Hydrogen-Bond Dynamics in the Excited State of Coumarin 102−Aniline Hydrogen-Bonded Complex†

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Comparison of the steady-state FTIR absorption spectra of coumarin-102 (C-102) in tetrachloroethylene with added aniline of various concentrations, in neat aniline and in neat *N*,*N*-dimethylaniline (DMA), indicates formation of a hydrogen-bonded complex between C-102 and aniline in solution. Subpicosecond time-resolved infrared absorption spectroscopy has been applied to study the dynamics of the hydrogen-bond following photoexcitation of C-102 chromophore in a C-102−aniline hydrogen-bonded complex. Upon photoexcitation at 400 nm, the hydrogen bond between C-102 and aniline breaks within 250 fs. Reformation of hydrogen-bond between the excited C-102 molecule and aniline takes place within about 30 ps. Biexponential temporal dynamics monitored at C═O stretching vibration (1736−1742 cm^{-1}) in neat aniline, which is a strongly structured solvent due to formation of intermolecular hydrogen bonds, reveals the biphasic solvation dynamics of aniline with solvation times 0.6 and 7.2 ps. These time constants have been assigned to nondiffusive and diffusive structural reorganization of the solvent.

1. Introduction

Photoinduced electron transfer (PET) reactions in hydrogen-bonded donor−acceptor complexes, in which the donor and acceptor molecules are linked to each other by a hydrogen bond, represents a new and unique area of research.[1] These investigations have clearly established that as photon absorption initiates the transfer of an electron from the donor to the acceptor, the hydrogen bond can act as an effective conduit to facilitate the electron transfer (ET) process. The interplay between proton motion and electron transfer has far-ranging implications in biology, chemistry, and physics.[2−7] One of the important aspects of the pathway model of Beraton and Onuchic is the prediction of the importance of hydrogen bonds in the mediation of electronic coupling.[8] Therein and co-workers have designed a number of model systems for investigating the efficacy of hydrogen bonds in mediating the coupling.[4] Because of directionality of hydrogen bonds, the separation distance and relative orientations of the donor and acceptor are well defined.[9] In general, the suggestion of the pathway model that a hydrogen bond is worth about two covalent bonds in mediating the electronic coupling has been supported.[10−12] Recently, efforts in supramolecular solid-state chemistry have been directed toward the rational design of coupled-electron/proton-transfer systems with novel electronic and photonic properties.[13−15] From a more fundamental point of view, the ET process in hydrogen-bonded systems steps beyond the outer sphere reactions treated by Marcus theory. The making and breaking of chemical bonds, which are not originally considered in this theory, may involve both ET and bond-forming/bond-breaking processes that accompany proton motion within the hydrogen-bond interface.[16−18]

The PET process between courmarin and aromatic amine solvents has been widely studied.[19−23] Interestingly, in the molecule of a coumarin dye, the C═O group is the only site that is responsible for both hydrogen bond formation and electron acceptance. Hence, it is an ideal system to explore the possibility of having a complete understanding about the role of hydrogen bond dynamics in the electron-transfer processes in hydrogen-bonded donor−acceptor molecular systems. The dynamics of intermolecular ET reactions, involving neat aromatic amine solvents, such as aniline (AN) and *N*,*N*-dimethylaniline (DMA), as the donors and the electronic excited states of coumarin dyes as the acceptors has been investigated by several groups using a fluorescence up-conversion technique.[19−23] In most coumarin−aniline systems, the ET dynamics takes place in a faster time domain than the solvation dynamics.[19−23] As a result, it should be accompanied by and possibly be coupled with the hydrogen-bond dynamics, since it has been shown that hydrogen-bond dynamics occurs in the subpicosecond time domain.[24−28] However, most of the experimental techniques applied so far to study the ET reaction dynamics, such as fluorescence up-conversion and transient absorption spectroscopy in the visible region, are not very sensitive to the local solute−solvent geometries and hence provided only limited insight into the microscopic dynamics.

Therefore, we plan to investigate the role of hydrogen-bond dynamics in intermolecular PET reaction in coumarin−amine hydrogen-bonded complex in solution, by applying the time-resolved vibrational spectroscopic technique. In our previous study, we observed a significant deuterium isotope effect on the electron-transfer dynamics in the coumarin−aniline systems when the amino hydrogen atoms are deuterated.[21] It indicated that the hydrogen-bond dynamics play a significant role in the PET process. The C═O group in C-102, has been reported to be a good hydrogen-bond acceptor to form hydrogen-bonded complexes with hydrogen bond donating solvents, such as

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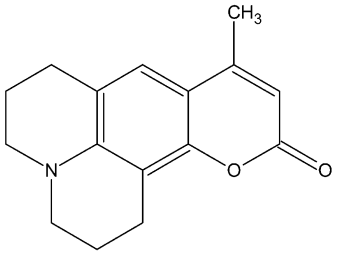
SCHEME 1: Chemical Structure of the Coumarin-102 Molecule



phenols.[19,22] Hence, C-102 is also expected to form a hydrogen-bonded complex with aniline in the ground state.

