Volume 1 | Number 1 | Jan 2013 | Pages 1–100

PCCP

Physical Chemistry Chemical Physics
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Solvation dependence of valence electronic states of water diluted in organic solvents probed by soft X-ray spectroscopy

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Abstract

The knowledge of hydrogen bonds is important in a wide range of scientific fields. However, information on the electronic state of hydrogen bonded molecules in liquids and solutions is still limited. We applied X-ray emission and absorption spectroscopy to observe the electronic state around oxygen of water and investigate the solvent dependence of occupied and unoccupied valence electronic states of water in acetonitrile, 3-methylpyridine, and ethylenediamine at room temperature under atmospheric pressure. Based on the direct comparison of the spectra, the pronounced variation of the unoccupied $2b_2$ state of water in acetonitrile and 3-methylpyridine was assigned to difference of the dipole-dipole interaction and the donor hydrogen bond. For ethylenediamine solution, an enhancement of the peak structure in the post-edge region of X-ray absorption spectra and an evident shoulder structure on the higher energy side of the occupied $1b_1$ state in X-ray emission spectra were observed. Although ethylenediamine has two amino groups that can form the hydrogen bonds as a proton donor, obtained results indicate that the amino groups of ethylenediamine also act as a proton acceptor in the hydrogen bond between water molecules. A systematic peak intensity variation of the pre-edge peak corresponding to the lowest unoccupied molecular orbital, $4a_1$, was also found through the comparison of three organic solvents. Since the peak intensity tends to decrease with increasing the number of hydrogen bonds, the results can be interpreted by the covalency of hydrogen bond.

Introduction

Intermolecular interactions play important roles in the properties and reactions of molecules in liquids. In particular, the hydrogen bond is important in a wide range of scientific fields, including physics, chemistry, and biology. For example, intramolecular hydrogen bonds retain the structure and function in biological molecules such as proteins and DNA. Hydrogen bonding in cellulose polymers of wood or cotton is responsible for their physical strength. In addition, the hydrogen bond is involved in the catalysis of enantioselective synthesis.[1] The hydrogen bond is also linked to the efficiency of dye-sensitized solar cells because the contamination of water in acetonitrile decreases the efficiency of the cell due to the adsorption of water on the surface by hydrogen bonding.[2] Since the understanding of the hydrogen bonding can promote a wide range of research, many spectroscopic techniques has been used to determine the structure and character of hydrogen bonding networks. However, the understanding of hydrogen bonds is still limited considering its

importance, and further information on the electronic state in liquids and solutions is required.

Recently, spectroscopic techniques using soft X-rays, such as X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS), have been applied to liquid water.[3-6] High resolution XES studies on liquid water revealed that XES is sensitive to chemical environments including hydrogen bonds, and exhibits two sharp peaks in the lone pair region.[7, 8] Since this discovery, XES spectra of liquid water have been extensively studied. [9-16] Spectral variations of water in XAS and XES have been reported for water molecules in a micelle lattice,[17] aqueous solutions,[13, 18] binary mixtures[19-22] and used as tools to detect the local environment around a water molecule. XAS and XES probes electronic states via electron transitions; i.e. XAS probes occupied valence electronic states via transitions of core electrons to valence unoccupied orbitals, and XES probes occupied valence electronic states via transitions of valence electrons filling core hole generated by electronic excitation such as X-ray absorption. Therefore, it is important to clarify the relationship between the spectra and intermolecular interactions for XAS and XES for further understanding of the electronic state in liquids and solutions.

In this report, we focus on the binary mixtures of water and organic solvents. There have been reports on XAS and XES of water/acetonitrile,[19, 20] heavy water/acetonitrile[21] and heavy water /3-methylpyridine[22], while the solvation dependence of the electronic structure of water in organic solvents is unclear. Therefore, we investigated the solvation dependence of O1s XAS and XES spectra of water molecules dissolved in organic solvents which do not contain oxygen atoms. Owing to the element selectivity of these methods, the use of organic solvents without oxygen atoms has the advantage because the obtained spectra directly reflect information about the molecular orbitals (MOs) of water in solvents. In our previous study of D_2O/3-methylpyridine mixture[22], we found that XES spectra of diluted solution exhibited simple three peaks structure similar to D_2O in the gas phase and concluded that the water molecules are solvated by the organic solvent without direct water-water interactions. Hence, highly diluted solutions were chosen as samples to observe interactions between water molecule and organic solvents.

The solvent dependence of O1s XAS and XES spectra for D_2O water diluted in solutions of acetonitrile (AN), 3-methylpyridine (3MP), and ethylenediamine (EDA) was successfully detected and the spectral variation of XAS for water in AN and 3MP was analyzed using theoretical calculations based on the density functional theory (DFT). The organic solvents compared here are typical solvents that have different interactions with water molecules. EDA has two amino groups that can form hydrogen bonds as donor. 3MP has a nitrogen atom in the pyridine ring that can act as an acceptor site for a hydrogen bond[23, 24]. The interaction between water and AN in the diluted solution was dominated by dipole-dipole interactions according to a study that used X-ray diffraction combined with IR spectroscopy.[25] Therefore, the results provide important information on how intermolecular interactions affect the occupied and unoccupied valence electronic structures, i.e., MOs, of water. In addition, the successful detection of pronounced solvation dependence in the spectra provides an experimental proof of the sensitivity of these methods for hydrogen bonds.

