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Solvent Dynamics probed by Photon Echo

Abstract

Solvent dynamics, which lies at the heart of 'femtochemistry' in solution, has been studied by femto-second photon echo and chirped four-wave mixing. A single Brownian oscillator is shown to provide an excellent description of the optical dynamics in the case of resorufin in dimethylsulphoxide. For pinacyanol in ethylene glycol at least three Brownian oscillators are needed to simulate the spectral and dynamical data. The different solvent behaviour is ascribed to hydrogen bonding effects in the case of ethylene glycol.

Introduction

The grasp of solvent dynamics is at the heart of the understanding of solution chemistry and henceforth much work has been devoted to this subject both experimentally and theoretically. In the past, liquid state dynamics has been accessed by coherent resonance Rayleigh mixing [Yajima et al., 1978], polarization spectroscopy [Song et al., 1978], resonance Raman scattering [Brafman et al., 1984; Nibbering et al., 1990], time-resolved hole burning [Brito-Cruz et al., 1986], optical Kerr effect measurements [McMorrow et al., 1988], and, more recently, by femtosecond photon echo [Becker et al., 1989; Bigot et al., 1991; Nibbering et al., 1991] and time-dependent Stokes shift measurements [Rosenthal et al., 1991]. The conclusion of all these experiments is that solvent dynamics has a component that proceeds on a femtosecond time scale. The same conclusion was drawn from molecular dynamics simulations of liquids [Maroncelli and Fleming, 1989]. For a better grip on 'femtochemistry' in solution detailed study of these ultrafast motions is therefore essential.

While the outcome of molecular dynamics simulations depends on knowledge of the intermolecular potentials, the conclusions drawn from experiments depend heavily on the dynamical model used to analyze the data. Recently it has been realized [Nibbering et al., 1990] that the optical dynamics, which is used as a probe for solvent dynamics, cannot be modelled using the optical analog of the Bloch equations. The fundamental reason is that in liquids there is not a clear separation of time scales, between bath fluctuations and optical coherence decay. A model that allows for dynamics in this regime is the so-called stochastic

modulation model. It has recently been applied successfully to the case of resorufin in dimethylsulphoxide [Nibbering et al., 1991]. Here the dynamics on all time scales -as expressed in the optical lineshape- were linked with the solvent dynamics on a femtosecond time scale, as probed by the two-pulse photon echo. However, this model does not account for the response of the solvent on optical excitation of the probe molecule. This solvation effect occurs on all time scales, but most notably at a sub 100 fs time scale [Rosenthal et al., 1991]. A model that does account for this effect is the so-called multimode Brownian oscillator (MBO) model. In this model the solvent motions that determine the dynamics are treated separately (projected out) from the solvent motions that have little effect on the optical dynamics. These Brownian oscillators are then used to 'dress' the electronic two-level system. Nuclear motion takes place on harmonic potential surfaces which are linearly displaced on optical excitation.

Fig. (1) shows how a displaced Brownian oscillator affects the optical response. Due to the fluctuations (damping) of the oscillatory movement, the width of the electronic transition increases. Due to the displacement of the potential surfaces, a nonequilibrium situation is created upon excitation with respect to the nuclear coordinate, which leads to a red or a blue shift of the electronic transition frequency, depending on the position of the 'particle' and 'hole' relative to the equilibrium minimum of the potential wells.

In this paper we will present and discuss some of our recent results of femtosecond photon echo and chirped four-wave mixing experiments on resorufin in dimethylsulphoxide (DMSO) and pinacyanol in ethylene glycol. We will show that the MBO model provides an excellent fit to all experiments in the case of resorufin. The first results on pinacyanol indicate that the solvent dynamics in this case are more complex and that therefore more than one oscillator is needed to model the dynamics. We further conclude that the dynamics for protic and aprotic solvents are different.

Prior to presenting our data the basic relaxation function will be discussed that emerges from the MBO theory. Further details on the MBO theory can be found, for instance, in a paper by Yan and Mukamel [1988].
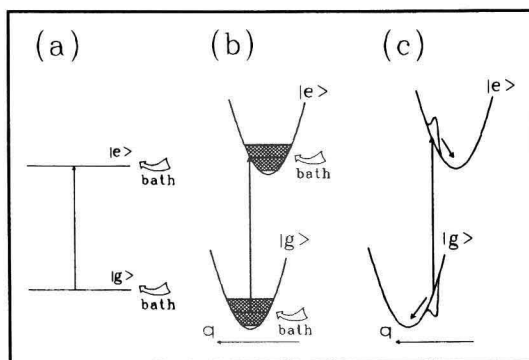

Fig. 1.   Modelling of non-Markovian two-level dynamics by the Brownian oscillator model.

