ACCOUNTS
of chemical research

Vibrational Dynamics of Hydrogen-Bonded Complexes in Solutions Studied with Ultrafast Infrared Pump−Probe Spectroscopy

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RECEIVED ON JANUARY 15, 2009

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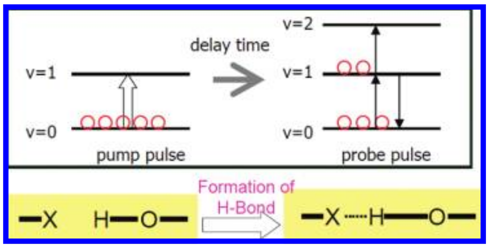

In aqueous solution, the basis of all living processes, hydrogen bonding exerts a powerful effect on chemical reactivity. The vibrational energy relaxation (VER) process in hydrogen-bonded complexes in solution is sensitive to the microscopic environment around the oscillator and to the geometrical configuration of the hydrogen-bonded complexes. In this Account, we describe the use of time-resolved infrared (IR) pump−probe spectroscopy to study the vibrational dynamics of (i) the carbonyl CO stretching modes in protic solvents and (ii) the OH stretching modes of phenol and carboxylic acid. In these cases, the carbonyl group acts as a hydrogen-bond acceptor, whereas the hydroxyl group acts as a hydrogen-bond donor. These vibrational modes have different properties depending on their respective chemical bonds, suggesting that hydrogen bonding may have different mechanisms and effects on the VER of the CO and OH modes than previously understood.

The IR pump−probe signals of the CO stretching mode of 9-fluorenone and methyl acetate in alcohol, as well as that of acetic acid in water, include several components with different time constants. Quantum chemical calculations indicate that the dynamical components are the result of various hydrogen-bonded complexes that form between solute and solvent molecules. The acceleration of the VER is due to the increasing vibrational density of states caused by the formation of hydrogen bonds.

The vibrational dynamics of the OH stretching mode in hydrogen-bonded complexes were studied in several systems. For phenol−base complexes, the decay time constant of the pump−probe signal decreases as the band peak of the IR absorption spectrum shifts to lower wavenumbers (the result of changing the proton acceptor). For phenol oligomers, the decay time constant of the pump−probe signal decreases as the probe wavenumber decreases. These observations show that the VER time strongly correlates with the strength of hydrogen bonding. This acceleration may be due to increased coupling between the OH stretching mode and the accepting mode of the VER, because the low-frequency shift caused by hydrogen bond formation is very large. Unlike phenol oligomers, however, the pump−probe signals of phenol−base complexes did not exhibit probe frequency dependence. For these complexes, rapid interconversion between different conformations causes rapid fluctuations in the vibrational frequency of the OH stretching modes, and these fluctuations level the VER times of different conformations.

For the benzoic acid dimer, a quantum beat at a frequency of around 100 cm^{-1} is superimposed on the pump−probe signal. This result indicates the presence of strong anharmonic coupling between the intramolecular OH stretching and the intermolecular stretching modes. From a two-dimensional plot of the OH stretching wavenumber and the low-frequency wavenumber, the wavenumber of the low-frequency mode is found to increase monotonically as the probe wavenumber is shifted toward lower wavenumbers.

Our results represent a quantitative determination of the acceleration of VER by the formation of hydrogen bonds. Our studies merit further evaluation and raise fundamental questions about the current theory of vibrational dynamics in the condensed phase.

Published on the Web 07/02/2009 www.pubs.acs.org/acr
10.1021/ar9000229 CCC: $71.50

Introduction

Hydrogen bonds are generally weaker than covalent bonds and stronger than intermolecular interactions such as van der Waals forces. This "intermediate" nature of hydrogen bonds governs various chemical and biological events.[1−3] For example, hydrogen bonds play an important role in determining the stability of the three-dimensional structures of many chemical complexes and biological macromolecules. In aqueous solutions, dynamical processes such as the formation, dissociation and structural relaxation of hydrogen bonds cause large fluctuations in the potential energy of the system, which exerts a great influence on chemical reactivity.[4]

Infrared (IR) spectroscopy is one of the most powerful methods for studying both the structure and the dynamics of hydrogen-bonded systems in the condensed phase.[5,6] In particular, vibrational modes such as the OH stretching mode are highly sensitive to the type and strength of hydrogen bonding. The formation of hydrogen bonds generally causes a red shift in the OH stretching band compared with that of a free OH. The vibrational frequency of the OH stretching mode depends on the molecular geometry of the hydrogen-bonded system, which results in an inhomogeneous distribution of the frequencies of the OH absorption band. Furthermore, in solution phases, extremely fast fluctuations in the surrounding environment induce dynamical changes in hydrogen-bonding interactions. This causes fluctuations in the frequency of the OH stretching mode in time, which also affects the shape of the absorption spectra.

