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Vibrational Transition Frequency Fluctuation of the NO Stretching Mode of Sodium Nitroprusside in Aqueous Solutions

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Frequency fluctuation of the NO stretching mode of the sodium nitroprusside, $[Fe(CN)_5NO]^{2-}$, in H_2O and D_2O was studied by three-pulse infrared photon echo spectroscopy. It is found that the time-correlation function of the frequency fluctuation of this mode is characterized by time constants similar to those of the triply degenerate T_{1u} mode of the CN stretching of $[Fe(CN)_6]^{4-}$, showing that the vibrational frequency fluctuation is not dominated by the time-dependent anisotropic solute–solvent interaction.

Third-order nonlinear infrared (IR) spectroscopy has become a powerful tool for investigating various dynamic processes in condensed phases over the last few decades.[1–3] The vibrational dynamics of the solute in solution provides information about the coupling between the vibrational mode of the solute and the bath degrees of the system. From polarization-sensitive IR pump–probe experiments, the vibrational population dynamics and rotational dynamics can be studied. Characteristics of the vibrational frequency fluctuation with multiples components with finite time scale in solution can be studied by three-pulse IR photon echo spectroscopy. Recently, we have investigated the vibrational dynamics of small ions and metal complexes.[4–7] The details of the temperature dependence of the vibrational frequency fluctuation of azide in D_2O was also studied.[6] The time-dependent frequency fluctuation, $\Delta\omega(t)$, is defined as

$$\Delta\omega(t) = \omega(t) - \langle\omega\rangle \qquad (1)$$

where $\omega(t)$ and $\langle\omega\rangle$ are the instantaneous vibrational transition frequency at time t and its time average, respectively. In previous studies, we obtained two major conclusions for the time-correlation function (TCF) of the frequency fluctuation in hydrogen-bonding solvents such as water and methanol. One is that the TCF is expressed by a biexponential function with a quasistatic term,

$$\langle\Delta\omega(t)\Delta\omega(0)\rangle = \sum_{i=1}^{2} {\Delta_i}^2 \exp(-t/\tau_i) + {\Delta_0}^2 \qquad (2)$$

The other is that the time constant for the slower part of the TCF, τ_2, does not significantly depend on the solute. In contrast, the amplitude for the slow component depends on both the solvent and the solute. In view of the above results, the major aim of this series of studies is to clarify what type of solute–solvent interaction determines the frequency fluctuation and what types of solvent dynamics govern the fluctuation. In particular, for degenerate vibrational modes, time-dependent anisotropic interaction due to the symmetry breaking may affect the vibrational frequency fluctuation.

In the previous work, we studied vibrational dynamics of the triply degenerate T_{1u} mode of the CN stretching of hexacyanoferrate ion $[Fe(CN)_6]^{4-}$ in H_2O and D_2O and that of hexacyanoruthenate $[Ru(CN)_6]^{4-}$ in D_2O.[4,8,9] For the system of $[Fe(CN)_6]^{4-}$ in D_2O, the transient grating signals in the magic angle condition show a biexponential decay upon the excitation of the T_{1u} mode of the CN stretching motion. A fast decaying component (ca. 700 fs) of the transient grating signal is attributed to the rapid equilibration between the T_{1u} mode and the Raman active modes. The time scale of the slow decaying component is around 23 ps, which corresponds to the vibrational population relaxation from the $v = 1$ state of the CN stretching mode. Anisotropy of the transient grating signal decays with a time constant of 2.6 ps, which is due to the time evolution of the superposition states of the triply degenerate T_{1u} modes. The three-pulse IR photon echo measurements showed that the TCF of the frequency fluctuations decays biexponentially with time constants of 80 fs and 1.5 ps. The time scales of the decay of the TCF are similar to those for other systems such as SCN^- in D_2O even though the coupling strength of the solute–solvent interaction depends on the systems. For the system of $[Ru(CN)_6]^{4-}$ in D_2O, we observed similar experimental results to the $[Fe(CN)_6]^{4-}$ case. Therefore, it is necessary to investigate how the mode degeneracy affects the TCF of the frequency fluctuation in order to understand the vibrational dynamics of the metal complexes. In this study we compare the results of the TCF of the frequency fluctuation of the NO stretching mode of $[Fe(CN)_5NO]^{2-}$ in H_2O and D_2O with that of the T_{1u} mode of the CN stretching mode of $[Fe(CN)_6]^{4-}$ in the same solvents.

