

# Vibrational Frequency Fluctuations in Solutions Studied by Infrared Nonlinear Spectroscopy

Keisuke Tominaga,<sup>1,2</sup> Junpei Tayama,<sup>1</sup> Akina Kariya,<sup>1</sup> Kaoru Ohta,<sup>2</sup> and Seiji Akimoto<sup>1,2</sup>

<sup>1</sup>Department of Chemistry, Graduate School of Science, Kobe University, Nada, Kobe 657-8501, Japan.

<sup>2</sup>Molecular Photoscience Research Centre, Kobe University, Nada, Kobe 657-8501, Japan.

**Abstract** Three-pulse photon echo measurements in the infrared region have been performed on various solute/solvent systems to obtain time correlation function of the vibrational frequency fluctuations. In order to compare the vibrational frequency fluctuations with solvation dynamics in the electronic states we have also conducted fluorescence dynamic Stokes shift experiments in the same solvents.

Molecular dynamics in liquids are strongly affected by the nature of intermolecular interactions. It is greatly important to obtain the molecular description on relation between the dynamics and interactions in liquids in order to elucidate the solvent dynamical effect on chemical reactions. Fluctuations of the vibrational transition energies, which are characterized by time correlation functions (TCF) of the frequency fluctuations, are very sensitive to the dynamics of surrounding environments. Therefore, it has been expected to investigate the microscopic view on liquid dynamics by probing the vibrational fluctuations. In recent years, a great deal of effort has been devoted to investigate solute-solvent interactions and vibrational frequency fluctuations with infrared (IR) nonlinear spectroscopy. These techniques give detailed information on the time scale of the vibrational fluctuation and the coupling strength to the solvent, which cannot be determined precisely by spectral analysis of the linear absorption.

Three-pulse photon echo measurements are a useful technique to probe energy fluctuations of optical transitions or spectral diffusion. This is because echo signals with three-pulse excitations can yield the dynamics of the inhomogeneous distribution, while the static inhomogeneous distribution of the transition frequency can be obtained by two-pulse photon echo measurements. The three-pulse photon echo technique has been applied to electronic transitions and, more recently, to vibrational transitions for small molecules in solutions and in protein environments.<sup>1,2</sup> This nonlinear spectroscopy is especially powerful when the spectral diffusion process is characterized by multiple time scales. We have performed three-pulse photon echo measurements on various solution systems to obtain the TCF of the frequency fluctuations.<sup>3,4</sup> The results are summarized in Table 1. We found that the TCF decays biexponentially with time constants of several tens of femtoseconds and a few picoseconds. The TCF can be expressed as,

$$\langle \omega(0)\omega(t) \rangle = \Delta_1^2 \exp(-t/\tau_1) + \Delta_2^2 \exp(-t/\tau_2) + \Delta_\infty^2.$$

The results show that the time scale of the TCF depends only on the solvent and independent of the solute, whereas the coupling strength of the solute-solvent interaction is dependent on both the solvent and solute. We have also found difference of the time scale of the TCF between H<sub>2</sub>O and D<sub>2</sub>O as a solvent and this isotope effect is smaller than that obtained for the fluctuations of the energy level of the electronic state.

In order to compare the results of the vibrational frequency fluctuations with energy fluctuations of the electronic transitions, we have also performed fluorescence dynamic Stokes shift experiments. Within the linear response theory the TCF of the energy fluctuation in the equilibrium state is equal to the response function in the non-equilibrium state. We have found that for some solvents the TCF of the vibrational frequency fluctuation is similar to the response function of the solvation dynamics, whereas for other solvents that does not hold. We discuss the difference of these findings.

**Table 1. Summary of the time correlation function of vibrational frequency fluctuations**

| solute                            | solvent                       | $\Delta_1$ (ps <sup>-1</sup> ) | $\tau_1$ (ps) | $\Delta_2$ (ps <sup>-1</sup> ) | $\tau_2$ (ps) | $\Delta_\infty$ (ps <sup>-1</sup> ) |
|-----------------------------------|-------------------------------|--------------------------------|---------------|--------------------------------|---------------|-------------------------------------|
| OCN <sup>-</sup>                  | CH <sub>3</sub> OH            | 1.3                            | 0.12          | 1.6                            | 4.5           | 0.55                                |
| SCN <sup>-</sup>                  | CH <sub>3</sub> OH            | 2.6                            | 0.09          | 3.6                            | 4.1           | 0.1                                 |
| SCN <sup>-</sup>                  | D <sub>2</sub> O              | 4.3                            | 0.08          | 2.7                            | 1.3           | 0.0                                 |
| N <sub>3</sub> <sup>-*</sup>      | D <sub>2</sub> O              | 2.6                            | 0.08          | 1.4                            | 1.3           | 0.3                                 |
| N <sub>3</sub> <sup>-</sup>       | H <sub>2</sub> O              | 4.0                            | 0.08          | 1.0                            | 1.2           | 0.2                                 |
| Fe(CN) <sub>6</sub> <sup>4-</sup> | D <sub>2</sub> O              | 2.8                            | 0.08          | 1.15                           | 1.5           | 0.0                                 |
| Fe(CN) <sub>6</sub> <sup>4-</sup> | H <sub>2</sub> O              | 2.95                           | 0.08          | 1.0                            | 1.4           | 0.0                                 |
| SCN <sup>-</sup>                  | formamide                     | 2.8                            | 0.09          | 1.8                            | 4.7           | 0.6                                 |
| SCN <sup>-</sup>                  | <i>N</i> -methylformamide     | 2.75                           | 0.09          | 2.55                           | 5.4           | 0.3                                 |
| SCN <sup>-</sup>                  | <i>N,N</i> -dimethylformamide | 2.4                            | 0.09          | 0.9                            | 5.3           | 0.05                                |
| SCN <sup>-</sup>                  | acetonitrile                  | 2.5                            | 0.09          | 0.8                            | 3.4           | 0.0                                 |

\*: from reference 1.

## References

<sup>1</sup>P. Hamm, M. Lim and R. M. Hochstrasser, Phys. Rev. Lett., **81**, 5326 (1998).

<sup>2</sup>M. Lim, P. Hamm and R. M. Hochstrasser, Proc. Natl. Acad. Sci. USA, **95**, 15315 (1998).

<sup>3</sup>K. Ohta and K. Tominaga, Bull. Chem. Soc. Jpn., **78**, 1581 (2005).

<sup>4</sup>K. Ohta, H. Maekawa and K. Tominaga, J. Phys. Chem. A., **108**, 1333 (2004).