Following photoexcitation of the coumarin chromophore with ultra short laser pulses of 400 nm, we follow the hydrogen-bond dynamics in real time by monitoring the temporal evolution of vibrational absorption due to C═O stretching in the 1700−1800 cm^{-1} region. In this paper, we report the results of our investigations on the hydrogen-bond dynamics in the excited state of coumarin-102 (C-102)−aniline hydrogen-bonded complex. While the PET process in many of the coumarin−amine systems is very fast (faster than the solvation time) and complete within a few picoseconds, the same process in the C-102−amine system is slow and takes about a few nanoseconds to be completed.[19−21] Hence, in this system we expect to observe only the hydrogen-bond dynamics isolated from the ET process, since the ET dynamics is much slower than the hydrogen-bond dynamics. Recently, Elsaesser and co-workers applied this technique to observe the changes in distinct functional groups involved in the hydrogen-bond formation, which provided site-specific insight into local dynamics. They observed that dynamics of hydrogen bonds occur on ultrafast time scales set by vibrational motions of the hydrogen bond between the donor and the acceptor.[24−28]

2. Experimental Section

Laser grade C-102 (chemical structure of C-102 is shown in Scheme 1), procured from Exciton, was used as it was received. Analytical reagent (AR) grade aniline and dimethylaniline (DMA) were distilled under nitrogen atmosphere just before their use. Spectrograde tetrachloroethylene (TCE) was used as received without further purification. The steady-state absorption and fluorescence spectra were recorded on Shimadzu UV-3100 absorption spectrophotometer and JASCO FP-777 spectrofluorimeter, respectively. FTIR spectra of the liquid samples taken in a 1 mm thin cell with CaF_2 windows were recorded on Thermo Nicolet AVATR-360 infrared spectrometer.

We performed subpicosecond time-resolved vibrational spectroscopy using a mid-infrared transient absorption spectrometer, which has been described in detail elsewhere.[29] Briefly, an amplified Ti:sapphire laser system, consisting of an oscillator (Tsunami 3960, Spectra Physics) and a regenarative amplifier ("Spitfire", Spectra Physics), produces 120-fs pulses centered at 800 nm with 1 kHz repetition rate. Subsequently, the 400 nm light for pump is generated via frequency doubling of the fundamental in a 1 mm thick BBO crystal. An OPA (OPA-800 from Spectra Physics), pumped by a fraction of the fundamental from the amplifier, is used to produce signal and idler beams in the region of 1.14 ∼1.6 μm and 1.98 ∼ 1.6 μm, respectively. The total powers of the signal and idler beams were mixed collinearly in a 2 mm thick crystal to generate the tunable mid-infrared probe (from 800 to 2800 cm^{-1}) pulses for probing the transient absorption. The experiments were performed on 200-

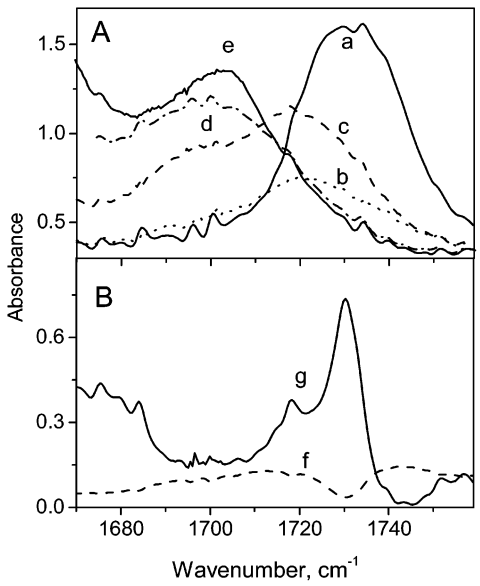


Figure 1. Steady-state FTIR spectra. (A) C-102 (1.5×10^{-2} mol dm^{-3}) in tetrachloroethylene (TCE) in absence (a) and in the presence of 1 and 3 mol dm^{-3} of aniline (curves b and c, respectively). C-102 in neat aniline (curve "d") and neat aniline only (curve "e"). (B) Neat DMA (curve "f") and C-102 (1×10^{-2} mol dm^{-3}) in DMA (curve "g").

μm thick liquid samples taken in a flow through cell. The temporal resolution was about 250 fs, as determined by measurement of the cross correlation in a 300 μm thick plate of silicon.

3. Results

3.1. Steady-State FTIR Spectra. Curve "a" in Figure 1 shows the steady-state FTIR spectrum of a solution of C-102 (15×10^{-3} mol dm^{-3}) in TCE. It shows a very strong absorption band having the maximum at ca. 1730 cm^{-1} due to stretching vibration of the C═O group. Vibrational spectra of C-102 were also recorded in the same solvent with varying concentrations of aniline, as well as in neat aniline (∼11 mol dm^{-3}, curve "d"). In the presence of 1 mol dm^{-3} of aniline (curve "b" in Figure 1), the absorption maximum due to C═O stretching mode appears at 1722 cm^{-1}. A red shift of about 8 cm^{-1} for the absorption maximum and a reduction in molar extinction coefficient of absorption, indicates the formation of an association complex between C-102 and aniline. In the presence of 3 mol dm^{-3} of aniline in TCE, the FTIR spectrum of C-102 has the absorption maximum at 1719 cm^{-1}, with an increase in absorbance as compared to that in curve "b", and a shoulder at 1698 cm^{-1}. In the case of C-102 in neat aniline (∼11 mol dm^{-3}), the absorption maximum due to the C═O group appears at 1698 cm^{-1} (curve "d"). All of these observations indicate formation of some kind of complex between C-102 and aniline. Curve "e" shows the FTIR spectrum of neat aniline. It has a maximum at 1703 cm^{-1}. However, this band is not observed in the FTIR spectrum of aniline in TCE if the concentration of aniline is less than 1 mol dm^{-3}. Hence this band could be assigned to some kind of self-association complex of aniline.[30−32] It is evident that the curve "d" represents the combined spectra due to neat aniline and the C-102−aniline association complex. We also observed a red shift of about 6 nm of the maximum wavelength in the steady-state fluorescence spectrum as well as a strong quenching of fluorescence intensity of C-102 in the presence of aniline in TCE. Curve "g" in Figure 1B shows the FTIR spectrum of C-102 in neat DMA. The absorption

