

DMSO–Water Clustering in Solution Observed in Soft X-ray Spectra

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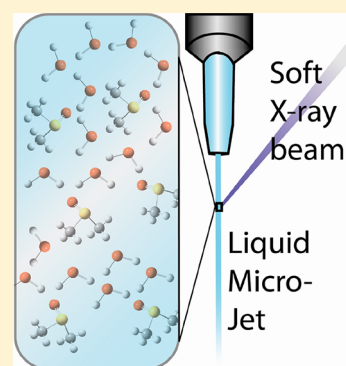
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ABSTRACT: The significant deviation from the ideality of dimethyl sulfoxide (DMSO)/water mixtures can be addressed based on the change of the local molecular orbitals of each solvent upon mixing. Oxygen K-edge absorption and emission spectra of DMSO/water solutions were measured using the liquid microjet technique. The spectra demonstrate that the hydrogen bond network in liquid water is already influenced at small DMSO concentrations, and at the molar fraction $x_{\text{DMSO}} = 0.43$ we find strong evidence of DMSO–water clustering reflected by the influence on the occupied molecular orbitals.



SECTION: Liquids; Chemical and Dynamical Processes in Solution

Dimethyl sulfoxide (DMSO) and water are important and widely used solvents in their neat form, and also aqueous solutions of DMSO have many applications in biology, chemistry, and pharmacology.^{1–7} Indeed, DMSO/water solutions have physical and chemical properties that are far from what is expected for an ideal solution and strongly deviate from ideality if plotted against the molar fraction.^{3–10} For example, the freezing point is depressed by 140 K at molar fraction $x_{\text{DMSO}} = 0.25$ to 0.3. The polarity of the DMSO molecules can primarily be associated with the sulfinyl group with excess charge at the oxygen site. In aqueous solution, hydrogen bonds (HBs) with H₂O are formed at this site,^{1–4,9–14} which are much stronger than the typical HBs in liquid water. There have been attempts to explain the dramatic lowering of the freezing temperature in terms of the formation of small weakly interacting subunits, and it has been suggested that a “stable” DMSO *n*-hydrate should be formed.¹¹ These issues have been investigated theoretically,^{3,4,8–11} by X-ray and neutron scattering and diffraction,^{6,13,14} infrared and Raman spectroscopy,^{1,2,6,15–18} and nuclear magnetic resonance,^{1,16} yet no consensus regarding the structure and molecular interactions in the solutions has been reached.

X-ray absorption (XA) and emission (XE) spectroscopy can reveal the local electronic structure at specific sites in complex liquids.^{19–21} Because of the local atom-specific nature of the core holes and the short lifetime of the excited states, XE spectra also give information about ultrafast (fs) dynamics. In the case of liquid water, we have unequivocally demonstrated that the spectra are very sensitive to HBs using our recently

developed high-resolution XE spectrometer on the microjet.^{22–24} The low-energy component of the sharp and dominant double feature, called d_2 ,²⁵ “fingerprints” the strength of the hydrogen bonding.^{22–24} Here we used XA, XE, and resonant inelastic X-ray scattering (RIXS) to study the effect of HBs in water/DMSO mixtures. Besides selectively separating the local electronic structure of the DMSO oxygen and the water oxygen, we probe the mixture without possible membrane-induced effects.²⁶ This allows us to show that the water HB network is substantially altered already at small DMSO concentrations, and huge effects in the spectra at higher concentrations show that the DMSO–water HBs are very strong, suggesting water–DMSO clustering.

The TFY spectra of neat DMSO, neat water, and their binary mixtures with volume fractions 25:75, 50:50, and 75:25 are presented in Figure 1. We recently discussed the XA spectrum of DMSO²⁷ and assigned the dominating peak at 533 eV to transitions to the two molecular orbitals 15a' and 8a'' of σ^* and π^* character, respectively. The XA spectrum of liquid water has been discussed at length in the literature.^{19,24} The large difference between gas- and liquid-phase water spectra is due to interaction between the molecules, and it is believed that the peaks correspond to different hydrogen-bond conformations. Still, pre-edge (~ 535 eV) and main-edge (~ 537 eV) intensity

