

Photoabsorption of liquid water in far-ultraviolet region

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Abstract:

Liquid water is very colorless and transparent in visible light region, but it is very photoabsorbing in the far-ultraviolet (FUV) region below 200 nm wavelength. FUV absorption of liquid water is ascribed to the first electronic transition ($\tilde{A} \leftarrow \tilde{X}$) of water molecules, and its band maximum appears around 150 nm. Because the FUV absorptivity of liquid water is significantly high (absorption coefficient: $\sim 10^5 \text{ cm}^{-1}$ at 150 nm), attenuated total reflection (ATR) technique employing an alumina prism is required to measure FUV spectra of liquid water and aqueous solutions.[1] Since the $\tilde{A} \leftarrow \tilde{X}$ transition of water is the excitation of nonbonding electrons on the oxygen atom, hydrogen bonding and hydration states of water molecules strongly affect the $\tilde{A} \leftarrow \tilde{X}$ bands.

Cation size effects on the $\tilde{A} \leftarrow \tilde{X}$ transition of hydrated water were studied with FUV spectroscopy and quantum chemical calculations.[2] ATR-FUV spectra of Group I nitrate electrolyte aqueous solutions (1 M, Fig. 1) show that the $\tilde{A} \leftarrow \tilde{X}$ bands of the hydrated water are shifted to higher energy side as the cation size is smaller from H^+ to Cs^+ . The energy shifts are linearly dependent on the hydration energies of the cations, indicating that the electrostatic interaction between the cations and the hydrated water affects the electronic state of hydrated water molecules. The EOM-CCSD and TD-DFT calculations of the $\tilde{A} \leftarrow \tilde{X}$ transitions of Group I cation-water clusters ($\text{M}^+(\text{H}_2\text{O})_6$, M^+ : $\text{H}^+ - \text{K}^+$) show that the electrostatic interactions with the cations lower the ground state energies of the hydrated water more significantly than the excited state energies.

ATR-FUV spectroscopy is suitable to study the electronic states of interfacial water on an alumina surface.[3] ATR method can linearly resolve the bulk and interfacial spectra by measuring various incident angle spectra based on Lambert's law. Figure 2 shows the resolved FUV spectra of the bulk and interfacial phases of liquid water and those of the ice states (hexagonal (I_h) and amorphous). The $\tilde{A} \leftarrow \tilde{X}$ bands of the bulk and interfacial phases are very different; specifically, the $\tilde{A} \leftarrow \tilde{X}$ band of the interfacial water is much closer to the ice spectra rather than the bulk water. Also, the red-tailing of the $\tilde{A} \leftarrow \tilde{X}$ band appears peculiarly for the interfacial water. This tailing is ascribed to the broken H-bond acceptor of water, which is probably associated with the slight hydrophobicity of the first adsorbed water layer on the alumina surface.

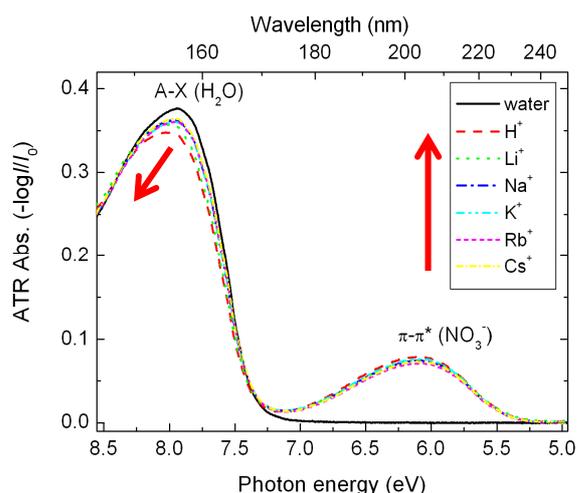


Figure 1. ATR-FUV spectra of Group I nitrate electrolyte aqueous solutions (1 M).

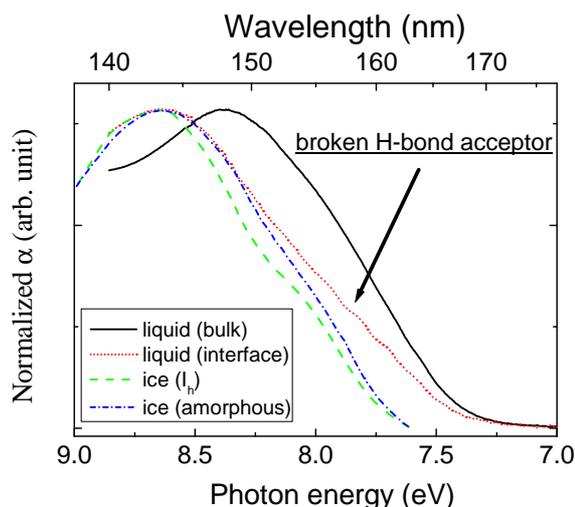


Figure 2. FUV spectra of the bulk and interfacial phases of liquid water and those of the ice states (I_h and amorphous).

References:

- [1] Ozaki, Y. and Kawata, S. (eds.) (2015) *Far- and Deep-Ultraviolet Spectroscopy*, Springer.
- [2] Goto, T.; Ikehata, A.; Morisawa, Y.; Higashi, N.; Ozaki, Y. *Phys. Chem. Chem. Phys.* **2012**, *14*, 8097.
- [3] Goto, T.; Ikehata, A.; Morisawa, Y.; Ozaki, Y. *J. Phys. Chem. Lett.* **2015**, *6*, 1022.