Vibrational Dynamics of Hydrogen-Bonded Complexes Studied by Infrared Pump-Probe Spectroscopy

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We have investigated vibrational dynamics of hydrogen-bonded complexes in solutions by sub-picosecond infrared (IR) pump-probe spectroscopy. The anharmonic coupling between the OH stretching mode of benzoic acid dimer and low-frequency mode was studied from analysis of the quantum beat observed in the pump-probe signal. The IR absorption spectrum of 9-fluorenone (FL) in alcohol shows three distinct contributions from the free FL, its complex with one alcohol molecule, and that with two molecules. The time constants of the vibrational energy relaxation (VER) of the CO stretching mode of the free FL and that of the 1:1 complex were obtained. The VER of the OH stretching mode of methanol was studied in the isotopically diluted methanol. The internal isotope effect on the VER is discussed.

Key Words: Infrared short pulse, Pump-probe spectroscopy, Hydrogen bond in solutions

1. Introduction

Hydrogen bond plays an important role in various chemical and biological events.1, 2) Hydrogen bonds greatly influence stability of three-dimensional structures of chemical complexes and biological macromolecules such as nucleic acid and proteins. Biological macromolecules often express and control their functions by rearranging hydrogen bonds. Furthermore, hydrogen bond forms a characteristic network structure of a finite size in hydrogen bonding liquids such as water and alcohol, which play an important role in chemical reactions and biological activities. In this work we have studied effect of hydrogen bond on vibrational energy relaxation by infrared (IR) pump-probe spectroscopy.

2. Experimental

Details of the IR pump-probe spectroscopy will be described elsewhere.3) We obtained IR pulses by difference frequency mixing with signal and idler pulses generated by a home-built optical parametric amplifier. The pulse duration of the IR pulse is approximately 200 fs. We split the IR pulse into pump, probe, and reference pulses. The probe and reference pulses were detected by an array detector after passing through a monochromator. The samples were contained in a cell with an optical path length of 0.05-0.5 mm depending on the systems. The samples were prepared so that the optical density was around 0.6 at the excitation wavenumber. The measurements were done at room temperature (20℃).

3. Results and Discussion

3.1 OH Stretching Mode of Benzoic Acid Dimer

Carboxylic acids in solutions are important model systems for studying hydrogen bonds. Benzoic acid (BA) is one of the carboxylic acids and forms dimer or complex with other molecules in various solutions.4) Intermolecular hydrogen bonds of these complexes have much effect on dynamics of the vibrational modes associated with hydrogen bonds. The effects of hydrogen bond on dynamics in the vibrationally excited state of the hydroxyl stretching mode have been extensively studied by time-resolved vibrational spectroscopy. Recently, Heyne et al. have studied the coupling between the hydroxyl stretch and low-frequency modes of acetic acid dimer by analyzing the quantum beat observed in the pump-probe signal.5,6) In this work we have studied vibrational energy relaxation (VER) of the OH stretching mode of the BA complex in solutions by IR pump-probe spectroscopy.

Figure 1 shows IR spectra of the OH stretching mode of BA-d5 in the solvents which do not form any strong hydrogen bond (CCl4, CDCl3, and benzene-d6). The peak wavenumber is located at around 3000 cm−1, and the spectra show a broad band with complicated structures.5,6) The spectra of the three solutions are identical to each other. From the dependence of the IR spectrum on the concentration of BA, the broad band at 3000 cm−1 is assigned to dimer of BA.

