

High-Resolution Soft X-Ray Photoelectron Spectroscopy of Liquid Water

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Water is the most important liquid since it is essential for life. The relationship between liquid water and biomolecules has been attracting great interest. However, the properties and dynamics of liquid water are rather peculiar due to its strong hydrogen-bonding (HB) network so that even now they cannot be completely explained in terms of intermolecular forces.

The average coordination structure of the HB network in liquid water is believed to be tetrahedral and each water molecule is thought to act as a double proton donor and a double proton acceptor (DDAA). However, the tetrahedral coordination is an average structure and there is a certain amount of thermal fluctuation. A critical question is: to what extent is the tetrahedral structure broken or distorted under normal conditions at room temperature? Eaves et al. performed two-dimensional infrared spectroscopy and molecular dynamics simulations of water and concluded that each distorted HB configuration endures for less than 200 fs. Consequently, they suggested that dangling H-bonds are insignificant species in liquid water. On the other hand, Wernet et al. used soft X-ray absorption spectroscopy and X-ray Raman scattering to investigate the structure of liquid water. They claimed that most water molecules in liquid water have only two H-bonds and that each molecule acts as a one proton donor and one proton acceptor (DA). This surprising report has been intensely discussed. Tokushima et al. made the even more interesting discovery that the soft X-ray emission band associated with the transition from the lowest valence $1b_1$ orbital to the $1a_1$ ($O1s$) core orbital of liquid water after core excitation exhibits an unexpected splitting. They attributed the splitting to tetrahedral and distorted HB configurations coexisting in liquid water and estimated their ratio to be ca. 1:2. The distortion in this case is partial disruption of the tetrahedral HB network in the same sense as that suggested by Wernet et al. Fuchs et al. and Forsberg et al. also obtained essentially the same result for the $1b_1 \rightarrow O1s$ splitting as that reported by Tokushima et al. However, Fuchs et al. attributed these two bands to signals from intact H_2O and dissociated OH after core-hole creation. In the present study, we reinvestigate X-ray PES of liquid water and examine the $1b_1$, $3a_1$, and $O1s$ bands with the highest spectral resolution attained so far (0.1 eV). Both H_2O and D_2O are studied. D_2O has slightly stronger H-bonds than H_2O since it has a lower zero-point energy, which might enhance the spectral resolution of PES.

Figure 1 shows the observed soft X-ray photoelectron spectra of H_2O and D_2O . We curve fitted the spectral region for $3a_1(\text{liq})$, $1b_1(\text{liq})$, $3a_1(\text{vapor})$, and $1b_1(\text{vapor})$. The most important result is that the $3a_1$ bands are well expressed by two overlapping bands separated by 1.38 eV (H_2O) or 1.39 eV (D_2O). The splitting of the $3a_1$ band in cubic ice has been ascribed to interactions with the neighboring $3a_1$ orbitals in the crystal

band structure. This interpretation is based on the crystal structure and is not readily applicable to disordered amorphous ice and liquid water. The most important interactions for the spectral shapes of amorphous ice and liquid water are those between ionized (“central”) water molecules and the first hydration shell. Beyond the first shell, the interactions are predominantly electrostatic and result only in the energy shift of each band of the central water molecule. Therefore, we investigated the origin of the $3a_1$ band splitting by *ab initio* Hartree-Fock molecular orbital calculations on small water clusters with extended basis functions and Koopmans’ theorem. The splitting of the $3a_1$ band is theoretically attributed to water molecules interacting with the first hydration shell as both a proton donor and an acceptor, which does not completely rule out contributions from non-tetrahedral coordination structures such as the DA-chain structure. However, the absence of splitting in the $O1s$ and $1b_1$ bands in photoelectron spectroscopy apparently contradicts the unmistakable splitting in $1b_1 \rightarrow O1s$ soft X-ray emission spectra. This result suggests that the splitting of the $1b_1 \rightarrow O1s$ emission band and its excitation energy dependence originate from the structure and dynamics in the excited state(s) after creation of an $O1s$ core hole.

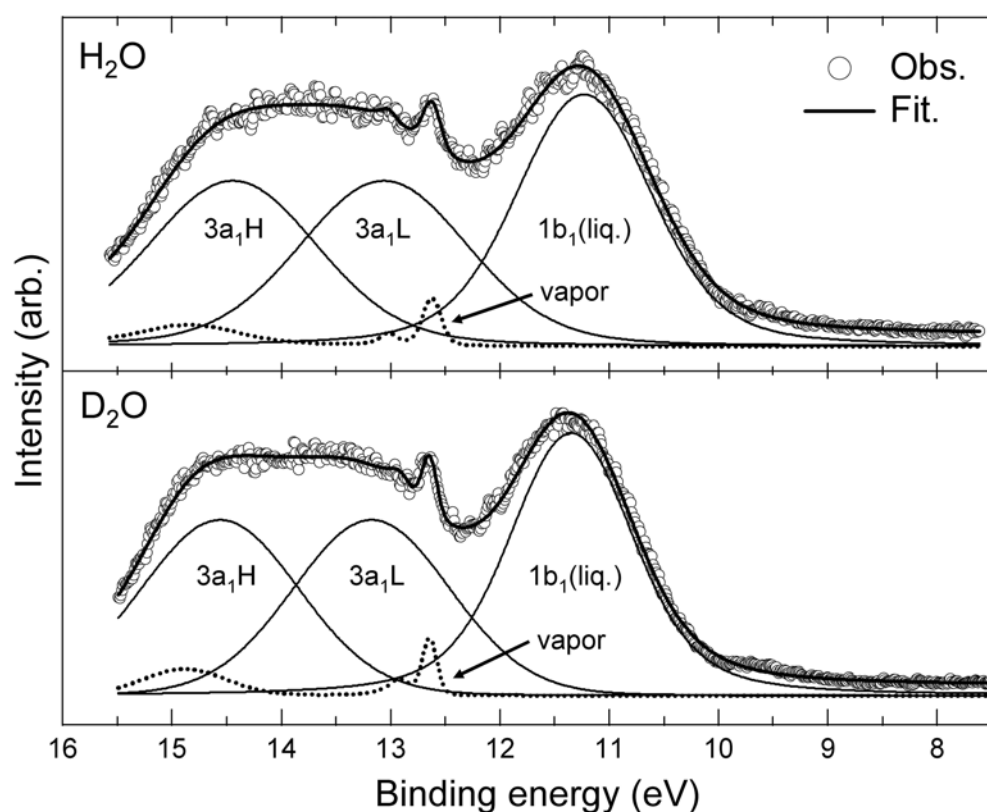


Figure 1 Curve fitting of the valence soft X-ray photoelectron spectra of H_2O and D_2O liquid beams measured at a photon energy of 516 eV. Symmetric Voigt profiles were assumed for every component. For the $3a_1$ region, two peaks with identical linewidths and heights are employed to reflect the top-flat feature in each spectrum.

Reference

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