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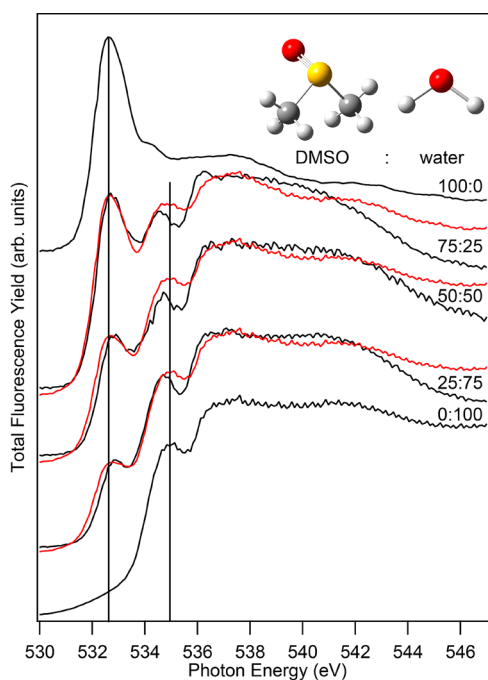


Figure 1. Measured TFY spectra (black) of neat DMSO, water–DMSO mixtures of three different concentrations, and neat water. For the mixtures we also include a best-fit superposition (red) of spectra for the pure liquids.

can be associated with the $4a_1$ and $2b_2$ orbitals of the water molecule, respectively.²² The FY spectrum shown in Figure 1 differs significantly from the true XA spectrum due to saturation effects.

In the mixtures, the oxygen atoms of both DMSO and water molecules contribute to the FY intensity. To describe the spectra, we compare to a superposition of the spectra from the pure liquids. In principle, deviations from this model indicate interactions between the molecules. In practice, one also must take saturation effects into account. This is complicated by the fact that saturation effects are very large for pure H_2O and significantly smaller for DMSO. We observe (Figure 1) that the superposition model works fairly well and the contributions of DMSO and water are clearly distinguishable at ~ 533 and ~ 535 eV, respectively. Although the observation of small energetic shifts indicates a change of the hydrogen bonding structure upon mixing, one cannot be conclusive due to saturation effects. Additionally, sharpening of the water-derived features and the relative depletion of the postedge feature are all in-line with saturation effects. It cannot be excluded that spectral changes also can be associated with rearrangement of HB conformation. In the light of the large rearrangement and the huge changes in the XE and RIXS spectra discussed in the following, the relative success of the superposition model is surprising.

The XE spectra for the same solutions excited at 537.7 eV are shown in Figure 2. We recently analyzed the XE spectrum of pure DMSO²⁷ and assigned the features by means of ab initio Hartree–Fock and configuration interaction calculations using the GSCF3 code.^{28,29} According to these calculations, the four peaks found in the spectrum are dominated by transitions from the $12a'$, $13a'$, $7a''$, and $14a'$ orbitals at 523.5, 524.8, 523.5, 526.9, and 527.7 eV, respectively, with $14a'$ as the highest occupied molecular orbital (HOMO). Whereas all orbitals are