Figure 2 shows a frequency-resolved pump-probe signal of the OH stretching mode of BA-d5 in CCl4, in which the signal is displayed as a function of the delay time and the probe frequency. The excitation and probe pulses have a central wavenumber at 3000 cm−1. In the lower-frequency side the ground state bleach and the stimulated emission is observed, and in the higher-frequency side the transient absorption is observed. Figure 3 displays a time profile of the signal at 3000 cm−1.
The signal shows a double exponential decay with a pronounced oscillation. The obtained time constants of the decay are 730 fs and 12 ps at 3000 cm$^{-1}$. At higher-frequency sides the signal turns to a transient absorption component instantaneously, which is followed by decay in a picosecond time scale. This transient absorption component in the higher-frequency side results from a blue shift of the spectrum in the vibrational ground state. This is caused by increase of weakly hydrogen-bonded complexes due to local heating around the oscillator. Therefore, the VER takes place within our time resolution (< 200 fs), and the pump-probe signals come from the vibrational ground state. We tentatively assign the fast and slow components to the VER of the low-frequency modes in the ground state of the OH stretching mode and cooling process in the environment locally heated, respectively.

We analyzed the oscillation in the pump-probe signals by Fourier transforming the oscillatory part. By subtracting the Fourier spectrum of the quantum beat. There is a single band located at around 100 cm$^{-1}$. This double exponential function.

Fig. 3. A pump-probe signal of 120 mM BA-d$_5$ in CCl$_4$. A blue curve is a result of fitting by a double exponential function.

Fig. 4 (left) The two-dimensional plot of the Fourier spectra. $\nu_{LF}$ and $\nu_{OH}$ denote frequencies of the low-frequency mode and OH stretching mode, respectively. (right) The dependence of the low-frequency mode ($\nu_{LF}$) on the OH stretching mode ($\nu_{OH}$). A blue is a least-squares fit for eye guidance.

Heyne et al. also observed a low-frequency mode at 145 cm$^{-1}$ which is coupled to the OH stretch of acetic acid dimer. They assigned this mode to in-plane dimer bending mode. In order to obtain the peak wavenumber of the low-frequency mode more accurately, we fitted the Fourier spectra with a Lorentzian function. The results are shown in Figure 4. Although the points are rather scattered, it is observed that the peak wavenumber of the low-frequency mode depends on the frequency of the OH stretching mode; as the frequency of the OH stretching mode increases, the frequency of the low-frequency mode becomes smaller.

Let us briefly discuss the possible origins for this dependence. First, the Fermi resonance may contribute to the oscillation. However, as discussed in detail by Heyne et al., oscillation due to the Fermi resonance should disappear within a dephasing time between the $v_0$ and $v_1$ states of the OH stretching mode. In this case the lifetime of the vibrationally excited state is shorter than the time resolution which is less than 200 fs. Therefore, it is unlikely that the Fermi resonance could contribute to the oscillation. Second, there may be two low-frequency modes around 100 cm$^{-1}$ which are coupled to the OH stretching mode. Bands due to these modes may overlap with each other, and the coupling strength of these modes may depend on the wavenumber. Then, the band shape changes with the probe wavenumber since the relative intensities of the two bands depend on the wavenumber, and, consequently, an effective peak position changes with the wavenumber. Finally, the high-frequency side of the OH stretching mode corresponds to weaker hydrogen bonds. Therefore, it may happen that the low-frequency inter-molecular mode depends on the hydrogen bond strength. It is true only when the band is massively inhomogeneously broadened. The key question is how large the inhomogeneity is for the OH stretching band, which can be clarified by an IR photon echo experiment.

3.2 CO Stretching Mode of 9-Fluorenone in Alcohol

In the hydrogen-bonded complexes various dynamical features such as reactivity and energy relaxation are strongly influenced by intramolecular hydrogen bonds as well as intermolecular ones. Among them, the effect of hydrogen bonds on VER has been recently investigated by time-resolved IR spectroscopy. For example, the OH stretching mode of
alcohols or water shows a significant red shift of about 300 cm$^{-1}$ by forming a hydrogen bond with other molecules, and the VER of the OH stretching mode is accelerated by more than one order of magnitude. In this work we focus on the hydrogen bond effect on the VER of the CO stretching mode. The carbonyl molecule chosen for the present study is 9-fluorenone (FL). We have studied the VER of the CO stretching mode of FL in non-hydrogen bonding solvent and in alcohol by sub-picosecond IR pump-probe spectroscopy.