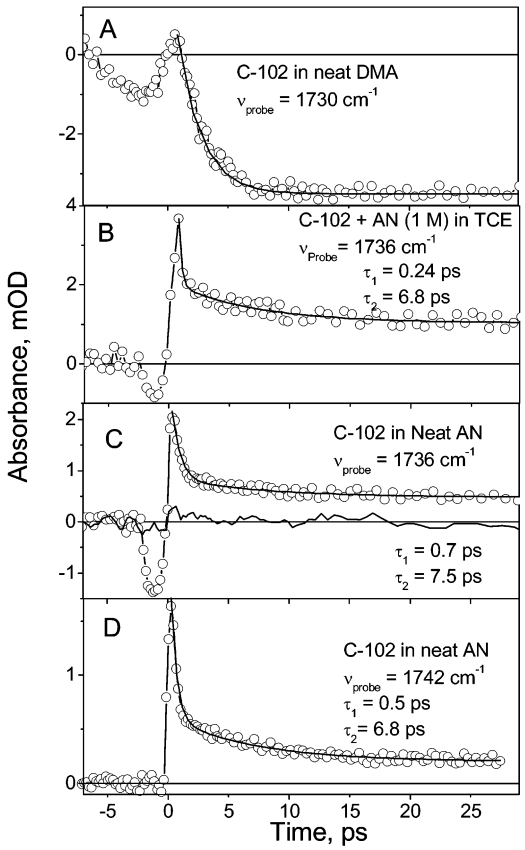


Figure 2. Time-resolved change of vibrational absorption monitored at different frequencies following optical excitation of C-102 chromophore (1.5×10^{-2} mol dm^{-3}) in neat DMA (A), in the presence of 1 mol dm^{-3} of aniline in TCE (B), and in neat aniline (C and D). The solid line in C indicates the transient absorption signal due to pure aniline. The lifetimes obtained by single- or two-exponential fittings of the data are given in the insets.

maximum due to the C═O group in neat DMA appears at 1730 cm^{-1}, which is nearly the same position at which the absorption due to C═O stretching of C-102 in TCE appears (curve "a"). However, the bandwidth of C═O absorption is reduced significantly in DMA as compared to that in TCE.

3.2. Time-Resolved Infrared Absorption Study. Time-resolved infrared absorption spectroscopic studies have been performed with the solutions containing C-102 in neat aniline and DMA and in TCE in the presence of 1 mol dm^{-3} of aniline. Upon photoexcitation of coumarin−amine systems by ultrashort (duration of about 150 fs) laser pulses of 400 nm, which is resonant to the electronic $S_1 \leftarrow S_0$ transition of C-102, only the C-102 chromophore is excited. Aniline and DMA molecules do not absorb at 400 nm, and hence they stay in their ground electronic states. The temporal evolution of the vibrational absorption due to the C═O stretching vibration of C-102 was monitored at both 1742 and 1736 cm^{-1} in the case of aniline as the donor, and at 1730 cm^{-1} for the C═O stretching vibration of C-102 in neat DMA.

Figure 2 presents the temporal profiles for vibrational absorption changes following optical excitation of C-102 in the presence of donors. Figure 2A shows the temporal profile of the transient absorption with C-102 in neat DMA at the probe frequency 1730 cm^{-1} (corresponding to the C═O stretching frequency of C-102 in DMA). It consists of a dip (negative absorption) at negative time delays, positive going change around zero delay, and a rise of negative absorption signal after the zero delay due to ground-state bleaching of C-102 following

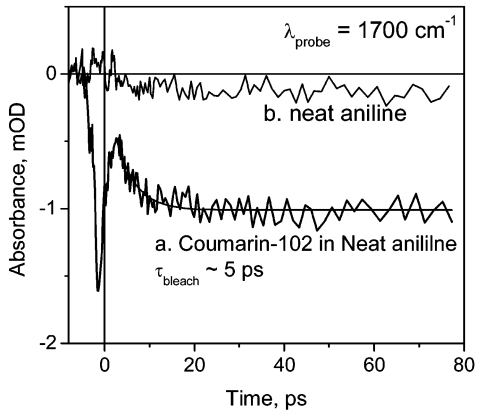


Figure 3. Time-resolved change of vibrational absorption at 1700 cm^{-1} after electronic excitation of C102 in neat aniline (curve a). Curve b represents the blank experiment with neat aniline only.

photoexcitation. The small dip (negative absorption) and a rise before and around the zero time is due to perturbed free induction decay as well as cross correlation with the exciting beam. The bleaching signal takes about 5 ps to grow to the maximum (growth lifetime is about 2 ps) and does not recover within the time-domain of our experiment, i.e., up to about 100 ps (Figure 2A).

Figure 2B presents the temporal profile of the transient absorption monitored at 1736 cm^{-1}, following photoexcitation of C-102 in the presence of 1 mol dm^{-3} of aniline in TCE. It consists of a dip (negative absorption) before the zero time delay due to the perturbed free induction decay and a sharp rise of the absorption to the maximum positive value around the zero time delay with instrument response time (∼250 fs). This is followed by a dual-exponential decay of the transient absorption to a residual value (about 15% of the peak value), which in its turn takes a few hundred picoseconds to decay (not shown in Figure 2). The lifetimes of the two components decaying in the early time domain are 0.25 and 6.8 ps.

The temporal profiles of the transient absorption monitored at 1736 and 1742 cm^{-1} following photoexcitation of C-102 dissolved in neat aniline are shown in the Figures 2C and 2D. The hydrogen-bonded complex has a weak absorption at 1736 cm^{-1} but no absorption at 1742 cm^{-1}. The free C═O group absorbs strongly at both the frequencies. The decay characteristics of the transient absorption presented in these figures are more or less similar to those shown in Figure 2B. The lifetimes of the two components decaying in the early time domain have been determined to be 0.6 ± 0.1 and 7.2 ± 0.4 ps. It is important to note that the free induction decay before the zero time delay is not observed in the case of the kinetic trace monitored at 1742 cm^{-1} (Figure 2D), at which the C-102−aniline complex does not absorb. The free induction decay before the zero time delay seems to be significant in the region where the C-102−aniline complex shows substantial absorption. Since the free induction decay originates from the perturbation of the probe-induced polarization of the pump pulse, if the probe pulse is not resonant to a molecular transition (here it is C═O stretching), there should be no polarization with a finite dephasing time, and thus the probe-induced free induction decay is absent in the transient absorption profile monitored at 1742 cm^{-1}.