Vibrational dynamics such as vibrational energy relaxation (VER) and vibrational dephasing have been studied by ultrafast IR spectroscopy for systems in the solution phase.[7,8] Hydrogen-bonded liquids have been extensively investigated using subpicosecond or femtosecond IR pump−probe techniques to examine the OH and NH stretching modes.[9−14] Heilweil and co-workers have performed pioneering work on the dependence of VER on hydrogen bond strength.[15,16] In particular, they measured the pump−probe signals of the NH stretching mode of pyrrole in complexes with proton acceptors[16] and investigated the relation between the pump−probe signal and the basicity of the proton acceptors. The VER time of the free pyrrole in CCl_4 is 49 ps, whereas this time ranges from 13 ps for a complex with acetone to 0.7 ps for a complex with triethylamine in CCl_4. They concluded that the VER time decreases monotonically as the basicity of the proton acceptor increases, which indicates that the magnitude of the enhanced VER is mostly dictated by the strength of the hydrogen bond and is relatively independent of the vibrational mode structure of the base. The acceleration of VER through hydrogen bonding has been also reported for a few other systems. For example, the VER time of the OH stretching mode of methanol monomers is reported to be 9 ps.[17] When methanol forms oligomers in CCl_4, the VER time of the OH mode decreases to the subpicosecond range.[18]

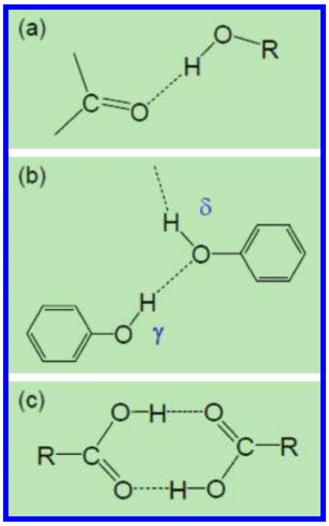

FIGURE 1. Hydrogen bonds investigated in this work: (a) complex of carbonyl compounds with alcohol; (b) phenol oligomer; (c) cyclic dimer of carboxylic acid.

Recently, it has been shown that two-dimensional (2D) IR spectroscopy, a vibrational analogue of 2D NMR, is a powerful tool for studying the dynamics of hydrogen-bonded systems, including the formation and dissociation of intermolecular hydrogen bonds.[19−23] The effects of hydrogen bonding on VER were investigated theoretically by using a model solute molecule in molecular dynamic simulations.[24] In the gas phase, the vibrational relaxation of the OH stretching mode of hydrogen-bonded phenol clusters was investigated using picosecond IR−ultraviolet pump−probe spectroscopy.[25,26]

In this Account, we review studies on the vibrational dynamics of intermolecular hydrogen-bonded systems by using subpicosecond IR pump−probe spectroscopy. This technique has been applied to the study of the vibrational dynamics of carbonyl CO stretching modes in protic solvents (Figure 1a).[27−29] We have also investigated the vibrational dynamics of the OH stretching modes of phenol and carboxylic acid (Figure 1b,c).[30,31] In these cases, the carbonyl group acts as a hydrogen bond acceptor, and the hydroxyl group acts as a hydrogen bond donor. Furthermore, certain properties of the chemical bonds, such as charge distribution and the force constant, are different between the carbonyl group and the hydroxyl group. This suggests different mechanisms through which hydrogen bonding affects VER, as well as different effects of hydrogen bonding on the VER of these modes. We discuss the effects of intermolecular hydrogen bonding and its dynamics on the VER of vibrational modes associated with hydrogen bonds.

Experimental Method

We performed ultrafast IR pump−probe experiments in order to observe vibrational dynamics. The details of the experimental apparatus and methods have been described elsewhere.[29] The output from a Ti:sapphire regenerative amplifier (800 nm, 100 fs, 350 mW, 1 kHz) was introduced into a handmade optical parametric amplifier (OPA). The outputs from the OPA in the near-IR region were passed through a $AgGaS_2$ window, which resulted in a difference frequency wave in the mid-IR region. The pulse energy was 1.4−2.0 μJ, depending on the peak wavenumber. The temporal width of the IR pulse was approximately 150 fs. The mid-IR pulse was divided into two pulses for use as the pump and the probe pulses. After passing through the sample, the probe pulse was analyzed with a monochromator and detected with a HgCdTe or an InSb detector. The relative polarization angle between the pump radiation and the probe radiation was set to the magic angle. The sample solution was introduced into a cell with two CaF_2 windows. The thickness of the cell was adjusted in such a way that the optical density of the vibrational mode of the sample was about 0.5.

Steady-State IR Spectra of Hydrogen-Bonded Systems

The wavenumber and the intensity of the peaks in vibrational spectra related to hydrogen bonding change through the formation of hydrogen bonds. This is due to changes in the electronic structure of the vibrational mode caused by the formation of the hydrogen bond. However, the degree of these changes depends on the vibrational mode and chemical system under investigation.

The IR spectra of carbonyl groups in hydrogen-bonding and non-hydrogen-bonding solvents are summarized in Figure 2. At wavenumbers between 1640 and 1740 cm^{-1}, the spectra exhibit absorption bands due to the CO stretching mode. For 9-fluorenone (FL) in cyclohexane, the absorption band shows a single Lorentzian peak resulting from "free" FL, while two peaks and one shoulder are observed for FL in 1-octanol.[27] The absorption band in 1-octanol is well approximated as the sum of three Lorentzian components. This result indicates that there are three different species in the solution, which are assigned as free FL (highest wavenumber band), the hydrogen-bonded complex of FL with one solvent molecule (1:1 complex), and the complex with two molecules (1:2 complex; lowest wavenumber band). These assignments are based on a comparison with the results of the quantum chemical calculations shown in Table 1. The IR absorption band shape of methyl acetate (MA) in methanol is qualitatively similar to that of FL in 1-octanol (Figure 2b).[28] The peak position of the absorption component in the highest wavenumber region corre-