Figure 5 shows an IR absorption spectrum of FL in cyclohexane, a non-hydrogen-bonding solvent. The CO stretching mode of FL shows a sharp band in cyclohexane with a peak wavenumber of 1725 cm$^{-1}$ and fwhm of 4.5 cm$^{-1}$. The IR absorption spectrum of FL in 1-octanol is superimposed in the figure. The spectrum shows pronounced structures with two peaks at around 1713 cm$^{-1}$ and 1721 cm$^{-1}$, and a shoulder at around 1700 cm$^{-1}$. In other alcohol solvents such as 1-propanol or 1-butanol (not shown here), similar spectral shapes with three bands were observed though the relative intensities of the three bands depend on the alcohol.

We have obtained optimized geometries and normal mode coordinates and their frequencies of the free FL and complexes in gas phase by performing DFT calculation with a basis set of 6-31+(d,p) using B3LYP functional. We chose methanol as an alcohol. The oxygen atom has two lone pairs which act as hydrogen bonding sites, and there are two possible hydrogen-bonding complexes with one and two methanol molecules. The wavenumber of the CO stretching vibration of free FL is 1784 cm$^{-1}$, and those of FL:MeOH and FL:(MeOH)$_2$ molecules are 1761 cm$^{-1}$ and 1736 cm$^{-1}$, respectively. The results show that the peak shifts to the lower-frequency side by forming complexes. Therefore, we assign the observed bands in the IR spectrum to different complexes of FL and solvent molecules, that is, the (a), (b), and (c) bands correspond to free FL, FL and one alcohol complex, and FL and two alcohol complex, respectively.

The IR pump-probe signal of FL in cyclohexane at 1727 cm$^{-1}$, which is close to the peak wavenumber, decays exponentially with a time constant of 4.3±0.1 ps. The signal decays to the recovery of the ground state bleach and the decay of the stimulated emission. The signal shows a sharp spike at around t = 0 ps, which we assign to a coherent artifact. For all the pump-probe signals investigated in this work, we fit the time profile of the signal from the delay time of 0.45 ps. Figure 6 shows a pump-probe signal in 1-octanol at 1723 cm$^{-1}$ that is close to the peak of the CO stretching vibration of the free FL. The signal decays exponentially with a time constant of 4.3±0.1 ps. The time constant is similar to that in cyclohexane. On the other hand, the figure in the lower panel is the pump-probe signal at 1712 cm$^{-1}$, closed to the peak of the CO stretching vibration of the FL:(1-octanol) complex. The signal decays exponentially with a time constant of 1.6±0.1 ps. From the global fitting for the frequency-resolved pump-probe signals we obtained decay the time constants for the free FL and FL:(1-octanol) complex as 4.7±0.1 ps and 2.3±0.1 ps, respectively. This results show that the VER is accelerated twice by the hydrogen bond formation.

The mechanism that speeds up the VER by hydrogen bond formation has been often discussed in terms of Fermi Golden Rule. Namely, the transition rate is determined by density of states, coupling strength, and energy gap. The formation of hydrogen bond could influence all the three factors. For example, the OH stretching of water shows a red shift of about 300 cm$^{-1}$ by hydrogen bond formation, that facilitates coupling with overtone of the bending mode. In the present case, the energy shift due to the bond formation is about 10 cm$^{-1}$, and it is not likely that the energy gap change is a major effect of the change of the VER time. Rather than that, the increase of the density of states may be a cause for this acceleration of the relaxation. The DFT calculation shows that there are intermolecular vibrational modes with frequencies of 19 cm$^{-1}$, 36 cm$^{-1}$ and 51 cm$^{-1}$ for the FL:MeOH complex, which may be accepting modes in the relaxation process.