Method

O 1s XES and XAS experiments were performed at the SPring-8 synchrotron radiation facility using the soft X-ray beamline BL17SU.[26, 27] All the spectra were measured using a liquid flow cell with a 150 nm-thick Au-coated thin-film SiC window (NTT Advanced Technology Co., Japan) to separate the liquid flow at atmospheric pressure from the high-vacuum region (see Ref.[28] for details of the liquid flow cell). The XAS spectra were recorded as total fluorescence yields using a standard 100 mm^2 Si photodiode (IRD AXUV-100, Opto Diode Corp., USA) facing the window. The photoelectrons emitted from the window were eliminated by placing an electrically biased mesh screen in front of the photodiode. Circularly polarized X-rays were used for both XES and XAS measurements to gain a higher photon flux. The energy resolution of the O 1s XAS measurements was about 0.1 eV. The energy resolution of the O 1s XES measurements was about 0.35 eV.

The samples were prepared by mixing the organic solvents, 3-methylpyridine (99.0%), acetonitrile (99.8%), and ethylenediamine (99.0%), with heavy water (D_2O 99.9%, Cambridge Isotope Laboratories, Inc., USA). All organic solvents were purchased from Wako Pure Chemical Industries Ltd., Japan and were used without further purification. Heavy water (D_2O) was chosen to minimize

the core-hole induced effect,[29] which results in the peak broadening of XES spectra. To investigate water molecules solvated without water-water hydrogen bonding interactions, low-concentration solution of D_2O was prepared. Appropriate concentration of diluted solutions of D_2O was determined with aid of previous studies. For AN-water mixture, an X-ray diffraction study combined with IR spectroscopy [25] revealed that the dipole-dipole interaction becomes a dominant interaction for lower concentration below water molar fraction of 0.3, while water-water hydrogen bonds are evident in the mixtures for higher concentration. For 3MP- water mixture, our previous study using XAS and XES [22] shows that D_2O molar fraction of 0.2 is almost enough to achieve solvated water molecule without water-water interaction. For EDA-water mixture, as far as we know, experimental information is still limited to decide appropriate concentration. However, ethylenediamine interact with water molecule by hydrogen bonds[30, 31] and should easily solvate water molecule through hydrogen bonds in the mixture. Thus, appropriate concentration for EDA-D_2O solution should not be far from that of AN and 3MP solution. Finally, samples with molar fraction X_{D2O}=0.1, which should be dilute enough to achieve solvated water molecule without water-water interaction for all of three organic solvents investigated here, were prepared for XAS measurements. In XES measurements, the signal intensity was low due to low acceptance angle of the spectrometer compared to the photodiode. As a result, we need to increase concentration to get reliable data to X_{D2O}=0.17, and that of 3MP solution was X_{D2O}=0.2 for AN solution and 3MP solution. However, selected concentration is still dilute enough to achieve solvated water molecule without water-water interaction according previous studies mentioned above.[22, 25]

All XAS and XES spectra were measured at room temperature. As detailed in our previous report,[22] the background signals from oxygen impurities in the SiC window, i.e., surface natural oxides, were estimated by measuring the XAS and XES spectra of pure solvents and subtracted them from the spectra of all samples.

Spectrum calculations for XAS were performed using half core-hole wave functions within the framework of a transition potential method[32] by the StoBe-deMon code, [33] which calculates the intensity of each peak structure in the XAS spectra by evaluating the dipole transition probabilities between core and valence orbitals.[34] The core-excited oxygen atom was described using the IGLO-III basis of Kutzelnigg et al.,[35] and the non-core-excited oxygen atom was described by effective core potentials.[36] (5211/411/1) and (311/1) basis sets were applied to the carbon and hydrogen atoms, respectively. To determine the energy position of the excited states, normal ΔKohn-Sham calculations were performed to compute the ionization energies of the highest occupied molecular orbital (HOMO) and core orbital. Because of the difficulty in determining a reliable model for the molecular geometry in solution, the molecular geometry was optimized as a complex of one water molecule and one or two molecules of organic solvent without surrounding solvents. Geometry optimizations of clusters were performed using Gaussian 09[37] at the MP2/cc-pVTZ level.

Results

The left panel of Fig. 1 shows the O 1s XES spectra of pure D_2O, and D_2O diluted in acetonitrile (D_2O/AN), 3-methylpyridine (D_2O/3MP), and ethylenediamine (D_2O/EDA). D_2O molar fractions (X_{D2O}) of the samples are around 0.1–0.2 as indicated in the labels besides each spectrum. The excitation energy for the XES measurement was 550 eV, i.e., non-resonant excitation. The non-resonant XES spectrum of water vapor (D_2O) reported previously by Weinhardt et al. [38] was also plotted for comparison. Because of the low signal intensity of the X-ray emission from diluted water in the solvents, the S/N ratio of each mixture sample spectra is worse than that the spectrum of pure D_2O water.

Since the selected organic solvents have no oxygen atoms in their molecular structures, O1s XES spectra reflect the electronic structure of D_2O molecule in the samples. The spectral features of O1s XES on water vapor reflect the occupied valence orbitals, $1b_2$, $3a_1$, and $1b_1$. [4] [6, 38] The corresponding three components are also well resolved in the XES profile of water in organic solvents. Compared to the spectra of liquid water, which shows peak splitting in the lone pair $1b_1$ state, XES spectra of diluted water in AN and 3MP exhibited simple spectral shapes with only three peaks seen for D_2O in the gas phase. This is because the water molecules are in a solvated state without water-water

interactions in contrast to the complex hydrogen bonding network of bulk liquid water.