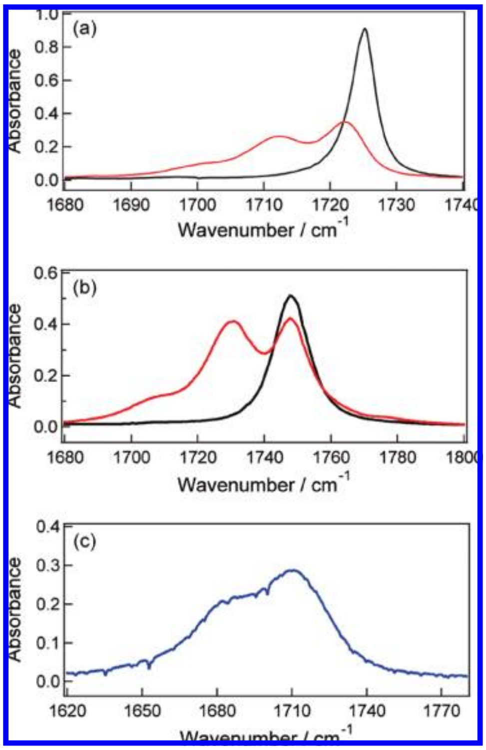

FIGURE 2. IR absorption spectra of carbonyl compounds: (a) 9-fluorenone in cyclohexane (25 mM, black) and 1-octanol (25 mM, red); (b) methyl acetate in CCl_4 (0.3 M, black) and methanol (0.3 M, red); (c) acetic acid (CH_3COOD) in D_2O (0.3 M).

TABLE 1. Summary of Calculations of the CO Stretching Frequencies

	Fluorenone (FL)[a]
Free FL	1784 cm^{-1}
FL:OcOH	1761 cm^{-1}
FL:$(OcOH)_2$	1736 cm^{-1}
	Methyl Acetate (MA)[b]
free MA	1752.6 cm^{-1}
MA/CH_3OH	1727.8 cm^{-1}, 1722.3 cm^{-1}[c]
MA/CH_3OD	1727.5 cm^{-1}, 1721.9 cm^{-1}
	Acetic acid (AA)[b]
free AA	1766 cm^{-1}
AA/D_2O	1712 cm^{-1}
AA/$(D_2O)_2$	1682 cm^{-1}

[a] The calculations were performed on the basis of density functional theory (DFT) with a basis set of 6-31++G(d,p) using a B3LYP functional with Gaussian 03.[33] OcOH denotes 1-octanol. [b] DFT calculations with a basis set of 6-311+G(d,p) using a B3LYP functional. The obtained vibrational wavenumbers were corrected by applying the wavenumber-linear scaling method.[34] [c] There are two possible configurations of the 1:1 complex.

sponds to that in CCl_4, indicating that this absorption component is due to free MA. The components in the lower wavenumber region are assigned as the modes of the 1:1 and 1:2 complexes. In aqueous solutions, the IR spectrum of the CO stretching mode is more red-shifted than that in alcohol. The band includes a peak at 1710 cm^{-1} with a shoulder at 1680 cm^{-1} in the IR spectrum of acetic acid (CH_3COOD; AA) in D_2O (Figure 2c).[29] The absorption band of this mode due to free AA in CCl_4 is located in the wavenumber range between 1760 and 1780 cm^{-1}.[32] Based on a comparison with the results of the quantum chemical calculations shown in Table 1, AA exists as a 1:1 complex and 1:2 complex. No evidence of free AA is observed in the IR spectrum, which is in sharp contrast with the results observed in the case of the alcohol solvent.

The fluctuations in the IR spectra of the OH stretching mode caused by hydrogen bond formation are more drastic. The IR spectra of phenol and phenol−base complexes in CCl_4 are shown in Figure 3.[30] In Figure 3a, the OH stretching mode of phenol in CCl_4 shows a sharp absorption band at about 3600 cm^{-1}. This band is assigned to that of the phenol monomer. The broad absorption band at lower wavenumbers is assigned to phenol oligomers. The dependence of the IR spectrum of the concentration is shown in Figures 3b,c, where the oligomer band increases as the concentration increases. In particular, as shown in Figure 3c, the absorption band of the oligomers includes two components, a peak at around 3350 cm^{-1} and a shoulder at around 3480 cm^{-1}. Based on studies of the methanol oligomers,[35,36] the absorption components at 3350, 3480, and 3600 cm^{-1} are assigned to γ-type (OH groups acting as donors but not as acceptors) and δ-type molecules (OH groups acting as both donors and acceptors) in the phenol oligomers, and the monomer, respectively (Figure 1b). The absorption spectra exhibit a broad absorption band in the wavenumber region lower than 3600 cm^{-1} when phenol forms a complex with a proton acceptor, as shown in Figure 3d. The peak wavenumber and the bandwidth change as the identity of the base changes. It is likely that the peak wavenumber decreases and the bandwidth increases as the strength of the hydrogen bond between phenol and the base increases.

When carboxylic acid forms a cyclic dimer, the band shape of the OH stretching mode changes drastically (Figure 1c). In a nonpolar solvent such as CCl_4, benzoic acid (BA) exists as a cyclic dimer at high concentrations.[37] The IR spectrum of C_6D_5COOH (BA-d_5) exhibits a broad absorption band with a complex structure between 2400 and 3400 cm^{-1} due to the OH stretching mode.[31] This band structure has been investigated theoretically and experimentally, and it is considered that these structures are due to anharmonic coupling with the intermolecular mode, Fermi resonance, and Davydov coupling.[8,37−39]

