Femtochemistry of Hydrogen Bonded Complexes after Electronic Excitation in the Liquid Phase: The Case of Coumarin 102

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We review our results on hydrogen bonding dynamics in the electronically excited state of coumarin 102 (C102), where we deduced that a hydrogen bond cleavage occurs within 200 fs. We compare the electronic absorption and emission properties of C102 hydrogen bonded to $CHCl_3$, phenol or 2,2-dimethyl-3-ethyl-3-pentanol. We introduce the technique of two-pulse photon echo to show that an optical coherence between the optically coupled electronic ground and excited states survives until 180−200 fs, in the case of C102−$(phenol)_{1,2}$ complexes, and argue that this is an indication that an electronic state hopping occurs around this time. By comparison with the previous pump−probe and grating scattering results we deduce that this state hopping is accompanied by a hydrogen bond cleavage.

1. Introduction

Intermolecular hydrogen bonding is a site-specific interaction between hydrogen donor and acceptor molecules. It is central to the understanding of microscopic structure and function in many molecular systems, such as hydrogen bonded networks in pure liquids such as water or alcohols[1] and the tertiary structure of proteins.[2] Dynamics of hydrogen bonds occur on ultrafast time scales mainly set by vibrational motions of the hydrogen donor and acceptor groups and are relevant both in thermal equilibrium and for nonequilibrium excitations. In thermal equilibrium, i.e., in the electronic ground state, vibrational and translational motions give rise to fluctuations in the hydrogen bonding geometries,[3] leading to e.g., proton-transfer reactions (proton hops) between water molecules (Grotthuss mechanism).[4,5] These charge-conducting "water wires" [6] are responsible for the operation of membrane protein channels[7,8] and photosynthetic reaction centers.[9]

Nonequilibrium vibrational excitations, e.g., by infrared absorption or Raman scattering, initiate a complex relaxation scenario including dephasing of the vibrational transition, intra- and intermolecular energy redistribution, and structural reorientation, processes in which hydrogen bonds can play a major role. In condensed phase systems, such phenomena have been studied by vibrational spectroscopy, both in the frequency and time domain. Experiments in the pico- and femtosecond time regime have the potential to monitor the microscopic dynamics in real time. A limited number of such experiments have been reported for water and alcohols, making use of resonant vibrational excitation by ultrashort infrared pulses.[10−14]

Even less is known on structural and relaxation dynamics after electronic excitation of molecules that are part of an intermolecular hydrogen bond. In solutions, a change of solute dipole moment induced by electronic excitation initiates a complex solvation process in which the energy of the dipole is reduced by solvent reorientation, resulting in a shift of electronic transition frequencies.[15] Here, local interaction between the solute and the first solvent shell is very important.[16−19] In addition, hydrogen bonds can be affected where proton transfer often happens and/or where the hydrogen bonds may be broken. These phenomena occur on ultrafast time scales and are thus a class of chemical reaction dynamics within the expanding field of femtochemistry.[20,21] The influence of such local interactions on electronic transitions is highly complex, and thus the study of transient absorption and emission bands gives only very limited insight into site-specific dynamics.

Most of the experimental techniques for studying the dynamics of hydrogen bonds have monitored changes in the transmission or the fluorescence yield of electronic transitions[22−28] or the ion yield or electron yield in time-of-flight mass spectrometry.[29−39] These observables measure the population of the electronic states that are typical for either hydrogen bonded or non-hydrogen bonded cases. In the gas phase these observables may well be good indicators of the actual events of hydrogen bond dynamics, such as proton transfer and bond-breaking, of small-to-mid-size molecules. In the liquid phase, however, these features will be masked by other effects caused by the rearrangement of nearby solvent molecules, such as transient shifts of emission bands due to solvation dynamics.[17,40,41]

The goal in femtochemistry is to determine the time evolution of chemical structures during chemical reactions. Ultimately, one attempts to resolve the spatial coordinates of the different constituents in time or, in other words, one has to determine structural dynamics of the molecular systems. Much effort is put in the development of ultrafast methods, such as X-ray diffraction,[42−44] X-ray spectroscopy,[45,46] or electron diffraction,[47] to probe structural dynamics. Technological limitations make it, until now, unfeasible to probe liquid phase reaction dynamics of, for instance, hydrogen bonds, and one has to rely on alternative experimental approaches. It is well known that with time-resolved vibrational spectroscopy one can grasp the dynamics of specific chemical bonds if the probed vibrations can be regarded as local modes. For instance, intramolecular proton transfer of 2-(2′-hydroxyphenyl)benzothiazole after electronic excitation[48,49] and the photodissociation of ICN[50] were studied with picosecond time resolution. In contrast, by probing

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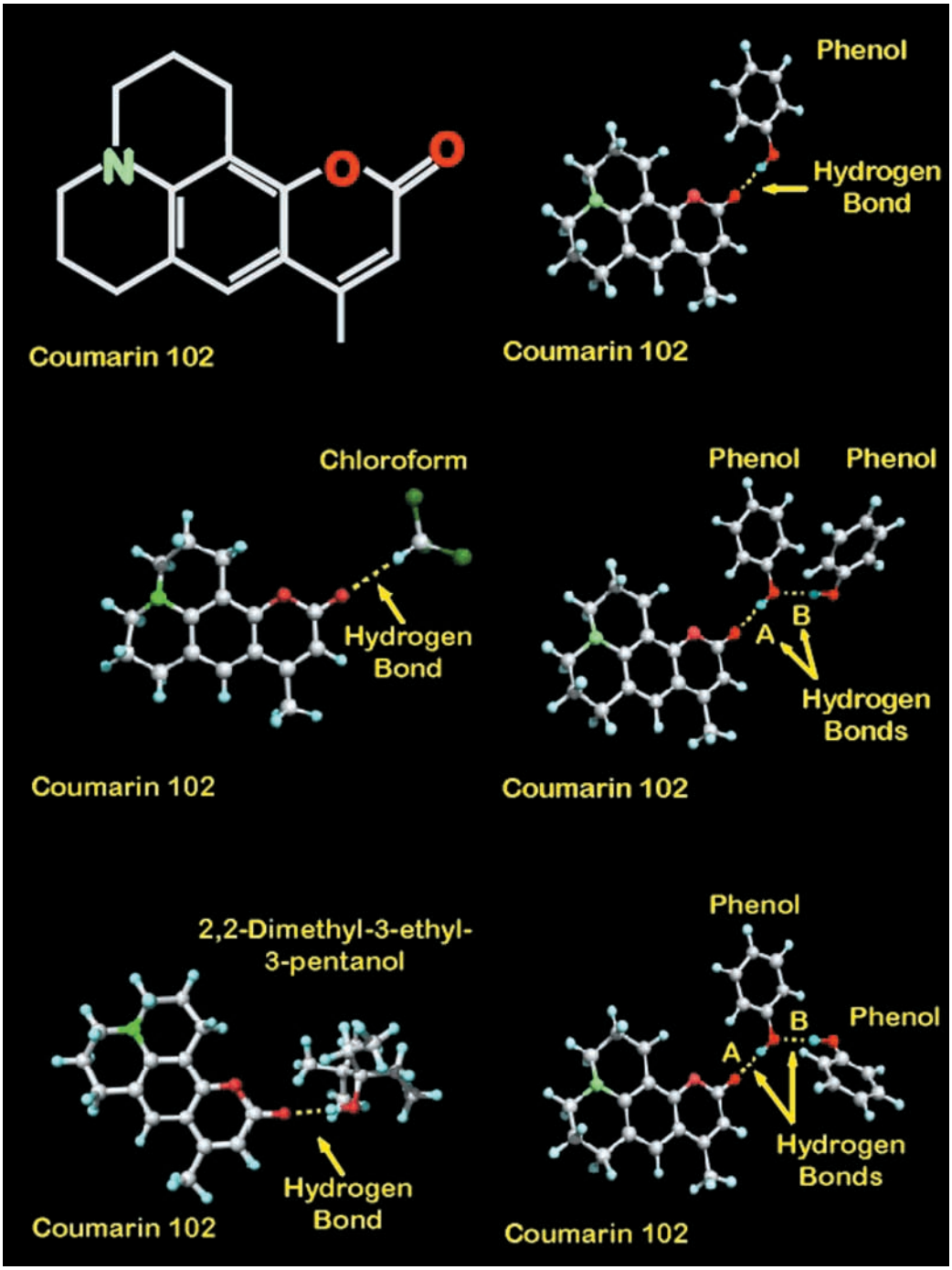