XES spectra of D_2O/AN mixture is consistent with previously reported XES spectra using liquid microjet[21] by taking differences of sample condition, such as pressure and temperature, into account (see Electronic Supplementary Information for a comparison of the spectra). The AN solution showed a fine peak for the $1b_1$ state with peak width of 0.8 eV (FWHM), which is slightly broader than the peak width for gaseous D_2O. The $1b_1$ peak was shifted about 0.35 eV toward lower energy compared to that in gaseous D_2O. The $1b_2$ state was also shifted about 0.35 eV lower energy compared to that in the gas phase. However, the peak width was almost the same as gaseous D_2O around 2 eV (FWHM). The structure corresponding to the $3a_1$ state appeared in between the $1b_1$ and $1b_2$ peaks. Interestingly, the peak shape was different from the gas phase D_2O peak and had a broad trapezoidal shape.

The 3MP solution also showed the $1b_1$ peak shifted by around 0.5 eV towards lower energy compared to that in gaseous D_2O. The $1b_2$ peak appeared at almost the same energy position and had a comparable width to that of the AN solution. The structure corresponding to $3a_1$ has a symmetric shape, which is different from the AN solution, but similar to that in the gas phase D_2O. The peak position shifted about 0.5 eV toward lower energy compared to that in the gas phase D_2O.

The EDA solution has a slightly different tendency in terms of its spectral shape. The EDA solution has the corresponding $1b_1$ structure, but it also has a shoulder structure on the higher energy side. The $3a_1$ structure is broad and ambiguous compared to that of the gas phase, AN, and 3MP solutions. The $1b_2$ structure appeared at around 0.6 eV higher energy position compared to that of the gas phase water.

The right panel of Fig. 1 shows the O 1s XAS spectra of heavy water (D_2O) diluted in AN, 3MP, and EDA mixtures, pure D_2O, and water (H_2O) in the gas phase reported by Myneni et $al.$[4] XAS spectra of the binary solutions were normalized to have the same intensity at a non-resonant region around 548 eV. The concentration of samples is 0.1 in water molar fraction (X_{D2O}) as indicated by the labels besides each spectrum. The peak structures in the measured spectrum of pure liquid D_2O were not clear because of the saturation effect on the fluorescence yield detection;[39] therefore, a correction for the saturation effect was necessary and applied based on a previous report of saturation correction for XAS.[39] Once corrected for the saturation effect, three structures, the pre-edge (535 eV), main-edge (537−538 eV), and post-edge (539−541 eV), become apparent and match the previously reported XAS spectrum for liquid water.[6] For highly diluted samples, the saturation effect is typically negligible.[40] In fact, XAS spectra of D_2O/AN are consistent with the previously reported spectra of H_2O/AN acquired using X-ray Raman scattering (XRS) which provides the same information of XAS without suffering the saturation effect by using high energy X-rays[20].

The $4a_1$ and $2b_2$ peaks of the water molecule show differences in solvation dependence. The electronic state corresponding to $4a_1$ commonly appears as a pre-edge structure around 534−535 eV. However, the peak energy and intensity are different in different solvents. $2b_2$ derived state appears as a pronounced peak structure at 536.5 eV in AN. In EDA and 3MP solutions, a broad structure around 537 eV is evident with a similar shape to that seen in pure D_2O. The post-edge structure observed around 540eV for liquid water also shows solvation dependence. While the post-edge structure almost disappears in the 3MP solution, the post-edge structure is enhanced in the EDA solution.

Here, it should be mentioned on the consistency of obtained spectra with the experimental data using a liquid microjet. Recently, an experimental study using a liquid microjet in vacuum reported that O1s XAS spectra using a liquid flow cell contain artifacts induced by "structuring due to interaction with a membrane" based on the comparison of experimental data using a liquid cell[41] and a liquid microjet[19]. However, the spectra obtained here resemble the reported spectra of liquid microjet.[19] Therefore, we concluded that the effect of membrane window is negligible for our liquid flow cell design[28].

Discussion

The three organic solvents investigated are different in terms of their expected interactions with water diluted in the solvents. EDA has two amino groups that can act as a hydrogen bond donor. According to calorimetric measurements of the 3MP solution of water,[24] water molecules have hydrogen bond that connects to a nitrogen site of 3MP, which act as a hydrogen bond acceptor, in the diluted sample. AN also has a nitrogen site that can form hydrogen bonds as an acceptor. However, the interaction between water and AN in the diluted solution, molar fraction of water $X_{H2O} \leq 0.1$, was dominated by dipole-dipole interactions according to a study of X-ray diffraction combined with IR spectroscopy.[25]

Spectral variations in O1s XAS and XRS for water molecules were reported for reverse micelles,[42] aqueous solutions,[13, 43, 44] and high-pressure, high-temperature water.[45] These variations were used as a tool for detecting the local environment around a water molecule. However, there are some arguments on the assignments of the variation in the O1s XAS spectra of water and aqueous solutions.[46, 47] Therefore, the discussion here will begin with a comparison of XAS spectra for a simpler system, water diluted in 3MP, where water molecules form hydrogen bonds as a donor to 3MP.

In terms of unoccupied MOs, the $2b_2$ state (536 eV in the gas phase) shows clear solvation dependence. The $2b_2$ is apparent only for the AN solution in the three investigated organic solutions. The 3MP and EDA solution shows a broad structure around 537 eV with a similar shape to that of liquid D_2O. Therefore, it is possible to consider the $2b_2$ state is sensitive to the presence of a hydrogen bond.

The Rydberg state, which appeared as a fine peak series at around 537–539 eV [4, 48, 49] for isolated gas phase water, did not have a corresponding peak for the water diluted in 3MP. The missing of Rydberg states were common for all the dilute D_2O solutions investigated in this report. According to the literature, the Rydberg states are sensitive to the hydrogen bond configuration.[50] Therefore, it is possible to assume that the Rydberg states disappear due to the solvation interaction in a solution.

