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LETTERS

Ultrafast Structural Response of Hydrogen Bonded Complexes to Electronic Excitation in the Liquid Phase

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The response of hydrogen bonded complexes to electronic excitation is studied by site-specific vibrational spectroscopy in the femtosecond domain, providing insight into local changes of hydrogen bonding geometries. For the prototypical organic complex coumarin 102−$(phenol)_{1,2}$ in solution, electronic excitation of the coumarin chromophore initiates a response of intermolecular hydrogen bonds on two distinct time scales: the hydrogen donor $(phenol)_{1,2}$ is released from the acceptor coumarin within 200 fs, followed by a reorganization of the $(phenol)_2$ moiety with an 800 fs time constant. This structural response results in strong changes of vibrational dipole moments which are monitored for the first time.

Intermolecular hydrogen bonding represents an important type of local interaction in which a hydrogen atom is linked to donor and acceptor groups on different molecules. Such bonds play a fundamental role for the structure and dynamics of hydrogen bonded liquids such as water,[1−3] binary complexes,[4] biomolecules such as double helix structures,[5] and solute−solvent complexes.[6] In liquids, intermolecular hydrogen bonding leads to the formation of extended molecular networks, the structure and dynamics of which are difficult to analyze, both from a theoretical and experimental point of view. Thus, the study of model systems of reduced complexity, e.g., hydrogen bonded complexes consisting of a small number of molecules, plays an important role for understanding microscopic structure and interactions. A prototypical case is hydrogen bonded complexes embedded in a nonpolar aprotic solvent, as the relative concentrations of the species forming the complex and, thus, the site geometry and molecular interactions can be varied over a wide range.

Dynamics of hydrogen bonds occur on ultrafast time scales set by vibrational motions of hydrogen donor and acceptor and are barely understood on a microscopic level. Ultrafast spectroscopy in the femtosecond domain has the potential to monitor such dynamics in real time. So far, most ultrafast experiments on hydrogen bonded systems have concentrated on changes of electronic absorption and emission spectra. For instance, solute−solvent interactions in polar liquids have been studied by monitoring transient red shifts of electronic emission bands of a chromophore in order to characterize the time scales of solvent response.[7] Such experiments give ensemble averaged time-correlation functions for liquid motion, providing very limited information on changes of microscopic solvent structure. In contrast, ultrafast vibrational spectroscopy of distinct functional groups in the hydrogen bonds can give site-specific insight into local dynamics.

In this paper, we address a fundamental problem of liquid dynamics, the ultrafast response of hydrogen bonded complexes to the creation of an electronic transition dipole in the complex. We demonstrate for the first time that the energy of the transition dipole is lowered by changing local hydrogen bonds. In this solvation scenario, ultrafast changes of local hydrogen bonds are monitored by site-specific femtosecond vibrational spectroscopy. Different stages of molecular reorientation are sepa-

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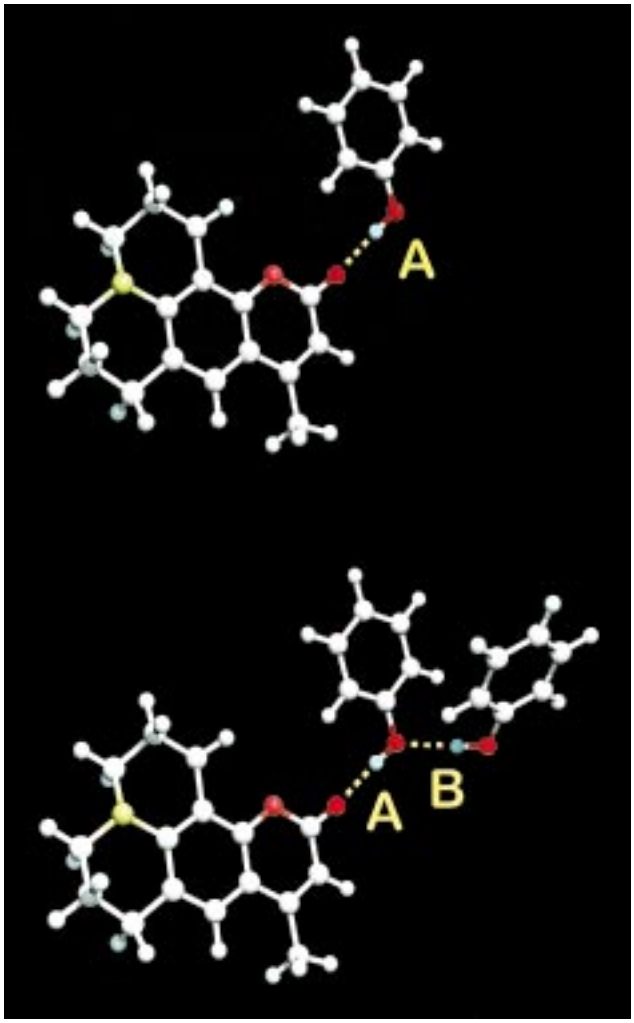