Figure 1. Molecular structures of the hydrogen bonded complexes of coumarin 102 (C102), C102−$CHCl_3$, C102−phenol, C102−$(phenol)_2$, and C102−DEP. The molecular complexes have been calculated with a low-level force field routine. Two examples of possible geometries for the C102−$(phenol)_2$ complexes are depicted indicating the hydrogen bonds A and B.

electronic states with optical frequencies additional arguments are necessary to determine whether certain chemical bonds are involved in the reaction pathways.

In this paper we focus on the dynamics of hydrogen bonded complexes of a laser dye, coumarin 102 (C102), induced by electronic excitation. We first review our ultrafast vibrational and optical pump−probe and grating experiments. We show that ultrafast vibrational spectroscopy is a sensitive probe of the dynamics of site-specific hydrogen bonding in the electronically excited state of complexes of an organic chromophore, coumarin 102 (C102), hydrogen bonded to donors $CHCl_3$ or $(phenol)_{1,2}$[51−53] (see Figure 1). We show that the dynamics can be characterized by two stages of evolution: (a) hydrogen bond cleavage within 200 fs and (b) reorganization of the molecular fragments and of the surrounding solvent shell. We then focus on results obtained with ultrafast optical spectroscopy, and show that effects of hydrogen bonding are also eminent in these data.[54] We then investigate whether the hydrogen bond is immediately broken when the electronic charge distribution is altered during optical excitation, or if the hydrogen bond cleavage occurs at later times. We tentatively show for the first time that a two-pulse photon echo can be measured on a reactive system. We perform the two-pulse echo on the electronic transition of hydrogen-bonded C102 and deduce from the echo results that a change of electronic state occurs around 180−200 fs.

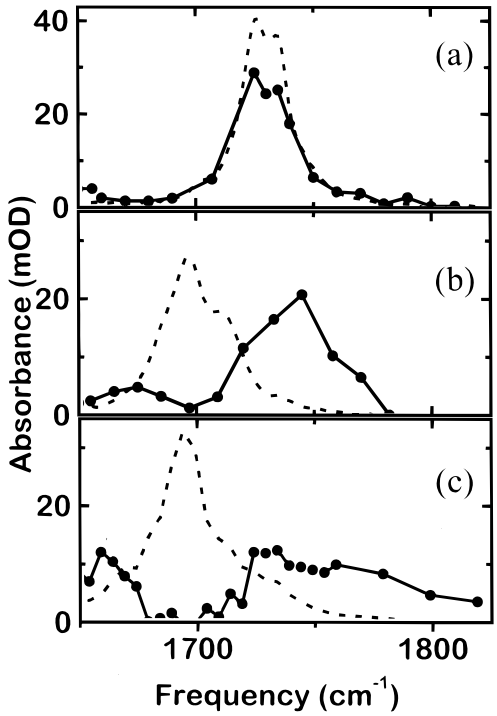

Figure 2. Ground state (dashed lines) and excited state (connected dots) C═O stretching bands of C102 in pure C_2Cl_4 (a), C102 in $CHCl_3$ (b), C102−$(phenol)_{1,2}$ complexes in C_2Cl_4 (c). The transient C═O bands in the S_1 state of C102 were recorded 500 fs (a/b) or 400 fs (c) after excitation.

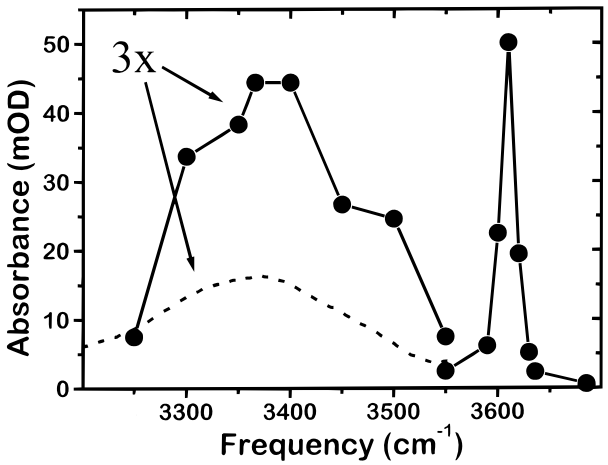

Figure 3. Ground state (dashed line) O−H stretching band of C102−$(phenol)_{1,2}$ complexes in C_2Cl_4. The transient O−H bands (connected dots) were recorded 400 fs after excitation to the S_1 state of C102. The narrow band located at 3610 cm^{-1} indicates free O−H groups, whereas the broad band between 3200 and 3550 cm^{-1} is due to hydrogen bonded O−H groups.

2. Femtosecond Vibrational Spectroscopy

In this section we review our results obtained with ultrafast vibrational spectroscopy on hydrogen bonded complexes of C102. We show that this method gives us site-specific information on the structural dynamics of these complexes, in particular the femtosecond chemical event of bond breaking, but also subsequent reorganization of the molecular fragments.

2.1 IR Analysis of the Hydrogen Bonded Complexes in the Electronic Ground State. We first summarize the results obtained with infrared spectroscopy of complexed C102 in the electronic ground state and compare the results with the uncomplexed case. Infrared spectroscopy is the standard tool for probing hydrogen bonding.[55−58] Intermolecular vibrational modes, σ stretching and δ in-plane and γ out-of-plane bending, are present only when a hydrogen bond is formed between two molecules. These modes usually can be found in the low-frequency part of the IR-spectrum. Very often these modes have small transition moments and are masked by solvent bands, as is the case for our C102 complexes. Intramolecular modes on either donor or acceptor molecules may change their characteristics upon the formation of a hydrogen bond. We have shown that the carbonyl stretch of C102 downshifts about 35−40 cm^{-1} when a complex is formed with either $CHCl_3$ or $(phenol)_{1,2}$, whereas the band is located at 1735 cm^{-1} for uncomplexed C102 in the nonpolar, weakly interacting solvent C_2Cl_4.[51−53] This is demonstrated in Figure 2 by the dashed lines. Such a markedly large shift has been ascribed to the formation of hydrogen bonds,[59] but alternative explanations without invoking site-specific hydrogen bonds have been proposed in the literature.[60]

By the use of $CHCl_3$ as hydrogen donor we are able to probe only the C═O stretch on the acceptor side. In principle the C−H stretch of $CHCl_3$ should exhibit a red shift upon formation of a hydrogen bond. This red-shifted band, however, will be masked by the bulk C−H band of the solvent. To obtain information on intramolecular modes on the donor side we need to focus on hydrogen-bonded complexes dissolved in an inert solvent. In the case of phenol as hydrogen donor we can also inspect the hydroxyl stretch (see Figure 3). Here it follows that under the working concentrations (5 mM C102 and 10 times as much (50 mM) phenol in C_2Cl_4) a narrow band exists at 3610 cm^{-1}, indicative of non-hydrogen bonded phenol molecules, and a broad band exists between 3200 and 3550 cm^{-1} that can only be due to hydrogen bonded O−H groups. These results show that the nature of complexation between C102 and phenol is that of hydrogen bonding. In this case the red shift of the carbonyl stretching band of C102 (Figure 2c) is practically identical to that of C102 in $CHCl_3$ (Figure 2b). We conclude that hydrogen bonding represents the dominant local interaction in both cases. We have performed a concentration-dependent study of IR spectra of C102 and phenol in C_2Cl_4.[53] It has been found that under the conditions of the time-dependent experiments C102 is either complexed to one or two phenol molecules (with some free phenol dimers as well). We estimated that larger complexes of the type C102−$(phenol)_n$, $n = 3, 4, \ldots$ make up only less than 10% of the total amount of complexes of C102[53] and may be discarded in the analysis of the transient experiments.