Detail of the experimental setup has been described elsewhere.[9,10] Briefly, a mid-IR pulse was generated by difference frequency generation on $AgGaS_2$ crystal between the two near-IR outputs (signal and idler pulses) from an optical parametric amplifier. A mid-IR pulse has a pulse width of about 150 fs with a repetition rate of 1 kHz and pulse energy of about 2 μJ/pulse. The peak frequency of the IR pulse was tuned to around 1935 cm^{-1}. The mid-IR pulse was split into three beams that were focused on the sample with a parabolic mirror. The homodyne-detected IR photon echo signal was measured as a function of the two delay times, τ and T. The delay time τ is defined as the time between the k_1 and k_2 pulses, and the delay time T is defined as the time between the k_2 and k_3 pulses for $\tau \geq 0$ and k_1 and k_3 pulses for $\tau < 0$. The sample was contained in a cell with an optical path length of 25 μm and CaF_2 windows. The concentration of the sample used for the three-pulse IR photon echo experiments was around 72 mM. Sodium nitroprusside $Na_2[Fe(CN)_5NO]$ and D_2O were purchased from Aldrich and used as received. H_2O (Milli-Q) was also used without additional treatment. The linear IR spectra were recorded using a JASCO FT-IR 6300 spectrometer. The parameters for the TCFs of the NO stretching mode of $[Fe(CN)_5NO]^{2-}$ in H_2O and D_2O are optimized by the iterative

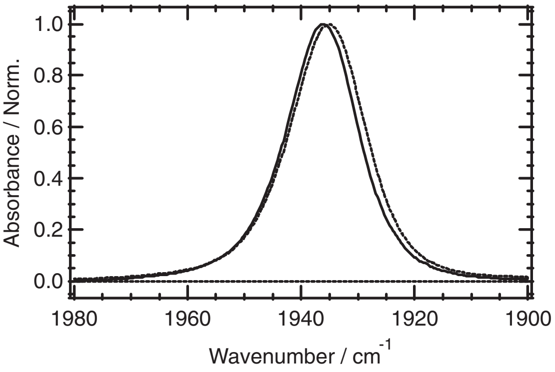

Figure 1. The IR absorption of the NO stretching mode of $[Fe(CN)_5NO]^{2-}$ in H_2O (solid line) and D_2O (dotted line).

numerical simulation of the linear and nonlinear IR signal with the standard procedure.[10–12]

The IR absorption spectrum of the NO stretching mode of $[Fe(CN)_5NO]^{2-}$ in H_2O and D_2O are shown in Figure 1. The width of this band (full width at half maximum) is 14.9 cm^{-1} in H_2O and 15.7 cm^{-1} in D_2O. The peak position of this band is 1936.2 cm^{-1} in H_2O and 1935.0 cm^{-1} in D_2O. This weak solvent dependence is conceivably caused by the difference of the mass of the tightly bound solvents around the NO moiety. We may leave the details of the origin of this frequency shift to our future publications.

Figure 2a shows the three-pulse photon echo signals of the NO stretching mode of $[Fe(CN)_5NO]^{2-}$ in D_2O at 293 K under the all-parallel polarization condition. At population times T earlier than 200 fs, the first moment of the photon echo signal along the τ axis

$$FM(T) = \frac{\int_{-\infty}^{\infty} d\tau \tau I(\tau, T)}{\int_{-\infty}^{\infty} d\tau I(\tau, T)} \qquad (3)$$