Brownian Oscillator Model

A Brownian oscillator is characterized by three parameters: frequency ω, damping $\gamma(t)$, and displacement d. A particular two-level system may be dressed with any number of oscillators, each with different parameters. Depending on whether $\gamma(t)$ is much larger or smaller than ω the Brownian oscillator is overdamped or underdamped. The underdamped modes are responsible for the vibrational structure in the optical spectra, while the overdamped modes dominate the dynamics. When it is further assumed that the solvent dynamics are fast compared to the oscillator dynamics the so-called Markovian limit of the MBO model is obtained. For this case a very simple expression for the correlation function of the strongly overdamped Brownian oscillator can be derived:

$$M_j(t) = \exp(-\Lambda_j t) \tag{1}$$

Here Λ_j is the inverse correlation time of the oscillator's correlation function, and defined by $\Lambda_j = \omega_j^2/\gamma_j$.

The various kinds of (non)linear optical responses that are probed in the different experiments are most conveniently expressed in terms of an overall line broadening function $g(t)$ [Yan and Mukamel, 1990; Mukamel, 1990], which consists of contributions from different Brownian oscillators $g_j(t)$. We are particularly interested in the form of this function in the case of strongly overdamped modes, because especially these modes contribute to line broadening and other dynamical effects. The line broadening function of an overdamped oscillator can be written as :

$$g_j(t) = i\frac{\lambda_j}{\Lambda_j}\left[1 - \exp(-\Lambda_j t)\right] + \frac{\Delta_j^2}{\Lambda_j^2}\left[\exp(-\Lambda_j t) + \Lambda_j t - 1\right] \tag{2}$$

λ_j is the reorganisation parameter, which is given by $\lambda_j = \omega_j d_j^2/2$. Δ is related to the frequency ω and displacement d of the oscillator by the relation: $\Delta_j^2 = \omega_j^2 d_j^2[n(\omega) + 1/2]$. In the high temperature limit ($kT \gg \hbar\omega_j$) this relation becomes $\Delta_j^2 \approx 2kT\lambda_j/\hbar$, thus relating Δ_j an λ_j directly. Therefore in the high temperature limit these strongly overdamped modes (SOMs) are characterized by only two parameters (Δ_j and Λ_j).

For further details on how to arrive at Eqs. (1) and (2) we refer to [Duppen et al., 1993].

It should be noted that when the imaginary part in Eq. (2) is ignored the line broadening function of the stochastic model is recovered [Nibbering et al., 1991]. As mentioned, in this model solvation is not accounted for.

Liquid state optical dynamics

We will present results of a number of linear and nonlinear optical experiments on the system resorufin in dimethylsulphoxide (DMSO). These results will be

discussed in the context of the multi-mode Brownian oscillator (MBO) model in its simplest form: a single, overdamped oscillator will be used to mimic the solvent dynamics. For pinacyanol some preliminary stimulated photon echo measurements will be shown. Here at least three Brownian oscillators are needed to simulate the liquid state dynamics.

Two-pulse photon echo experiments

The fastest experiment is a two-pulse photon echo. In this experiment two short optical pulses with wavevectors k_1 and k_2 excite the system in an impulsive way. Conventionally the rephasing of the polarization leading to echo formation is supposed to arise from a static distribution of transition frequencies (inhomogeneous broadening). Homogeneous broadening causes a decay of the echo amplitude when the pulse separation τ is increased. In a liquid the presence of inhomogeneous broadening is not crucial for a photon echo to be generated. Instead, the correlation function Eq. (1) provides the necessary phase memory, but only for a time corresponding to the correlation time Λ^{-1}. Rephasing and echo formation will thus be possible for pulse separations up to this time.

The experimental decay of the echo intensity is shown for resorufin in DMSO in Fig. 2. These signals were measured with a beam geometry shown in the inset. The two optical pulses were generated with a Colliding-Pulse Mode-Locked (CPM) laser and amplified with a copper-vapor laser, which gave transform-limited 50 fs pulses with a repetition-rate of 8.3 kHz. These pulses were subsequently chirped in a single-mode optical fiber to a duration of 1.2 ps with a center wavelength of 620 nm and a bandwidth of 3000 cm^{-1}, and subsequently compressed to a duration of about 9 fs using a combination of two gratings and four prisms [Nibbering et al., 1991]. The pulses were crossed at an angle of about 4.5° in a 60 μm thick jet of the dye solution (10^{-3} M). The nonlinear signals in the phase-matched direction $2k_2 - k_1$ were detected with a photomultiplier and a lock-in amplifier.
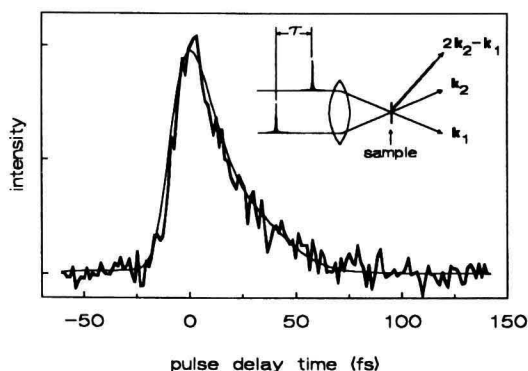

Fig. 2. Two pulse photon echo signal of resorufin in DMSO at room temperature as a function of relative pulse delay time τ (dotted line). The beam geometry is shown in the inset.