With these findings in mind we have constructed the molecular structures of Figure 1. We note that the depicted molecular structures have been calculated with a low-level force field routine and are to be regarded as a simple representation of the complexes. It would be of great importance to calculate the ground state conformations of these hydrogen bonded complexes with a sophisticated quantum chemical method, preferably with the nonpolar, yet highly polarizable, solvent C_2Cl_4 surrounding it. We note that it is known from quantum-chemical calculations based on semiempirical methods[16,18,61,62] that coumarin dyes have a strong charge density on the carbonyl oxygen. Together with the fact that in the steady state and transient IR spectra the C═O-stretch shows large shifts when a hydrogen bond is formed, we expect the hydrogen bond to form with the carbonyl group. However, the nitrogen in the julolidine group also has negative charge according to these semiempirical calculations, and as such this group may also function as the hydrogen acceptor site. The electron pair on the nitrogen atom, however, will be conjugated with the π-electron orbitals, and we may expect that a possible attachment of a hydrogen donor

on the nitrogen atom will lead to strong changes in the electronic energies of the π-orbitals. On the other hand, for the carbonyl oxygen electron density is also present in the molecular plane, and these lone pairs are strong candidates for the formation of a hydrogen bond. We nevertheless aim to analyze further the vibrational spectra of C102 to see whether a local C−N stretch vibration can be identified as such, and whether this vibration is affected by hydrogen bonding.

2.2 Early-Time Dynamics in the Electronic Excited State: Hydrogen Bond Cleavage. Femtosecond vibrational spectroscopy enables us to follow the hydrogen bond dynamics of the C102 complexes after electronic excitation. By inspection of the C═O and O−H stretch vibrations as a function of delay between an optical pump pulse, tuned in such a way that the S_1 electronic excited state is generated without additional vibrational energy and an IR-pulse tuned at the C═O and O−H vibrational resonances, we may follow the evolution of the hydrogen bond between C102 and $CHCl_3$ or $(phenol)_{1,2}$. It follows that large changes already occur within 200 fs, the time resolution of the experiments. The uncomplexed C102 in C_2Cl_4 appears to have a carbonyl stretch resonance in the S_1 state at about the same position as in the S_0 state (accuracy better than 3 cm^{-1}), as shown in Figure 2. This means that upon electronic excitation of C102 at the red edge of the electronic absorption band, no energy is converted into the low-frequency modes (heating effects), after which through anharmonic coupling the C═O stretch may change its characteristics, in contrast to, e.g., the ultrafast photoisomerization of azobenzene.[63] We note that direct excitation of the $v = 1$ state of the C═O band in the S_1 state is not possible by tuning the optical pump near the red edge of the electronic absorption band. The total amount of energy given to the nearby solvent shells through intermolecular interactions, as given by the total Stokes shift, is not more than 1100 cm^{-1} in this case.

We observe different features for the initially hydrogen bonded complexes (Figures 2 and 3). We ascribed the large blue shift of 40 cm^{-1} of the C═O band in the case of C102−$CHCl_3$ to a hydrogen bond cleavage induced by electronic excitation.[51] The same feature occurs in the case of the C102−$(phenol)_{1,2}$ complexes.[52] We note that, in contrast to the carbonyl stretching band, other modes of C102 in the same frequency range, e.g., skeletal modes near 1600 cm^{-1}, do not show such large frequency shifts. This finally underlines that the C═O group is involved in a local hydrogen bond. In the case of the C102−$(phenol)_{1,2}$ complexes we are also able to probe the O−H stretch region. We observe an increase of signal at the band located at 3610 cm^{-1}, corresponding to free O−H groups, the strength of which is identical to the amount of complexes initially excited.[53] From these observations we derive that a hydrogen bond cleavage between donor and excited acceptor occurs for all studied complexes on a time scale with an upper limit of 200 fs, the temporal resolution of the experiment. In the case of C102−$(phenol)_2$ the hydrogen bond B between the two phenol units is not broken and thus retains a contribution to the hydrogen bonded O−H stretch region between 3200 and 3550 cm^{-1}.

The question now remains whether the hydrogen bond is directly broken upon electronic excitation, a direct consequence of the rearrangement of the electronic distribution in the complex after interaction with the pump light field, or whether a hydrogen bonded state exists after electronic excitation, only to evolve with a finite lifetime ($\tau < 200$ fs) toward a non-hydrogen bonded state. Until now, femtosecond technology has not enabled us to perform femtosecond vibrational experiments with higher time resolution, partly because of the available pulse durations of about 100 fs, partly because of group velocity mismatch between optical pump and infrared probe pulses over sample widths of about 200 μm, and partly because of unwanted coherent artifacts masking all other dynamics at these early delay times.

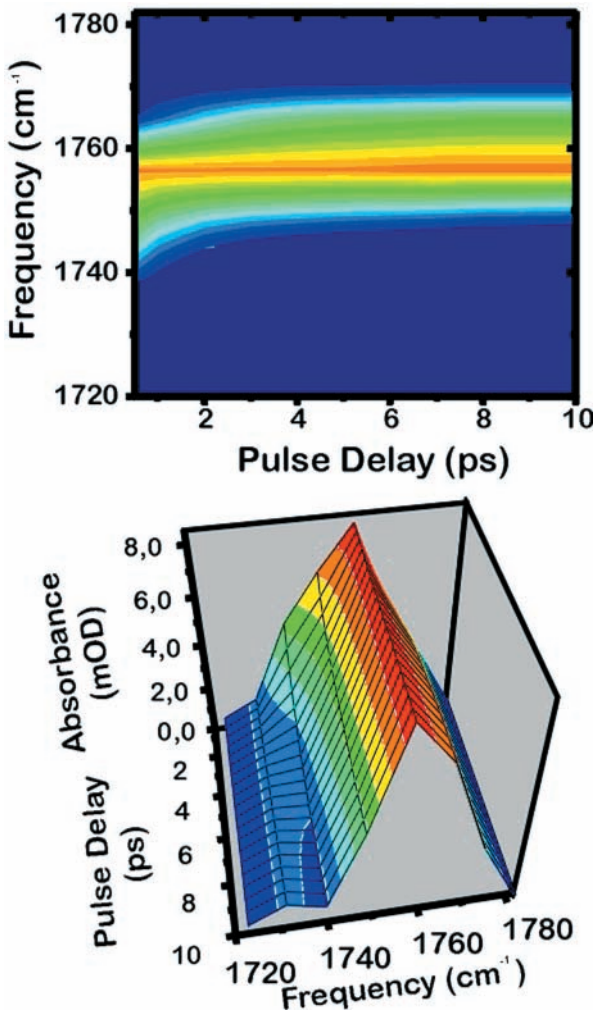

Figure 4. Contour and 3D plots of the picosecond dynamics of the C═O band of C102 in $CHCl_3$, showing the frequency upshifting vibrational Stokes shift with a time constant of 2.5 ps.

