

Frequency fluctuations of non-ionic vibrational probe in water studied by 2DIR spectroscopy and molecular simulation

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Frequency fluctuations of the CN stretching mode of 2-nitro-5-thiocyanatobenzoic acid are examined by 2D-IR spectroscopy and classical molecular dynamics simulation. The 2D-IR experiment revealed that the frequency-frequency correlation function contained the decay component of 1.1 ps, which is attributed to the rearrangement of hydrogen-bond network around the solute.

In aqueous solution, three-dimensional hydrogen bond network are formed among water molecules. The network evolves continuously in time due to the rearrangement of hydrogen bonds. Therefore, thorough solute-solvent interactions, such a collective dynamics strongly perturbs solutes, resulting in fluctuations of the electronic and vibrational states. So far, we examined the vibrational frequency fluctuations of ions, such as N_3^- , in water in order to discuss solute-solvent interactions and solvation dynamics [1]. In this study, we investigate the frequency fluctuations of the CN stretching mode of 2-nitro-5-thiocyanatobenzoic acid (NTBA) with two-dimensional infrared (2D-IR) spectroscopy. Because the SCN group in NTBA covalently binds to the aromatic ring, we can study the hydrophobic effects on the frequency fluctuations by comparing the results for ions. From the decay curve of the center line slope of 2D-IR spectra of NTBA in H_2O (Fig. 1) [2], it is found that the frequency-frequency correlation function (FFCF) of NTBA decays with the time constants of about 1 ps, and, according to the previous results of ions in water, this decay is related to the collective motion of waters around NTBA [1]. Moreover, no static component is contained in FFTCF of NTBA. Consequently, it could be considered that the water dynamics around NTBA is similar to those around ions. To obtain molecular pictures for the frequency fluctuations of NTBA in water, we also performed the molecular dynamics (MD) simulation. Based on the theoretical method to analyze the frequency shifts of the CN stretching mode in water [3], it is revealed that interactions between NTBA and water molecules not only in but also out of the first hydration shell are important for the frequency fluctuations of NTBA (Fig. 2)

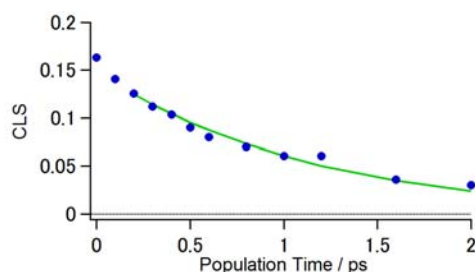


Figure 1. CLS curve from each 2D-IR spectra of NTBA in H_2O plotted against population time. Green line indicates the numerically calculated CLS [2].

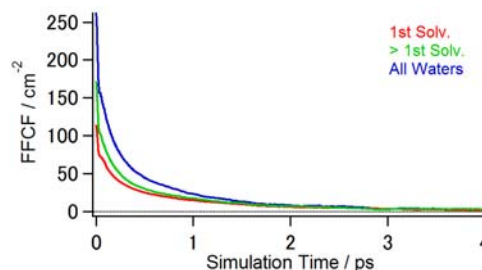


Figure 2. FFCF of NTBA in H_2O theoretically calculated with MD simulation [3]. Based on the radial distribution function obtained from MD simulation, we determine the hydration shell of NTBA, and calculated space-resolved FFCF: (red) within and (green) out of the first solvation shell, and (blue) whole simulation box.

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