S, Catalano T and Bozek J D 2002 Surface relaxation in liquid water and methanol studied by x-ray absorption spectroscopy *J Chem. Phys.* **117** 7738-44

[5]   Coulman D, Puschmann A, Hofer U, Steinruck H P, Wurth W, Feulner P and Menzel D 1990 Excitation, Deexcitation, and Fragmentation in the Core Region of Condensed and Adsorbed Water *J Chem. Phys.* **93** 58-75

[6]   Kuo I F W and Mundy C J 2004 An ab initio molecular dynamics study of the aqueous liquid-vapor interface *Science* **303** 658-60

[7]   Matsumoto M and Kataoka Y 1989 Molecular-Orientation near Liquid Vapor Interface of Methanol - Simulational Study *J Chem. Phys.* **90** 2398-407

[8]   Patel S and Brooks C L 2005 A nonadditive methanol force field: Bulk liquid and liquid-vapor interfacial properties via molecular dynamics simulations using a fluctuating charge model *J Chem. Phys.* **122** -

[9]   Wilson K R, Rude B S, Catalano T, Schaller R D, Tobin J G, Co D T and Saykally R J 2001 X-ray spectroscopy of liquid water microjets *J. Phys. Chem. B* **105** 3346-9

[10]   Diercksen G H F, Kraemer W P, Rescigno T N, Bender C F, Mckoy B V, Langhoff S R and Langhoff P W 1982 Theoretical-Studies of Photo-Excitation and Ionization in H2o *J Chem. Phys.* **76** 1043-57

[11]   Kim D Y, Lee K, Ma C I, Mahalingam M, Hanson D M and Hulbert S L 1992 Core-Hole Excited-States of H2o - Symmetries and Relative Oscillator-Strengths *J Chem. Phys.* **97** 5915-8

[12]   Parent P, Laffon C, Mangeney C, Bournel F and Tronc M 2002 Structure of the water ice surface studied by x-ray absorption spectroscopy at the OK-edge *J Chem. Phys.* **117** 10842-51

[13]   Jaeger R, Stohr J and Kendelewicz T 1983 X-Ray-Induced Electron-Stimulated Desorption Versus Photon Stimulated Desorption - Nh3 on Ni(110) *Surface Science* **134** 547-65

[14]   Jaeger R, Stohr J and Kendelewicz T 1983 Ion Desorption from Surfaces Following Photon Excitation of Core Electrons in the Bulk *Physical Review B* **28** 1145-7

[15]   Hermann K, M. P L G, Casida M E, Daul C, Goursot A, Koester A, Proynov E, St-Amant A, Salahub D R, Carravetta V, Duarte H, Godbout N, Guan J, Jamorski C, Leboeuf M, Malkin V, Malkina O, Nyberg M, Pedocchi L, Sim F, Triguero L and Vela A 2004 StoBe Software v.2.0.

[16]   Cavalleri M, Ogasawara H, Pettersson L G M and Nilsson A 2002 The interpretation of X-ray absorption spectra of water and ice *Chem. Phys. Lett.* **364** 363-70

[17] Jungwirth P and Tobias D J 2002 Ions at the air/water interface [Review] *J Phys. Chem. B* **106** 6361-73

[18] Wernet P, Nordlund D, Bergmann U, Cavalleri M, Odelius M, Ogasawara H, Naslund L A, Hirsch T K, Ojamae L, Glatzel P, Pettersson L G M and Nilsson A 2004 The structure of the first coordination shell in liquid water *Science* **304** 995-9

[19] Smith J D, Cappa C D, Messer B M, Drisdell W S, Cohen R C and Saykally R J 2006 Probing the local structure of liquid water by x-ray absorption spectroscopy *J. Phys. Chem. B* **110** 20038-45

[20] Cappa C D, Smith J D, Wilson K R, Messer B M, Gilles M K, Cohen R C and Saykally R J 2005 Effects of alkali metal halide salts on the hydrogen bond network of liquid water *J. Phys. Chem. B* **109** 7046-52

[21] Triguero L, Pettersson L G M and Agren H 1998 Calculations of near-edge x-ray-absorption spectra of gas-phase and chemisorbed molecules by means of density-functional and transition-potential theory *Phys. Rev. B* **58** 8097-110

[22] Cappa C D, Smith J D and Saykally R J Unpublished results

[23] Teo B K, Joy D C and Materials Research Society. 1981 *EXAFS spectroscopy, techniques and applications* (New York: Plenum Press)