2.3 Vibrational Dynamics in the Electronic Excited State at Longer Times: Reorganization. Following the initial hydrogen bond breaking, the C═O and O−H stretch bands exhibit dynamics at (sub-)picosecond time scales. In the case of C102 in $CHCl_3$, the C═O stretch acquires an additional blue shift of 7 cm^{-1} with a time constant of 2.5 ps (see Figure 4). Since no dynamics of this band is observed in uncomplexed C102 in C_2Cl_4, we can exclude the possibility of heating effects due to anharmonic coupling with low-frequency modes. The additional blue shift has thus its origin in coupling with the polar solvent $CHCl_3$, which can be related to the dielectric relaxation dynamics of bulk $CHCl_3$.[53] One may regard this coupling with presumably low-frequency solvent modes to result in a vibrational Stokes shift,[13] very much in the same way as in the case of electronic transitions. However, now the sign of the coupling constant between C═O mode and the solvent modes leads to a frequency upshift of the carbonyl band, whereas the electronic Stokes shift always exhibits a downshift in frequency.

In the case of the C102−$(phenol)_{1,2}$ complexes in C_2Cl_4, no further signal at 3610 cm^{-1} is generated at later times. From this we conclude that after 200 fs no additional hydrogen bonds

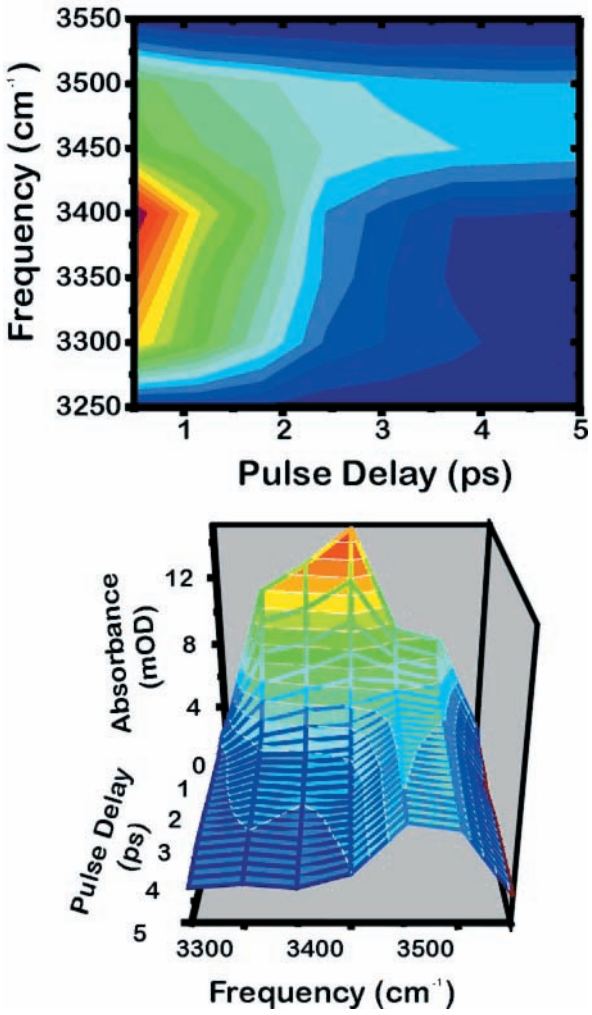

Figure 5. Contour and 3D plots of the dynamics of the broad hydroxyl band, allocated to hydrogen bond B of the phenol dimer, where reorganization to a smaller band occurs, similar to that of equilibrated $(phenol)_2$, with a time constant of 800 fs.

are broken. We do observe additional dynamics in the O−H stretch region corresponding to hydrogen-bonded hydroxyl groups, which we allocated to the hydrogen bond between the two phenol units inside the dimer that has been released from C102. The broad band initially present from 200 fs rearranges to a more confined band that is identical to the O−H band of the phenol dimer with a time constant of 800 fs (Figure 5). It may come to mind that we might observe a vibrationally hot O−H mode, and because of anharmonicity the signal at 3300 cm^{-1} is due to transient absorption from the $v = 1$ to $v = 2$ transition. The disappearance of this signal with the 800 fs time constant should then be nothing more than vibrational relaxation to the $v = 0$ state of the dimer. However, the total electronic Stokes shift of C102 in this case is about 1500−2000 cm^{-1}. Even though it seems unlikely that such a large fraction of this energy would end up in the hydrogen bond between the two phenol units after electronic excitation of C102, it is just not sufficient to produce the $v = 1$ state, for which at least 3300 cm^{-1} is necessary.

The question now is whether this rearrangement is due to a phenol dimer that has to relax to the new equilibrium configuration, or whether two entities exist, an already relaxed phenol dimer giving the signal near 3500 cm^{-1}, and another one leading to the signal at 3300−3400 cm^{-1}. The latter possibility can be excluded because the disappearance of the O−H signal at 3300−3400 cm^{-1} due to, e.g., heating effects[64] should lead to new signals at other frequencies, and that is not observed. The gradual change from a broad band with center frequency at 3350 cm^{-1} to a smaller band at 3500 cm^{-1} demonstrates that we observe the dynamical rearrangement of the hydrogen bond properties of the phenol dimer. The frequency downshift and increase in transition moment of an O−H stretch band is directly correlated to the strength of the hydrogen bond.[57] It then follows that the observed dynamics should indicate a weakening of the hydrogen bond between the two phenol units. The reason for that may be that the two phenol units undergo a rearrangement where the orientation relative to each other but also to the nearby C102 changes. An indication for that is the fact that the new C═O band located at 1740 cm^{-1} diminishes its strength somewhat with the same time constant of 800 fs, although it does not show additional frequency shifts.[52]

It is now well known that several mechanisms are responsible for the broad absorption line shapes of O−H stretch modes in the case of hydrogen bonding.[65,66] The anharmonic coupling between the high-frequency O−H stretch and a low-frequency mode, e.g., the O···H−O stretch, is thought to induce a Franck−Condon-like progression in the O−H vibrational band, where the temperature, frequency, and coupling constant of this low-frequency mode play a role. In addition, dephasing mechanisms by the nearby solvent molecules, either directly on the O−H mode or indirectly through the anharmonically coupled low-frequency mode, lead then to the observed spectral breadth. This anharmonic coupling strength is directly related to the strength of the hydrogen bond. It thus seems promising to further investigate this O−H stretch region, both in the electronic ground state and after electronic excitation. We hope that by elucidating the underlying mechanisms for this spectral line shape we can grasp the characteristics of molecular motion of the phenol dimer.

3. Femtosecond Optical Spectroscopy

In this section we first mention some of our previously reported results on the optical transition of hydrogen bonded complexes of C102, where we discuss the possibility of a direct influence of the formation of a hydrogen bond on the electronic levels of C102. We then present new results obtained on C102 complexed with a sterically hindered alcohol, 2,2-dimethyl-3-ethyl-3-pentanol (DEP), and photon echo results measured on C102 complexed with phenol.