The temporal profile "a", shown in Figure 3, represents the transient infrared absorption signal monitored at 1700 cm^{-1}, at which both the self-association complex of aniline and the C-102−aniline hydrogen-bonded complex absorb. This shows a large negative absorption dip before zero delay time due to free induction decay. The partial recovery of the negative

absorption signal around the zero delay time is followed by another small rise of the negative absorption signal with a growth lifetime of about 5 ps. Since we could not observe the same kind of temporal profile with neat aniline alone (temporal profile "b"), the transient absorption signal "a" definitely represents the characteristic of the excited C-102−aniline hydrogen-bonded complex in neat aniline solvent. This bleach signal has not recovered within our experimental time domain (i.e., up to about 100 ps).

4. Discussion

4.1. C-102−Aniline Hydrogen-Bonded Complex. The position of the absorption band due to C═O stretching in the FTIR spectrum of the C-102 molecule in neat DMA has not been affected as compared to that of C-102 in TCE, which is a noninteracting solvent. However, in the presence of aniline, not only is the position of C═O absorption red-shifted but also the absorption coefficient has been reduced significantly. The fact that aniline has the ability to form a hydrogen bond with the C═O group of C-102 molecule, but not DMA, suggests that the formation of complex between C-102 and aniline occurs via formation of a hydrogen bond between the C═O group of C-102 and the H−N group of aniline (C═O···H−N). However, due to a small shift between the absorption maxima of the C═O group in free C-102 and the C-102−aniline complex in TCE, as well as considerable overlap between the absorption spectra of C-102−aniline complex and self-associated complex in neat aniline solvent, it has not been possible to determine the association constant for C-102−aniline complex. The larger red shift and increase in absorbance of the C-102−aniline complex in the presence of higher concentrations of aniline in TCE or in neat aniline could possibly be explained by postulating higher association constants for the C-102−aniline hydrogen-bonded complex in the solvents of higher polarity of the solvent medium (dielectric constants are 6.7 and 2.3 for aniline and TCE, respectively). One point to note here is that the bandwidth of the vibrational absorption band due to C═O stretch in neat DMA is narrower than that in TCE. Narrower bandwidth of C═O absorption in neat DMA may possibly indicate a charge-transfer type of interaction between C-102 and DMA.

4.2. Hydrogen-Bond Dynamics in the Excited State of C-102−Aniline Hydrogen-Bonded Complex. We mentioned earlier that the lifetimes of the S_1 state of C-102 in neat aniline and DMA are 1.4 and 2.4 nanoseconds, respectively.[19−21] Since the process of PET from amines to the excited C-102 molecule occurs on a few nanosecond time scale (see Introduction), the time dependent absorbance changes, as shown in Figure 2, indicate the role of hydrogen-bond in the excited state dynamics of C-102 in aniline, rather than in the dynamics of ET reactions between the dye and aniline. The difference in dynamics of the excited C-102 molecule in the presence of aniline and DMA obviously suggests the involvement of the hydrogen-bond dynamics in the solvation of the S_1 state of C-102 in aniline. In the case of C-102 in DMA (Figure 2A), the transient absorption profile monitored at the probe wavelength 1730 cm^{-1}, indicates the bleaching of absorption, while in the case of C-102−aniline systems, we observe the instrument response time limited rise of the transient absorption due to free or unbound C═O stretching vibration monitored in the region 1730−1742 cm^{-1} (Figures 2B, 2C, and 2D). The negative absorption signal, which we observe due to bleaching of the ground state of C-102 in DMA following optical excitation to its S_1 state, indicates the decrease of the vibrational transition moment for the $v = 0$ to $v = 1$ transition in the S_1 state as compared to that in the S_0 state. Nibbering et al.[24,25] found a decrease in the oscillator strength of the $v = 0$ to $v = 1$ transition in the excited state without a significant spectral shift upon optical excitation at 400 nm.[25] However, while the growth of the bleach signal should follow the instrument response time, in C-102-DMA system, we observe a growth lifetime of about 2 ps. Possibly, we could not observe the instantaneous bleach because of unwanted coherent artifacts masking all the dynamics at very early delay times. The growth lifetime of about 2 ps could possibly be due to the nondiffusive component of the dipolar solvation of the excited state of C-102 in DMA. This time constant has been measured to be about 3 ps by the fluorescence dynamic Stokes shift method.[22]

The increase in transient absorption immediately following the electronic excitation of the coumarin chromophore in the C-102−aniline hydrogen-bonded complex indicates the instantaneous (<250 fs) appearance of transient absorption due to free C═O because of dissociation of the hydrogen bond between C-102 and aniline. Elsaesser and co-workers reported that in the case of the C-102−phenol and C-102−$CHCl_3$ hydrogen-bonded complexes in solution, the hydrogen bond breaks within 200 fs following optical excitation of the hydrogen bonded complex.[24−28] The cleavage of the hydrogen-bond is driven by the changes of local charge distribution in the excited state of C-102. As suggested by semiempirical calculations of charge distribution in the S_1 state of C-102, the polarity, and thus the hydrogen affinity of the C═O group, decreases on photoexcitation.[33] Instantaneous cleavage of hydrogen-bond following optical excitation of C-102 is a consequence of a rearrangement of electron density upon photoexcitation. The ultrashort time scale (<250 fs) for cleavage of the hydrogen bond dictates the involvement of the low-frequency vibrations of the hydrogen-bonded groups, in the 100−200 cm^{-1} range.[25] The impulsive enhancement of the transient absorption following optical excitation represents a nonequilibrium geometry of the cleaved hydrogen bond. Since 85% of the transient infrared absorption signal, which is characteristic of the C═O group, decays within a few tens of a picosecond (this is much shorter than the lifetime of the S_1 state of C-102 in aniline), it could be correlated with the process of reformation of hydrogen-bond after its cleavage in the S_1 state. However, this new hydrogen-bond, reformed between C-102 in the S_1 state and aniline molecules in the ground state, have equilibrium geometry and electronic structure that are different from those formed between aniline and C-102 in the ground state.