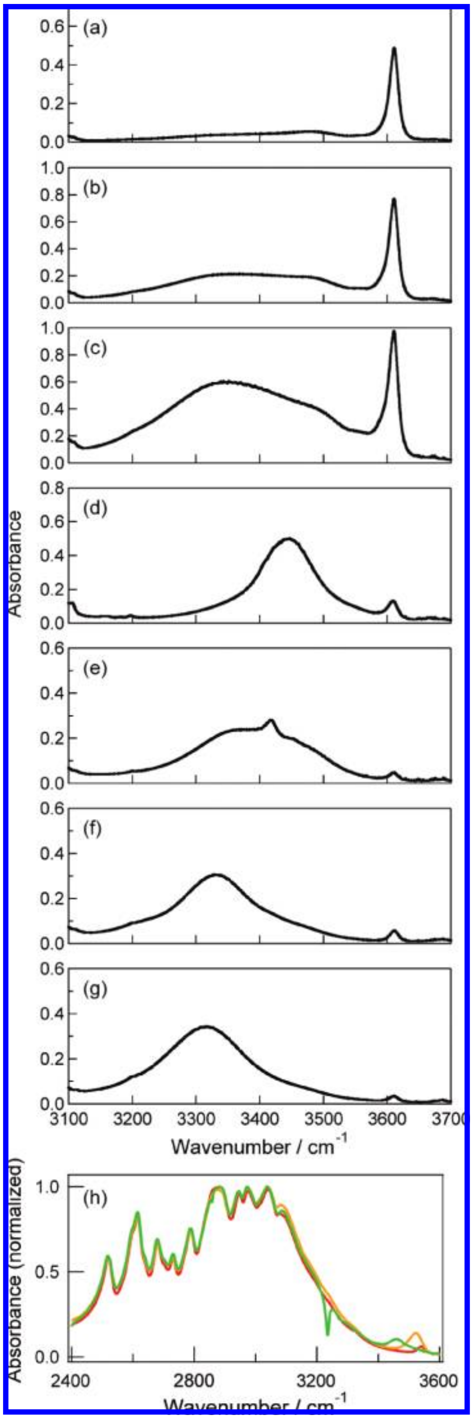

FIGURE 3. IR absorption spectra of (a) phenol (0.15 M), (b) phenol (0.3 M), (c) phenol (0.5 M), (d) phenol (0.15 M)−benzonitrile (1.0 M), (e) phenol (0.1 M)−acetone (1.0 M), (f) phenol (0.1 M)−diethylether (1.0 M), (g) phenol (0.1 M)−tetrahydrofuran (1.0 M) in CCl_4, and (h) benzoic acid-d_5 (0.12 M) in CCl_4 (red), $CDCl_3$ (yellow), and C_6D_6 (green).

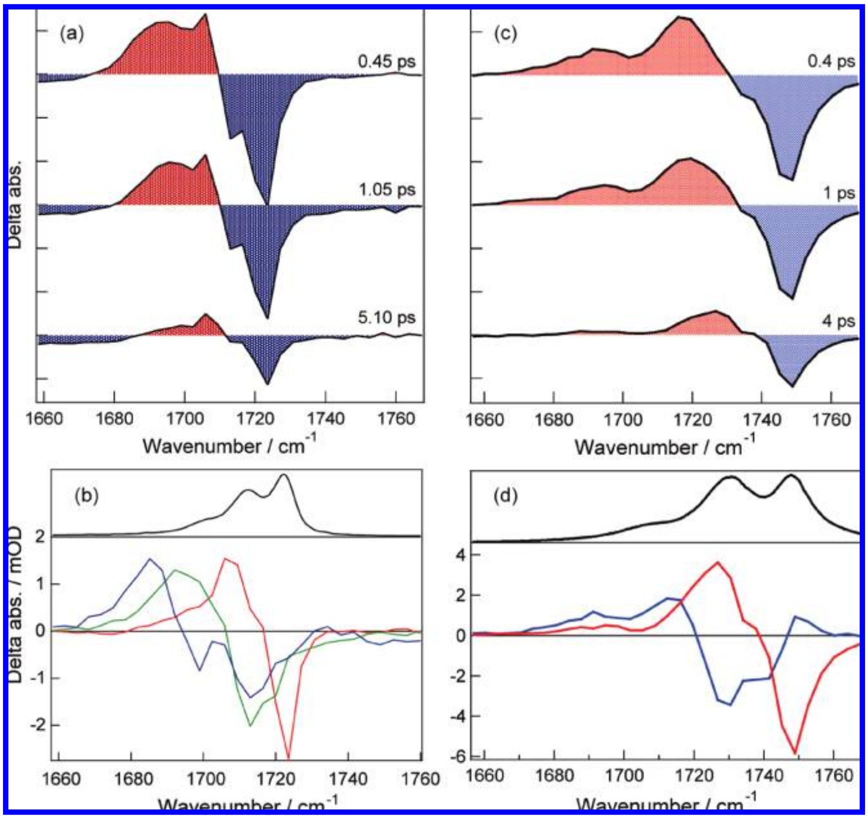

FIGURE 4. Time-resolved difference spectra after excitation of the CO stretching mode of (a) 9-fluorenone in 1-octanol and (c) methyl acetate in methanol. Time delays are shown in the figure. (b) Decay-associated spectra of the 0.27 (blue), 2.3 (green), and 4.7 ps (red) components for 9-fluorenone in 1-octanol and (d) those of 1.2 (blue) and 4.0 ps (red) components for methyl acetate in methanol. Solid lines at the top represent the absorption spectra in the ground state.

