FUV spectroscopic investigations for water and aqueous solutions

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Summary: The wavelength region shorter than 200 nm, far-ultraviolet (FUV) region, is very rich in information about the electronic states and structure of a molecule. Since the molar absorption coefficient is very high (~10^5 mol-1 dm3 cm-1) in the FUV region, FUV spectral measurement of liquid water and aqueous solutions had been limited. Thus, for liquid samples generally either absorption spectroscopy or specular reflection spectroscopy was difficult to observe. Accordingly, FUV spectroscopy for liquid samples has been a relatively undeveloped research area. To solve the above difficulties of FUV spectroscopy we have recently developed a totally new FUV spectrometer based on attenuated total reflection (ATR) that enables us to measure spectra of liquid samples in the 140–280 nm region. This paper shows the studies by the attenuated total reflection far-ultraviolet (ATR-FUV) spectroscopy for the first electronic (*A* ← *X*) transition of liquid water and effect of cation on the *A* ← *X* transition in the aqueous solutions.

Introdution: Far-ultraviolet (FUV) spectroscopy holds great potential in revealing electronic transitions and structure of a wide range of molecules in condensed phases [1-5]. FUV spectroscopy in the 145-200 nm region has recently been a matter of intense interest because many kinds of organic [6-11] and inorganic [12-18] materials in the condensed phase show bands coming from electronic transitions in the FUV region. The spectroscopy is available not only for basic studies but also for various applications such as monitoring of the quality of semiconductor wafer clearwing [4, 19, 20]. For example, the photo catalytic activities of metal-modified TiO2 were studied by using an attenuated total reflection (ATR)-FUV spectroscopy [17, 18]. Such rapid progress in FUV spectroscopy has been introduced by the development of ATR-FUV spectrometer, which has enabled us to measure the spectra in the complete FUV region for liquid and solid samples without facing problems such as peak saturation [4, 5]. Moreover, significant progress of quantum chemical calculations for electronic excitation states of molecules improve our interpretations of the FUV spectra. In the series of studies, we investigated the FUV region of various molecules by ATR-FUV spectroscopy; namely, water and aqueous solutions [12-16], alcohols [6], n- and branched alkanes [7, 8], ketones [9], amides [10], and nylons [11] in the liquid or solid phase. The ATR-FUV spectroscopy enables us to examine the existence of confined Rydberg transitions in the liquid phase.

Results and Discussion: Molecules with oxygen atom have a transition of lone pair electron (n orbital). Because an electron in lone pair orbital plays an important role in a hydrogen bonding, it is interesting to know how the transition behaves in the liquid phase. As to water the *A* ← *X* transition is assigned to n-σ* and prtly n-3*s* Rydberg transition. The band maximum of the *A* ← *X* transition of water are measured at 168, 148-150 , 144 nm for the gas, liquid, and solid states, respectively. Fig. 1 shows ATR-FUV spectra of H_2O and D_2O at different temperature (10-70^{o}C). The maximum abosorptions for D_2O spectra were observed in shorter wavelength than those for H_2O spectra. Difference in peak maximum between D_2O and H_2O arises from the difference in the vibrational zero-point energy of the ground electronic state between H_2O and D_2O because the first electronic excitation (A) state has repulsive potential along the OH bond length.

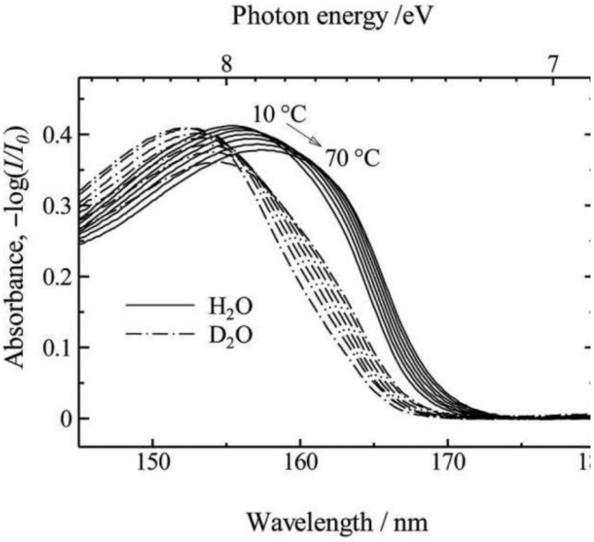

Fig. 1 ATR-FUV spectra of H2O and D2O at different temperature (ref. [12])

The *A* ← *X* transition of H2O on an sapphire substrate was ivestigated using variable angle attenuated total reflection far-ultraviolet (VA-ATR-FUV) spectroscopy in the wavelength region 140–180 nm. [16] The measurements with different penetration depth (25–19 nm) of the evanescent wave of a probe light took place by different incident angle (58.4^{o} to 71.8^{o}). The FUV spectra associated with bulk water (distance from the alumina surface >2 nm) and interfacial water (<2 nm) were calculated with the alternating least-squares (ALS) method. We found that the $\tilde{A} \leftarrow \tilde{X}$ band of the interfacial water was markedly blue-shifted and red-tailed relative to the bulk water. The electronic state difference of the interfacial water from the bulk water mainly arose from the hydrogen-bond structure and energy affected by the alumina surface.

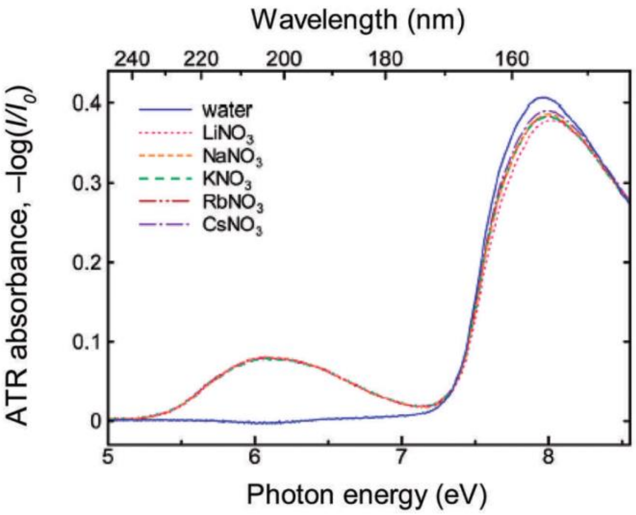

Fig. 2 ATR-FUV spectra of aqueous solution of 1M alkali metal nitrates at 25°C [13]

We also have studied for the $A \leftarrow X$ transition of water in aqueous solutions. Fig.2 shows ATR-FUV spectra of aqueous solution of 1M alkali metal nitrates. Since all the solution contain same counter anion, nitrate, with same concentration, the absorption band peaked at 6.1 eV (203 nm) which is assigned to p-p* transition of nitrate was perfectly same in each solutions. On the other hand, the the $A \leftarrow X$ transitions of H_2O shift to higher energy of the order of CS^+, Rb^+, K^+, Na^+, and Li^+. The amount of blue shift correlates with the hydration energies of the cation [13, 14].

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