[24] Stanners C D, Du Q, Chin R P, Cremer P, Somorjai G A and Shen Y R 1995 Polar Ordering at the Liquid-Vapor Interface of N-Alcohols (C-1-C-8) *Chemical Physics Letters* **232** 407-13

[25] Wolfrum K, Graener H and Laubereau A 1993 Sum-Frequency Vibrational Spectroscopy at the Liquid Air Interface of Methanol - Water Solutions *Chemical Physics Letters* **213** 41-6
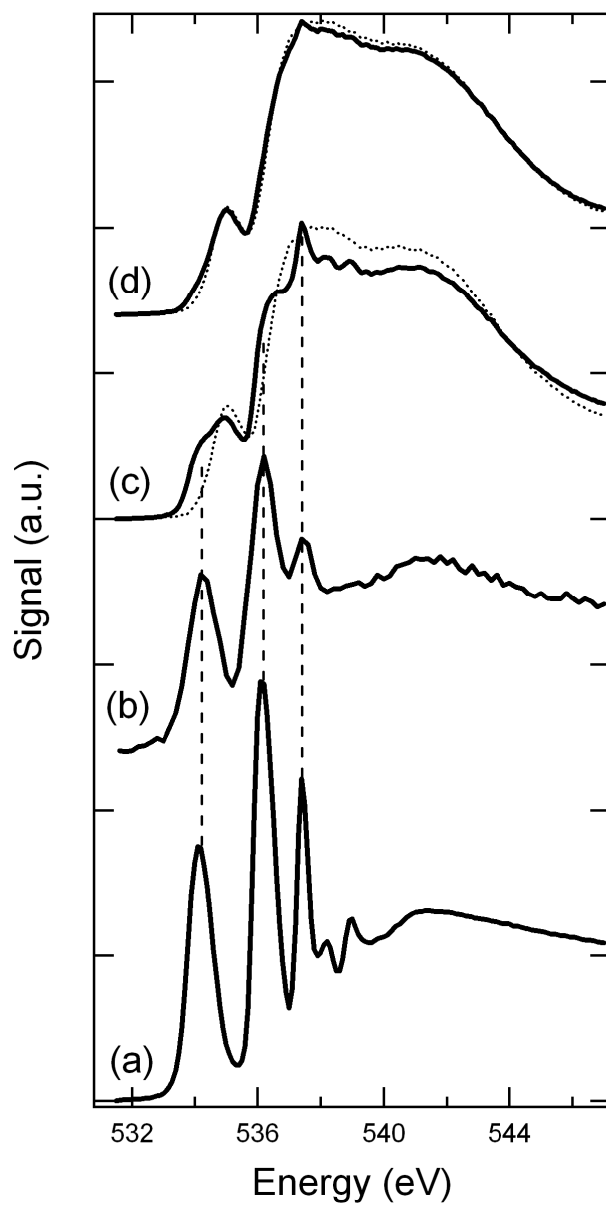
Figure 1. Observed XA spectra of water (solid lines). (a) The TIY spectrum of gas-phase water. (b) The previously observed "old" liquid water TIY spectrum [1, 9]. (c) A more