Vibrational Dynamics Studied by IR Pump–Probe Spectroscopy

There have been a number of theoretical treatments of VER in condensed phases.[40–42] One of the most prevalent approaches is a method based on the Golden Rule. In this case, the Hamiltonian of the system can be written in the following form:

$$\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{SB}$$

where the "system" Hamiltonian $\hat{H}_S$ describes intramolecular motion that is assumed to be harmonic.[42] The harmonic bath model has often been used for the bath Hamiltonian $\hat{H}_B$, where $\hat{H}_B$ is represented as a sum of normal-mode Hamiltonians. We denote the eigenvalues and the eigenstates of the bath Hamiltonian as ε_α and $|\alpha\rangle$. $\hat{H}_{SB}$ represents the oscillator–bath coupling. If we consider the transition rate between two molecular levels i and f with energies E_i and E_f, which are eigenstates and eigenvalues of $\hat{H}_S$, it is necessary to evaluate this rate on the basis of the eigenstates of $\hat{H}_S + \hat{H}_B$. The transition under consideration is between the group of states $\{|i,\alpha\rangle\}$ and $\{|f,\alpha'\rangle\}$ averaged over the thermal distribution in the $\{\alpha\}$ manifold and summed over all final states α'. Thus, the rate is[42]

$$k_{f\leftarrow i} \propto \sum_{\alpha} e^{-\varepsilon_\alpha/(kT)} \sum_{\alpha'} |(\hat{H}_{SB})_{i\alpha,f\alpha'}|^2 \delta(E_i + \varepsilon_\alpha - E_f - \varepsilon_{\alpha'})$$

The transition rate is determined by the vibrational density of states (VDOS), the coupling strength, and the energy gap. The formation of a hydrogen bond can influence all of these factors.

CO Stretching Mode. The time-resolved difference spectra after the excitation of the CO stretching mode of FL in 1-octanol and MA in methanol are shown in Figure 4.[27] For both systems, the depletion of the ground-state absorption and the transient absorption are observed in the higher and lower wavenumber regions, respectively. The spectral shape of the difference spectrum changes as a function of the time delay. This result indicates the presence of several components with different time constants in the pump–probe signal. We analyzed the temporal changes of the difference spectra by global fitting with a sum of two or three exponential components:

$$\Delta A(\tilde{\nu}, t) = \sum_n a_n(\tilde{\nu}) \exp\left(-\frac{t}{\tau_n}\right)$$

where $\Delta A(\tilde{\nu},t)$ is the obtained pump–probe signal at wavenumber $\tilde{\nu}$ and delay time t and $a_n(\tilde{\nu})$ is the spectrum of the component decaying with a time constant τ_n. For FL in 1-octanol, the decay time constants were found to be 0.27, 2.3, and 4.7 ps, and the decay-associated spectra of the three decay components are shown in Figure 4b. The depletion peaks in the decay-associated spectra of the 2.3 and 4.7 ps components correspond well to the peaks in the IR absorption components due to the 1:1 complex and the free FL, respectively. Therefore, the time constants of 2.3 and 4.7 ps are the VER time constants of the 1:1 complex and the free FL, respectively. The fastest decay component with a time constant of 0.27 ps may be that of the 1:2 complex. However, the depletion peak of the decay-associated spectrum of this component does not correspond to the position of the shoulder in the ground-state absorption band. It is probable that a coherent artifact contributes to the pump–probe signal in the fast time domain.[43]

The results for the system of MA in methanol were also analyzed by global fitting similarly to the analysis of FL.[28] The obtained decay-associated spectra correlate well with the IR spectra. The time constants of 1.3 and 4.0 ps were obtained by the fitting, and the decay-associated spectra of the two components are displayed in Figure 4d. The 1.3 and 4.0 ps components are assigned to the 1:1 complex and the free MA, respectively.

The acceleration of the VER is also observed in aqueous solutions. The frequency-resolved pump–probe signal of AA in D_2O can be reconstructed by two dynamical components, which are obtained by global fitting analysis.[29] The obtained time constants were 450 and 980 fs. The decay-associated spectra of the components are shown in Figure 5. The depletion peak positions in the fast and the slow spectra correspond to the peak positions of the ground-state absorption components due to the 1:2 and the 1:1 complexes, respectively. The VER times of the CO stretching modes of the 1:2 and the 1:1 complexes for deuterated AA (CD_3COOD) were also determined as 390 and 930 fs, respectively, which are identical to those of CH_3COOD within the margins of experimental error. This indicates that the vibrational energy deposited to the CO stretching mode is first distributed between the kinetic modes localized in the COOD moiety.

The VER process is accelerated by a factor of 2 through the formation of an intermolecular hydrogen bond. The results are summarized in Figure 6. Unlike the VER of the OH stretching mode of water, the energy shift due to the bond formation of the CO stretching vibration is about 10 cm^{-1}, and it is not likely that the energy gap change has a major effect on the VER time. Instead, an increase in the VDOS may be the cause for this acceleration of the relaxation. Quantum chemical calculations show that there are several intermolecular vibrational modes with frequencies less than 100 cm^{-1} for the FL/methanol complex, which may be accepting modes in the relaxation process. It is likely that the effective dissipation of energy from the CO stretching mode in the hydrogen-bonded complexes results from the increase in the VDOS through a combination of intramolecular fingerprint and intermolecular low-frequency modes. However, further studies are needed to clarify the details of the role of hydrogen bonding in VER.