Figure 1. Molecular structures of coumarin 102 (C102)−phenol (top) and C102-(phenol)$_2$ (bottom), indicating the hydrogen bonds A and B in yellow. After electronic excitation of C102, bond A cleaves within 200 fs, after which the geometry of bond B changes with an 800 fs time constant.

rated in time, and the changes of the microscopic structure are determined via transient vibrational spectra.

In our experiments, hydrogen bonded complexes between the organic chromophore, coumarin 102 (C102), serving as hydrogen acceptor, and hydrogen-donating phenol molecules are investigated (Figure 1). Such complexes are dissolved in the nonpolar solvent tetrachloroethene, C_2Cl_4. First, the steady-state vibrational spectra of both the hydrogen donor and acceptor groups are investigated in the electronic ground state. The stretching band of the carbonyl (C═O) group of C102, the hydrogen acceptor (concentration $c = 5 \times 10^{-3}$ M), is shown in Figure 2(a) for the pure nonpolar solvent (dashed line) and the complexes (solid line). In pure C_2Cl_4, one finds the stretching band of a free C═O group around 1735 cm^{-1}.[8] Addition of phenol (concentration 4×10^{-2} M) leads to a downshift of the band to 1695 cm^{-1}. This red shift by 40 cm^{-1} is due to the formation of a strong C═O···H−O hydrogen bond between the C═O group and an O−H group of phenol with a binding energy on the order of 60 kJ mol^{-1}.[9]

Formation of the C═O···H−O hydrogen bond strongly affects the O−H stretching bands of the phenol molecules (Figure 3). The spectrum of pure phenol in C_2Cl_4 ($c = 4 \times 10^{-2}$ M) shown in Figure 3(a) displays a stretching band at 3610 cm^{-1} which is caused by free O−H groups not being part of a

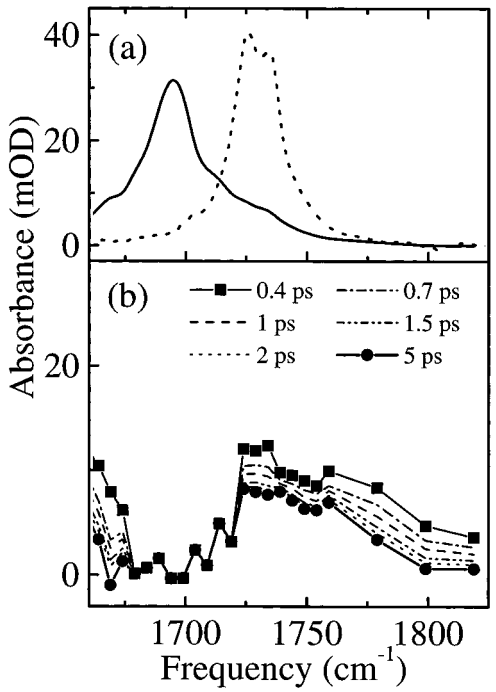

Figure 2. (a) Ground-state C═O stretching bands of C102 in pure C_2Cl_4 (dashed line) and of C102−(phenol)$_n$ complexes in C_2Cl_4 (solid line). The C102 and phenol concentrations were 5 mM and 40 mM, respectively. (b) Transient C═O stretching band of C102 in the complexes after excitation to the S_1 state of C102. The spectra are shown for different time delays after excitation.