recently obtained "new" liquid water TIY spectrum. (d) The bulk sensitive TEY spectrum of liquid water. The dotted lines show the spectra after vapor subtraction.
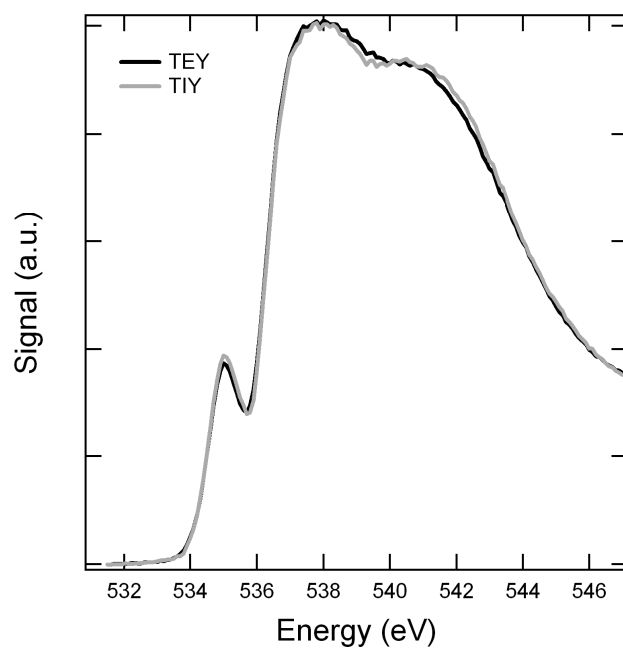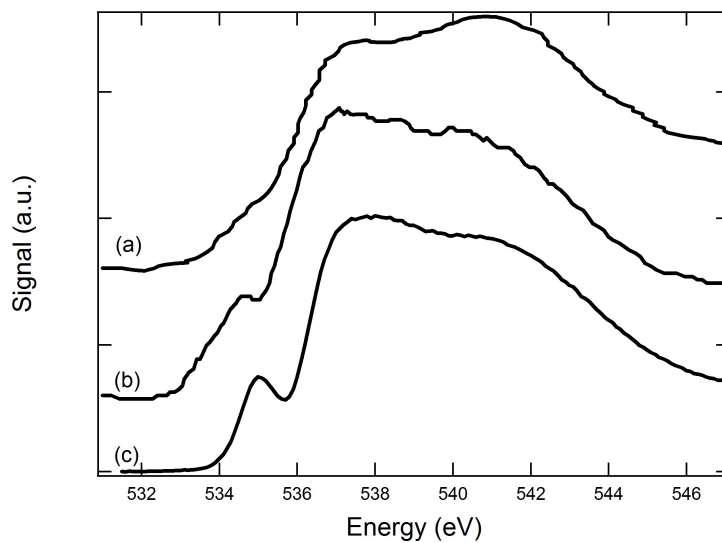
Figure 2. Experimental TEY and TIY spectra of liquid water after gas-phase subtraction. The raw spectra are shown in Figure 1.
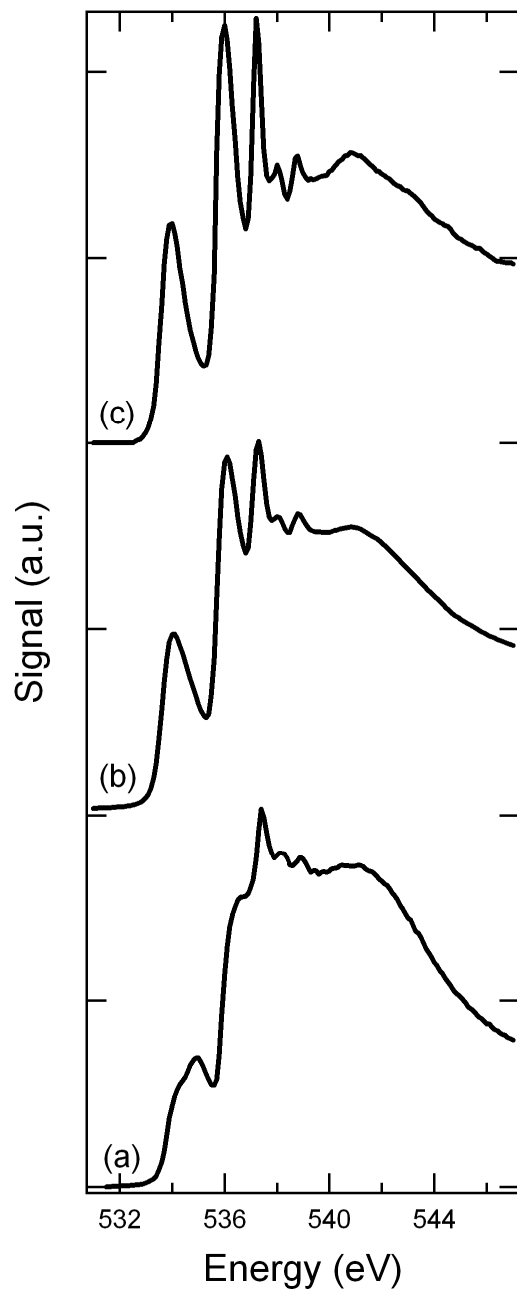
Figure 3. "New" experimental TIY-XA spectra of liquid water for a (a) ~20% vapor contribution, (b) ~40% vapor contribution and (c) ~70% vapor contribution to the observed spectrum.