### 3.3 OH Stretching Mode of Methanol

The hydroxyl stretching vibrations of alcohols are very sensitive to microscopic environment around the hydrogen bond, and the vibrational spectra of the mode are a good probe to investigate hydrogen bond dynamics. Methanol is the simplest alcohol and is a model system to investigate static and dynamics effects of the hydrogen bond on the OH stretch. Recently, the VER of the OH stretch of methanol has been measured by time-resolved vibrational spectroscopy. For example, in CCl$_4$ methanol forms clusters, and IR pump-probe experiments were conducted on the OH$^+$ and OD$^+$ stretch of this system. Dlott and coworkers studied the VER in pure methanol (CH$_3$OH) by IR pump-Raman probe technique. It is found that lifetime of the OH stretch depends on the strength of the hydrogen bond; for isolated methanol, the VER times ($T_1$) are in a picosecond order, and it becomes shorter than 1 ps when it forms hydrogen bond.
This may be due to changes of density of states, coupling strength, and energy gap by hydrogen bond formation. In this work we have measured VER times of the OH and OD stretching in isotopically diluted methanol. Furthermore, we have studied isotope effect of the methyl group on the VER of the OH and OD stretching modes. We prepared the following four different isotopically diluted solutions: CH3OH/CH3OD, CD3OH/CD3OD, CH3OD/CH3OH, and CD3OD/CD3OH. The volume ratio of the solute and solvent is 1:19.

Figure 7 shows IR absorption spectra of the OH and OD stretch region of methanol in isotopically diluted solutions. The absorption spectra of the OH stretching mode have a peak at 3340 cm\(^{-1}\) with FWHM of 210 cm\(^{-1}\), and the two spectra of the CH3OH/CH3OD and CD3OH/CD3OD (not shown here) systems are identical with each other. The spectrum of the OD stretch, on the other hand, has a narrower spectral width of about 140-150 cm\(^{-1}\). The CH3OD/CH3OH system shows a shoulder at around 2450 cm\(^{-1}\), which was attributed to the Fermi resonance with an overtone of the methyl rocking mode.

Figure 8 shows a pump-probe signal of the CH3OH/CH3OD system. The time profiles of the signals were fitted well by a single exponential function. To avoid complication due to coherent artifact at around \(t = 0\) ps, we fitted the time profiles of the signal from \(t = 0.20\) ps. A small offset \(A_0\) at long delay times has been often observed in other systems such as ethanol, which was attributed to be a cooling process of the locally heated environment.

The CH3OD/CH3OH system shows the fastest decay (0.83 ps) of the pump-probe signal of the OH stretch. This is because strong Fermi resonance with other modes enhances the relaxation process. Consequently, it is suggested that the pathway of the VER after the excitation of the OD stretch of CH3OD is different from the hydroxyl stretches of the other isotopically substituted methanol. In CCl4, Fayer and coworkers observed a decay of the OD stretching mode of CH3OD with a similar time constant.

The VER of the OH stretching mode of CH3OH takes place about 20% faster than that of the OH stretch of CD3OH. This fact suggests mechanism of the energy relaxation of the OH stretching mode. Dlott and coworkers performed IR-pump and Raman-probe experiment on methanol to study energy relaxation pathways after exciting the OH stretch. They observed an instantaneous rise of the other vibrational modes such as \(\nu(CH_3)\), \(\delta(CH_3)\), \(\delta(COH)\), \(\gamma(CH_3)\), and \(\nu(CO)\) modes within the time resolution of their setup of 1 ps, leading to a conclusion that an intramolecular process is important for the VER. Our observation is consistent with their conclusion. For example, a combination band of \(\delta(CH_3)\) and \(\delta(COH)\) can be one of the accepting modes for the energy relaxation of the OH stretch. The frequency of this combination band is about 2900 cm\(^{-1}\) for CH3OH and 2400 cm\(^{-1}\) for CD3OH, resulting in a larger energy gap from the OH stretching mode by deuteration of the methyl group. The intramolecular isotope effect on the VER in methanol can be rationalized in terms of the Fermi golden rule in a qualitative level.

In summary, effects of hydrogen bond on vibrational dynamics in solutions have been studied by sub-picosecond IR pump-probe spectroscopy for the three different species. The mechanisms of the anharmonic coupling between the modes and the acceleration of the population relaxation due to hydrogen bond were discussed.

References