3.1 Spectral Analysis and Time-Resolved Experiments on the Electronic Transition. Coumarin 102 (C102), a member of the coumarin class of laser dyes, has been used as a probe molecule to sample the response of solvent motion to a sudden change of electronic charge distribution (solvation dynamics).[67−69] The structurally closely related coumarin 153 (C153) is even more popular in solvation dynamics studies.[16,61,62,70−77] C153 has a trifluoromethyl group instead of a methyl group on the 9-position, so it can be expected that the electronic structures of the S_0 and S_1 states are similar. It has been shown by Maroncelli and co-workers[70] that by plotting the absorption and emission spectral shifts of C153 as a function π^* solvent polarity a distinct difference is found when dealing with hydrogen donating solvents as compared to non-hydrogen donating solvents. In contrast, theoretically more sophisticated methods based on, e.g., dielectric continuum models[73] do not indicate a significantly large effect of hydrogen bonding. This is furthermore substantiated by time-resolved Stokes shift measurements on C153, where no clear distinction in rotation time−viscosity correlation is found when comparing protic with aprotic polar solvents.[72] Molecular dynamics simulations[16,62] and our vibra-

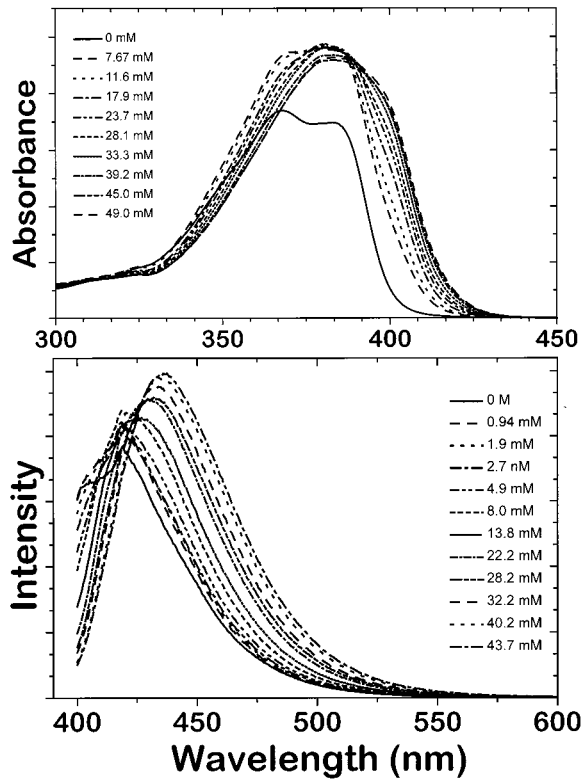

Figure 6. Absorption (top) spectra of 5 mM C102 and phenol at various concentrations in C_2Cl_4. Emission spectra (bottom) are measured in the back-reflection configuration. Excitation wavelengths for the emission spectra are $\lambda = 390$ nm with 0.5 mM C102.

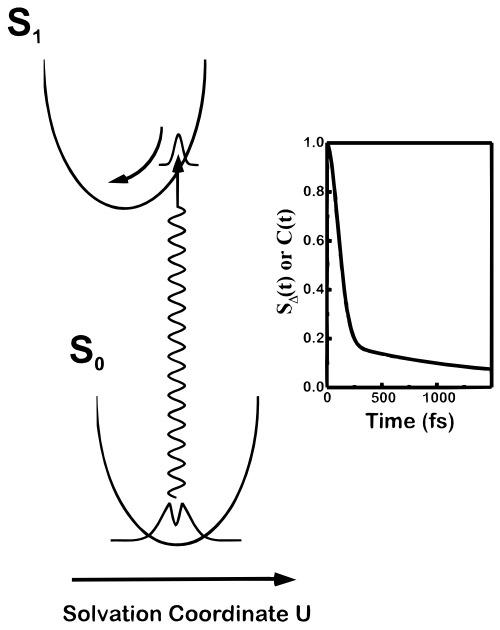

Figure 7. Schematic depiction of standard description of solvation dynamics. After electronic excitation, a collective solvent mode reorganizes to the equilibrium position in the excited state. Dynamics of this mode on multiple time scales is reflected by a solvation correlation function $S_\Delta(t)$ (or the electronic frequency correlation function $C(t)$) that has decay characteristics with a more complex time behavior.

tional spectroscopic results[51−53] indicate that C102 or C153 will form hydrogen-bonded complexes at the carbonyl site if hydrogen donating species are present in solution. Furthermore, time-resolved measurements on hydrogen bonded complexes of C102 with 2,2,2-trifluoroethanol have indicated that the rotation times can be understood as due to long-lived solute−alcohol complexes as a whole.[67] However, it has been mentioned (ref 101 in ref 70) that for C102 half of the emission shifts between nonpolar and alcoholic solvents are already present when dealing with 1:1 probe−alcohol complexes. Moreover, as discussed in section 2 of this paper, our results obtained with femtosecond vibrational spectroscopy of hydrogen bonded C102 have unequivocally demonstrated the dynamics of hydrogen bond cleavage within 200 fs after electronic excitation. This has led us to inspect the optical properties of these complexes, to see whether a more indirect indication of hydrogen bond dynamics could be obtained by studying the dynamics of the electronic transitions. We have performed an optical spectral analysis, where we indicated that hydrogen bonding also affects the electronic absorption and fluorescence properties of C102 complexed with phenol[54] (see Figure 6). This, however, is not a clear proof of a change in electronic transition frequency caused by the formation of a hydrogen bond. The relative concentrations of C102 and phenol are such that in addition to the directly linked phenol molecules several other polar phenol molecules might be preferentially located near this polar complex. These additional phenol molecules can contribute to the observed absorption and emission shifts. In addition, upon excitation these uncomplexed phenol molecules might then contribute to the solvation dynamics observed, as has been observed in MD simulations of solvation dynamics of C153 in alkane/alcohol mixtures.[62] In that respect, the deductive analysis of absorption and emission properties by decomposition of the overall spectra into relative contributions of uncomplexed C102, C102−phenol, and C102−$(phenol)_2$ might not be completely correct. We used a set of parameters for the chemical equilibria of these different species derived from steady-state IR spectra.[54] With these parameters we deduced a red shift of the absorption and emission spectra upon the formation of a hydrogen bond between C102 and phenol. In addition, the spectra of C102−$(phenol)_2$ is even more red shifted. The fact that the emission properties alter when the excitation wavelength is changed indicates that this trend is correct. Nevertheless, the influence of the additional uncomplexed nearby phenol molecules might lead to changes in, e.g., center frequencies and extinction coefficients of the different species.

We performed pump−probe and grating scattering experiments on the electronic transition of C102 and showed that a dynamical response occurs with an exponential time constant of 170 ± 40 fs that has to be correlated with the hydrogen bond dynamics, since it is absent in the case of C102 dissolved in nonpolar C_2Cl_4.[54] However, this feature is not a direct proof that the hydrogen bond cleaves with this time constant. It could also be that the dynamics is due to a fast component in the solvation process by rearrangement of instantaneously released polar $CHCl_3$ and $(phenol)_{1,2}$ units in what usually is referred to as the inertial component in dielectric relaxation.[78,79] In the latter case the electronic state is regarded as remaining the same, with a solvent collective mode adjusting at multiple time scales along the solvation coordinate (see Figure 7). Such a collective solvent mode has been modeled in solvation studies with, e.g., Brownian oscillators[80−83] or instantaneous normal modes.[17,84] Pump−probe and grating scattering do not directly show when the molecular system changes its state, since they could also have contributions from the electronic ground state (such as ground-state vibrational coherences) and from possible product states (e.g., excited-state absorption).

3.2 Experimental Section. For the experiments we have used a home-built chirped-pulse amplified femtosecond kHz laser system with frequency conversion scheme to the violet-blue

region of the electromagnetic spectrum. After compression the system delivers 30−40 fs pulses of 1.2−1.5 mJ centered at 795 nm. Frequency conversion to the violet-blue is then achieved with the second harmonic generation and the hollow waveguide technique.[85]

For the pump−probe experiments on C102 complexed with 2,2-dimethyl-3-ethyl-3-pentanol (DEP) we used the second harmonic of the laser output as pump and probe pulses. Pulses with energies up to 1 μJ for the pump and 0.2 μJ for the probe were focused on a rotating cell with a 500 μm thickness and fused silica windows. We did not use a free-standing jet because of reasons of safety and cost.