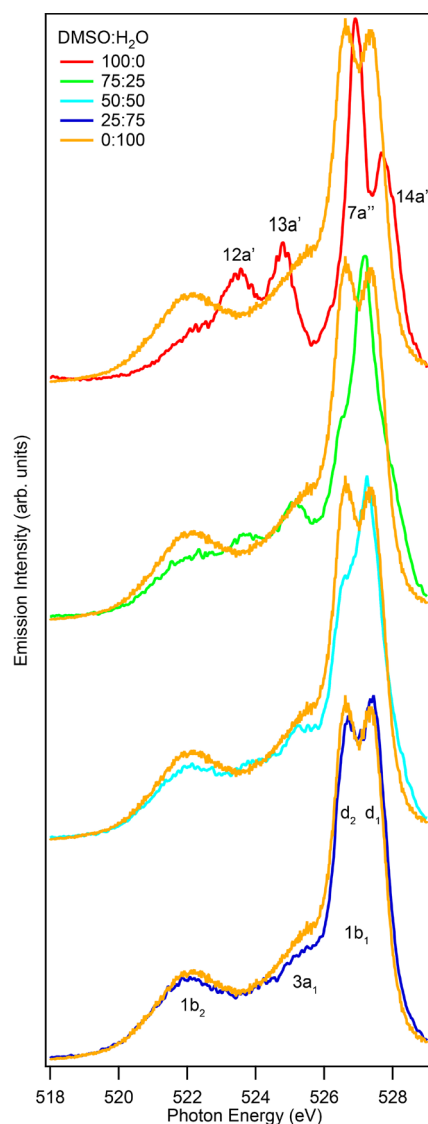


Figure 2. Nonresonantly excited (537.7 eV) XE spectra of neat DMSO (red), DMSO–water mixtures with 75:25 (green), 50:50 (light blue), 25:75 (dark blue), and the neat water spectrum (yellow).

fairly delocalized, the HOMO is lone-pair-like at the oxygen site, and the HOMO-1 has S–O π bonding character. We found that the spectrum for a single DMSO molecule well-reproduces the spectrum of the neat liquid.^{27,30} This is not the case for the water spectra. The gas-phase spectrum shows peaks corresponding to three molecular orbitals, $1b_2$, $3a_1$, and $1b_1$ in order of increasing energy and with $1b_1$ as the HOMO. The liquid spectrum is significantly different, revealing four peaks, where the two dominating features have been labeled d_2 and d_1 in order of increasing energy.²⁵ Whereas the exact interpretation of the differences is being discussed,^{19,22,23,25} studies have unambiguously shown that the relative d_2 intensity increases with HB coordination.²²

Like in the FY spectra, oxygen atoms both in DMSO and water contribute to nonresonantly excited XE spectra of their mixtures. In solutions with large water content (25 and 50 vol % DMSO), we consider the spectra to be dominated by emission from water because features reminiscent of DMSO are not very prominent. An obvious difference from the spectrum of neat water is, however, the relative reduction of the d_2

intensity. In line with our previous result,^{22,23} we interpret this observation as a “fingerprint” for breaking of HBs in the water network when DMSO molecules are introduced. A noticeable effect is already observed at 25 vol %, and at 50% concentration the reduction is comparable to dissolution of water in 25% acetonitrile.²² Whereas the HBs between DMSO and water at the DMSO oxygen site are much stronger than typical HBs in liquid water, it is indeed to be expected that the HB network in water is disrupted as DMSO is introduced.

For larger DMSO concentrations (75:25), we observe a spectrum that is very different from the spectra of both the neat liquids (Figure 2). Opposite to our previous observation for XA spectra, attempts to combine the spectra of the neat liquids to simulate the measured spectrum fail to reproduce the main features (Figure 3), and it is not even straightforward to relate

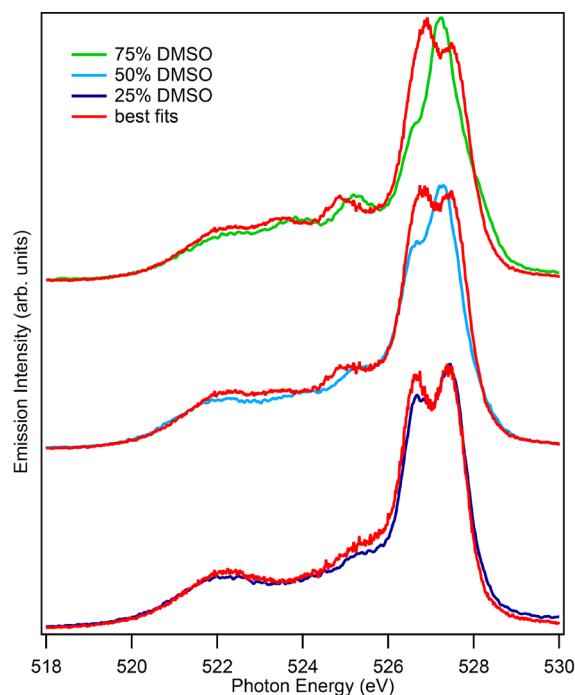


Figure 3. XE spectra of the binary mixtures with volume ratios 25:75, 50:50, and 75:25 of DMSO and water along with their best fits from the superposition of neat water and DMSO spectra are presented. The best fit for the mixture with 25 vol % DMSO is the pure water spectrum.