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The notable asymmetry in the trace of Fig. (2) indicates that dephasing of resorufin in DMSO is not irreversible. Apparently partial rephasing occurs when pulse 2 interacts with the sample at a time τ after pulse 1, which makes it ligitimate to call these signals photon echoes.

It can be shown [Nibbering et al., 1991] that for delta pulse excitation the two-pulse echo intensity has the following expression:

$$I_{2PE}(t, \tau) \sim \exp[-2Re[2g(t) + 2g(\tau) - g(t + \tau)\}]$$ (3)

with the delay time τ defined to be positive (pulse $\mathbf{k}_2$ after pulse $\mathbf{k}_1$).

The result of Eq. (3) is remarkable, especially with regards to solvation. A possible time dependent shift of the system frequency is incorporated in the imaginary part of the lineshape function $g(t)$. Since Eq. (3) only involves the real part of $g(t)$, it follows that the photon echo signal is insensitive to net rearrangements of the solvent shells upon excitation of the probe molecule! The reason for this behaviour is that only coherent superposition states are involved in the generation of the echo signal, and that an inversion of phase occurs when the second pulse is applied. Only fluctuations (damping) are important for the decay of the signal. In the case of a strongly overdamped oscillator, the expression for $I_{2PE}(t, \tau)$ is identical to that of the stochastic model of optical dynamics [Nibbering et al., 1991; Duppen et al., 1993], since the line broadening function for the stochastic model is identical to the real part of an overdamped $g(t)$. So, when Eq. (2) is inserted in Eq. (3) the same expression is obtained that was used previously to analyze these data in the context of the stochastic model [Nibbering et al., 1991]:

$$I_{2PE}(t, \tau) \sim \exp\left[\frac{-2\Delta^2}{\Lambda^2} \times \{2e^{-\Lambda t} + 2e^{-\Lambda \tau} - e^{-\Lambda(t + \tau)} + \Lambda(t + \tau) - 3\}\right]$$ (4)

To compare this theoretical expression with experiment, the finite pulse width and the detector response have to be considered. The assumption of delta pulses that was made in Eq. (4) is an idealization of the actual pulse width of about 9 fs. However, as long as the pulses are short enough to ignore the system dynamics during the optical interaction, the impulsive treatment is still valid. The observed signal can then be calculated by convolving the calculated delay dependence with the experimental time resolution. Also, the detector integrates the echo signal that is generated after the interactions with both pulses over all times t. The experimental trace that was obtained for resorufin in DMSO therefore has to be compared to the following theoretical expression:

$$S_{2PE}(\tau) = \left\{\int_0^\infty dt\, I_{2PE}(t, \tau)\right\} \otimes T(\tau)$$ (5)

where $T(\tau)$ is a measure of the time resolution and $\otimes$ designates a convolution.

When Eq. (5) is fitted to the experiment on resorufin in DMSO, the smooth curve in Fig. (2) is obtained. The parameter values of the fit are: $\Delta = 41$ THz

(rad/sec) and $\varLambda = 27$ THz (sec^{-1}). In the MBO model $\varDelta$ is a measure of the Franck-Condon allowed frequency range of the optical transition and is related to the reorganization parameter λ, while $\varLambda$ is the inverse of the correlation time of the Brownian oscillator motion ($\tau_c = \varLambda^{-1} = 37$ fs). In the stochastic model, $\varDelta$ is the root mean square amplitude and $\varLambda$ the correlation time of the frequency fluctuations of the optical transition. Next to the electronic absorption at 595 nm only one vibronic transition at 576 nm was taken into account in the calculation of the signal of Fig. (2). This gives rise to a very weak beat in the observed decay. All other vibronic transitions are either too weak to contribute to the nonlinear signals, or they are outside the bandwidth of the optical pulses. The full vibronic structure of resorufin in DMSO will be discussed more extensively below.

Chirped four-wave mixing

In chirped four-wave mixing [Duppen et al., 1993] two or three chirped optical pulses interact in a sample to generate a nonlinear signal. These chirped pulses are strongly non-transform limited, but their optical phases are well-defined at all times. The carrier frequency is explicitly time dependent, which for a linearly chirped pulse can be written as:

$$\omega(t) = \omega_0 + bt \tag{6}$$

Here ω_0 (rad/sec) is an off-set frequency and b is the chirp rate (rad/sec^2). Typically, in chirped four-wave mixing the durations of the pulses are long compared to the dynamics. The time scale of the experiment is determined by the ratio of the width of the optical transition and the chirp rate, i.e. by the time it takes the optical field to sweep across the material resonance.

