Probing solvation dynamics with femtosecond vibrational spectroscopy

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Abstract. We explain why solvent reorganization can induce both red- and blue-shifting of vibrational transitions of a particular probe molecule upon excitation to the \( \Delta_1 \) electronic state. We observe with femtosecond vibrational spectroscopy, after hydrogen-bond cleavage dynamics, an additional blue shift of the carbonyl stretch of coumarin 102 of 7 cm\(^{-1}\) when dissolved in chloroform.

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Much effort has been put into the unraveling of liquid motion at ultrafast time scales, where it is understood that solvation dynamics occurs within 100 fs or less [1, 2]. The reason for this effort is that the outcome of chemical reactions will be determined by these motions, one clear example being the cage effect where molecular fragments of a photodissociated molecule bounce back at the first solvent shell and then recombine [3]. Moreover, when a molecular dissociation occurs, the actual movement of the molecular system over the transition barrier may not be the most direct pathway. Collisions with the nearby solvent molecules may lead to a more diffusive type of motion, as explained by Kramers equation [4, 5]. Due to the large magnitude of degrees of freedom of modeling these interactions with the solvent shells, stochastic theories based on for instance the Langevin equation have been extensively [6].

The amount of degrees of freedom that play a role in a chemical reaction is rather staggering. For this reason, several groups have resorted to the study of liquid motion by probing the dynamics of the solvent after an abrupt change of electronic charge distribution of a specific probe molecule that does not lead to subsequent chemical reaction dynamics. This change of charge distribution is induced by electronic excitation from the electronic ground state to the excited state. The solvent shells are initially in a configuration in equilibrium with the probe molecule in its electronic ground state. After electronic excitation the solvent has to respond by reorientation to the more energetically favorable situation (Fig. 1). This process of adjustment of free energy is called solvation dynamics, where it is believed that knowledge about this process will enable the interpretation of solvent motion around a reacting molecule.

For more than a decade, solvation dynamics has been studied by the technique of time-resolved fluorescence Stokes-shift measurement, with which the time-delayed adaptation of the solvent to the new charge distribution in the probe molecule is directly measured [7, 8]. Based on the assumption of linear response of the solvent from these measurements, a two-point time-correlation function can be determined, that then should represent the equilibrium fluctuations of the solvent, irrespective of which probe molecule is chosen for these studies.

Alternatively, a large class of femtosecond four-wave-mixing experiments has been reported, where the coherence properties of electronic transitions of probe molecules in solution have been investigated [9, 10]. From these studies on certain probe molecules, again with the assumption of linear response, the two-point time-correlation functions of several solvents have been derived. By use of a Brownian-oscillator model to mimic the solvent response, a connection can be made between the broadening mechanism of the optical line shapes (that is determined by the optical coherence loss, or dephasing, of the transition) and the time-dependent Stokes shift (that is determined by solvent nuclear rearrangement coupled to the electronic state) [11]. These studies have shown that the nuclear dynamics of the rearranging solvent occurs on a multitude of time scales, from the first few hundred femtoseconds, up to picoseconds or even longer times.

The limitation of the aforementioned methods lies in the fact that intrinsically the influence of the solvent motion is contained within this two-point time-correlation function [12]. This limitation is not overridden if one would resort to higher-order perturbative \( \chi(5) \)- or \( \chi(7) \)-spectroscopy on the electronic transition of the probe molecule, since the outcome will always be determined by line-shape functions that will be a linear combination of (time-integrated) two-point time-correlation functions [11]. One has to rely on methods of probing the solvant motions directly by use of for instance femtosecond THz-spectroscopy [13] and femtosecond IR-spectroscopy [14–17]. The additional advantage lies in
the fact that the obtained information can be highly site-specific, if one probes vibrational modes that are localized in one section of the molecular systems (Fig. 1). This feature is omnipresent in the system we have studied recently, the hydrogen-bonded complexes of the dye molecule coumarin 102 (C102). In contrast, electronic spectroscopy will always lead to results where it is difficult to extract specific nuclear motions from the overall response [17, 18].

