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Subpicosecond UV-pump and IR-probe Spectroscopy of 9-Fluorenone in Deuterated Acetonitrile and Methanol

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The vibrational dynamics of the CO stretching mode of 9-fluorenone (FL) in CD_3CN and CD_3OD were studied by subpicosecond UV-pump and IR-probe spectroscopy. We found that the CO stretching band is blue-shifted by hydrogen-bond formation in the S_1 state but red-shifted in the S_0 state. In both CD_3CN and CD_3OD, the time evolution of the transient absorption spectrum was observed on a picosecond time scale, likely because of vibrational cooling and hydrogen-bond dynamics.

Chemical reactions occurring in hydrogen-bonding (H-bonding) solvents such as water and alcohols are strongly influenced by solvent properties that arise from H-bonding. For example, the electronic states and vibrational structures of solute molecules are often altered by H-bonding with solvent molecules. Moreover, H-bonding solvents form characteristic network structures, which fluctuate continuously with time. In this work, we used 9-fluorenone (FL) as solute and deuterated methanol or acetonitrile as solvent to investigate the effects of H-bonding on the vibrational structures and vibrational dynamics in the electronically excited state. In the ground state, FL is a rigid planar molecule with a carbonyl group that exhibits a strong infrared (IR) absorption band. Accordingly, FL is an ideal probe for studying the effects of H-bonding on the CO vibrational mode. Recently, we reported that the IR spectrum of FL in alcohol shows structures in the CO stretching band, owing to the presence of H-bonded FL and non-H-bonded FL (free FL).[1,2] Furthermore, since an oxygen atom has two H-bonding sites, two types of H-bonded complexes (FL:methanol (1:1 complex) and FL:$(\text{methanol})_2$ (1:2 complex)) are observed. By subpicosecond IR pump–probe spectroscopy, we found that the formation of H-bonds accelerates the vibrational population relaxation several fold. UV-pump IR-probe spectroscopy is a suitable technique for investigating the effects of H-bond dynamics on the vibrational states after photoexcitation. The H-bond dynamics between coumarin 102 and phenol in solution have been investigated by this technique, revealing that the H-bonds are cleaved within 200 fs after the photoexcitation.[3] The dynamics of 4-(dimethylamino)benzonitrile in the excited state in methanol have also been investigated.[4] In this Letter, we extend our work on the vibrational dynamics in H-bonding solvents to the electronically excited state of FL.

Details of the experimental setup are as follows. The pump pulse was generated by frequency tripling the output of a Ti:sapphire regenerative amplifier. The tunable IR pulse was generated by difference frequency mixing of the signal and idler output of the optical parametric amplifier. The probe and reference pulses were obtained using the reflection of a CaF_2 wedged window. The pump and probe pulses were focused onto the sample with a fused-silica lens ($f = 300$ mm) and a parabolic mirror ($f = 152.4$ mm), respectively. The probe and reference pulses were dispersed by a monochromator, and the absorption changes were measured with an MCT (HgCdTe) array detector. The experiments were conducted using 100-μm-thick liquid samples in a rotating cell. FL, CD_3CN, and CD_3OD were purchased from Sigma-Aldrich and used without purification. The concentration of FL was 38 mM.

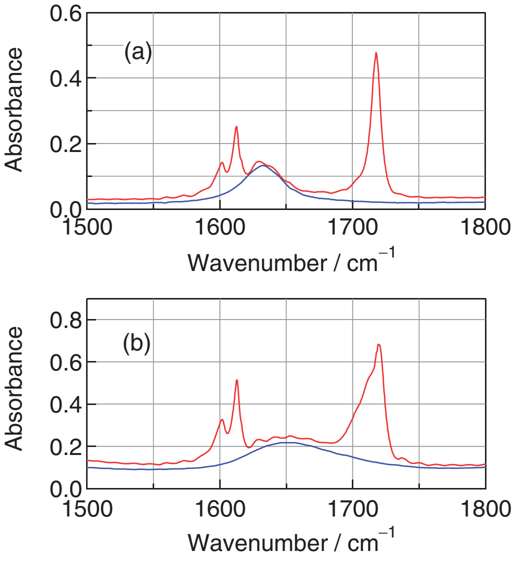

Figure 1. IR spectra of FL in (a) CD_3CN and (b) CD_3OD (red solid line). Solvent absorption is also shown (blue solid line). Reference for measurement is a blank cell.

Figures 1a and 1b show the IR absorption spectra of FL in CD_3CN and CD_3OD, respectively. The CO stretching band at around 1700 cm^{-1} is symmetric in CD_3CN but broad and asymmetric in CD_3OD because of the presence of free FL and the 1:1 and 1:2 complexes of FL. Figure 2 shows the transient IR spectra of FL in CD_3CN and CD_3OD. The pump wavelength is 267 nm, which excites the $\pi\pi^*$ state of FL. We also conducted pump–probe measurements for the neat solvents, CD_3CN and CD_3OD (data not shown). The transient measurements for both neat solvents revealed a broad band covering the entire mid-IR region, which is probably due to multiphoton absorption in the CaF_2 window under UV pulse irradiation. In Figure 2, the baseline is shifted because of this broad absorption component, and the baseline of each measurement is shown in the figure.