For the photon echo experiment on C102 complexed with phenol we used the laser output at 795 nm upconverted to the second harmonic in a BBO crystal, after which we generated a violet-blue continuum in a hollow waveguide with subsequent compression to 15 fs pulses with energies up to 1 μJ centered around 397 nm.[85] We characterized the pulses with the self-diffraction technique[86,87] in 100 μm BBO crystals. We carried out the photon echo experiments on a 100 μm thick jet of solutions of 5 mM C102. For the experiments on complexes of C102 with phenol, the concentration of the latter was about 10 times higher (44 mM) than that of C102. Pulse intensities at the focus were about $10^{10}-10^{11}$ W/cm^2.

We purchased C102 from Lambda Physik, 2,2-dimethyl-3-ethyl-3-pentanol (DEP) from Aldrich, phenol and the solvents tetrachloroethene (extra pure) and chloroform (Uvasol) from Merck. We used all compounds without further purification.

3.3 Spectral Analysis and Pump−Probe Experiments on Coumarin 102 Complexed with 2,2-Dimethyl-3-ethyl-3-pentanol. From our IR-studies on C102 complexed to phenol we have learned that under our working conditions various complexes with varying sizes can exist, as depicted in Figure 1, since the alcohol phenol can act either as hydrogen donor or as hydrogen acceptor. Similar features can be expected to occur for the ordinary alcohols such as methanol or ethanol, that are known to form hydrogen-bonded chain-like structures. To study the spectroscopic features due to a single hydrogen bond between C102 and a donor, without additional attached molecules, we have to rely on a different hydrogen donor. At the same time we maintain C_2Cl_4 as the inert background solvent, so that competing hydrogen bonds between donor and solvent do not influence the complexation process. We decided to use 2,2-dimethyl-3-ethyl-3-pentanol (DEP) as hydrogen donor (see Figure 1), which is known to form only dimers at high concentrations due to steric hindrance.[88,89] This is the reason DEP has been used for IR studies of the hydrogen bonds of alcohols.[90−92]

We depict the electronic absorption and emission spectra in Figure 8. While keeping the concentration fixed for C102 in C_2Cl_4, we increased the DEP concentration. Initially the extinction coefficient increases, but the spectral shape does not alter significantly. When 200 times more DEP is in solution than C102, additional red shifting can be observed in the electronic spectra. Comparing these spectra with the IR spectra of the carbonyl stretch of C102 measured on the same solutions, it follows that the increase of extinction coefficient occurs without a significant amount of hydrogen bonded complexes in solution (see Figure 9). This follows from the fact that the C═O stretch corresponding to free C102 does not disappear. Only when a relatively large amount of DEP is in solution does this C═O band diminish its strength, and a red-shifted band located at 1708 cm^{-1} appears, corresponding to hydrogen-bonded C102. We conclude from these data that the red shift

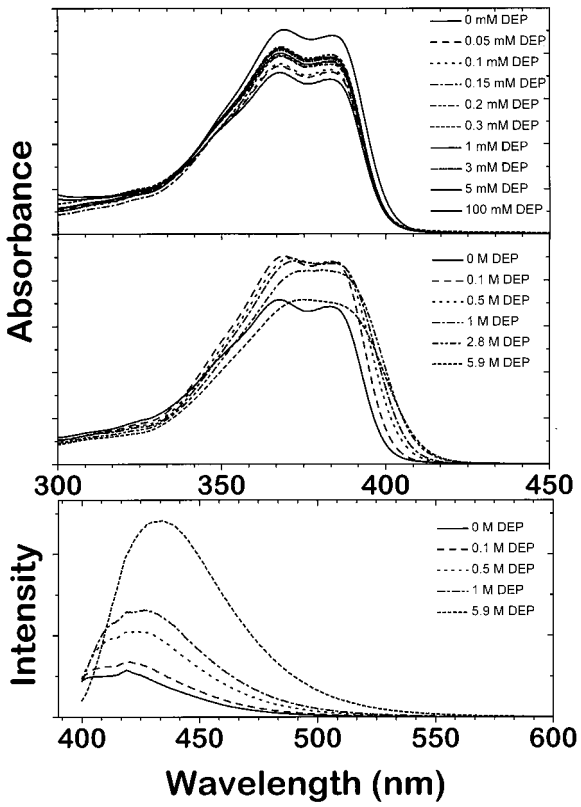

Figure 8. Absorption (top and middle) and emission spectra (bottom) of 0.5 mM C102 and DEP at various concentrations in C_2Cl_4. Emission spectra are measured in the back-reflection configuration. Excitation wavelengths for the emission spectra are $\lambda = 390$ nm. A concentration of 5.9 M DEP corresponds to the situation where DEP is the solvent and no C_2Cl_4 is present.

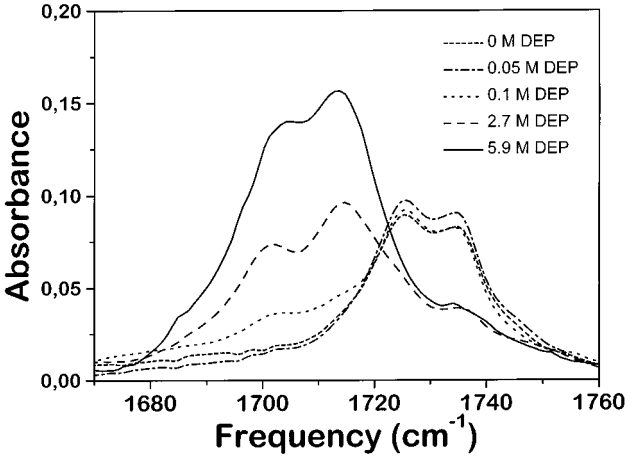

Figure 9. IR spectra of 5 mM C102 + DEP at various concentrations in C_2Cl_4 showing the carbonyl stretch region of C102. A concentration of 5.9 M DEP corresponds to the situation where DEP is the solvent and no C_2Cl_4 is present.

in electronic spectra is accompanied by the occurrence of hydrogen-bonded C102. We note that the study of the O−H stretch in the IR spectrum is difficult: due to the large fraction of DEP in solution, the O−H stretch region corresponding to hydrogen-bonded hydroxyl groups is mostly due to $(DEP)_2$ complexes.

The gradual increase of the extinction coefficient in the electronic absorption spectrum at moderate concentrations of DEP can be understood by inspection of the refractive index changes when going from C_2Cl_4 ($n_D = 1.506$) to DEP ($n_D = 1.442$). Lewis and Maroncelli have shown that by making a

correction for refractive index changes the real transition moments of C153 in electronic absorption and emission turn out to be solvent independent with an error of less than 10%.[76] Our data on C102 dissolved in mixtures of DEP and C_2Cl_4 hint at a similar trend. However, the additional changes are more drastic than can be explained by refractive index changes. In fact, at low DEP concentrations the absorption and emission bands of C102 only increase in strength without changes in spectral shape. This is a strong indication of preferential solvation of C102 by DEP molecules, as one would expect that a situation of polar C102 and polar DEP being nearest neighbors is energetically more favorable than a situation where C102 or DEP are close to the nonpolar solvent C_2Cl_4.