To further investigate the variation of XAS spectra, spectral calculations of O1s XAS were performed. A complex containing one water molecule was chosen because the systems under investigation are highly diluted solutions. For simplicity, 1:1 complex of water-3MP and AN-water were calculated at first.

Fig. 2 shows the calculated O1s XAS spectra for an isolated water molecule, a water-AN complex and a water-3MP complex. Optimized geometries of each complex are schematically shown in the left side of the figure (see Electronic Supplementary Information for optimized geometries in xyz coordinates). The calculated XAS spectrum of an isolated water molecule shows pronounced $4a_1$ and $2b_2$ peaks resembles the experimental XAS spectra of gas phase water. While the water-AN complex shows an evident $2b_2$ peak structure, this peak structure is completely diminished in the water-3MP complex. Hence, one can conclude that the overall trend of variation in the calculated XAS spectra qualitatively agrees with the experimental data.

The major difference in the calculations for these complexes is the relative configuration of water and organic molecule. While the N atom of 3MP is almost on the axis of O-H for the water-3MP complex, the N atom of AN is not on the O-H axis for the water-AN complex. In addition, the O-N distance in the AN-water complex is 1.11 times longer than that of the 3MP-water complex. Because 3MP has a nitrogen atom in the pyridine ring, which can form hydrogen bonds between water molecules, a linear configuration of O-H and N is the result of an O-H···N hydrogen bond. In the water-AN complex, the C-N axis of AN is almost parallel to the principal axis of the water molecule, and hence the configuration of the water-AN complex should correspond to the dipole-dipole interaction. This calculation result indicates that the missing $2b_2$ peak structure in the O 1s XAS spectrum of D_2O in 3MP is attributable to perturbation induced by hydrogen bond formation with 3MP, i.e., O-D···N hydrogen bond.

While calculation results for the 1:1 complex show a pronounced $2b_2$ peak, the experimental XAS spectra for the AN-water mixture show a broad structure beneath the pronounced peak structure for $2b_2$ state. For further investigation of the origin of this broad structure, 1:2 complexes were additionally calculated. As shown in Fig. 2, the calculated results for the 1:2 complex show a broadened peak structure. In solution, a water molecule should form a complex with more than one AN molecule through dipole-dipole interactions. It is reasonable to think that multiple interactions of

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water molecules with AN molecules are the origin of the broad structure beneath the $2b_2$ peak. XES spectra also support this conclusion. XES spectra of $D_2O/3MP$ and D_2O/AN almost show three peak structures with narrow widths comparable to gas D_2O peaks. One remarkable exception is $3a_1$. The peak shape of $3a_1$ for D_2O/AN is different from that of gas phase D_2O and $D_2O/3MP$ and is a broad trapezoidal shape. The broad peak shape of $3a_1$ may imply that there are variations in the surrounding environment of water due to multiple dipole-dipole interactions.

The influence of hydrogen bonding and dipole interactions on XAS spectra makes O1s XAS a useful method for detecting the interaction of a water molecule with the surrounding solvent molecules in a binary solution of water and organic solvent. Using XAS and XES spectra as an indicator for the interaction between water and organic solvents, the hydrogen bonding of water in EDA solutions is discussed further.

Compared to AN and 3MP solutions, the EDA solution of water shows a pronounced difference in XAS and XES spectra. The XAS spectrum shows a broad peak structure in the post-edge region (539−541 eV). In the XES spectrum, the $1b_1$ state of the EDA solution has a peak with a shoulder structure. It is reasonable to exclude the water-water interactions as the origin of the peak structure in XAS and the shoulder structure in XES because the sample concentration of the EDA solution, X = 0.1, is even more dilute than the concentration of other sample solutions of AN and 3MP. For aqueous solutions, hydroxide ions should be listed as a possible reason for the difference in XAS and XES spectra since the amino groups of amines tend to protonate and generate hydroxide ions in the solution. However, differently from aqueous solution which contains huge amount of water molecule, organic solution investigated here only contains quite low amount of water molecule. According to previous study of Fuchs et $al.,$[7] hydroxide ions (OH^- and OD^-) in aqueous solution has a peak structure at around 533.2eV in O1s XAS spectra. In the XAS spectra of EDA solution of water presented in Fig.1, no peak structure around 533.2eV was observed.   Hence, one can conclude that probability of deprotonation of water molecule in ethylenediamine solution should be negligible. Hydroxide ions generated in the solution due to deprotonation of water can be also excluded from the reason of the pronounced difference in XAS and XES spectra. Another possibility is the effect of core-hole induced dynamics.[29] However, it is natural to consider that core-hole induced dynamics are suppressed by the choice of heavy water for the sample. In addition, the core-hole induced dynamics of a water molecule at non-resonant excitation is quite small according to experimental studies of water in the gas phase.[38] Indeed, the core-hole induced dynamics is appeared only in XES spectra in principle. The peak structure in XAS spectra cannot be explained by core-hole dynamics. Hence, the solvation structure around water molecules remains as an origin of the difference of XAS and XES in the EDA solution.

While a simple structure of a solvated water molecule with an acceptor hydrogen bond with the EDA molecule was expected, a previously reported theoretical study using molecular dynamics concluded that the amino groups of EDA could simultaneously act as a donor and acceptor for hydrogen bonds.[51] In highly diluted EDA solutions of water, water molecules tend to form hydrogen bonds as a donor because of a lack of acceptor sites.[51] Therefore, a hydrogen bond donor should be included as a possible interaction in addition to the hydrogen bond acceptor; in other words, the amino groups of EDA would form O-H···N hydrogen bonds in addition to N-H···O hydrogen bonds with water molecules.