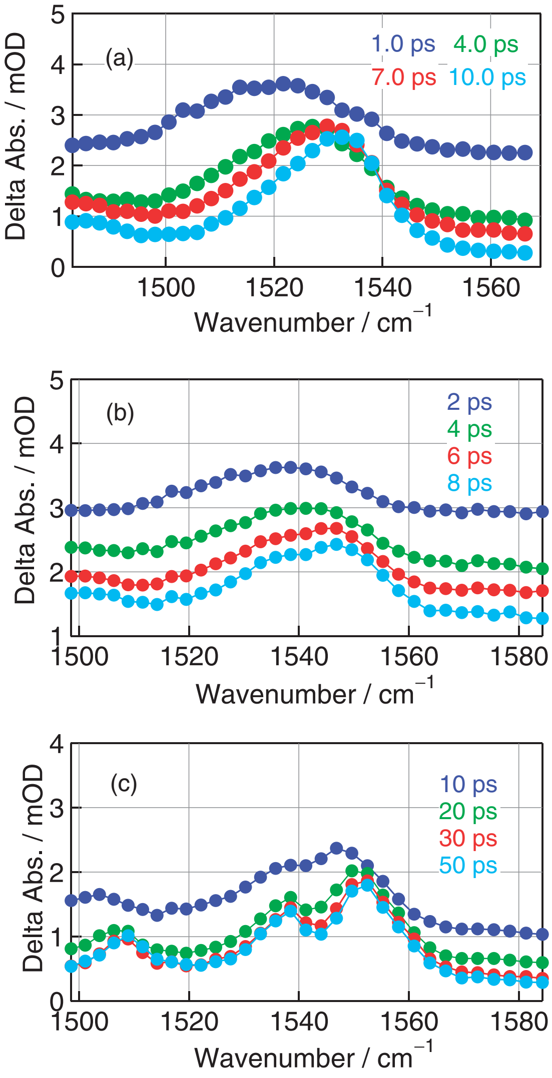

Figure 2. Transient absorption spectra after UV excitation: (a) FL in CD_3CN, (b) and (c) FL in CD_3OD. Baseline is shifted because of the signal from the CaF_2 window.

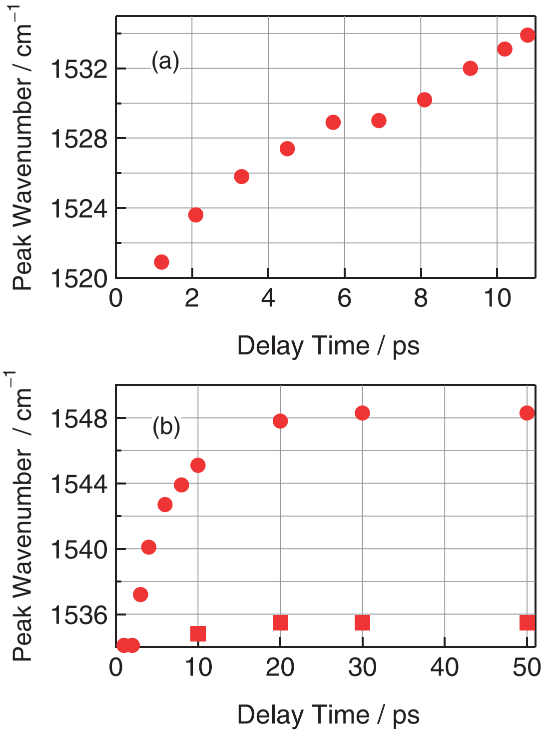

Figure 3. Peak wavenumbers of transient absorption bands as a function of delay time. Solvents are (a) CD_3CN and (b) CD_3OD. In CD_3OD, two bands are observed after 10 ps.