We can now compare the new spectral results of hydrogen-bonded complexes between C102 and DEP with the previously published data on C102 complexed on phenol (as shown in Figure 6). In the latter case, a small increase in absorption is detectable when the amount of phenol rises, although the red shift is much more pronounced. We infer from this that preferential solvation also occurs in the case of C102 and phenol. Although the hydrogen bond formation of C102 is much more preferable with phenol than with DEP, we cannot exclude that a significant amount of phenol molecules are near C102 without linking through a hydrogen bond, even at low concentrations of phenol. Through changes in the refractive index near C102 the extinction coefficient is slightly altered, making a straightforward reduction of the electronic spectra into contributions of free C102, C102−phenol, and C102−$(phenol)_2$ species impossible. This is probably the reason for the peculiar strong changes in calculated absorption and emission strengths of these species as published previously.[54]

On the other hand, the markedly large spectral red shifting of C102 when phenol or DEP is added is largely due to the formation of hydrogen bonds, but polarity changes also play an important role.[70] Since in both cases of phenol and DEP an excess of the hydrogen donating alcohol is added to solutions of C102, these two contributions are not separable in a straightforward way. This would be possible for a donor with a much larger hydrogen donating capacity, so that clearly defined 1:1 complexes occur without possible extended chain-like structures. However, an inert nonpolar solvent should still be used to avoid the possible additional effects by polarity changes of the solvent.

Pump−probe measurements on C102−DEP mixtures are shown in Figure 10 for two cases. In curve (a) the response is shown for 5 mM C102 and 50 mM DEP in C_2Cl_4. This case corresponds to a situation where no hydrogen bonds are formed. After a strong signal around zero delay, which we ascribe to cross-phase modulation effects in the solvent and/or cell windows, we see a slow decay with a time constant of 3.9 ps. We believe that reorganization of nearby DEP molecules in response to the electronic excitation of C102 causes these dynamics on longer time scales. This has also been observed in MD simulations of solvation dynamics of C153 in methanol/hexane mixtures, where more methanol molecules are close to C153 in its excited state than in the ground state.[62] In curve (b) the response is shown for 5 mM C102 in DEP, i.e., DEP is used as the solvent. Again a strong signal occurs around zero delay, and the subsequent bleach does not show any dynamics on a time scale of 4 ps. Possible reorganization of the solvent DEP does not have a strong impact on the pump−probe signal. What is more surprising is a nonappearance of a possible fast component in the dynamics. We ascribed the occurrence of a fast component on a time scale of 200 fs in $CHCl_3$− and phenol

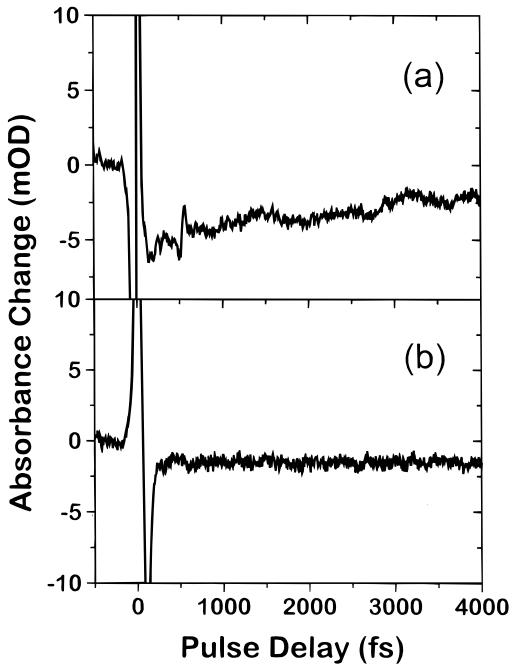

Figure 10. Pump−probe transients of 5 mM C102 and 50 mM DEP in C_2Cl_4 (a), and of 5 mM in DEP (b) measured at 400 nm, showing a picosecond reorganization response in case (a).

complexes to an effect of the hydrogen bond dynamics of C102, since such a component is not detected in free C102 in C_2Cl_4.[54] It could be that, since the hydrogen bond of C102 with DEP is much weaker, the dynamics of hydrogen bond cleavage is much faster, maybe even instantaneous. A more trivial explanation that a possible fast component with a small magnitude is hidden behind the large signal around zero delay, unfortunately, cannot be fully excluded.

3.4 Femtosecond Two Pulse Photon Echo on C102−$(phenol)_{1,2}$ Complexes. In this section we address the point of whether initially a hydrogen bonded excited state of C102 exists, which subsequently decays into an unbound state. We present as a new approach to this problem first two-pulse photon echo results on the complexes of C102 with phenol with which we obtain new insight in the dynamics of these complexes in the first few hundreds of femtoseconds. The idea is as follows (see Figure 11): an electronic coherence between two states is only present as long as dephasing processes have not caused the destruction of this coherence. Dephasing (described by a time constant T_2) can be due to either lifetime processes (T_1) or pure dephasing processes (T_2*), as exemplified by the basic formula $1/T_2 = 1/2T_1 + 1/T_2$*.[93−95] When a jump from electronic state E_I (in which a hydrogen bond exists) occurs to an electronic state E_{II} (where the hydrogen bond is broken), a typical T_1 process, the electronic coherence between state E_I and the (hydrogen-bonded) ground state G_I should be destroyed. Usually T_1 processes are much slower than T_2* processes in the case of electronic dephasing in liquids;[82] however, in the present case they could occur on the same time scale. Recurrences, a flow back from state E_{II} to state E_I, should occur according to Figure 11, when both states have bound potentials and when the system is isolated from its surroundings, e.g., in the gas phase. In the case that state E_{II} is a dissociative state, no flow back will occur. In the liquid phase, moreover, the nearby solvent might drive the two fragments away.

Photon echo measurements, the utmost suitable technique to determine electronic coherences, may thus reveal whether such a postulated quantum-state jump occurs.[96] The fact that in liquids

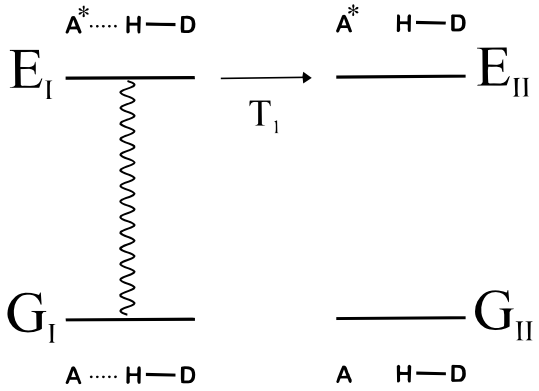

Figure 11. Schematic depiction of the relevant electronic states when the hydrogen bond cleavage is noninstantaneous. Upon electronic excitation an electronic coherence exists between the hydrogen bonded complex in its ground state G_I and excited state E_I. The electronically excited hydrogen bonded complex has a finite lifetime T_1, where the state jump leads to a non-hydrogen bonded situation E_{II}, where the coherence is destroyed.