By inspection of certain spectator modes, like the carbonyl stretch of C102 and the O–H stretch of the hydrogen-donor phenol, we were able to derive that hydrogen bonds exist between C102 and hydrogen donors when C102 is in the electronic ground state. For instance, the C = O stretch of C102 red shifts 35 cm\(^{-1}\) when C102 is dissolved in CHCl\(_3\) as compared to the band position when C102 is dissolved in C\(_2\)Cl\(_4\), where no hydrogen bonds occur. Upon electronic excitation of C102 this band upshifts again to about the position of the C = O stretch of C102 dissolved in C\(_2\)Cl\(_4\), either in the S\(_0\) or S\(_1\) state since in C\(_2\)Cl\(_4\) no shifts occur [14]. Probing the spectator C = O mode enables us to derive that a hydrogen bond with the solvent CHCl\(_3\) is formed when C102 is in the S\(_0\) state, and that within 200 fs (the time resolution of the experiment) this hydrogen bond breaks if C102 is promoted to the S\(_1\) state.

We observed that after the hydrogen-bond cleavage an additional blue shift of 7 cm\(^{-1}\) with a time constant of 2.5 ps occurs. We ascribed this feature to the effects of solvation dynamics (solvation reorganization) of CH\(_3\) on a picosecond time scale \([14, 16]\). In this Letter we explain why solvation reorganization leads to an upshifting of the vibrational transition.

The experimental setup of the optical pump/mid-infrared probe experiment with a time resolution of 200 fs is based on a 1 kHz Ti:sapphire chirped pulse regenerative amplifier providing 100 fs pulses from 780–830 nm with pulse energies up to 400 \(\mu\)J. Pump pulses of 30 \(\mu\)J energy and 100 fs are generated in the wavelength range from 390 to 415 nm by frequency-doubling pulses of 100 \(\mu\)J energy at the fundamental in a 300-\(\mu\)m-thick BBO crystal. The mid-infrared probe pulses in the range of 2–12 \(\mu\)m are generated by parametric infrared generation \([19]\). This system consists of optical parametric generation (OPG) in a temperature-controlled lithium triborate (LBO) crystal of 5-mm length (z-cut, non-critical type-II phase matching), followed by optical parametric amplification (OPA) in a BBO crystal of 4-mm length (\(\Theta = 20^\circ\), type-I phase matching). The OPG and OPA are pumped by the fundamental and generate near-infrared pulses from 1 \(\mu\)m to 2.5 \(\mu\)m with pulse energies of \(> 1 \mu\)J. In a second parametric stage, the difference frequency of the near-infrared signal and idler pulses is generated in an AgGaS\(_2\) crystal of 2-mm length. Signal and idler pulses are separated by dichroic mirrors to adjust the polarization and to optimize the temporal and spatial overlap in the AgGaS\(_2\) crystal. Wavelength tuning is achieved by varying the temperature of the LBO crystal and adjusting the phase-matching angles of the BBO and AgGaS\(_2\) crystals. The tunable mid-infrared pulses have pulse durations of 130 fs and pulse energies of about 5 \(\mu\)J.

The pump and probe beams are focused into a 200-\(\mu\)m-thick jet. The focus diameter is 500 \(\mu\)m for the pump and 100 \(\mu\)m for the probe. After interaction with the sample, the probe beam is dispersed in a monochromator and recorded by a liquid-nitrogen-cooled HgCdTe detector.

Commercially available C102 (Lambda Physik) was used without further purification. For the femtosecond measurements, one liter of solution is prepared with chloroform as solvent (Merck, Uvasol-grade). The concentration of C102 is 0.005 mol/l in all measurements.

Figure 2 shows our main results. It follows that after initial cleavage of the hydrogen bond the C = O stretch is located at 1738 cm\(^{-1}\), subsequently exhibiting a blue shift with a time constant of 2.5 ps. The C = O stretch shifts 7 cm\(^{-1}\) to higher values. In the following we explain why solvent reorganization can alter the vibrational frequency of the C = O mode.

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**Fig. 1.** Schematic drawing of the solvent reorganization induced by electronic excitation of the probe molecule (top). Infrared spectroscopy reveals site-specific information if local vibrational modes are probed, as opposed to electronic spectroscopy where all molecular motions contribute to the signal (bottom).

**Fig. 2.** 3D and contour plots of the 1710–1775 cm\(^{-1}\) frequency range in the fingerprint region of C102 dissolved in CHCl\(_3\), after electronic excitation at time zero. The plots show the long-time-scale dynamics after 500 fs.