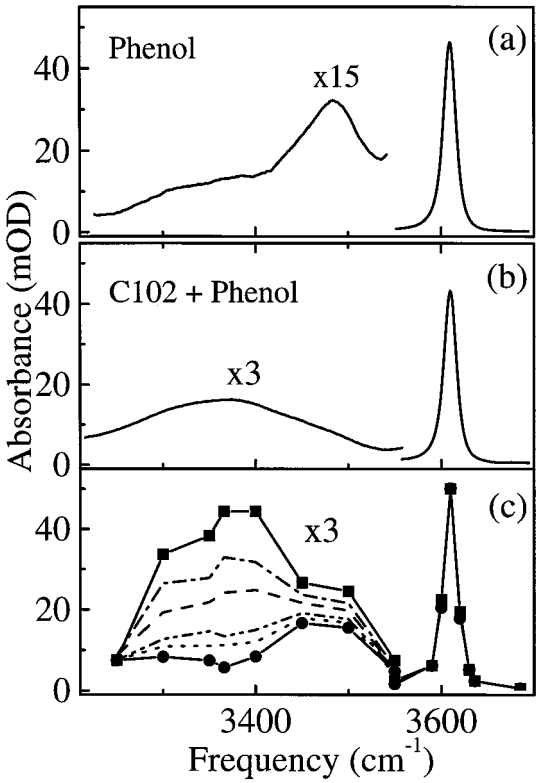

Figure 3. (a) Steady-state O−H stretching bands of phenol dissolved in C_2Cl_4 (concentration $c = 30$ mM). (b) Ground-state infrared spectrum of C102−(phenol)$_n$ complexes ($c = 5$ mM for C102, $c = 40$ mM for phenol). (c) Transient vibrational spectra of the (phenol)$_n$ units in the complexes after excitation of C102, recorded at the same delays as in Figure 2b.

hydrogen bond, and a broader band between 3450 and 3550 cm^{-1}. The latter is predominantly due to 1:1 phenol−phenol

complexes[10] where an intermolecular O···H−O hydrogen bond exists between the two phenols. Addition of C102 (concentration 5×10^{-3} M) leads to the formation of an additional broad band with a strongly red-shifted maximum around 3380 cm^{-1} (Figure 3b). This band is due to O−H groups in the C═O···H−O hydrogen bonds with C102. Additional experiments (not shown here) in a wide range of relative concentrations of C102 and phenol give the following quantitative information. In the case of the time-resolved data presented below we have: (i) only one phenol binds to a C102 molecule, (ii) 92% of the C102 molecules are complexed, of which 44% form C102−phenol and 56% C102−$(phenol)_n$ complexes with $n \geq 2$. All of those complexes contribute to the broad O−H band between 3200 and 3550 cm^{-1}.

To study the ultrafast response of the complexes to an electronic dipole, the C102 chromophore is excited by a 100 fs pulse at 400 nm, resonant to the purely electronic S_0-S_1 transition, whereas the phenol molecules stay in their electronic ground state. The resulting changes of vibrational absorption of both the C102 and phenol molecules are monitored by mid-infrared probe pulses tunable in the range of the C═O and O−H stretching bands. We performed femtosecond vibrational spectroscopy using an amplified Ti:sapphire laser system with 100 fs pulses centered at 800 nm with 1 kHz repetition rates. Subsequent frequency conversion of the fundamental laser pulses to the second harmonic was achieved with a 300 μm thick nonlinear BBO crystal. Mid-infrared pulses with 130 fs duration tunable between 2 and 10 μm were generated as described before.[11] The experiments were performed on a 200 μm thick jet of a mixture of 5 mM coumarin 102 (Lambda Physik) and 40 mM phenol dissolved in tetrachloroethene (both Merck UVASOL grade). Pulse intensities on the sample were 10^{11} W/cm^2 for the pump and 10^7 W/cm^2 for the probe. The temporal resolution was 200 fs, as determined by measurement of the cross-correlation in a 300 μm thick plate of silicon. The change of vibrational absorption $\Delta A(\nu,t_D)$ is measured at about 50 fixed spectral positions ν as a function of delay time t_D between excitation and probe. A selection of such transients is plotted in Figure 4. Combining the absorption changes for different spectral positions at a fixed t_D and estimating the amount of excited molecules, we derive the transient infrared spectra of the excited complexes in Figures 2(b) and 3(c).