If water molecules in an EDA solution form hydrogen bond as acceptor (N-H···O) in addition to a hydrogen bond as donor (O-H···N), the experimental results can be explained by the hydrogen bonding configuration. XAS spectra of the EDA solution show an enhancement of the post-edge structure, which is also known to be enhanced for ice I_h.[6, 52] The hydrogen bond configuration of ice I_h is a four-fold coordination with four hydrogen bonds (two donors and two acceptors). Because the hydrogen bond configuration of water molecules in EDA solution becomes two donors-two acceptors configuration by adding two donor hydrogen bonds to the EDA molecule, one can expect some part of the water molecule takes a similar configuration as a four-fold coordination.

Interestingly, the post-edge region of the XAS spectra of D_2O/EDA is evident compared to that of liquid water. Based on assignments of the post-edge peak in XAS,[6, 52] this result implies the amount of water with a four-fold coordination hydrogen bond is larger than liquid water. Because the previous molecular dynamics study[51] predicts an increase in the average number of hydrogen bonds

for a water molecule upon the addition of EDA, the enhancement of the post-edge structure is consistent with the simulation. Finally, we conclude that the experimental results indicate water diluted in EDA solution has hydrogen bond with both of donor and acceptor between EDA molecules; i.e. the amino groups of EDA are acting as a donor and acceptor for hydrogen bonds simultaneously.

It might be interesting to see the connection between the results of X-ray spectroscopy and ultraviolet absorption, because the temperature dependence of UV absorption detects a red shift of the lowest energy UV absorption band in liquid water upon increasing temperature.[53] In the UV region, the energy shift of the lowest energy UV absorption band of liquid water was interpreted to be a result of hydrogen bonding.[54] To the best of our knowledge, there are no reports on the direct observation of a UV absorption band for 3MP and EDA solutions. However, we can compare the variation of the energy separation between $1b_1$ in XES spectra and $4a_1$ in XAS spectra, because the lowest energy UV absorption band of water corresponds to the electronic excitation between $1b_1$ and $4a_1$ MOs.

For a 3MP solution, both of the $1b_1$ and $4a_1$ peaks shift toward lower energy for almost the same amount. Therefore, the variation in the energy separation is small. On the other hand, an EDA solution shows an energy shift in the main part of the $1b_1$ peaks toward lower energy without a further shift of $4a_1$, i.e., the energy separation increases in the EDA solution. According to the interpretation of the energy shift in the UV region, the magnitude of the blue shift depends on the number of acceptor hydrogen bonds, and there is no evident shift due to donor hydrogen bonds.[54] While donor hydrogen bonds are the dominant interaction for 3MP solutions, both acceptor and donor hydrogen bonds coexist in the EDA solution. Therefore, the increase in the energy separation in the XES and XAS spectra of the EDA solution is consistent with the interpretation of UV absorption.

Because the electronic state information obtained by XAS and XES was utilized to investigate the covalent nature of interactions such as metal-ligand bonds in a complex[55] and the surface-adsorbate interaction of adsorbate molecules on a low-temperature clean surface,[56] it should be interesting to seek an indicator of covalency in the obtained spectra of the binary solutions. Although the partial covalent nature of hydrogen bonds was confirmed experimentally by Compton scattering experiments,[57, 58] detailed information on how MOs vary due to hydrogen bonds has still not been revealed.

For occupied states, it is not easy to analyze the XES spectra, especially for liquid water and water molecules in the EDA solution because of overlapping peaks and peak splitting of the $1b_1$ peak from the complex liquid structure. However, there are no evident new features that provide a clue of covalency in the occupied valence state observed by XES at least. For unoccupied states, the $2b_2$ orbital shows a pronounced variation as discussed above. In addition, the pre-edge peak corresponding to the $4a_1$ orbital, i.e. lowest unoccupied molecular orbital (LUMO), shows an evident peak intensity variation. The intensity of the pre-edge peak for the $D_2O/3MP$ solution is about 70% of the peak intensity of D_2O/AN. The intensity is further decreased in D_2O/EDA solutions and is about 45% of the intensity of D_2O/AN. For pure water, the intensity in the saturation corrected spectra is about 50% and is slightly higher than that of the water molecules dissolved in EDA. The pre-edge peak intensity clearly tends to decrease as the number of hydrogen bonds increases; in AN solution, water molecules dissolve with the dipole-dipole interaction, and there should be no hydrogen bond. Water molecules diluted in 3MP only have one or two hydrogen bonds as donor.[23, 24] For a water molecule in EDA solution, the average number of hydrogen bonds is greater than in pure liquid water according to the previous molecular dynamics study[51].

The pre-edge peak in O1s XAS corresponds to electronic transitions from a core O1s orbital to the valence MO corresponds to $4a_1$. The core orbitals such as O1s are strongly localized around the atom and insensitive to the chemical environment except for an energy level shift known as chemical shift. Thus, the observed intensity decrease can be directly connected to variation in the $4a_1$ orbital (LUMO). These results can be explained by MO mixing of LUMO orbital[50, 59] or charge transfer from acceptor to donor[60] associated with hydrogen bonding. However, separate electronic state information for the acceptor and donor is necessary to make a concrete conclusion about the covalency of hydrogen bonding. Therefore, X-ray spectroscopy of nitrogen 1s of AN and 3MP in

aqueous solutions may be important and of interest in further investigations.

Conclusion

We investigated D_2O water dissolved in AN, 3MP, and EDA at room temperature under atmospheric pressure using O 1s XES and XAS and successfully detected solvation dependence in the spectra. Because XAS and XES probe unoccupied and occupied valence electronic states via the electronic transitions between core and valence orbitals, these results provide information on how intermolecular interaction affects on valence MOs of water.