In Figure 2, we observe that the transient absorption due to free C═O group of C-102 in its S_1 state, which appears immediately after photoexcitation of the C-102−aniline complex, undergoes a nonexponential decay process. It has been shown earlier that two-photon absorption by C-102 at 400 nm excitation is of minor importance.[27] In addition, the vibrational excess energy in the S_1 state is much smaller than the vibrational energy of about 1700 cm^{-1} of the modes studied here. Excitation does not create population of the $v = 1$ or higher levels in these vibrations.[27] Similarly, the $v = 1$ of these modes in the unexcited molecules shows a population very small compared to the purely electronic, and consequently excitation from the $v = 1$ levels in S_0 can be neglected.[27]

We mentioned earlier that aniline is a strongly self-associated solvent due to formation of intermolecular hydrogen-bonds.[30,31] Immediately after excitation of the C-102−aniline hydrogen-bonded complex, cleavage of hydrogen bond is accompanied by the redistribution of electron density in the aniline molecule, which has been directly involved in hydrogen-bond formation

with C-102, as well as in the other aniline molecules associated with the former. Any kind of change in the charge distribution in intermolecularly hydrogen-bonded solvent molecules, surrounding the C═O group, acts back on it and causes a change in vibrational absorption characteristics of the C═O group. Earlier, the experimental results, obtained by Elsasser and co-workers on the C-102−(phenol)$_n$ hydrogen-bonded complex, demonstrated the ability of the ultrafast time-resolved vibrational spectroscopy to reveal the dynamics of the hydrogen bond not only involving the phenol unit directly linked to C-102 but also the dynamics in hydrogen-bonding network further away from the initially excited hydrogen-bond acceptor.[24−27]

The distinct differences observed in the temporal profiles of transient absorption monitored at 1700 cm^{-1} in neat aniline and C-102-aniline systems (Figure 3) clearly reveal the involvement of some kind of dynamical process following photoexcitation of C-102−aniline hydrogen-bonded complex. A large negative signal around zero delay time due to perturbed free induction decay also supports this observation. Due to overlapping of the bleach signal with that due to free induction decay at around zero delay time, it is not possible to assign the amount of contribution of the instantaneous bleach signal immediately following photoexcitation of the hydrogen-bonded complex. However, the rise time of about 5 ps for the small amount of bleach signal after zero-delay could be correlated with the reorganization of the electron distribution in the neighboring aniline molecules associated with the C═O group to attain a new equilibrium geometry of the hydrogen bond in the excited state of coumarin molecule.

4.3. Can Hydrogen-Bond Dynamics Be Considered as Solvation Dynamics? Although a dipole−dipole or van der Waals interaction is considered a nonspecific interaction, and interaction between the solute and solvent via hydrogen bonding is considered a "specific" interaction, they may be considered not very different.[34] Popular measures of electronic-state solvation, such as the $E_T(30)$ scale, are known to be as much a measure of hydrogen bonding to the solvent as a measure of interaction with the solvent dipole.[35−37] From this viewpoint, reformation of hydrogen bond is just a change in solute−solvent interaction resulting from the reorganization of the solvent, i.e., it is a type of solvation dynamics.[38] The standard picture of nonspecific solvation dynamics assumes relatively weak intermolecular interactions.[39−42] The interactions of the solute with each of a large number of solvent molecules, are equally important, and the dynamics involve motion along a coordinate representing the collective movements of many solvent molecules. The barriers to these motions are small compared to the thermal energies. As a result, the solute is generally regarded as the system and all of the solvent molecules form the bath. However, since the hydrogen-bond dynamics observed here can also be considered as a transfer between two distinct states, nonbonded and hydrogen-bonded C═O group, the reformation of the hydrogen bond is more naturally described as a chemical reaction than as a solvation process. In reality, hydrogen-bond dynamics should represent a case intermediate between nonspecific solvation and bond-breaking. However, if we consider the fact that the free energy change associated with reformation of an O···H−N hydrogen-bond is small (although not negligible as compared to the thermal energy), the hydrogen-bond dynamics we observe following photodissociation of the C-102−aniline hydrogen-bonded complex may possibly be described as solvation dynamics.

On the basis of these arguments, we propose a model in which hydrogen-bond breaking is followed by solvent reorganization on two time scales. After initial bond-breaking, the fragments are rapidly, but incompletely, solvated to leave a "dangling" hydrogen bond. The component with 0.6 ps lifetime associated with the temporal profiles shown in Figures 2C and 2D, which represent the vibrational dynamics of the C═O group of C-102 in neat aniline, possibly have arisen due to this rapid nondiffusive component of solvation. The small amplitude of this motion leads to rapid relaxation. Hochstrasser and co-workers experimentally determined the free rotor anisotropy decay time constant of aniline (4×10^{-2} mol dm^{-3}) to be 0.94 ps in isopentane solvent.[43] Applying the extended diffusion theory to aniline−isopentane anisotropy decay, the collision time of 0.21 ps has been determined. This implies that the aniline molecule in isopentane rotates about 20° between collisions, and hence the orientational motion of aniline in isopentane is significantly nondiffusive.[43]

To complete the equilibration of the product state, the dangling bond must be fully incorporated into the hydrogen-bond structure of the solvent. This process occurs on a longer time scale related to the rate of hydrogen-bond reorganization in the bulk solvent. In hydrogen-bonding solvents, the longest component of the Debye dielectric relaxation is generally assumed to be associated with the rate of hydrogen-bond reorganization in the solvent.[44,45] Thus the slower decay process having the lifetime of about 7 ps could be correlated to the diffusive restructuring of the first solvation shell around the C═O group of C-102 in the S_1 state.