Figure 4. Experimentally observed TEY. (a) The TEY reported in Ref. [9] that was obtained around the same time as the "old" TIY. (b) The TEY reported in Ref. 1. (c) A more recent TEY that is known to be correct.
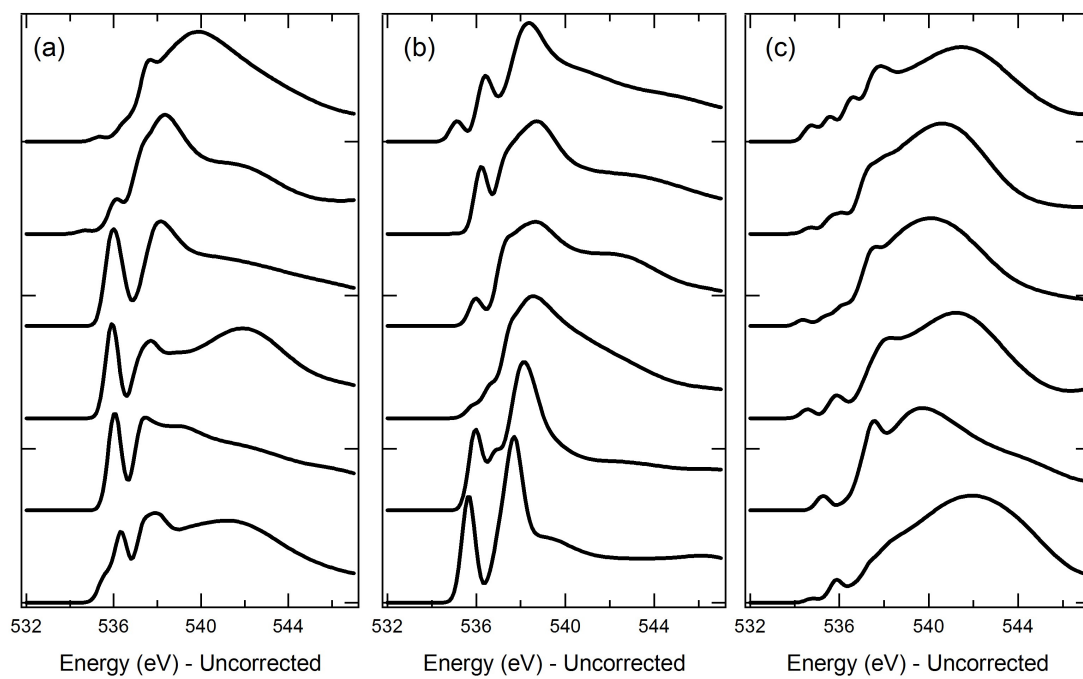
Figure 5. Calculated XA spectra of individual liquid "surface" molecules. Panel (a) shows only no-donor (i.e. acceptor-only), (b) single-donor and (c) double-donor species.
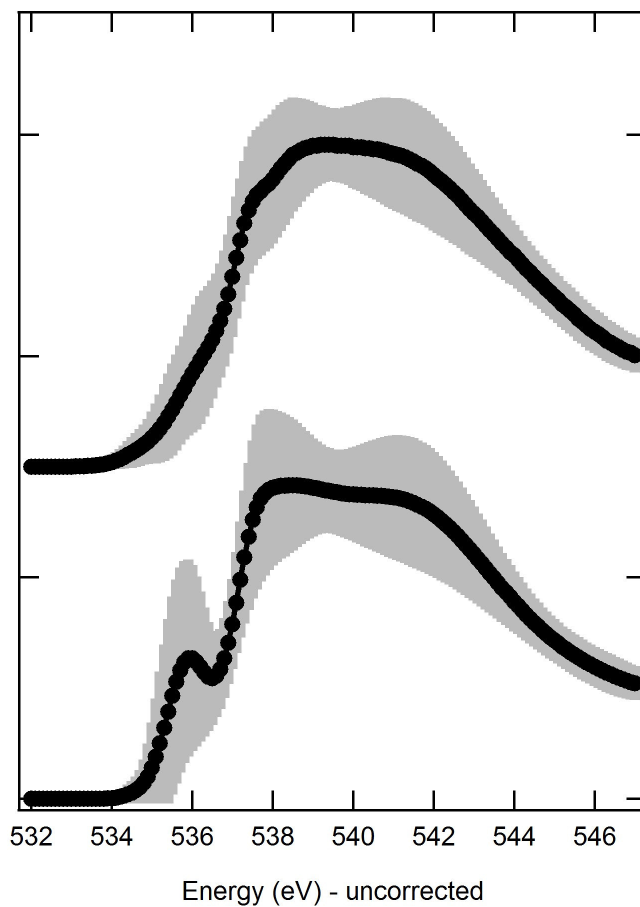
Figure 6. Calculated bulk (top) and surface (bottom) average XA spectrum. The bulk spectrum is the