In CD_3CN, the UV-induced difference IR spectra exhibit transient absorption bands at around 1535 and 1480 cm^{-1}. Tanaka et al. have studied the excited state dynamics of FL in CD_3CN by nanosecond UV-pump and IR-probe spectroscopy.[5] They assigned the transient absorption band at 1544 cm^{-1} to the CO stretching mode of FL in the S_1 state. Considering the mode assignment by Tanaka et al., we concluded that the transient absorption band at around 1535 cm^{-1} is due to the CO stretching mode of FL. According to molecular orbital calculations, the HOMO of FL does not have any electron density in the carbonyl group; all the electrons are localized in the aromatic ring.[6] However, the LUMO of FL has antibonding character for the CO bond. Since the S_1 state contains an electron in the LUMO, the bond order of the CO bond is decreased by the photoexcitation. The band at around 1480 cm^{-1} probably corresponds to the transient absorption band at 1496 cm^{-1} observed by Tanaka et al., although the mode has not yet been accurately assigned. The peak wavenumber and the width of the band at 1535 cm^{-1} change on a picosecond time scale as shown in Figure 3a. This may be due to vibrational relaxation from the highly excited vibrational state, because the excess energy from the 00 transition in the S_1 state is about 15000 cm^{-1}. The anharmonicity of the CO stretching mode of FL in the S_0 state is observed at about 20 cm^{-1}.[2] If the anharmonicity in the S_1 state is similar to this value, the $v = 1 \rightarrow 2$ transition occurs at around 1515 cm^{-1}. This suggests that the intramolecular vibrational energy relaxation takes place in several picoseconds. Similar feature, i.e., blue shift of the vibrational bands, was reported for azobenzene and riboflavin.[7,8] Samant et al. reported a subpicosecond pump–probe study on FL in various solvents including methanol and acetonitrile.[9] They excited FL at 400 nm and observed time evolution in the transient absorption with a time constant of 1.4 ps. They hypothesized a dynamic process in which the vibrationally hot molecules in the S_1 state transfer their excess vibrational energy to the surrounding solvent molecules. Although our pump wavelength is different from theirs, we observed a time scale longer than 1.4 ps, suggesting that the other process may also contribute to the time evolution in the transient IR spectra. Iwata and Hamaguchi studied vibrational cooling of the C=C stretching mode of *trans*-stilbene in various solutions by picosecond time-resolved Raman spectroscopy.[10] They observed the peak shift of the C=C stretching mode with delay time on a picosecond time scale; this finding was interpreted as cooling of the locally heated environment around the solute. Although the solute and solvent are different from the previous work, the time scale of the band change is similar to that of *trans*-stilbene, suggesting that the observed time evolution of the band on a slower time scale is due to the cooling of the locally heated environment.

The UV-pump IR-probe measurements on FL in CD_3OD show three transient absorption bands at 1506, 1536, and 1550 cm^{-1} at 50 ps as shown in Figure 2c. In contrast to the results for FL in CD_3CN, we assign the band at 1536 cm^{-1} to the CO stretching mode of free FL in the S_1 state. The fluorescence spectra suggest that there is a greater amount of 1:1 complex than free FL because the spectrum due to the 1:1 complex at 565 nm has higher intensity than that due to the free FL at 514 nm.[9] Therefore, since the intensity of the band at 1550 cm^{-1} is larger than that at 1536 cm^{-1}, the band at 1550 cm^{-1} is assigned as the CO stretching mode of the 1:1 complex. This finding sharply contrasts with the electronic ground state where free FL is the dominant species. This result suggests that after photoexcitation, some amount of free FL should form H-bonds with methanol. Although the assignment of the band at 1506 cm^{-1} is unclear, this probably corresponds to the band at 1496 cm^{-1} reported by Tanaka et al.[5]

Interestingly, the peak shift due to the formation of H-bonding in the case of the CO stretching mode of FL in the S_1 state is opposite to that in the S_0 state. On the one hand, the peak wavenumber of the CO stretching mode of FL in the electronic ground state is red-shifted by 10 cm^{-1} by H-bonding with methanol. On the other hand, this stretching mode is blue-shifted by about 14 cm^{-1} by H-bonding in the S_1 state. As mentioned above, the LUMO of FL has antibonding character for the CO bond. If other molecular orbitals with bonding character for the CO bond are mixed with the LUMO by H-bond formation, the peak wavenumber of the CO stretching mode will be blue-shifted. This behavior was predicted in theoretical work on the S_1 state by Zhao and Han, although the shift was calculated to be only 3 cm^{-1}.[6] They demonstrated that intermolecular hydrogen bond between FL and methanol molecules becomes stronger in the electronic excited state.[6] Further studies are necessary to discuss the discrepancy of the frequency shift between experimental results and theoretical calculations quantitatively.

Similar to the CD_3CN case, we observed a blue shift and sharpening of the transient absorption bands at around 1530–1560 cm^{-1} in CD_3OD. The time evolution of the transient spectrum reflects the vibrational cooling process, similar to the case of CD_3CN. Before 5 ps, a broad single band at around 1535 cm^{-1} is observed, which is split into two bands at 1536 and 1550 cm^{-1}. The dependence of the peak wavenumbers on delay time is shown in Figure 3b. After 10 ps, the second highest peak due to free FL is also seen, together with the peak due to the 1:1 complex. The band at 1534 cm^{-1} due to free FL does not shift after 10 ps. However, the 1550-cm^{-1} band evolves even after 10 ps, which may reflect the H-bond dynamics between FL and methanol; the H-bond formation for FL in the S_1 state occurs on a time scale of 10 ps. In the time evolution of the transient absorption spectrum of FL, Samant et al. observed time constants of 5.7 and 16.3 ps in methanol.[9] The faster process was assigned to the reformation of the H-bonded complex, accompanied by equilibration of the H-bond network structure of the solvent, which corresponds to the slower process. The slow dynamics observed for the 1:1 complex in the present experiment may correspond to this rearrangement of the H-bond network structure. However, because of the broad background, it is difficult to discuss the faster dynamics of this band quantitatively. Experiments with 400 nm excitation will be useful to address the issue on the vibrational cooling and hydrogen-bonding dynamics more clearly.

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