Vibrational Dynamics of Nitrosyl Stretch of Ru Complex in Aqueous Solution Studied by Two-Dimensional Infrared Spectroscopy

Kaoru Ohta[1], Kyoko Aikawa[2], and Keisuke Tominaga[1,2]
[1] Molecular Photoscience Research Center, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501, Japan
[2] Graduate School of Science, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501, Japan
e-mail address: kohta@kobe-u.ac.jp

Abstract: Vibrational frequency fluctuation of NO stretch of $[RuCl_5(NO)]^{2-}$ in water was studied by two-dimensional infrared spectroscopy. Observed temperature dependence provides evidence that collective dynamics of hydrogen bonding network controls the time scale of frequency fluctuation.
OCIS codes: (000.1570) Chemistry; (300.6340) Spectroscopy, infrared; (320.7100) Ultrafast measurements;

1. Introduction

Solute-solvent interaction plays an important role in chemical reaction dynamics and in many relaxation processes in the condensed phase. In particular, hydrogen bonding dynamics in aqueous solution occurs on a picosecond time scale which may facilitate proton transfer and ion transport. Furthermore, the hydrogen bonding interactions are substantially influenced by the presence of charged species. Understanding of such interaction requires detailed knowledge of dynamical properties of the solvent molecules at the microscopic level. It is known that small ionic molecules such as SCN^- and N_3^- are excellent vibrational probes for studying the local interaction with the surrounding environment. Recently we studied the vibrational dynamics of the anti-symmetric stretching mode of SCN^- and N_3^- in various polar solvents by using three-pulse infrared (IR) photon echo methods [1,2]. Our results showed that there exists a clear difference of the vibrational dynamics between protic and aprotic solvents. Hydrogen bonding interaction plays an important role in the structural fluctuations of the solution.

To understand the molecular origin of vibrational dynamics in detail, we chose the NO stretching mode of $[RuCl_5(NO)]^{2-}$ as a vibrational probe. Here we investigated the temperature dependence of the vibrational frequency fluctuation of the NO stretching mode in aqueous solution and compared with our previous studies of a couple of different ionic probe molecules. Temperature dependence of the vibrational dynamics of the solute in solution provides the systematic information about the coupling between the vibrational mode of the solute and the bath degrees of the system.

2. Results and Discussion

To quantify the frequency-frequency correlation functions of vibrational transitions, we used two-dimensional IR spectroscopy. Home-built optical parametric amplifier and difference frequency generator were used to produce a mid-IR pulse at around 1900 cm^{-1}. 2D IR spectra were measured with a collinear pulse pair pump-probe geometry. From the FT-IR spectra of the NO stretching mode of $[RuCl_5(NO)]^{2-}$, the peaks of the absorption spectrum are located at around 1882 cm^{-1} in D_2O and H_2O. We measured the vibrational population relaxation for this mode by ultrafast IR pump-probe spectroscopy. We found that vibrational relaxation takes place on 31 ps in D_2O and 7.7 ps in H_2O, respectively. Similar fast relaxations in H_2O were observed for the other vibrational modes such as anti-symmetric stretching modes of N_3^- and SCN^- [2]. This is because the vibrational bands at around 1900 cm^{-1} couples strongly with a combination band of the bending and librational modes of H_2O. Spectral overlap of the solvent vibrational modes enhances the vibrational energy transfer from solute to solvent.

Figure 1 displays 2D-IR spectra of the NO stretching mode of $[RuCl_5(NO)]^{2-}$ in D_2O taken at 283 K and 313 K. At small values of population times, the 2D IR line shape is elongated along diagonal axis which reflects a positive correlation between the initial (ω_{pump}) and final (ω_{probe}) frequencies. At longer population times, the shape becomes more round, reflecting the loss of the correlation of transition frequency. To determine the form of the frequency-frequency correlation function from 2D IR spectra, we used center line slope (CLS) analysis. From the previous studies, the temporal profiles of the CLS mirror the frequency-frequency correlation function of the vibrational transitions. Figure 1(c) shows the decay profiles of CLS at different temperatures. At 293 K, the decay time constant of CLS is 1.0 ps. This process reflects the hydrogen bonding dynamics under thermal equilibrium condition. The obtained time constant is very similar to that observed in the other ionic vibrational probes [1,2]. This means

that time scales of the vibrational frequency fluctuation are not simply determined by the interaction between solute and nearest solvent. Collective dynamics of the solvent molecules around solute play a major role in determining the time scales of the vibrational frequency fluctuations in aqueous solutions.