Based on the direct comparison of experimental XAS spectra of D_2O/3MP and D_2O/AN, the pronounced variation of the unoccupied $2b_2$ orbital of water diluted in 3MP and AN was assigned to difference of interactions; while the dipole-dipole interaction is dominant for water diluted in AN, donor hydrogen bonding is dominant for water diluted in 3MP. The XAS and XES spectra of water in EDA solution shows a pronounced difference compared to that of AN and 3MP solutions. In XAS spectra of EDA solutions, an enhancement of the peak structure in the post-edge region, similar to that seen in ice I_h, was observed. The XES spectrum also detects an evident shoulder structure on the higher energy side of the $1b_1$ state. These results can be explained by assuming the amino groups of ethylenediamine act as an acceptor site for hydrogen bonds from water molecule in addition to donor site and is consistent with previously reported molecular dynamics study of water/EDA mixture.[51]

We also found a systematic peak intensity decrease of the pre-edge peak corresponding to the $4a_1$ orbital (LUMO), which tended to decrease with increasing the number of hydrogen bonds. Although separate electronic state information on the acceptor and donor of hydrogen bonds is necessary to make a concrete conclusion, these results can be interpreted by the covalency of hydrogen bonding, i.e. the mixing of LUMO orbital[50, 59] or charge transfer from hydrogen bond acceptor to donor.[60]

The present results of solvation dependence demonstrate that the combination of XAS and XES is a powerful tool to investigate solvation interactions in solution. Further insights into hydrogen bonding should be obtained through the investigation of a wide variety of hydrogen-bonded molecules with different inter-atomic distances and bond strengths[58] using X-ray spectroscopy.

References

1.   M. S. Taylor and E. N. Jacobsen, *Angew. Chem.*, 2006, **45**, 1520-1543.
2.   M. Sumita, K. Sodeyama, L. Y. Han and Y. Tateyama, *J. Phys. Chem. C*, 2011, **115**, 19849-19855.
3.   J. H. Guo, Y. Luo, A. Augustsson, J. E. Rubensson, C. Såthe, H. Ågren, H. Siegbahn and J. Nordgren, *Phys. Rev. Lett.*, 2002, **89**, 137402.
4.   S. Myneni, Y. Luo, L. Å. Näslund, M. Cavalleri, L. Ojamäe, H. Ogasawara, A. Pelmenschikov, P. Wernet, P. Vaterlein, C. Heske, Z. Hussain, L. G. M. Pettersson and A. Nilsson, *J. Phys.: Condens. Matter*, 2002, **14**, L213-L219.
5.   S. Kashtanov, A. Augustsson, Y. Luo, J. H. Guo, C. Såthe, J. E. Rubensson, H. Siegbahn, J. Nordgren and H. Ågren, *Phys. Rev. B*, 2004, **69**, 024201.
6.   P. Wernet, D. Nordlund, U. Bergmann, M. Cavalleri, M. Odelius, H. Ogasawara, L. Å.

Näslund, T. K. Hirsch, L. Ojamäe, P. Glatzel, L. G. M. Pettersson and A. Nilsson, *Science*, 2004, **304**, 995-999.

7. O. Fuchs, M. Zharnikov, L. Weinhardt, M. Blum, M. Weigand, Y. Zubavichus, M. Bär, F. Maier, J. D. Denlinger, C. Heske, M. Grunze and E. Umbach, *Phys. Rev. Lett.*, 2008, **100**, 027801.

8. T. Tokushima, Y. Harada, O. Takahashi, Y. Senba, H. Ohashi, L. G. M. Pettersson, A. Nilsson and S. Shin, *Chem. Phys. Lett.*, 2008, **460**, 387-400.

9. J. Forsberg, J. Gråsjö, B. Brena, J. Nordgren, L.-C. Duda and J.-E. Rubensson, *Phys. Rev. B*, 2009, **79**, 132203.

10. C. Huang, K. T. Wikfeldt, T. Tokushima, D. Nordlund, Y. Harada, U. Bergmann, M. Niebuhr, T. M. Weiss, Y. Horikawa, M. Leetmaa, M. P. Ljungberg, O. Takahashi, A. Lenz, L. Ojamäe, A. P. Lyubartsev, S. Shin, L. G. M. Pettersson and A. Nilsson, *Proc. Natl. Acad. Sci. USA*, 2009, **106**, 15214-15218.

11. M. Odelius, *J. Phys. Chem. A*, 2009, **113**, 8176-8181.

12. M. Odelius, *Phys. Rev. B*, 2009, **79**, 144204.

13. K. M. Lange, R. Könnecke, S. Ghadimi, R. Golnak, M. A. Soldatov, K. F. Hodeck, A. Soldatov and E. F. Aziz, *Chem. Phys.*, 2010, **377**, 1-5.

14. M. P. Ljungberg, A. Nilsson and L. G. M. Pettersson, *Phys. Rev. B*, 2010, **82**, 245115.

15. T. Tokushima, Y. Horikawa, H. Arai, Y. Harada, O. Takahashi, L. G. M. Pettersson, A. Nilsson and S. Shin, *J. Chem. Phys.*, 2012, **136**, 044517-044517.

16. Y. Harada, T. Tokushima, Y. Horikawa, O. Takahashi, H. Niwa, M. Kobayashi, M. Oshima, Y. Senba, H. Ohashi, K. T. Wikfeldt, A. Nilsson, L. G. M. Pettersson and S. Shin, *Phys. Rev. Lett.*, 2013, **111**, 193001.