the features to those in the spectra of the neat liquids. Thus, we can conclude that there is a dramatic structural change upon mixing of the substances and that the molecules interact strongly. We believe that both the water and DMSO emission, reflecting the local electronic structure at the oxygen sites, are subject to large changes. We briefly discuss the phenomenology in the 75% DMSO solution in the following. The main peak at 527.3 eV in the spectrum of the solution is situated between the d_1 peak in the spectrum of pure water and the $7a''$ (HOMO-1) peak in the DMSO spectrum. Although the peak must originate from both species, it is too sharp to be constructed as a simple superposition of the two features in the neat liquid spectra. This suggests that both corresponding orbitals are significantly distorted by the intermolecular interaction. The peak corresponding to the d_2 peak in the water spectra, which is associated with water–water HBs, is further attenuated as the DMSO concentration increases. This is in line with the

expectation that water–water HBs are increasingly broken upon mixing with DMSO. We further note that the two peaks assigned to the $12a'$ and $13a'$ states at 523.8 and 525.2 eV in the DMSO spectrum are also observed in the spectrum of the solution. However, these counterparts show a blue shift compared with the pure liquid. We attribute this shift to a weakening of the S–O bond associated with strong HBs. This conclusion is based on the notion that the overlap between the atomic orbitals determines the energy spacing of the molecular orbitals, a simple scheme that we recently used to compare spectra of acetone and DMSO.²⁷ In aqueous mixtures, increased dipole moment of the S–O group was predicted¹¹ and strong hydrogen bonding was observed, for example, as a red shift in Raman spectra.¹⁸ This supports the suggestion that the S–O bond is stretched due to the strong HBs with water, viz., a weakening of the S–O bond that leads to the observed larger dipole moment. Finally, we see that there is no obvious peak in the liquid corresponding to the $14a'$ (HOMO) in pure DMSO. Any reminiscence is hidden in the high-energy flank of the main peak. Thus, in the solution, the DMSO HOMO loses intensity or shifts toward the HOMO-1 peak. A shift is in line with the weakening of the S–O bond, as previously described. We note that the $14a'$ orbital is fairly delocalized, and we recently showed that it gives rise to much less relative spectral weight than the corresponding orbital in acetone.²⁷ This is counterintuitive because DMSO is much more polar than acetone with partial charge on the oxygen site. We found that the larger dipole is due to polarization of the inner orbitals, thus weakening the S–O bond.²⁷ In aqueous solution, the dipole moment of DMSO is very large compared with neat DMSO,¹¹ and by simply extrapolating the trend found in this comparison, we would expect a further polarization of the inner orbitals and delocalization of the $14a'$ orbital, thereby weakening the S–O bond,^{11,18} resulting in an additional reduction of the relative intensity associated with the HOMO orbital upon dissolution in water.

Concerning the RIXS spectra, we excite at the first DMSO resonance (Figure 4), which is energetically situated below the threshold for water excitations. The excited electron is localized

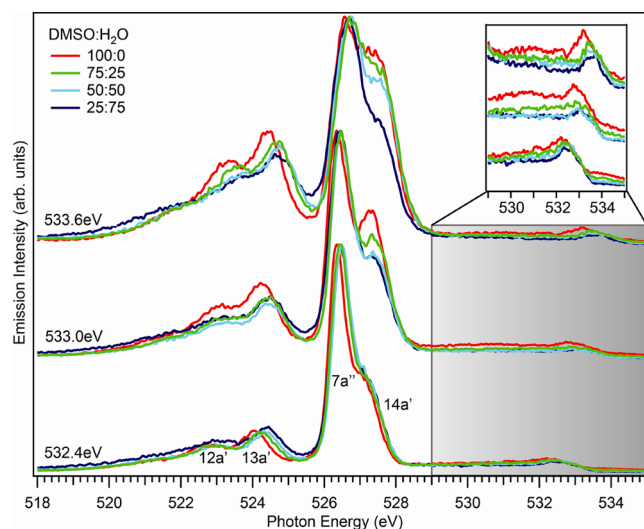


Figure 4. RIXS spectra of neat DMSO and its mixtures with water with volume ratios 25:75, 50:50, and 75:25 are presented for excitation energies labeled above the spectra. The elastic peaks are presented separately in the inset for better visibility.