The component with decay time constant of 0.25 ps, which represents the vibrational dynamics of C═O group of C-102 in the presence of 1 mol dm^{-3} of aniline in TCE, may have arisen due to inertial and/or nondiffusive solvation of the S_1 state of C-102 immediately after hydrogen-bond dissociation. Considering the instrument response of our spectrometer to be 250 fs, decay lifetime of this component obviously could not be ascertained with reasonable accuracy. The possibility that this decay component, which appears like an absorption spike at around the zero delay time, has arisen due to coherent multiple IR photon absorption concurrent with the visible excitation of the C-102−aniline complex also can not be excluded.[25]

4.4. Solvation Dynamics in Aniline. Since we propose to correlate the time constants for the decay of vibrational absorption of the C═O group in the S_1 state of C-102 in aniline solvent determined in this work ($\leq$0.25, 0.6 and 7.1 ps) with the solvation times, it is important to compare these time constants with the solvation times of the same solvent determined earlier using other methods. Table 1 records the different solvation times of aniline determined by different groups using different methods. The longitudinal relaxation time (τ_L) in liquid aniline, which is predicted to be the solvation time by the simplest continuum theory, has been determined to be 8.1 ps.[39,40]

Among the different methods that have been adopted by the chemists to unravel the dynamics of solvation on the ultrafast time scale, the dynamic fluorescence Stokes shift method is the most widely used and has been proven to be most successful. C-102 has been widely used by a number of groups of scientists as a fluorescent probe for solvation dynamics study.[46−48] Yoshihara and co-workers, who measured the dynamic fluorescence Stokes shift in aniline using C-102 as the probe, reported the biphasic solvation in aniline.[41] The measured solvation times are 1.2 and 17.8 ps, with average solvation times of 13.2 ps. However, the solvation times of aniline obtained from the dynamic fluorescence Stokes shift measurement using LDS 750 dye as the probe has been fitted both to biphasic solvation dynamics with solvation times 0.6 and 24.7 ps as well

TABLE 1: Solvation Times of Aniline Determined by Using Different Methods

	solvation times, ps	method	refs
1.	8.1	longitudinal relaxation time	ref 50
2.	1.2, 17.8	fluorescence upconversion using C-102 as the probe	ref 48
3.	0.3, 5.6, 26.5	fluorescence upconversion using LDS-750 as the probe	ref 49
4.	0.1, 0.8, 10.6	super continuum model	Do
5.	0.3, 8.56, 17.7	dynamical mean spherical approximation	Do
6.	1.2, 14	OHD-OKE in neat aniline	ref 54, 55
7.	0.2, 14	OHD-OKE in dilute aniline solution in CCL_4	ref 55
8.	0.6, 7.2	transient IR absorption, using C-102 in neat aniline	this work
9.	0.25, 6.8	transient IR absorption, using C-102 in aniline/TCE	this work

as triphasic solvation dynamics with solvation times 0.3, 5.6, and 26.5 ps.[48] These solvation times were compared with those of the expected values calculated using both the simple continuum model (solvation times are 0.1, 0.82, and 10.6 ps) and dynamical mean spherical approximation (DMSA) (solvation times are 0.3, 8.56, and 17.7 ps).[49]

Although the dynamic Stokes shift method has been widely used to determine the solvation times, one of the central assumptions in interpreting and generalizing the results obtained using this method is that of linear response.[50,51] Reported results obtained by using the molecular dynamics simulation method indicate that the assumption of the linear response is reasonable for a number of solute − solvent systems. The accuracy of the linear response for a given solvent depends on the size and charge density of the model solute as well as the nature of specific interaction between the solute and the solvent.[52−54] Considering these facts, the assumption of linear response in a strongly self-associated solvent such as aniline, possibly may not be valid, and hence the solvation times determined by using dynamic Stokes shift method may have some uncertainties.

Since, in the case of solvation, solvent orientational dynamics is the dominant mechanism, the ultrafast liquid dynamics as observed in the optically heterodyne detected optical Kerr effect (OHD-OKE) experiment could be used to calculate the solvation time correlation function. Smith et al. measured the OHD-OKE technique in the femtoscond time domain to construct the solvation correlation function in liquid aniline.[55,56] The solvation correlation function calculated from the complete OHD-OKE data showed an initial rapid nonexponential component of the Gaussian profile, a weak oscillation around 0.2 ps, followed by a longer nonexponential decay, characterized by two solvation times of about 1.2 and 14 ps.[55] The ultrafast component of 0.25 ps duration was assigned to the inertial motion of the solvent molecules. This was ascribed to the librational motion of molecules on a potential surface formed by interaction with a cage of other neighbors. The shorter (1.2 ps) of the two exponential relaxations was too fast to be ascribed to diffusive orientation, and hence the possible physical origin to this nondiffusive picosecond component was assigned to the dissociation or disruption of short-range structure in the liquid. This short relaxation time was sensitive to dilution, and this component was not well resolved at high dilution. This result agrees well with our observation. This suggests that intermolecular interactions in aniline are important in determining the magnitude of the contributions of the decay components. The slowest relaxation time was shown to behave at least qualitatively, as predicted by the hydrodynamic models of orientational diffusion. However, quantitative analysis suggested that some of the assumptions concerning the molecular shape or hydrodynamic boundary conditions were inadequate to completely describe diffusional orientational motion in aniline. Beningo et al. also observed that the solvent dynamics affecting hydrogen bonds are well correlated with the dielectric relaxation times of the pure solvents but uncorrelated with their viscosities.[38] This result suggests that the polarizability anisotropy relaxation dynamics, as observed by the OHD-OKE method, is sensitive to the dynamic processes in the liquid, which are dependent on the intermolecular interaction and local liquid structure, in addition to the orientational motion of the solvent molecules. The latter process has been suggested to be the dominant mechanism in solvation dynamics by molecular dynamic simulation.