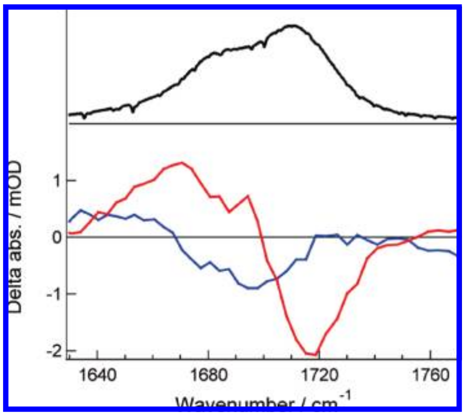

FIGURE 5. Decay-associated spectra of 450 fs (blue) and 980 fs (red) components in the IR pump–probe signal of acetic acid in D_2O. Black line at the top represents the IR absorption spectrum in the ground state.

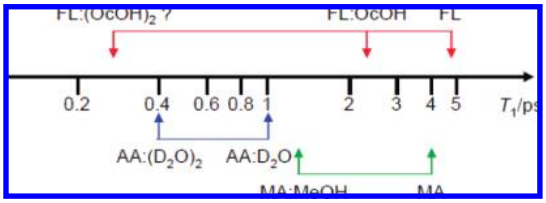

FIGURE 6. Summary of VER times of the CO stretching modes.

To continue with the dynamics of hydrogen bonds, in liquids, hydrogen bond formation and dissociation occurs continually. If the time scale of the dynamics is comparable with that of the vibrational dephasing or the VER, it affects the vibrational line shape and VER processes. In the case of FL complexes, the spectral components due to free FL and 1:1 complexes are well separated by the global fitting analysis. This result indicates that the formation and dissociation of the hydrogen bonds proceeds more slowly than the VER processes (2.3 and 4.7 ps). It has been reported that the dynamics of hydrogen bond formation and cleavage proceed on a time scale of 10–15 ps for *N*-methylacetamide in methanol.[19]

The dynamics between FL and 1-octanol may also proceed on almost the same time scale or a slower one. Such hydrogen bond dynamics are a suitable subject for 2D IR spectroscopy. Fayer and co-workers used this technique to investigate the dynamics of a phenol-*d*-benzene complex in nonpolar solvents.[22] By observing the temporal evolution of the off-diagonal peaks in the 2D IR spectrum, they obtained kinetic information on the chemical exchange process.

OH Stretching Mode. The acceleration of the VER through the formation of hydrogen bonds is also observed for the OH stretching mode. The major difference between the IR spectra of the CO and OH stretching modes is the significantly broadened OH stretching band due to the high sensitivity of its transition frequency to the local geometry of the hydrogen bond. In other words, it may be possible to investigate the relation between the VER of the OH stretching mode and the strength of hydrogen bonding.

The time profiles of the depletion of the OH stretching absorption band of phenol are shown in Figure 7.[30] The time profile of the signal is described well by a single-exponential function in all cases. The time constants are displayed in the figure. It should be noted that unlike the case of CO vibration, the decay time of the pump–probe signal does not necessarily correspond to the VER time in this case. This is because it is necessary to consider the spectral diffusion of such a broad spectrum when we discuss the pump–probe signal of this mode, which will be discussed below. Here, we regard the decay time of the signal as the VER time. For phenol oligomers in CCl_4 (Figure 7a–c), the VER time is also shown in the figure. For phenol–base complexes (Figure 7d–g), as the peak wavenumber of the IR absorption band decreases by changing the base, the VER time decreases monotonically. As discussed above, the peak wavenumber of the absorption band correlates with the strength of the intermolecular hydrogen bond in the complex. Therefore, the rate of VER for the OH stretching mode of phenol is higher when the intermolecular hydrogen bond is stronger.

The mechanism by which hydrogen bonding accelerates the VER of the OH and NH stretching modes may be slightly different from that of the CO stretching mode. As the energy gap between the OH or NH stretching mode decreases due to hydrogen bonding, the perturbed OH or NH stretching vibration becomes closer to the resonance of the accepting mode. Elsaesser and co-workers have studied the vibrational dynamics of the NH stretching mode of 7-azaindole.[44,45] The VER time of the monomer in $CDCl_3$ (10 ps) is significantly longer than that of the cyclic dimer (350 fs). They suggest that the acceleration of the VER is the result of a decrease in the NH stretching frequency by ~400 cm^{-1}, which causes frequency matching between the NH stretching and overtones of the NH bending modes. It is likely that frequency matching between the OH stretching mode and accepting modes, such as an overtone of the OH bending mode, results in the dependence of the VER time on the solvent.