and has finite probability to recombine with the core hole, reflected by the so-called elastic peak around 533 eV. The shift relative to the nominal excitation energy and the long tails toward lower energies are due to vibrational excitations in the final electronic ground state. The excited electron does influence the spectrum, and the final states are neutral excited states rather than ionized as in the XE spectra. Accordingly, additional information is obtained by the combination of RIXS and XE. We recently showed that the two different states contributing to the absorption resonance in neat DMSO have quite different RIXS spectra.²⁷ Thus, the variation of the intensity ratio of the two main features (Figure 4) as the excitation energy is increased over the resonance was attributed to a variation of the cross section for scattering over the 15a' (LUMO) and the 8a'' (LUMO+1) orbitals. At the lowest excitation energy, the 15a' scattering channel dominates. Intriguingly, the effects of water mixing seem to be quite small. However, already at the lowest water concentration, in line with the observation in the spectra excited above threshold, the features associated with the 12a' and 13a' features are shifted. Again, this can be associated with a weakening of the S–O bond. The interpretation that the sulfinyl bond is weakened is in line with the reduction of the energetic spacing between the states, as described above, n.b., not including the HOMO–LUMO gap. Such reduction is directly observed here, given a relatively large shift of the lower valence states upon mixing without a significant shift of the HOMO and HOMO-1.

The changes in the intensity ratios between the two main peaks are less pronounced in the spectra of the aqueous solution than in neat DMSO and are further attenuated as the water concentration increases. This again indicates a strong water–DMSO interaction, and we suggest two possible mechanisms. A shift of the resonant 8a'' orbital, which has local S–O π^* antibonding character, due to the interaction with water is possible. This would reduce the excitation energy dependence in the RIXS spectra as the first resonance would be dominated by the 15a' channel at all excitation energies. The other possible mechanism is that the reduction of the HOMO related intensity in the high-energy part of the structure is similar to what was discussed for the XE spectra.

We investigated the molecular interaction between DMSO and water solution with high-resolution XA, XE, and RIXS spectroscopy using the microjet technique. Besides the power of this membrane-free method, we demonstrated that the interaction between DMSO and water is strong and clearly reflected in the XE and RIXS spectra. Already in water-rich solutions the DMSO molecules distort the HB network of water, and at 75 vol % (43 mol %) DMSO the interaction between the molecules has a dramatic effect on the spectra and suggests that clustering indeed occurs, which has been proposed as one mechanism for the extreme lowering of the mixtures' freezing temperature.¹¹ Additionally, the interactions between the molecules lead to a reduction of the relative spectral intensity of the 14a' (HOMO) of DMSO, suggesting a loss of oxygen 2p character, which is in line with a weakening of the sulfinyl bond. The weakening of the sulfinyl bond is also reflected in the RIXS spectra in a reduction of the energy spacing between the electronic states in aqueous solutions. We are convinced that the observed significant changes of the molecular orbitals of DMSO and water upon mixing will inspire further theoretical modeling and hope that future progress sheds further light on these phenomena.

■ EXPERIMENTAL DETAILS

DMSO with purity greater than 99% was obtained from Sigma-Aldrich and used without further purification. Binary mixtures of 0.25 (0.08), 0.50 (0.20), and 0.75 (0.43) DMSO volume fraction (molar fraction) were produced by diluting DMSO with Milli-Q water. Total fluorescence yield (TFY) XA, resonant inelastic X-ray scattering (RIXS), and XE spectra at the O K edge were recorded using a liquid microjet setup^{31,32} at the U41-PGM undulator beamline of BESSY II at Helmholtz-Zentrum Berlin. TFY spectra were recorded using a GaAsP photodiode, and for the RIXS and XE measurements a Rowland-circle geometry spectrometer with a grating of 7.5 m radius and 1200 lines per mm was used. The energy calibration of the RIXS and XE spectra was performed using the elastic scattering features, and whereas the relative energy of the beamline was well-calibrated, absolute calibration was performed by shifting the XA spectra of water such that the features fit the commonly described spectral positions.^{22–24,31–36} Details of the experimental setup have been previously described.^{22,31}

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Notes

The authors declare no competing financial interest.

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