is located at around 200 fs, indicating the presence of an inhomogeneous distribution of the vibrational frequency. The slice at $T = 500$ fs of the photon echo signal is shown in Figure 2b. The first moment of the echo signal along the τ axis shifts toward zero as the population time T increases (Figure 2c). This behavior shows that the local environment of each oscillator is inhomogeneously distributed and evolves on a time scale of a few picoseconds. As the delay time T increases, the time evolution of the local environment "destroys" the inhomogeneity of the distribution of the vibrational transition frequency obtained near $T = 0$. Therefore, the first moment of the photon echo signal is a sensitive measure for degree of "transient inhomogeneity" in the distribution of the transition frequencies, and the time scale of the decay is approximately proportional to that of the TCF of the frequency fluctuation.[13–15] The first moment decays on a time scale of 1.4 ps and is close to zero at $T = 6$ ps. The time scale of the decay of the first moment of the photon echo signals in H_2O is similar to that in D_2O.

The TCFs of the vibrational transition frequency fluctuation of the NO stretching mode of $[Fe(CN)_5NO]^{2-}$ in H_2O and D_2O are evaluated by the iterative numerical simulation of the temporal profile of the three-pulse IR photon echo signals and

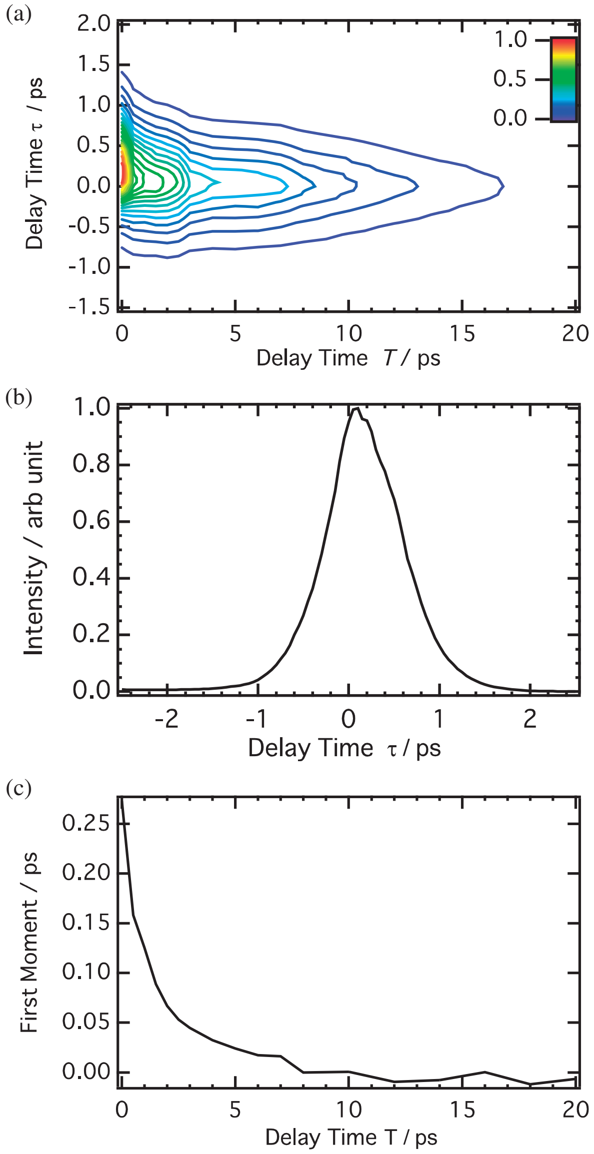

Figure 2. (a) Three-pulse IR photon echo signals of the NO stretching mode of the $[Fe(CN)_5NO]^{2-}$ ion in D_2O. (b) The slice of the three-pulse IR photon echo signal of the NO stretching mode of $[Fe(CN)_5NO]^{2-}$ in D_2O at $T = 500$ fs. (c) First moment of the photon echo signals of the NO stretching mode of $[Fe(CN)_5NO]^{2-}$ in D_2O.

