

## Molecular Structure of Alcohol-Water Mixtures

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We use x-ray emission spectroscopy to elucidate the molecular structure of liquid methanol, water, and methanol-water solutions. We find that molecules in the pure liquid methanol predominantly persist as hydrogen-bonded chains and rings with six and/or eight molecules of equal abundance. For water-methanol solutions we find evidence of incomplete mixing at the microscopic level. Our results provide a new explanation for a smaller entropy increase in the solution due to water molecules bridging methanol chains to form rings.

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Despite a great deal of effort spanning four decades, no general consensus has been reached concerning the structural properties of liquid alcohols and their solutions with water. Already for the simplest system, pure methanol, contradicting conclusions were reached even using the same experimental techniques. The early hypothesis of cyclic structures by Pauling [1] has both been supported [2] and contested [3] by neutron diffraction analysis, the competing interpretation being that the majority of liquid molecules are ordered in chains with up to ten members [3,4] or linear trimer-tetramer chains [5]. This uncertainty is accentuated when one considers alcohol-water solutions. The observed entropy increase upon mixing alcohol and water is much smaller than expected for an ideal solution. Early neutron diffraction data provide structure information of water cages around hydrophobic headgroups in solution [6–9]. Recently, a new neutron diffraction analysis demonstrated that incomplete mixing at the molecular level is essential to explain the smaller than expected entropy increase [10]. This contrasts with the prevailing view that a rearrangement of the water network around hydrophobic methyl groups of the methanol clusters is the main feature behind the unusual thermodynamic properties [11]. However, a convincing description of the details of the incomplete mixing at the molecular level is lacking.

Using x-ray absorption (XA) and selectively excited x-ray emission (XE) spectroscopy to probe unoccupied and occupied electronic states, we establish a firm interpretation for the unusual thermodynamic properties of alcohol-water solutions. Furthermore, we elucidate finer details of the structural properties of liquid methanol as well as of methanol-water solutions. XA and XE spectra reflect the local electronic structure of the various conformations; in this case, the oxygen line shape is sensitive to the hydrogen bonding configurations [12,13](see Fig. 1). The electronic structure of selected species in a complex system can be studied by these methods using resonant excitation of synchrotron radiation. The experiments

were performed at beam line 7.0 at the Advanced Light Source, with the same setup as in Ref. [12]. The measured XA spectrum of liquid methanol (inset of Fig. 1) is assigned to transitions from the O  $1s$  level to the unoccupied states, with the intensity directly relating to the local O  $p$  character of these states. Because of the multitude of different molecular arrangements, the measured XA spectrum of a liquid constitutes a superposition of spectra associated with atoms in several inequivalent sites. Using tunable synchrotron radiation it is thus possible to enhance particular conformations and study their specific XE spectra. Spectra A–C in Fig. 1 are assigned to transitions from the occupied valence orbitals to the core vacancy. The intensities are directly associated with the local oxygen  $p$  character of the occupied states.

A comparison of the theoretical XE spectra (in Fig. 1) associated with possible molecular arrangements makes it obvious that both rings and chains are present in liquid methanol. Structures of rings and chains up to ten methanol molecules, and mixtures of water clusters and methanol rings/chains are fully optimized by the hybrid density functional theory (DFT) at the Becke's three-parameter hybrid functional and the Lee-Yang-Parr correlation functional (B3LYP) level with 6-31G basis set using GAUSSIAN 98 [14]. The theoretical XE spectra of water, methanol, and the water-alcohol mixtures were generated by the group theory formulation developed by Luo *et al.* [15], using the adiabatic approximation (ground state electronic structure) for intensities as established for molecules and clusters [16]. All transition moments and orbital energies were calculated at the canonical Hartree-Fock level with Sadlej basis set by using the DALTON program [17]. For small clusters, the results are found to be in excellent agreement with those from DFT calculations with a larger basis set. Within the Hartree-Fock approach, the long-range molecular interactions have been treated as embedding the clusters into a dielectric medium.

