

1P062

イオン液体の固液界面近傍における
光誘起電子移動反応に対する全反射吸収分光
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**ATR Absorption Spectroscopic Study on Photo-induced Electron Transfer Reaction
nearby the Solid-Ionic Liquid Surface**

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Introduction

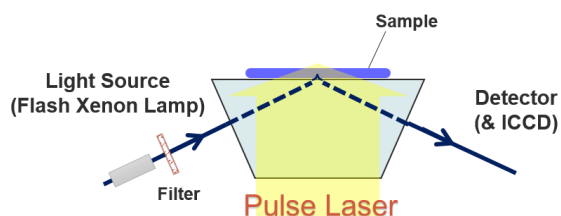
Ionic Liquids (ILs) consists of ionic molecules, and the interaction between them is characterized by strong Coulomb and van der Waals forces as well as hydrogen bonding. In addition, cation and anion in ILs exhibit poorly coordinated, resulting in salt-like material existed in liquid phase at room temperature. In this two decades, ILs are expected to be applied as a solvent for synthesis, catalysis novel electrolyte and so on. In these applications, a new question of physical phenomena caused by their natural high viscosity such as the rotational-translational process and mesoscopic chemical environment like interfacial structure of molecular layering have been pointed out recently.

This work focuses on the mesoscopic region, especially the interface of solid-ionic liquid, aims to measure the photochemical reaction (photo-induced electron transfer process) in the ILs. The methodology of this nearby interfacial study is using evanescent wave (EW) formed by the attenuate total reflection (ATR) phenomenon. We built a hand-made ATR spectroscopy covering UV-Vis region and develop it into transient observation combining with laser spectroscopy to investigate this phenomenon in nanometer-region. According to this measurement on the photo-chemical properties and dynamic information of several well-known chemical systems, the unique features of the ILs near interfacial region will be discussed combining with theoretical discussion.

Experiment

MATERIALS: ILs, 1-butyl-2-methylimidazolium dicyanamide, [C₄mim][DCN], was used as purchased form Io-li-Tec in high purity grade without further purification. Dye molecules, tetraphenylporphyrin tetrasulfonic acid hydrate (TPPS) and Erythrosine B were purchased from Tokyo Chemical Industry co., LTD. and used after recrystallization. All the samples were fabricated in room temperature and observed after vacuum dehydration.

SETUP: The UV-Vis ATR spectra were measured using a hand-made ATR spectroscopic unit, whose diagram is the center part shown in Scheme 1. The incidence light was supplied by Deuterium-Halogen Light Source (BH-2000-



Scheme 1 Diagram of developed UV-Vis ATR spectroscopy and transient observation combining with laser spectroscopy. Probe light transports from UV-Vis light source with optical fiber, and the incidence angle is controlled by graduation.

BAK), and transported to the sapphire dove prism through the optical fiber. Incidence angle was controlled by graduation before entering into the sapphire dove prism. Reflected light was detected by a UV-Vis spectrometer (Black-Comet; StellarNet Inc), and the spectrum of ATR absorbance was gathered with computer. In the transient ATR experiment, selected wavelength's laser was provided by a Nd:YAG and optical parametric oscillation. Light source was used by a flash xenon with frequency of 10 Hz. The reflected light was transported to the spectrometer, which is equipped with a photomultiplier. Intensity decay of the transient ATR signal was displayed by an oscilloscope and recorded by a computer. In the experiment of transient ATR observation, samples were deoxidized with argon gas bubbling procedure.

Results and Discussion

Figure 1 shows the UV-Vis ATR absorption spectra of 9.8 mM Erythrosine B in $[C_4mim][DCN]$ observed in different incidence angle. The absorbance decreases with incidence angle increasing, for EW penetration distance changing small. Comparing with absorption result, an inconspicuous peak shift caused by anomalous dispersion of absorbing material's refractive index was observed. By using the optical constant observed by UV-Vis absorption spectrum and anomalous dispersion, the simulated

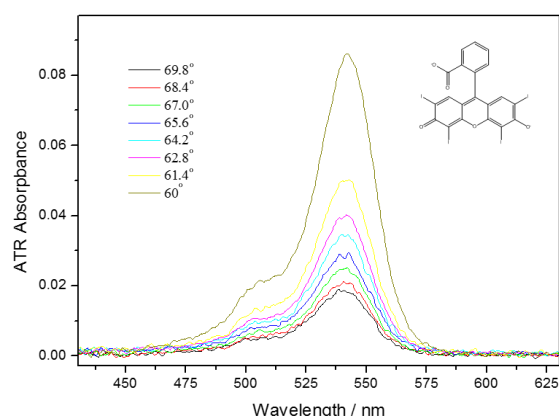


Figure 1 UV-Vis ATR absorption spectra of Erythrosine B in different incidence angle.

ATR absorption spectrum is similar to the observation. It is considered that there is no distinct electrical transition change in the solid-ionic liquid surface region; in other words, there is no interfacial phenomenon or not significant.

For the dynamic information in this interfacial region, transient ATR absorption spectroscopy was used to investigate a well-known triplet-triplet (T-T) annihilation process of TPPS. From the data analysis, T-T annihilation's reaction rate constant of the interfacial region is slower than that in bulk phase. It is considered that viscosity is a key factor in this microscopic region, namely, it is much more crucial than that in bulk. It affects how to estimate diffusion process in theoretical procedure, which is usually using diffusion controlled approximation in conventional solvents previously. In this stage, the reason of the different diffusion process is considered as ILs' special local environment nearby sapphire-ionic liquid interface with orderly arrangement, which is reported by Megzer.¹ In the presentation, results and discussion of transient ATR spectra will be talked, meanwhile up-to-date analysis of interfacial photo-induced reaction and the details of developed setup, UV-Vis ATR spectral correction will be also included.

1. Mezger, M.; Schramm, S.; Schroeder, H.; Reichert, H.; Deutsch, M.; De Souza, E. J.; Okasinski, J. S.; Ocko, B. M.; Honkimaki, V.; Dosch, H., Layering of BMIM (+)-based ionic liquids at a charged sapphire interface. *Journal of Chemical Physics* **2009**, *131* (9).