The time-resolved data give the first direct insight into microscopic dynamics of the complexes and reveal two distinct time scales of structural response, relating to the different types of hydrogen bonds in the system.

(i) Fast Dynamics within the First 200 fs after Excitation. Upon excitation of C102, the stretching band of the C═O group of C102 at 1695 cm^{-1} disappears and is replaced by a weaker broad band with a maximum at about 1740 cm^{-1} (Figure 2b). This position is characteristic of a free C═O group for both the ground state (cf. Figure 2a) and the S_1 state of C102.[8] Concomitantly, the excited complexes exhibit a stretching band of free phenol O−H groups at 3610 cm^{-1} (Figure 3c). A quantitative analysis of the spectrum shows that there is one free O−H group per excited complex. All changes build up within the time resolution of the experiment of 200 fs, as is evident from Figures 4 (a−c).

We conclude that the C═O···H−O hydrogen bond in both the C102−phenol and the C102−$(phenol)_{n\geq 2}$ complexes (denoted as A in Figure 1) break within 200 fs after excitation of C102, representing the fastest response of the complex to the creation of the electronic dipole. The cleavage of this bond is driven by changes of the local charge distribution of C102. In particular, the polarity, and thus the hydrogen affinity, of the C═O group decreases in the S_1 state of C102, as is suggested by semiempirical calculations of the S_1 charge distribution.[12] Cleavage of the hydrogen bond can be an instantaneous process owing to an rearrangement of electronic density upon excitation. It can also involve nuclear motion on a time scale set by the period of low-frequency vibrations of the hydrogen bonded groups in the 100−200 cm^{-1} range. Such frequencies translate into time constants < 200 fs, in agreement with the dynamics found here.

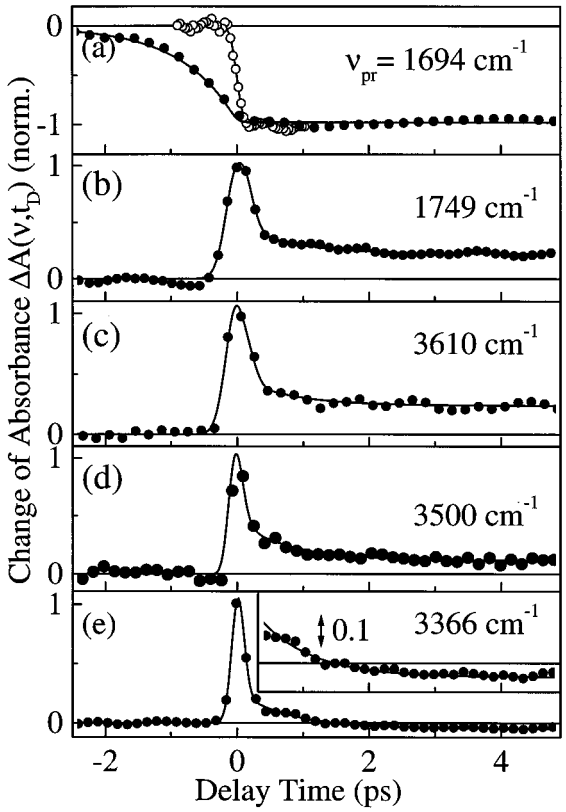

Figure 4. Time-resolved change of vibrational absorption at different spectral positions after electronic excitation of C102. (a) Bleaching of the ground-state C═O stretching band of C102 (solid circles). Open circles: time integrated cross correlation of pump and probe. (b) Increase of the stretching band of free C═O groups of excited C102. (c) Increase of free O−H stretching absorption of phenol. (d, e) Bleaching of hydrogen bonded O−H stretching absorption of phenol and $(phenol)_2$. The slow rise at negative delays in (a) is due to the so-called perturbed free induction decay, and the spike at zero delay for the other transients is due to a multiphoton absorption effect; both are not relevant in the analysis of this work. Note that a perturbed free induction decay does not appear in the transient at 3610 cm^{-1}, since the signal is due to newly generated phenol species that do not exist before electronic excitation.