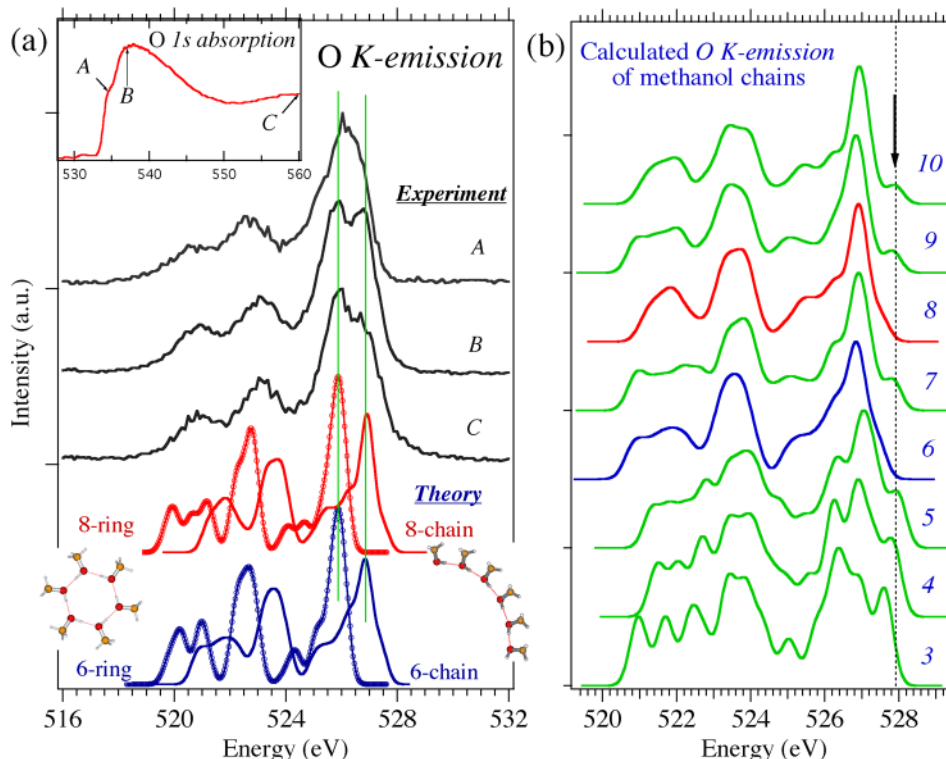


FIG. 1 (color online). Left: Experimental oxygen XE spectra of methanol recorded at 534.5 (A), 537 (B), and 560 eV (C) excitation energies in comparison with theoretical XE spectra of different structures: 6-, 8-chains and rings. The XA spectrum of methanol is shown in the inset. Right: Theoretical XE spectra of a series of methanol chains of different lengths.

The maxima at 526 and 527 eV can be assigned to ring and chain structures, respectively. In addition, we find that the measured spectra are typical for rings and chains consisting of six and eight molecules. Configurations with fewer than six molecules do not give representative predictions, and odd-numbered configurations yield an unobserved high-energy feature at 528 eV. Chains with more than ten molecules are unlikely in light of neutron diffraction data [3,4]. Therefore, the 6- and/or 8-membered rings and chains provide the predominant structures in liquid methanol. From the excitation-energy dependence we can state that the preshoulder in the XA spectrum is due to ring structures (A) and that the onset of absorption in the chains is located to the main absorption band (B). From the emission spectrum corresponding to high-energy excitations (C) we estimate that the relative abundance of chains and rings in liquid methanol is equal.

XE spectra of an equimolar mixture of methanol and water are compared to the spectra from the pure liquids in Fig. 2. The excitation energies are the same as for spectra B and C of Fig. 1 (above threshold). We find that a 1-to-1 combination of the pure liquid spectra reproduces the solution spectra to considerable detail (inset of Fig. 2). The spectra are very sensitive to the changes in the local electronic structure and this observation indicates incomplete mixing at the microscopic level. In particular,

any appreciable amount of “free-swimming” water molecules without hydrogen bonds would have given a completely different result. We note, however, that there is a significant discrepancy when the excitation energy emphasizes the chain structures (spectrum B). Here, the solution spectrum shows a relative intensity decrease in the  $E'_1$  region, indicating a depletion of methanol chains in the solution.

