

An *ab initio* study of an excited-state intramolecular proton transfer reaction in ionic liquids

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[Introduction]

Room-temperature ionic liquids (RTILs) are expected to be the novel solvents as a reaction medium due to their inherent properties. Nevertheless, the strong electrostatic interaction of solvent molecules makes it difficult to perform theoretical studies of chemical reactions in RTILs.

Combining multi-component RISM theory with RISM-SCF-SEDD [1], we have established a procedure by which chemical reactions in RTILs can be handled in the first principle manner. Thanks to its analytical treatment of correlation functions, RISM-SCF-SEDD is free from statistical error, which is severe problem in theoretical treatment of RTILs. By using RISM-SCF-SEDD in the coupling of DFT and TD-DFT, we investigated an excited-state intramolecular proton transfer reaction of DEAHF (Scheme 1) in typical ionic liquid, [bmim][PF₆]. Kimura *et al.* reported [2] the dependency of proton transfer rate on the excitation wavelength, which suggests the inhomogeneous structure in RTILs affects the chemical reactions. The purpose of the present study is elucidating the mechanisms of the proton transfer reaction at the molecular level.

[Results and Discussions]

We adopted the difference of the O_N-H and O_T-H distances as the proton coordinate (Scheme 1),

$$q = r(\text{O}_N - \text{H}) - r(\text{O}_T - \text{H}).$$

The energy changes of S₀ and S₁ states in gas phase and in [bmim][PF₆] are shown in Fig. 1. In the S₁ state, two minima are found, which is consistent with the experiment that two emission spectra were observed [2]. The S₁ state in the normal form is stabilized due to considerable solvation effects. This is because the dipole moment of the S₁ state in normal form becomes larger (20.0 |D|) compared with that of the S₀ state (8.8 |D|), originating in charge transfer from the amino group.

The absorption and emission energies are summarized in Table 1. Here we assumed that the transitions is fast enough to leave the solvation structure and geometry frozen at the initial state. The obtained results are in good agreement with the experimental ones, while the emission energy from tautomer form is overestimated by 0.21 eV.

The drastic solvation change gives rise to the solvation relaxation after the excitation, which affects the free energy profiles along the proton coordinate.

The nonequilibrium free energy changes due to the solvation relaxation [3] and detailed mechanisms of the proton transfer will be presented.

[References]

- [1] Yokogawa, D.; Sato, H.; Sakaki, S. *J. Chem. Phys.* **2007**, *126*, 244504.
- [2] Kimura, Y.; Fukuda, M.; Suda, K.; Terazima, M. *J. Phys. Chem. B*, **2010**, *114*, 11847.
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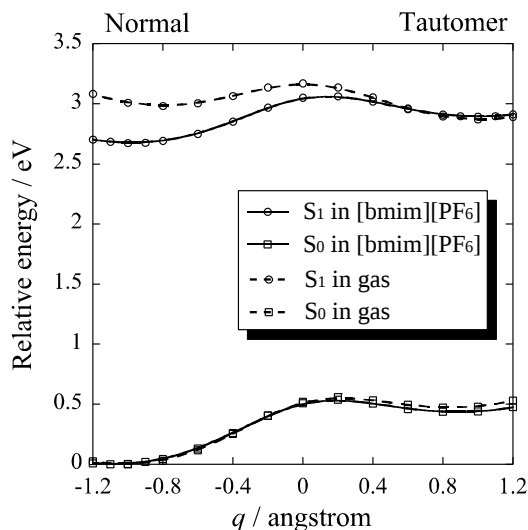
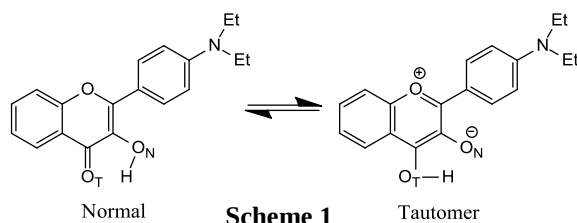


Figure 1. Relative energy along the proton coordinate.

Table 1. Summary for absorption and emission energies.

	calc. / eV	exptl.[2] / eV
Absorption	2.99	2.95
Emission (normal)	2.34	2.34
Emission (tautomer)	2.37	2.16