IR absorption spectrum simultaneously. Sando et al. study the vibrational and rotational dynamics of $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, and $[Fe(CN)_5NO]^{2-}$ in protic solvents.[16] They focused on the vibrational population relaxation and anisotropy decay of these systems. The time constants for in H_2O, $T_{10} = 7.3$ ps, $T_{21} = 3.65$ ps, $T_R = 16$ ps, and for in D_2O, $T_{10} = 22$ ps, $T_{21} = 11$ ps, $T_R = 20$ ps, where T_{10}, T_{21}, and T_R are the population relaxation time for $v = 1$–0 transition, the population relaxation time for $v = 2$–1 transition, and the rotational relaxation time, respectively, and anharmonicity, $\Delta = 28$ cm^{-1}, is used in the numerical simulation of the photon echo signal and the linear IR absorption spectrum of the NO stretching mode of $[Fe(CN)_5NO]^{2-}$ in H_2O and D_2O.[16–18] Optimized parameters for

Table 1. Parameters for the time-correlation function of the vibrational frequency fluctuations

System	Parameters for the correlation function					
	$\Delta_1/\mathrm{ps}^{-1}$	τ_1/ps	T_2^*/ps	$\Delta_2/\mathrm{ps}^{-1}$	τ_2/ps	$\Delta_0/\mathrm{ps}^{-1}$
T_{1u} mode of the CN stretching mode of $[Fe(CN)_6]^{4-}$						
In H_2O[8]	2.95	0.08	1.4	1.0	1.4	0.0
In D_2O[9]	2.8	0.08	1.6	1.15	1.5	0.0
T_{1u} mode of the CN stretching mode of $[Ru(CN)_6]^{4-}$						
In D_2O[4]	3.0	0.08	1.4	0.8	1.4	0.1
NO stretching mode of $[Fe(CN)_5NO]^{2-}$						
In H_2O	3.1	0.09	1.2	1.0	1.1	0.0
In D_2O	2.7	0.08	1.7	1.2	1.1	0.1

the TCF of the vibrational frequency fluctuation are listed in Table 1. It should be noted that fastest decaying components in the correlation function falls into the motional narrowing limit. Only the values of $\Delta_1{}^2\tau_1$ are important to describe the fast dephasing process. Pure dephasing time, $T_2{}^*(= \Delta_1{}^2\tau_1)$ is used to describe this component in the correlation function as shown in Table 1.

The obtained time constant of the slow decaying component of the TCF of the vibrational frequency fluctuation of the NO stretching mode of $[Fe(CN)_5NO]^{2-}$ in H_2O (1.1 ps) is similar to that in D_2O (1.1 ps), as well as those of $[Fe(CN)_6]^{4-}$ in D_2O (1.5 ps), $[Ru(CN)_6]^{4-}$ in D_2O (1.4 ps), SCN^- in D_2O (1.3 ps), and $N_3{}^-$ in D_2O (1.3 ps at 293 K). Fayer and co-workers showed that the temperature dependence on the pure dephasing of $[Rh(CO)_2(C_5H_7O_2)]$ is different from that of $[W(CO)_6]$ in the same solvent.[19] They proposed that this difference results from the difference in mode degeneracy. For $[W(CO)_6]$, local fluctuations in solvent give rise to the energy separation among the triply degenerate modes, causing a dephasing mechanism not seen in $[Rh(CO)_2(C_5H_7O_2)]$. Even though the vibrational dephasing could be caused by both the energy gap fluctuation between the $v = 0$ and $v = 1$ states for the T_{1u} mode and the fluctuation of the energy splitting among the triply degenerate T_{1u} modes, our result shows that the time scale of the spectral diffusion process for $[Fe(CN)_6]^{4-}$ is controlled by the same mechanism as that for SCN^-, not by the time-dependent anisotropic solute–solvent interaction. Symmetry breaking due to the solute–solvent interaction induces the energy splitting among the T_{1u} modes of solute. This would cause the additional source of the frequency fluctuation. We may observe different dynamics of the vibrational dephasing processes between $[Fe(CN)_5NO]^{2-}$ and $[Fe(CN)_6]^{4-}$. However, the time scale of these processes is similar to each other. We considered that the contribution of the vibrational dephasing originating from the fluctuation of the energy splitting among the triply degenerate T_{1u} modes is small.

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