Details in the water-methanol interaction are revealed in the XE spectra generated at excitation energies near threshold. The XA spectrum of the solution (inset of Fig. 3) shows similarities to the spectra of the two pure liquids. There are, however, distinct structures prior to the main absorption edge, at 532 eV, which are absent in the spectra of both pure liquids. These structures directly reflect the local electronic interaction between water and methanol molecules. Correspondingly, XE spectra excited in this region (Fig. 3) are significantly different from the XE spectra of the pure liquids. The 0.8 eV linewidth of the main peak is narrower than any XE feature of either liquid phase: water (1.0 eV) and methanol (1.9 eV). The main peak,  $E_1$ , shifts towards higher energy as the excitation energy is lowered from 532.5 down to 531.5 and 530.6 eV. We also note that the spectrum excited at 530.6 eV shows depletion of intensity in the region around 525 eV. One can conclude that specifically bonded structures involving both water and methanol are

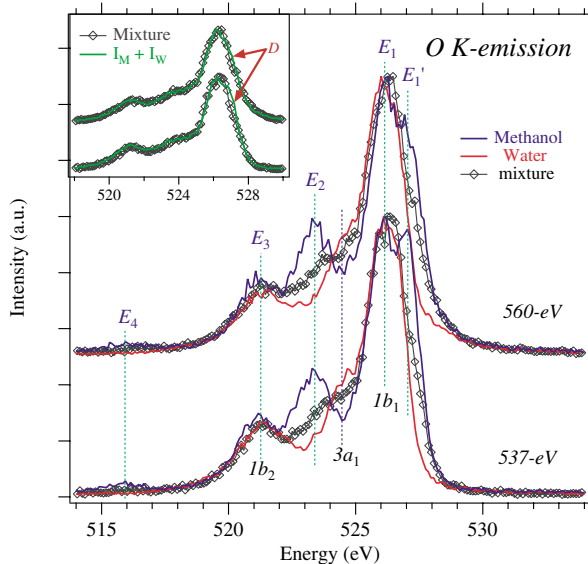


FIG. 2 (color online). The 537 (B) and 560 eV excited (C) XE spectra of liquid water, methanol, and their equimolar mixture. The linear combination of the two former ( $I_M + I_W$ ) reproduces the latter almost in detail (inset). Note, however, a significant difference regarding the  $E_1'$  feature (marked D), indicating a depletion of methanol chains in the solution.

responsible for this spectral behavior. The same behavior was observed in the methanol-water mixture of 7:3 molecular concentration.

To analyze the structural information inherent in these additional preedge structures we have simulated XE spectra of a multitude of possible configurations, a select number are presented in Fig. 4. The narrow spectral feature shown in the resonant emission spectra holds the key for identifying the structures. Based on the simulations of resonant emission spectra of water and methanol in both gas and liquid phases, one can conclude that this narrow spectral feature can be generated only from the emission of a water molecule that is “isolated” from the rest of the water network. Theoretical spectra of a methanol molecule in various methanol-water local structures are computed and do not show such a narrow spectral feature under any circumstances. Furthermore, the depletion of methanol chains in the solution indicates that there must be an interaction between water and methanol chains. This results in a significant reduction of the number of possible trial structures. We find that the only way to obtain a reasonable correspondence between theoretical and experimental results is to assume that the emission originates from water molecules that bridge methanol chains to form rings. The excitation-energy dependence can be well reproduced if the lowest excitation energy (530.6 eV) enhances configurations with eight methanol and 1–2 water molecules, whereas configurations with six methanol molecules and 2–4 water molecules are selectively excited at 531.5 eV. Further up

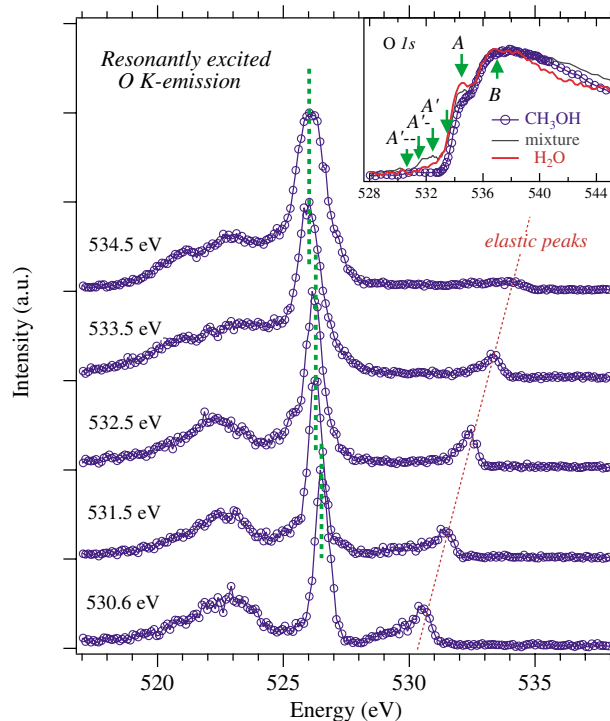


FIG. 3 (color online). A new prepeak appears at 532.5 eV in the XA spectrum of the water-methanol mixture (inset). The main emission peak becomes narrower in the XE spectra resonantly excited at 532.5, 531.5, and 530.6 eV. The depleted intensity at 525 eV and the opposite shift of emission peaks to the elastic peak suggest the existence of new chemical species.