17. J. Gråsjö, E. Andersson, J. Forsberg, E. F. Aziz, B. Brena, C. Johansson, J. Nordgren, L. Duda, J. Andersson, F. Hennies, J. E. Rubensson and P. Hansson, *J. Phys. Chem. B*, 2009, **113**, 8201-8205.

18. J. H. Guo and Y. Luo, *J. Electron Spec. Rel. Phenom.*, 2010, **177**, 181-191.

19. K. M. Lange, R. Könnecke, M. Soldatov, R. Golnak, J.-E. Rubensson, A. Soldatov and E. F. Aziz, *Angew. Chem.*, 2011, **50**, 10621-10625.

20. N. Huang, D. Nordlund, C. Huang, U. Bergmann, T. M. Weiss, L. G. M. Pettersson and A. Nilsson, *J. Chem. Phys.*, 2011, **135**, 164509-164506.

21. K. M. Lange, M. Soldatov, R. Golnak, M. Gotz, N. Engel, R. Könnecke, J.-E. Rubensson and E. F. Aziz, *Phys. Rev. B*, 2012, **85**, 155104.

22. H. Arai, Y. Horikawa, K. Sadakane, T. Tokushima, Y. Harada, Y. Senba, H. Ohashi, Y. Takata and S. Shin, *Phys. Chem. Chem. Phys.*, 2012, **14**, 1576-1580.

23. I. Papái and G. Jancsó, *J. Phys. Chem. A*, 2000, **104**, 2132-2137.

24. W. Marczak, J. K. Lehmann and A. Heintz, *J. Chem. Therm.*, 2003, **35**, 269-278.

25. T. Takamuku, M. Tabata, A. Yamaguchi, J. Nishimoto, M. Kumamoto, H. Wakita and T. Yamaguchi, *J. Phys. Chem. B*, 1998, **102**, 8880-8888.

26. H. Ohashi, Y. Senba, H. Kishimoto, T. Miura, E. Ishiguro, T. Takeuchi, M. Oura, K. Shirasawa, T. Tanaka, M. Takeuchi, K. Takeshita, S. Goto, S. Takahashi, H. Aoyagi, M. Sano, Y. Furukawa, T. Ohata, T. Matsushita, Y. Ishizawa, S. Taniguchi, Y. Asano, Y. Harada, T. Tokushima, K. Horiba, H. Kitamura, T. Ishikawa and S. Shin, *AIP Conf. Proc.*, 2007, **879**, 523-526.

27. Y. Senba, H. Ohashi, H. Kishimoto, T. Miura, S. Goto, S. Shin, T. Shintake and T. Ishikawa, *AIP Conf. Proc.*, 2007, **879**, 718-721.

28. T. Tokushima, Y. Harada, Y. Horikawa, O. Takahashi, Y. Senba, H. Ohashi, L. G. M. Pettersson, A. Nilsson and S. Shin, *J. Electron Spec. Rel. Phenom.*, 2010, **177**, 192-205.

29. M. Odelius, H. Ogasawara, D. Nordlund, O. Fuchs, L. Weinhardt, F. Maier, E. Umbach, C. Heske, Y. Zubavichus, M. Grunze, J. D. Denlinger, L. G. M. Pettersson and A. Nilsson, *Phys. Rev. Lett.*, 2005, **94**, 227401.

30. U. R. Kapadi, D. G. Hundiwale, N. B. Patil and M. K. Lande, *Fluid Phase Equilibria*, 2003, **205**, 267-274.

31. Å. U. Burman and K. H. U. Ström, *Journal of Chemical & Engineering Data*, 2008, **53**,