Hence to rationalize the different values of solvation times of aniline obtained by using different experimental and theoretical methods, it is important to consider that different methods have limitations to probe different aspects of solute−solvent interactions. It is also important to consider how the reactant (probe) and solvent dynamics are coupled. Recently, several groups have investigated the dynamics of the hydrogen bond in water, both theoretically and experimentally.[56−60] It is assured that the hydrogen-bond dynamics in water is nonexponential and could be explained by biphasic or triphasic dynamics. Our work shows the nonexponential nature of the hydrogen-bond dynamics in aniline, too. However, it is yet to establish how the hydrogen-bond dynamics is affected by the nature of the probe.

5. Conclusion

To summarize, C-102 in its ground state forms hydrogen-bonded complex with aniline, which is a self-associated liquid due to formation of intermolecular hydrogen bonds. Following photoexcitation of the coumarin chromophore of the C-102-aniline hydrogen bonded complex, the hydrogen bond dissociates within the time resolution (250 fs) of our ultrafast spectrometer. Following photodissociation of the hydrogen-bonded complex, the aniline molecules around the excited coumarin molecule reorient themselves to solvate it via reformation of the hydrogen bond with a new equilibrium geometry. The temporal dynamics of the vibrational absorption of the C═O group of C-102 is shown to reveal the detailed dynamics of solvation, although the C═O group is not directly attached to all the solvent molecules in the solvation shells. The biexponential dynamics of vibrational absorption of the C═O group have been correlated with the nondiffusive and diffusive structural dynamics of aniline.

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References and Notes

(1) Piotrowiak, P. *Chem. Soc. Rev.* **1999**, *28*, 143. (b) Ward, M. D. *Chem. Soc. Rev.* **1997**, *26*, 365. (c) Williamson, A.; Bowler, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 10902. (d) Prasad, E.; Gopidas, K. R. *J. Am. Chem. Soc.* **2000**, *122*, 3191. (e) Smitha, M. A.; Prasad, E.; Gopidas, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 1159. (f) Fukuzumi, S.; Yoshida, Y.; Okamoto, K.; Imahori, H.; Araki, Y.; Ito, O. *J. Am. Chem. Soc.* **2002**, *124*, 6794.

(2) Peltier, H.; Kraut, J. *Science* **1992**, *258*, 1748.

(3) Nocek, J. M.; Zhou, J. S.; DeForest, S.; Priyadarshy, S.; Beraton, D. N.; Onuchic, J. N.; Hoffman, B. M. *Chem. Rev.* **1996**, *96*, 2459.

(4) Lawrence, D. S.; Jiang, T.; Levett, M. *Chem. Rev.* **1995**, *95*, 2229.

(5) Cukier, R. L.; Nocera, D. G. *Annu. Rev. Phys. Chem.* **1998**, *49*, 337.

(6) de Rege, P. J. F.; Williams, S. A.; Therien, M. J. *Science* **1995**, *269*, 1409.

(7) Chang, C. J.; Brown, J. D. K.; Chang, M. C. Y.; Baker, E. A.; Nocera, D. G. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley: New York, 2000; Vol. III, p 409.

(8) Onuchic, J. N.; Beraton, D. N.; Winkler, J. R.; Gray, H. B. *Annu. Rev. Biophys. Biomol. Struct.* **1992**, *21*, 349. (b) Onuchic, J. N.; Beraton, D. N. *J. Chem. Phys.* **1990**, *92*, 722.

(9) Philip, D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154.

(10) Yang, J.; Seneviratne, D.; Arbatin, G.; Anderson, A. M.; Curtis, J. C. *J. Am. Chem. Soc.* **1997**, *119*, 5329. (b) Sessler, J. L.; Satiosatham, M.; Brown, C. T.; Rhodes, T. A.; Wiederrecht, G. *J. Am. Chem. Soc.* **2001**, *123*, 3655. (c) Prasad, E.; Gopidas, K. R. *J. Am. Chem. Soc.* **2000**, *122*, 3191. (d) Cukier, E.; Daniels, S.; Vinson, E.; Cave, R. J. *J. Phys. Chem. A* **2002**, *106*, 11240.

(11) Medvedev, D. M.; Daizadeh, I.; Stuchebrukhov, A. A. *J. Am. Chem. Soc.* **2000**, *122*, 6571

(12) Zhao, X. G.; Cukier, R. I. *J. Phys. Chem.* **1995**, *99*, 645.

(13) Birge, R. R. *Annu. Rev. Phys. Chem.* **1990**, *41*, 2339.

(14) Scherl, M.; Haarer, D.; Fischer, J.; DeCian, A.; Lehn. J.-M.; Eichen, Y. *J. Phys. Chem.* **1996**, *100*, 16175.

(15) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155.

(16) Gertner, B. J.; Hynes, J. T. *Science* **1996**, *271* 1563.

(17) Saevant, J.-M. *Acc. Chem. Res.* **1993**, *26*, 455.

(18) Robert, M.; Saevant, J.-M. *J. Am. Chem. Soc.* **2000**, *122*, 514.

(19) Yoshihara, K. In *Electron Transfer: From Isolated Molecules to Biomolecules, Part Two*; Jortner, J., Bixon, M., Eds.; *Adv. Chem. Phys. Ser.*; 1999; Vol. 107, p 371.

(20) Nagasawa, Y.; Yartsev, A. P.; Tominaga, K.; Bisht, P. B.; Johnson, A. E.; Yoshihara, K. *J. Phys. Chem.* **1995**, *99*, 653.