(532.5 eV) we find 8-chains of methanol bridged by three water molecules. With more water molecules involved, the outermost spectral feature becomes even broader.

The findings presented here are consequential for the current disparate views of microscopic structure and order of water-alcohol mixtures. The anomalously small entropy increase upon solution of alcohols in water is traditionally explained in terms of a hydrophobic interaction with the apolar alcohol headgroups, which induces an icelike structure in the surrounding water [11]. It is also a widespread view that, because the alcohol is fully soluble in water in all proportions, it must be homogeneously mixed at the molecular level. However, our results show that most water and methanol molecules in the solution persist in structures similar to the ones found in the pure liquids; thus the results do not support the cherished view of icelike structure formations in the water. Instead, the results show that the small mixing entropy to an incomplete mixing at the molecular level.

Our finding is also incompatible with the appreciable presence of free-swimming water molecules without hydrogen bonding [10]. A portion of 13% of the water molecules would imply extensive hydrogen bond breakage between water molecules and would have a large

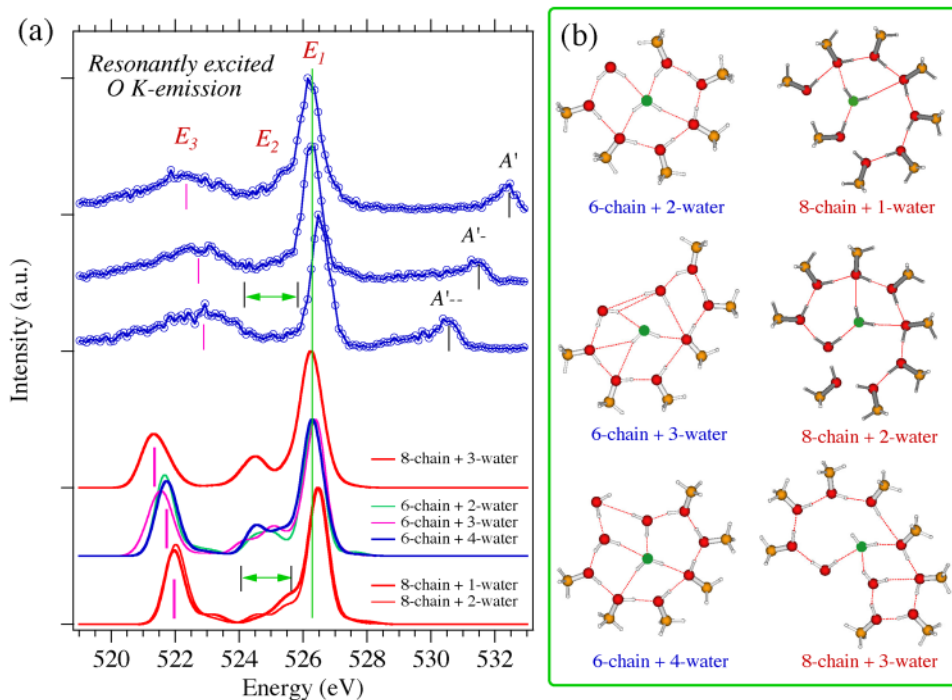


FIG. 4 (color online). The experimental resonant XE spectra are in good agreement with the prediction for the water clusters associated with methanol 6- and 8-chain configurations.

impact on the XA spectrum of the solution in the region of the pre-shoulder. This is at variance with our results since the intensity of this shoulder is known to be very sensitive to the amount of hydrogen bonds [12,13] in liquid water. We find that one origin of entropy decrease upon mixing is that the interaction of the two species gives rise to new ordered structures where water molecules bridge methanol chains to form ring structures (Fig. 4).

In conclusion, selectively excited XE spectroscopy provides a unique approach to determine the properties of liquids and solutions. Via comparison to theoretical predictions information about the molecular arrangements can be obtained. We find that liquid methanol is a combination of 6- and 8-rings and chains, and we learn that the solute-solvent interaction takes place mainly between chains and water molecules. In this manner we have substantially refined both the knowledge of structure and order present in methanol and methanol-water solutions and the understanding of the unusual thermodynamic properties.

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