A Theoretical Study of Intermolecular Vibrational Couplings in Aqueous Solutions

Junichi Ono[1], Yoshitaka Tanimura[1], and Shinji Saito[2]

[1]*Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa, Sakyoku, Kyoto 606-8502, Japan*

[2]*Department of Theoretical and Computational Molecular Science, Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan*

E-Mail Address to Ono: ono@kuchem.kyoto-u.ac.jp

Knowledge about the intermolecular dynamics is indispensable to elucidate chemical reactions in condensed phases such as aqueous solutions. Recently, it was found that the intermolecular mode couplings between the translational and librational motions play essential roles in the ultrafast energy redistribution in liquid water [1]. Therefore, it is important to investigate the intermolecular vibrational couplings between water molecules in liquid mixtures in order to understand chemical reactions in aqueous solutions.

We have theoretically investigated the intermolecular dynamics of binary mixtures of liquid water with formamide (FA) in terms of the fifth-order two-dimensional (2D) Raman spectroscopy [2]. 2D-Raman spectroscopy is sensitive to vibrational mode couplings arising from both the nonlinear polarizability and the anharmonicity of potential [2]. We have analyzed the microscopic origin of the 2D-Raman signals of mixtures by using equilibrium-nonequilibrium hybrid molecular dynamics (MD) simulations [3]; especially we focused on the intermolecular vibrational couplings between water molecules in mixtures.

Figure 1 shows the composition dependence of intermolecular mode couplings between water molecules in FA-water mixtures, which can be obtained by evaluating off-diagonal peaks in 2D-Raman spectra. The librational motions of water are located between 400 and 1000 cm^{-1}, and intermolecular translational motions are seen less than 400 cm^{-1}; the peaks at 60 and 200 cm^{-1} are assigned to the O…O…O bending and O…O stretching motions of hydrogen bonded water, respectively. It is found that the anharmonic couplings with translational motions of water molecules are significantly reduced by adding FA, while vibrational couplings between librational motions of water molecules are not affected by mixing.

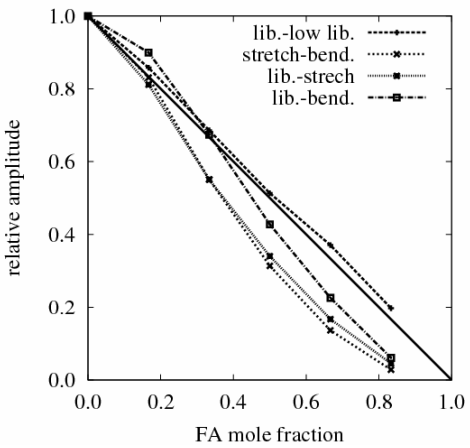

Figure 1. Composition dependence of intermolecular vibrational mode couplings between water molecules in mixtures.

REFERENCES

[1]. Y. Yagasaki and S. Saito, *J. Chem. Phys*. **128**, 154521 (2008).

[2]. S. Saito and I. Ohmine, *J. Chem. Phys.* **125**, 084506 (2006).

[3]. T. Hasegawa and Y. Tanimura, *J. Chem. Phys*. **125**, 074512 (2006).