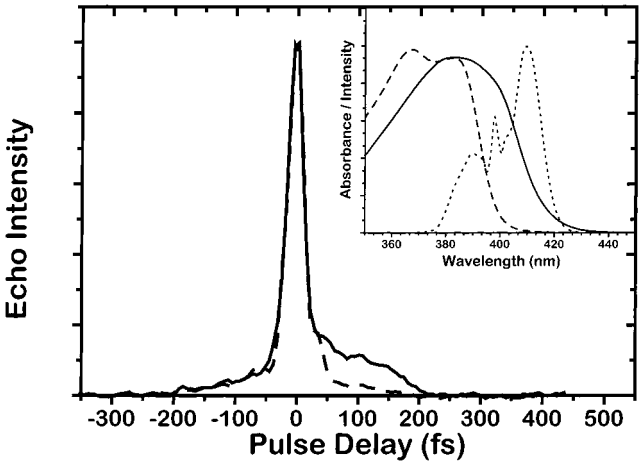

Figure 12. Two-pulse photon echo result on C102−$(phenol)_{1,2}$ complexes in C_2Cl_4 (solid line). The signal obtained on pure C_2Cl_4 (dashed) is added to indicate the nonresonant contributions of the solvent. Traces identical to the pure C_2Cl_4 signal were obtained for the cases C102 only in C_2Cl_4 and $(phenol)_{1,2}$ only in C_2Cl_4. The inset shows the corresponding spectra of the laser pulses (dotted) and electronic absorption of the C102−$(phenol)_{1,2}$ complexes (solid) and of free C102 in in C_2Cl_4 (dashed).

one cannot describe the pure dephasing processes with an exponential behavior (Markovian dynamics with a single electronic decay parameter), but sophisticated non-Markovian descriptions are more appropriate,[40,82,83,97,98,99] is not relevant for the present discussion.

Figure 12 shows the two-photon echo results obtained on C102−$(phenol)_{1,2}$ in C_2Cl_4. For comparison, a curve obtained on pure C_2Cl_4 is added to the Figure. Around zero delay a strong four-wave mixing signal is detected that is partly due to resonant contributions of C102−$(phenol)_{1,2}$ and partly due to nonresonant contributions of C_2Cl_4. We note here that for the cases of C102 only in C_2Cl_4 or of phenol only in C_2Cl_4 we observed the same signals as in pure C_2Cl_4. The reason for this is that free C102 or free phenol does not have a strong absorption at 400 nm, the center wavelength of the laser pulse. As a consequence, there is no resonance enhancement in their four-wave mixing signals, making the signals to weak to be detected. Since the nonresonant solvent C_2Cl_4 has a much larger concentration, its contribution to the overall signal is substantial, making the analysis around zero delay cumbersome. We thus focus our attention on the signal at positive delays where no overlap occurs between pulse 1 and pulses 2 and 3. For C102−$(phenol)_{1,2}$ this signal remains at positive delays that decay slowly until a sharp drop to zero occurs around 200 fs. The pulse intensities are rather high, so high-intensity artifacts might show up in the signals. For instance, it could be that higher-order effects due to a multitude of field interactions may alter the signal, $\chi^{(5)}$, or cascaded $\chi^{(3)}$, contributions, with terms describing Liouville pathways comprising electronic and nuclear coherences, or where pumping to higher electronic levels occurs. Lower excitation intensities at higher repetition rates may give more insight on these detrimental effects. However, for now we argue that these effects are not a problem for the interpretation of the two-pulse photon echo decay at positive delays, since the time-ordering implicit in the two-pulse photon echo experiment dictates that in any case an electronic coherence between ground and excited-state exists during the delay time between the arrivals of pulse 1, and of the pulse pair 2/3. Another complication is the fact that we deal here with two types of complexes, C102−phenol and C102−$(phenol)_2$, of which we have estimated that their absorption strength is about the same at the laser excitation wavelength. We know here that the initial hydrogen bond dynamics of these complexes is very similar, both with respect to the vibrational dynamics and the optical dynamics (as the pump−probe and grating scattering data show). However, under the present circumstances the question whether the echo signal is due to either one of the species or due to both cannot be solved completely.

The fact that we observe a photon echo signal for pulse delays up to 200 fs means that the optically coupled state E_I has a lifetime that is at least as long as that. Pure dephasing processes could cause the decline of the coherence and the lifetime might be longer. However, in conjunction with the grating scattering and pump−probe data it is now definitely clear that a process of electronic state hopping occurs around 200 fs. This means that pure dephasing is much slower than has usually been observed for probe molecules in polar aprotic and protic solutions. This suggests that the nonpolar solvent C_2Cl_4 does not have as strong an impact on the dephasing as polar solvents have. As a consequence, a larger fraction of the optical line breadth should be caused by processes with time scales much longer than that of the state hopping, and thus these processes can be denoted as inhomogeneous broadening. We note here that the experiment is performed on the C102 part of the complex. Rotational reorientation times of a dye molecule like C102 are much longer than the time span we are looking at in the echo experiment,[72] even after it is detached from the $(phenol)_{1,2}$ moiety. Any changes in absorbance due to rotational anisotropy can thus be discarded.

This leads us to conclude that if the hydrogen bonding dynamics is coupled to the electronic dynamics (as both electronic spectra and the pump−probe and grating scattering results imply), it is very likely that the hydrogen bond cleavage causes the change of electronic state. The other option, that the hydrogen bond is already directly broken during the electronic excitation, requires that an additional process should be postulated for the electronic state change, e.g., internal conversion to a nearby electronic state, or intramolecular vibrational redistribution. It may be worthwhile to note that electronic structure calculations with density functional theory for the case of coumarin 153 (C153), which is almost identical in molecular structure to C102, i.e., C153 has a trifluoromethyl-group instead of a methyl-group on the 9-position, have shown that internal conversion to other electronic states is unlikely, since they lie at much higher energies.[61] The effects of reorganization of

vibrational degrees of freedom may be another possibility that needs to be inspected more carefully, but, in the light of the experimental results presented previously[54] and in this paper, these effects should then lead to a change of electronic state. If one would assume that the electronic state remains the same after optical excitation of C102, one can only explain the ultrafast components in pump−probe and grating scattering experiments by assuming a time-dependent electronic transition moment (in other words, the Condon approximation does not hold).[100−103] So far there is no indication for such an effect in resonant excitation of large dye molecules such as C102 in the literature. Additional photon echo experiments in full resonance with the aborption band of C102−$(phenol)_{1,2}$ in C_2Cl_4 could give information on this issue. In any case, the absence of an ultrafast component in the pump−probe data on C102 in C_2Cl_4 excludes a full intramolecular effect.

4. Conclusions and Prospects

We first review our femtosecond infrared results on the hydrogen bonded complexes of coumarin 102 (C102) and $CHCl_3$ or phenol. We then focus on the electronic absorption and emission properties of these complexes and compare them with those of a complex between C102 and the sterically hindered alcohol 2,2-dimethyl-3-ethyl-3-pentanol (DEP). We argue that the interpretation of these spectra in terms of hydrogen bond contributions and polarity effects is in principle possible, but due to the excess of hydrogen donor complications arise in the analysis.

Using conclusions from previous ultrafast vibrational and optical studies, we introduce the method of two-pulse photon echo to show that in the case of hydrogen-bonded complexes of coumarin 102 (C102) and phenol, C102−$(phenol)_{1,2}$, dissolved in a nonpolar surroundings, C_2Cl_4, an electronic state jumping occurs that is completed around 200 fs after electronic excitation. We thus believe to have measured a photon echo on a reactive system. Under the assumption that no detrimental higher order effects occur due to the high-excitation intensities, we derive from the echo result that pure dephasing processes for these complexes are not as dominant as in traditionally surveyed polar solvents, and that the T_1 lifetime contribution is observable. We note that three-pulse stimulated echo results also exhibit features due to this T_1 effect and are presently pursuing a more thorough analysis of these results. We argue that hydrogen bonding is coupled to the electronic transition and that the hydrogen bond cleavage is responsible for the electronic state change. Naturally a thorough picture of the problem will only arise if reliable quantum-chemical calculations of the excited state potential energy surfaces can be made, especially the question has to be solved whether the potential is purely dissociative along the hydrogen bond coordinate or not. We expect that further improvement of ultrashort laser pulses in the violet-blue, shorter pulses with better phase characteristics at higher repetition rates, will enable a more careful analysis of the ultrafast optical dynamics of these hydrogen-bonded complexes.

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