Recently, the candidate has investigated electronic excitation spectra of ionic liquids by an attenuated total-reflectance (ATR) far-ultraviolet (FUV, <200 nm) and deep-ultraviolet (DUV, <300 nm) spectroscopy [**PCCP**, 18, 22526 **(2016)**; **Analyst**, 143, 2539-2545 **(2018)**]. In addition, the candidate developed a novel ATR spectroscopic system that operates under electrochemical conditions in order to investigate the electronic states of materials near the electrode surface [**Anal. Chem.**, 91, 3436-3442 **(2019)**]. In the FUV-DUV region, the penetration depth, which corresponds to the light path length for the ATR method, is less than 50 nm. Such a short light path length (i.e. surface sensitivity) is a strong advantage for investigations of physical chemistry under electrochemical environment because the materials/electrode interface where an electronic double layer forms is essentially important.

Despite providing rich information on electronic states, absorption spectra of ionic liquids in the FUV-DUV region were difficult to measure without saturation due to very strong absorbance. Herein, the candidate succeeded to record the FUV-DUV spectra of various ionic liquids systematically using the ATR-FUV-DUV spectroscopy and theoretically assign the obtained spectra based on quantum chemical calculations. Ionic liquids containing pyrrolidinium or ammonium cations and fluorine-containing anions exhibited weak absorbance below 200 nm that could not be measured by conventional UV-Vis spectroscopy. The quantum chemical calculations revealed that the absorbance was mainly due to intramolecular excitation in the anion. On the other hand, imidazolium-based ionic liquids with the fluorine-containing anions showed distinct absorption bands around 200 nm that could be reproduced by single-cation-model calculations. In addition, imidazolium-based ionic liquids with halide anions showed characteristic charge transfer (CT)-related absorbance. Thus, the ATR-FUV-DUV spectroscopy can contribute to investigations of a fundamental understanding of the electronic processes (e.g., intramolecular excitations and CT transitions) and molecular designs used in electrochemical devices.

Subsequently, upon application of voltage to an ionic liquid consisting of imidazolium cations and iodide anions, electronic transition spectra in the 150−450 nm range varied. In particular, absorbance due to charge transfer from the anion to the cation drastically increased at positive potentials. According to the molecular dynamics simulations, the density of iodide anion near the electrode surface drastically changed depending on the electrode potential, which contributed to the spectral changes. The extent of spectral change and contact area between the electrode and the ionic liquid were positively correlated, and thus, it was concluded that the interfacial ionic liquids on the electrode altered the ATR-FUV-DUV spectra. In addition, the spectral changes continued for several tens of minutes before reaching a steady state. This time scale was much longer than that of the charge redistribution process on the electrode, and such a slow dynamics was known as a unique behavior of the ionic liquids. Hysteresis was observed which was also corresponded with existing evidence from other spectroscopic techniques. The new electrochemical ATR system is the first experimental method for the measurement of electronic excitation spectra in the bulk solid/liquid interface, and it is not limited to ionic liquids and can be used for other electrochemical materials. For example, studies of organic semiconductors and hydrogen-storage polymers are in progress.