With decreasing temperature, the decay of CLS becomes slower as clearly seen from Fig.1(c). In our previous studies, we investigated the temperature dependence of the vibrational frequency fluctuation of the anti-symmetric stretching mode of N_3^- in D_2O by three-pulse IR photon echo experiments [3]. The decay component of frequency-frequency correlation function varies from 1.4 to 1.1 ps in the temperature range from 283 K to 353 K. The observed temperature dependence is very similar to that of current results. Furthermore, the dynamics of hydrogen bonding network in water have been intensively investigated by ultrafast IR spectroscopy in conjunction with molecular dynamics (MD) simulations. In these experiments, the vibrational frequency fluctuation of OH (OD) stretching mode was monitored for a solution of HOD in D_2O (H_2O). Temperature dependent studies suggested that the mechanism of vibrational frequency fluctuation, reorientational relaxation of OD stretch, and hydrogen bond rearrangement are strongly correlated and frequency-frequency correlation function follows a slightly non-Arrhenius behavior [4,5].

Together with these observations, we can conclude that picosecond vibrational dephasing dynamics of small ionic probes in aqueous solutions are driven by the electric field fluctuations originating from collective reorganization of hydrogen bonding network. Since the dynamic range of the 2D IR measurement is limited by the vibrational lifetime of the chromophore under investigation, the NO stretching mode of $[RuCl_5(NO)]^{2-}$ is a good vibrational probe for watching the local fluctuations of solvation structures of water in various environments on a longer time scale.
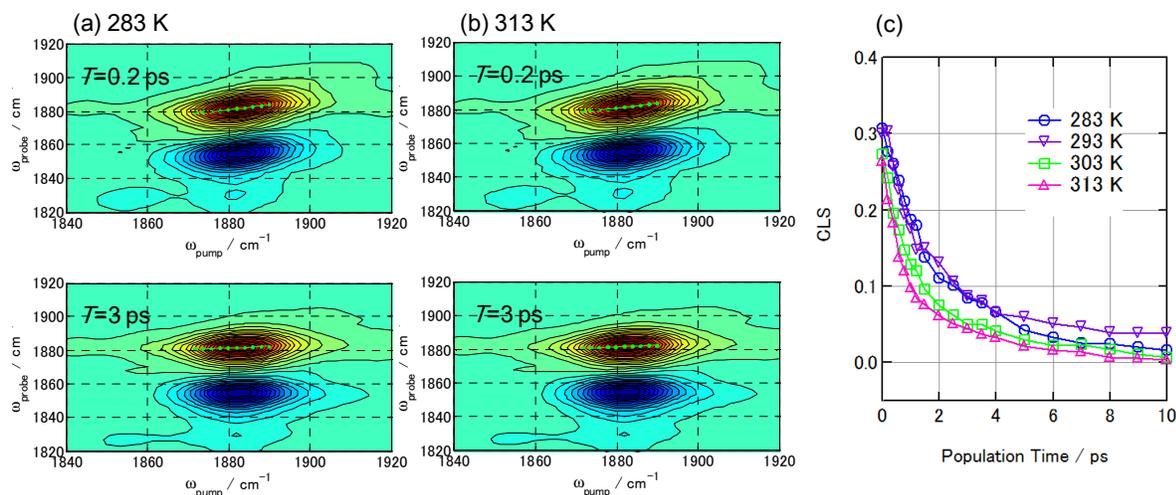

Fig. 1. (a) 2D IR spectra measured at 283 K with the population times of 0.2 ps and 3 ps. (b) 2D IR spectra measured at 313 K. Green lines and dots are the center line slopes. (c) Temporal profiles of CLS at temperatures of 283 K, 293 K, 303 K and 313 K.

3. References

[1] K. Ohta, J. Tayama, and K. Tominaga, "Ultrafast vibrational dynamics of SCN⁻ and N_3^- in polar solvents studied by nonlinear infrared spectroscopy", Phys. Chem. Chem. Phys. **14**, 10455-10465 (2012).

[2] K. Ohta, J. Tayama, S. Saito and K. Tominaga, "Vibrational frequency fluctuation of ions in aqueous solutions studies by three-pulse infrared photon echo method", Acc. Chem. Res. **45**, 1982-1991 (2012).

[3] J. Tayama, A. Ishihara, M. Banno, K. Ohta, S. Saito, and K. Tominaga, "Temperature dependence of vibrational frequency fluctuation of N_3^- in D_2O", J. Chem. Phys. **133**, 014505 (2010).

[4] R. A. Nicodemus, S. A. Corcelli, J. L. Skinner, and A. Tokmakoff, "Collective hydrogen bond reorganization in water studied with temperature-dependent ultrafast infrared spectroscopy", J. Phys. Chem. B **115**, 5604-5616 (2011).

[5] F. Perakis and P. Hamm, "Two-dimensional infrared spectroscopy of supercooled water", J. Phys. Chem. B **115**, 5289-5293 (2011).