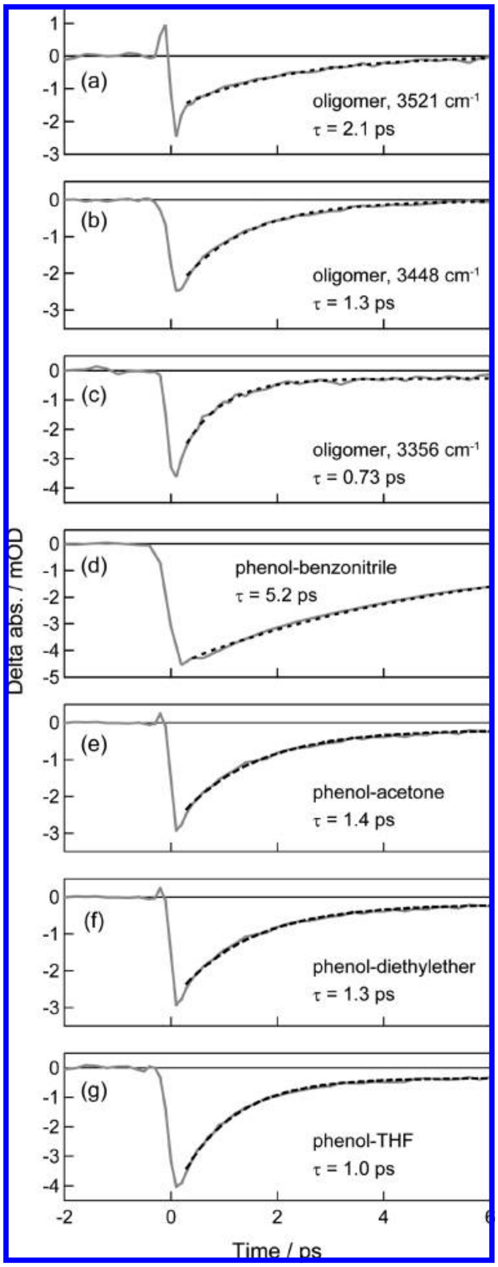

FIGURE 7. Time profiles of IR pump–probe signals of the OH stretching mode of phenol oligomers and phenol–base complexes. Decay time constants are shown in the panels. Dotted lines represent the results of the fitting.

Figure 8 shows the relation between the probe frequency and the decay time constants of the pump–probe signals for hydrogen-bonded phenol complexes in CCl_4. For phenol–acetone complexes, the decay at 3333 cm^{-1} is slightly faster

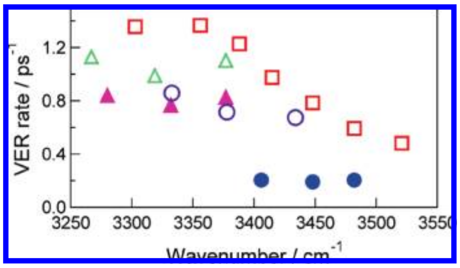

FIGURE 8. Plot of VER rates vs probe wavenumber. Phenol oligomers (□), phenol−benzonitrile (●), phenol−acetone (○), phenol−diethylether (▲), and phenol−tetrahydrofuran (△) complexes.

than that at the other two probe frequencies. For the other complexes, it was found that the decay time does not exhibit a notable dependence on the probe frequency. On the other hand, the decay of the pump−probe signals of phenol oligomers depends strongly on the probe frequency.

The dependence of the OH and OD stretching lifetime on the frequency is also an important factor in other hydrogen-bonded systems. In water, the dependence of the relaxation rates on the probe frequency is different for the OH and OD stretching modes of HOD in D_2O and H_2O.[46,47] For HOD in D_2O, the lifetime of the OH stretching mode was reported to be dependent on the frequency, with the relaxation time fluctuating between 0.5 ps at 3270 cm^{-1} and 1.0 ps at 3600 cm^{-1}.[46] On the other hand, for HOD in H_2O, the VER time of the OD stretching mode was reported to be 1.45 ps, which is independent of the frequency.[47] This lack of frequency dependence was attributed to the rapid spectral evolution of the OD stretching frequency. On the time scale of VER, the OD stretching wavenumber fluctuates over all environments, and the VER time is observed as an average value. Similarly, the lack of dependence on the probe frequency for phenol−base complexes results from the rapid interconversion between different conformations having different hydrogen bond strengths. This rapid interconversion between conformations causes rapid fluctuation of the OH stretching frequency. As a result, the VER times are averaged over all conformations. On the other hand, we found that in the case of phenol oligomers in CCl_4, the decay of the pump−probe signal depends strongly on the probe frequency. A possible explanation for this is that the OH stretching mode of the δ-type phenol molecule may have faster VER than that of the γ-type since the energy gap between the OH stretching mode and the accepting mode is smaller for the δ-type phenol. These different processes are not averaged by spectral diffusion due to the rapid VER.

The BA dimer in CCl_4 exhibits a spectrum with the most pronounced red shift among the OH stretching bands of the hydrogen-bonded complexes examined in this work. This suggests that this system has the fastest decay of the VER of the OH stretching mode. The frequency-resolved pump−probe signal of BA-d_5 in CCl_4 is shown in Figure 9a. In addition, the time profiles at the wavenumbers of 3000 and 3124 cm^{-1} are shown in Figure 9b,c. As shown in figure, the pump−probe signal consists of decaying and oscillating components. The decaying component at 3000 cm^{-1} is well reproduced by a biexponential function with time constants of 730 fs and 13 ps. At 3124 cm^{-1}, the absorbance change is negative around time zero and immediately becomes positive. Thus, the vibrational energy deposited to the OH stretching mode is distributed among other kinetic modes in the BA dimer within the time resolution of the experiment of about 200 fs. For the AA dimer, it was also reported that the VER process from the OH stretching mode proceeds with a time constant of less than 200 fs.[8,39] Analogous to the discussion on the AA dimer, the two decaying components are attributed to the energy dissipation from the BA dimer to the surrounding solvent and the cooling of the locally hot environment around the dimer, respectively.