(21) Nagasawa, Y.; Yartsev, A. P.; Tominaga, K.; Johnson, A. E.; Yoshihara, K. *J. Chem. Phys.* **1994**, *101*, 5717.

(22) Pal, H.; Nagasawa, Y.; Tominaga, K.; Bisht, P. B.; Yoshihara, K. *J. Phys. Chem.* **1996**, *100*, 11964.

(23) Castner, E. W., Jr.; Kennedy, D.; Cave, R. J. *J. Phys. Chem. A* **2000**, *104*, 2869.

(24) Englaitner, S.; Steel, M.; Zinth, W. *J. Phys. Chem. A* **1999**, *103*, 3013.

(25) Chudoba, C.; Nibbering, E. T. J.; Elsasser, T. *Phys. Rev. Lett.* **1998**, *81*, 3010.

(26) Chudoba, C.; Nibbering, E. T. J.; Elsasser, T. *J. Phys. Chem.* **1999**, *103*, 5625.

(27) Nibbering, E. T. J.; Chudoba, C.; Elsasser, T. *Isr. J. Chem.* **1999**, *39*, 333.

(28) Nibbering, E. T. J.; Tschirschwitz, F.; Chudoba, C.; Elsasser, T. *J. Phys. Chem. A* **2000**, *104*, 4236.

(29) Rubstov, I. V.; Zhang, T.; Yoshihara, K. *J. Spectrosc. Soc. Jpn.* **2000**, *49*, 6.

(30) Wolf, H.; Mathies, D. *J. Phys. Chem.* **1973**, *77*, 2087.

(31) Medhi, K. C.; Kartha, G. S. *Ind. J. Phys.* **1963**, *37*, 139 and 237.

(32) Sugawa, K.; Miyasaka, J.; Nakanaga, T.; Tako, H.; Lembach, G.; Djafari, J.; Barth, H.; Brutschy, B. *J. Phys. Chem.* **1996**, *100*, 17145.

(33) Kumar, P. V.; Maroncelli, M. *J. Chem. Phys.* **1995**, *103*, 3038.

(34) Mataga, N.; Kubota, T. *Molecular Interactions and Electronic Spectra*; Marcel Dekker: New York, 1970.

(35) Marcus, Y. *J. Solution Chem.* **1991**, *20*, 929.

(36) Fowler, F. W.; Katritzky, A. R.; Rutherford, R. J. D. *J. Chem. Soc. B* **1971**, *3*, 460.

(37) Reid, P. J.; Ales, S.; Jarzeba, J.; Schlief, R. E.; Johnson, A. E.: Barbara, P. F. *Chem. Phys. Lett.* **1994**, *22*, 93.

(38) Beningo, A. J.; Ahmed, E.; Berg, M. *J. Chem. Phys.* **1996**, *104*, 7382.

(39) Maroncelli, M. *J. Mol. Liq.* **1993**, *57*, 1.

(40) Barbara, P. F.; Jarzeba, W. *Adv. Photochem.* **1990**, *15*, 1.

(41) Beningo, A. J.; Berg, M. *J. Chem. Phys.* **1993**, *99*, 8552.

(42) Ma, J.; Vanden, B.; Merg, M. *J. Chem. Phys.* **1995**, *103*, 9146.

(43) Pereira, M. A.; Share, P. E.; Sarisky, M. J.; Hochstrasser, R. M. *J. Chem. Phys.* **1991**, *94*, 2513.

(44) Bertolini, D.; Casseteri, M.; Salvetti, G. *J. Chem. Phys.* **1983**, *78*, 865.

(45) Garg, S. K.; Smyth, C. P. *J. Phys. Chem.* **1965**, *69*, 1294.

(46) Kahlow, M. A.; Kang, T.-J.; Barbara, P. F. *J. Chem. Phys.* **1988**, *88*, 2372.

(47) Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1987**, *86*, 6221; **1990**, *92*, 3251.

(48) Pal, H.; Nagasawa, Y.; Tominaga, K.; Kumazaki, S.; Yoshihara, K. *J. Chem. Phys.* **1995**, *102*, 7758.

(49) Smith, N. A.; Meech, S. R. *J. Phys. Chem. A* **2000**, *104*, 4223.

(50) Rossky, P. J.; Simon, J. D. *Nature* **1994**, *370*, 263.

(51) Chandler, D. *Introduction to Modern Statistical Mechanics*; Oxford University Press: New York, 1987.

(52) Fonseca, T.; Ladyani, B. M. *J. Mol. Liq.* **1994**, *60*, 1. Fonseca, T.; Ladyani, B. M. *J. Phys. Chem.* **1991**, *95*, 2116.

(53) Ando, K.; Kato, S. *J. Chem. Phys.* **1993**, *98*, 5679.

(54) Smith, N. A.; Meech, S. R.; Rubtsov, I. V.; Yoshihara, K. *Chem. Phys. Lett.* **1999**, *303*, 209.

(55) Smith, N. A.; Lin, S.; Meech, S. R.; Yoshihara, K. *J. Phys. Chem. A* **1997**, *101*, 3641.

(56) Kropman, M. F.; Neinhuys, H.-K.; Woutersen, S.; Bakker, H. J. *J. Phys. Chem. A* **2001**, *105*, 4622.

(57) Pal, S. K.; Peon, J.; Bagchi, B. Zewail, A. H. *J. Phys. Chem. B* **2002**, *106*, 12376.

(58) Balasubramanian, S.; Pal, S.; Bagchi, B. *Phys. Rev. Lett.* **2002**, *89*, 115505.

(59) Yeremenko, S.; Pshenichnikov, M. S.; Weirsma, D. A. *Chem. Phys. Lett.* **2003**, *369*, 107.

(60) Lawrence, C. P.; Skinner, J. L. *Chem. Phys. Lett.* **2003**, *369*, 472.