(ii) Slower Dynamics Extending into the Picosecond Regime: The fast cleavage of the C═O···H−O hydrogen bond is manifested in the steplike increase of free O−H absorption at 3610 cm^{-1}, with a possible hint of dynamics on a picosecond time scale (Figure 4c). In contrast, strong changes of the broad O−H band between 3200 and 3550 cm^{-1} are found upon electronic excitation of C102 for delay times up to 5 ps. There is a strong increase of infrared absorption in this frequency range, followed by a reshaping of the spectrum. The absorption between 3200 and 3400 cm^{-1} disappears completely within the first few picoseconds, giving rise to a persistent bleaching (Figure 4e). In contrast, absorption is enhanced between 3400 and 3550 cm^{-1} (Figure 3c). The reshaping of the spectrum occurs with a characteristic time constant of 800 fs (Figure 4d,

e). The vibrational band found after about 5 ps stays unchanged for even later times and is very close to the stretching band of hydrogen bonded O−H groups in the phenol dimers (cf. Figure 3a). The absorption changes disappear on a time scale of nanoseconds with the decay of the S_1 state of C102, i.e., the decay of the electronic dipole. It should be noted that the strength of the new C═O stretching band of C102 also changes within the first 5 ps after excitation (Figure 2b). In addition, the transient of the free O−H band at 3610 cm^{-1} hints at a small change in absorbance on the same time scale.

The transient enhancement of infrared absorption at early times represents an effect which has not been anticipated and is observed here for the first time. It reflects the nonequilibrium geometry of the complexes immediately after cleavage of the C═O···H−O hydrogen bond. Cleavage is accompanied by a redistribution of electron density in the phenol molecule close to C102, both on the oxygen atom and in the aromatic ring. First, this change acts back on the neighboring C═O group of C102 being sensitive to the electronic charge of phenol, thereby changing the strength of the C═O band. Second, the change of charge densities along the other still intact hydrogen bonds in $(phenol)_n$ ($n \geq 2$) (denoted as B in Figure 1) leads to changes in hydrogen bond strength and the vibrational transition moments of the bridged OH-groups. Subsequently, the released $(phenol)_n$ moiety reorganizes itself to a new equilibrium configuration, mainly by reorientation of the phenol units relative to each other and to the excited C102 molecule. This structural reorganization of $(phenol)_n$ with a time constant of 800 fs is directly monitored in our measurements (Figures 3c, 4d, e). The new band between 3400 and 3550 cm^{-1} has a shape very close to the infrared absorption of 1:1 phenol−phenol complexes (Figure 3a). We conclude that the major fraction of C102−$(phenol)_n$ ($n \geq 2$) are C102−$(phenol)_2$ complexes, releasing $(phenol)_2$ after electronic excitation (see Figure 1). The experimental magnitude of the absorbance change for this band corresponds well with the assumption that larger complexes with $n \geq 2$ are not significant for the interpretation. The reorientation time of 800 fs corresponds to a low-frequency motion of about 40 cm^{-1}, a frequency typical for librational motions that could well represent the relative tilting of the rings in $(phenol)_2$.

A quantitative analysis of the transient infrared bands and the final orientation of the molecules require theoretical calculations combining molecular dynamics simulations with a treatment of the Coulomb interaction between the charges on the different molecules and their influence on hydrogen bonding geometries and vibrational spectra. To our knowledge, such calculations have not been performed yet. Our experimental results allow a clear separation of the different structural changes and will help to develop such theoretical models.

In conclusion, new insight into the ultrafast structural response of hydrogen bonded complexes to an electronic dipole excitation has been gained by femtosecond vibrational spectroscopy. In coumarin−phenol complexes, ultrafast cleavage of C═O···O−H hydrogen bonds within 200 fs is followed by a reorientation of phenol molecules with a time constant of 800 fs, changing the geometry of their mutual O···H−O hydrogen bond. In particular, we observe dynamics involving the phenol unit not directly bonded to C102, demonstrating the potential of femtosecond vibrational spectroscopy for probing dynamics in hydrogen bonding networks at a finite distance from the directly excited groups. Thus, future application of this technique to larger hydrogen bonded complexes, e.g., those with water, and to light-harvesting systems, where proton pumping through membranes occurs,[13] seems very promising. From a more fundamental point of view, this work provides a microscopic view of hydrogen bonding dynamics in an electronically excited system, being a major test for the recent efforts in mixed quantum-mechanical/classical molecular dynamics simulations.[14−18]

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