average of 107 individual spectra, and the surface spectrum is the average of 55 individual spectra. The gray regions indicate the 1σ variation in the calculated spectra.
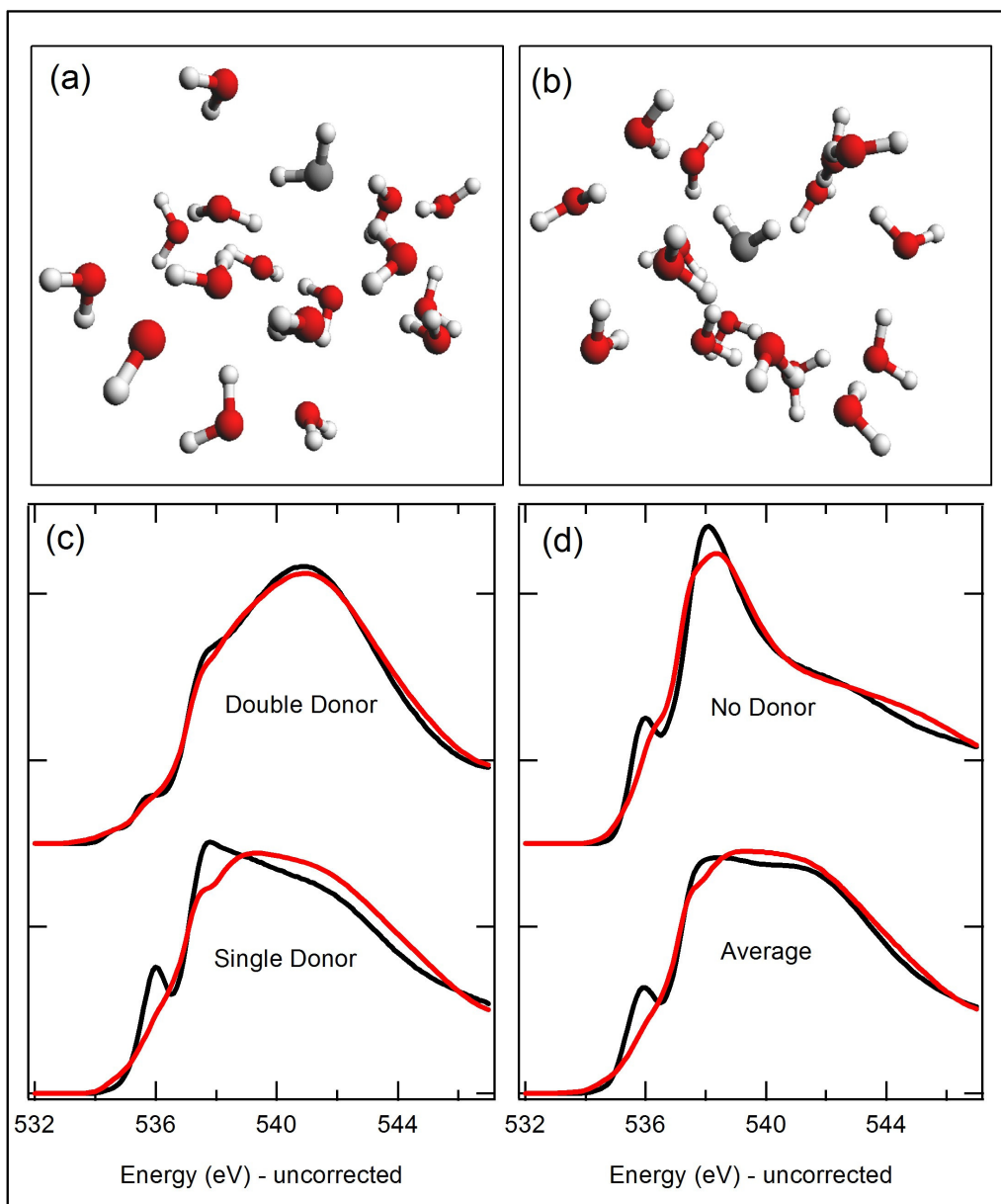
Figure 7. Sample configurations for single-donor (a) surface and (b) bulk molecules demonstrating the differing nature of the "free" –OH bond. The water molecule of interest is shown in gray. The calculated average spectrum for (c) single and double-donor molecules and (d) no-donor molecules and the total average for the bulk (red) and the surface (black).