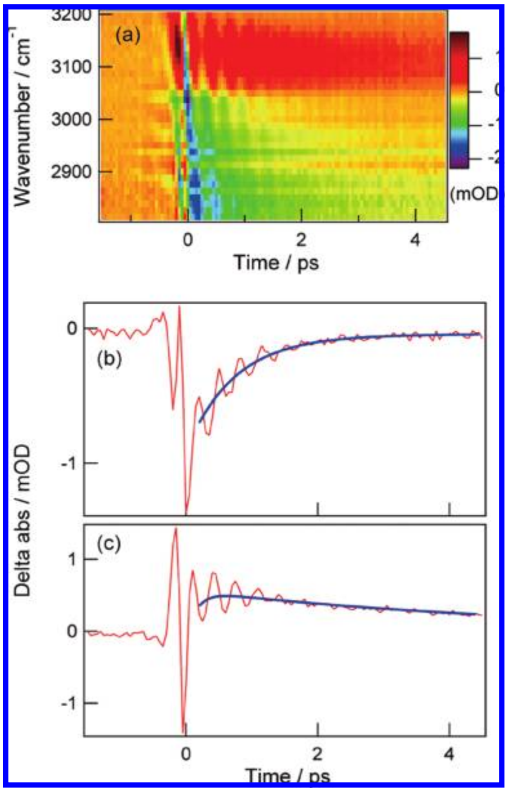

FIGURE 9. (a) Frequency-resolved pump−probe signal of the OH stretching mode of benzoic acid-d_5 dimer in CCl_4 and time profiles at (b) 3000 cm^{-1} and (c) 3124 cm^{-1}.

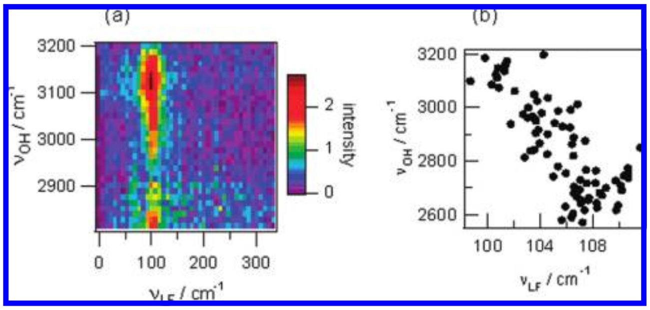

FIGURE 10. (a) 2D plot of Fourier spectra in the entire probe wavenumber region. ν_{LF} and ν_{OH} denote the wavenumbers of the low-frequency mode and OH stretching mode, respectively. (b) Dependence of the low-frequency mode (ν_{LF}) on the probe wavenumber of the OH stretching mode (ν_{OH}).

Outlook: Coupling between the High- and Low-Frequency Modes

The most interesting finding in these works is that the acceleration of VER by the formation of hydrogen bonds has been determined quantitatively. While a full theoretical description of such findings is beyond the scope of this Account, this certainly raises interesting questions regarding the current theory on vibrational dynamics in the condensed phase. As mentioned previously, in order to interpret the enhancement of the VER rate that occurs as a result of hydrogen bond formation, we may need to account for factors such as the effect of spectral diffusion, the dynamics of the formation and dissociation of hydrogen bonds, and inhomogeneity of the band shape. Among these, formulating a theoretical treatment regarding the effect of the low-frequency intermolecular mode of hydrogen bonding on the VER of the high-frequency intramolecular mode is of particular interest. Recently, Nibbering and Elsaesser have shown that the quantum beat observed in the pump–probe signal of the OH stretching mode of an AA dimer in CCl_4 is due to the intermolecular mode of the hydrogen bond.[8,39] This observation raises the possibility for a study of the anharmonic coupling between the high- and low-frequency modes in hydrogen-bonded complexes. Here, we demonstrate a new type of 2D plot to investigate the correlation between the high- and low-frequency vibrational modes of a complex.

The pump–probe signal of the BA dimer system also exhibits a quantum beat (Figure 9). We performed a Fourier transform on the oscillatory part after subtraction of the exponentially decaying component from the signal. The obtained Fourier spectrum is plotted against the probe wavenumber in Figure 10a. In the wavenumber region between 2800 and 3200 cm^{-1}, the Fourier spectrum shows a peak at around 100 cm^{-1}. This result indicates that the OH stretching mode couples with a vibrational mode at around 100 cm^{-1}. Quantum mechanical calculations show that the BA dimer has two intermolecular vibrational modes (dimer stretching and dimer in-plane bending modes) at 112.9 and 106.7 cm^{-1}, respectively.[48,49] The magnitude of the cubic anharmonicity between the OH stretching and the dimer stretching modes is about four times larger than that between the OH stretching and the dimer in-plane bending modes, indicating that the quantum beat is due to anharmonic coupling with the dimer stretching mode.[31] The peak position of the Fourier spectrum is plotted against the probe wavenumber in Figure 10b. The peak wavenumber of the Fourier spectrum increases monotonically as the probe wavenumber decreases. The physical origin of this correlation has not yet been clarified. One possible explanation is the inhomogeneity of hydrogen bond strength. When the intermolecular hydrogen bonds in the BA dimer become stronger, the wavenumber of the intramolecular OH stretching decreases and that of the intermolecular hydrogen bond vibrational modes increases. The key question concerns the degree of inhomogeneity of the OH stretching band of the BA dimer, which can be studied with 2D IR spectroscopy.

Conclusion

The VER process in intermolecular hydrogen-bonded complexes in solutions was investigated by time-resolved IR pump–probe spectroscopy. For the CO stretching modes of carbonyl compounds in protic solvents, which act as hydrogen-bond donors, different solute–solvent hydrogen-bonded structures are separated in terms of spectra and dynamics by the VER process. For the OH stretching modes of phenol and BA, the VER times change depending on the wavenumber of the OH stretching vibration. In both cases, the VER constant exhibits strong correlation with the hydrogen bond strength, where the VER time constant decreases as the strength of the hydrogen bond increases. It has been demonstrated that observation of the VER process is a powerful method for investigating the vibrational dynamics as well as the structures of solute–solvent hydrogen-bonded systems.

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