2307-2310.
32. L. Triguero, L. G. M. Pettersson and H. Ågren, *Phys. Rev. B*, 1998, **58**, 8097-8110.
33. deMon-KS StoBe version 5.3, K. Hermann, L. G. M. Pettersson, M. E. Casida, C. Daul, A. Goursot, A. Koester, E. Proynov, A. St-Amant, D. R. P. a. Salahub, V. Carravetta, H. Duarte, N. Godbout, J. Guan, C. Jamorski, M. Leboeuf, V. Malkin, O. Malkina, M. Nyberg, L. Pedocchi, F. Sim, L. Triguero and A. C. a. Vela, 2005.
34. A. Föhlisch, J. Hasselström, P. Bennich, N. Wassdahl, O. Karis, A. Nilsson, L. Triguero, M. Nyberg and L. G. M. Pettersson, *Phys. Rev. B*, 2000, **61**, 16229-16240.
35. W. Kutzelnigg, U. Fleischer and M. Schindler, *NMR-Basic Principles and Progress*, Springer-Verlag, Heidelberg, 1990.
36. L. G. M. Pettersson, U. Wahlgren and O. Gropen, *Chem. Phys.*, 1983, **80**, 7-16.
37. Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
38. L. Weinhardt, A. Benkert, F. Meyer, M. Blum, R. G. Wilks, W. Yang, M. Bär, F. Reinert and C. Heske, *J. Chem. Phys.*, 2012, **136**, 144311-144316.
39. L. Å. Näslund, D. C. Edwards, P. Wernet, U. Bergmann, H. Ogasawara, L. G. M. Pettersson, S. Myneni and A. Nilsson, *J. Phys. Chem. A*, 2005, **109**, 5995-6002.
40. Y. Horikawa, H. Arai, T. Tokushima and S. Shin, *Chem. Phys. Lett.*, 2012, **522**, 33-37.
41. K. M. Lange, K. F. Hodeck, U. Schade and E. F. Aziz, *J. Phys. Chem. B*, 2010, **114**, 16997-17001.
42. I. Waluyo, D. Nordlund, U. Bergmann, L. G. M. Pettersson and A. Nilsson, *J. Chem. Phys.*, 2009, **131**, 031103.
43. I. Waluyo, C. Huang, D. Nordlund, U. Bergmann, T. M. Weiss, L. G. M. Pettersson and A. Nilsson, *J. Chem. Phys.*, 2011, **134**, 064513.
44. I. Waluyo, C. Huang, D. Nordlund, T. M. Weiss, L. G. M. Pettersson and A. Nilsson, *J. Chem. Phys.*, 2011, **134**, 224507.
45. C. J. Sahle, C. Sternemann, C. Schmidt, S. Lehtola, S. Jahn, L. Simonelli, S. Huotari, M. Hakala, T. Pylkkänen, A. Nyrow, K. Mende, M. Tolan, K. Hämäläinen and M. Wilke, *Proc. Natl. Acad. Sci. USA*, 2013, **110**, 6301-6306.
46. D. Prendergast and G. Galli, *Phys. Rev. Lett.*, 2006, **96**, 215502.
47. T. Pylkkänen, A. Sakko, M. Hakala, K. Hämäläinen, G. Monaco and S. Huotari, *J. Phys. Chem. B*, 2011, **115**, 14544-14550.
48. J. Schirmer, A. B. Trofimov, K. J. Randall, J. Feldhaus, A. M. Bradshaw, Y. Ma, C. T. Chen and F. Sette, *Phys. Rev. A*, 1993, **47**, 1136-1147.
49. K. Okada, K. Ueda, T. Tokushima, Y. Senba, H. Yoshida, Y. Shimizu, M. Simon, H. Chiba, H. Okumura, Y. Tamenori, H. Ohashi, N. Saito, S. Nagaoka, I. H. Suzuki, E. Ishiguro, I. Koyano, T. Ibuki and A. Hiraya, *Chem. Phys. Lett.*, 2000, **326**, 314-320.
50. M. Cavalleri, H. Ogasawara, L. G. M. Pettersson and A. Nilsson, *Chem. Phys. Lett.*, 2002, **364**, 363-370.
51. A. V. Gubskaya and P. G. Kusalik, *J. Phys. Chem. A*, 2004, **108**, 7165-7178.
52. T. Pylkkänen, V. M. Giordano, J. C. Chervin, A. Sakko, M. Hakala, J. A. Soininen, K. Hämäläinen, G. Monaco and S. Huotari, *J. Phys. Chem. B*, 2010, **114**, 3804-3808.
53. A. Ikehata, N. Higashi and Y. Ozaki, *J. Chem. Phys.*, 2008, **129**, 234510.
54. P. C. do Couto and D. M. Chipman, *J. Chem. Phys.*, 2012, **137**, 184301.

55.   T. Glaser, B. Hedman, K. O. Hodgson and E. I. Solomon, *Accounts. Chem. Res.*, 2000, **33**, 859-868.
56.   A. Nilsson, M. Weinelt, T. Wiell, P. Bennich, O. Karis, N. Wassdahl, J. Stöhr and M. G. Samant, *Phys. Rev. Lett.*, 1997, **78**, 2847-2850.
57.   E. D. Isaacs, A. Shukla, P. M. Platzman, D. R. Hamann, B. Barbiellini and C. A. Tulk, *Phys. Rev. Lett.*, 1999, **82**, 600-603.
58.   E. Arunan, G. R. Desiraju, R. A. Klein, J. Sadlej, S. Scheiner, I. Alkorta, D. C. Clary, R. H. Crabtree, J. J. Dannenberg, P. Hobza, H. G. Kjaergaard, A. C. Legon, B. Mennucci and D. J. Nesbitt, *Pure Appl. Chem.*, 2011, **83**, 1619-1636.
59.   T. K. Ghanty, V. N. Staroverov, P. R. Koren and E. R. Davidson, *J. Am. Chem. Soc.*, 2000, **122**, 1210-1214.
60.   S. J. Grabowski, *Chem. Rev.*, 2011, **111**, 2597-2625.

Figure Captions

Figure 1
XAS and XES spectra of D_2O diluted in AN, 3MP, and EDA mixtures. Concentration of each sample is indicated by the labels on each spectra. The right panel shows O 1s XAS spectra, and the left panel shows O 1s XES spectra. Previously reported XAS spectra of H_2O water in the gas phase by Myneni *et al.*[4] and D_2O water in the gas phase by Weinhardt *et al.*[38] are also included in the figure for comparison. XAS spectra of the binary solutions were normalized to the same intensity at a non-resonant region at ~548 eV. The XES spectrum of the D_2O/3MP mixture is a part of the data in our previous report.[22] Concentrations of each sample are indicated in the figure as molar fraction of D_2O.

Figure 2
Calculated O1s XAS spectra for isolated water, water-AN complex (1:1 and 1:2 complex), and water-3MP complex.

O 1s XES

1b$_1$

2b$_2$

XAS

D$_2$O Water
Gas phase
(Weinhardt et al.)

3a$_1$

4a$_1$

H$_2$O Water
Gas phase
(Myneni et al.)

1b$_2$

AN/D$_2$O

X$_{D_2O}$ = 0.17

X$_{D_2O}$ = 0.10

3MP/D$_2$O

X$_{D_2O}$ = 0.20

X$_{D_2O}$ = 0.10

EDA/D$_2$O

X$_{D_2O}$ = 0.10

X$_{D_2O}$ = 0.10

D$_2$O Water
Liquid phase

Intensity [arb.units]

515   520   525   530   535   540

Photon energy [eV]

O1s XAS
(Theoretical calculation)

Oxygen

Hydrogen

Water (isolated)

Carbon
Nitrogen

Water + AN

Water + 2 AN

Water + 3MP

Intensity (arb. units)

Photon energy (eV)