An experimental result of chirped four-wave mixing on resorufin in DMSO is shown in Fig. (3). In this experiment two pulses were used with a beam geometry shown in the inset. These pulses were generated with the same set-up that
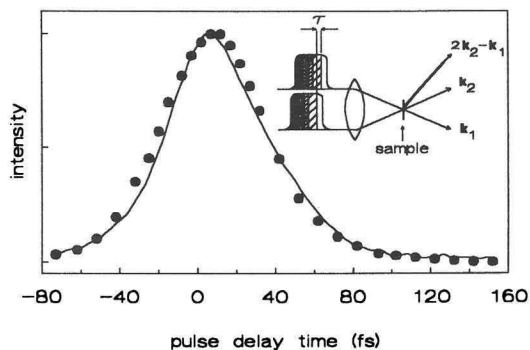

Fig. 3. Two pulse chirped four-wave mixing signal of resorufin in DMSO at room temperature as a function of relative pulse delay time τ (solid line). The beam geometry is shown in the inset; the different shades in the pulses indicate the frequency chirp.

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was used for the photon echo experiment, only the compression stages were left out. This means that the pulse duration was about 1.2 ps with a spectral width of about 3000 cm^{-1}, while the chirp rate was 2.6 cm^{-1}/fs. As indicated in the inset of Fig. (3), a relative delay τ implies an instantaneous frequency difference between both beams of $\delta\omega = b\tau$ (Eq. 6). The solid dots in Fig. (3) present the result of a numerical calculation [Duppen et al., 1993] using the same parameters as in the fit to the photon echo. Except for the overall intensity of the signal there is no fitting parameter involved in the numerical calculation. Yet, the calculated and measured traces of Fig. (3) agree very well. It is precisely this consistency in the modelling of the ultrafast photon echo and the chirped four-wave mixing signals that substantiates our Brownian oscillator approach to optical dynamics.

Absorption and emission

It is straightforward to calculate the absorption and emission spectra of a two-level electronic system dressed with Brownian oscillators. The absorption spectrum $S_A(\omega)$ can be written as:

$$S_A(\omega) = 2\omega Re\left\{\int_0^\infty dt \exp[i(\omega - \omega_{eg})\,t] \exp[-g(t)]\right\} \qquad (7)$$

were ω is the frequency of the absorbed light and ω_{eg} is the transition frequency of the electronic two-level system, which is centered in between the absorption and the emission maxima. The line broadening function $g(t)$ for an overdamped mode is given by Eq. (2). The steady state emission spectrum $S_F(\omega)$ is:

$$S_F(\omega) = 2(\omega)^3 Re\left\{\int_0^\infty dt \exp[i(\omega - \omega_{eg})\,t] \exp[-g^*(t)]\right\} \qquad (8)$$

where ω is the frequency of the emitted light and $g^*(t)$ is the complex conjugate of $g(t)$. By inspection of Eqs. (7) and (8) it is clear that the fluorescence spectrum $S_F(\omega)$ is practically the mirror image of $S_A(\omega)$ around the center frequency ω_{eg}.

In Fig. 4 the calculated absorption and emission spectra of resorufin in DMSO at room temperature are compared with the experimental results.

Again, just as in the calculation of the photon echo decay and the chirped four-wave mixing signal, a single overdamped oscillator was assumed to determine the optical response, with parameter values $\Delta = 41$ THz and $\Lambda = 27$ THz. The different vibronic components were considered as separate transitions, with absorption intensities as indicated by the structure underneath the spectra. Both the positions of these vibronic lines and their relative intensities are known from a report on resorufin in a glass [Van den Berg and Völker, 1988].

The enlarged part of Fig. (4) shows the origin region of the electronic transition of resorufin in DMSO. The one overdamped Brownian oscillator does not
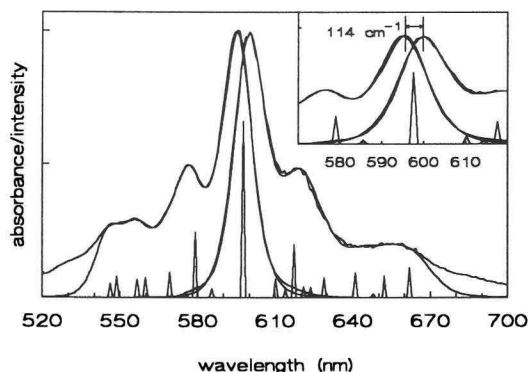
Fig. 4. Room temperature absorption and emission spectra of resorufin in DMSO. The fits are based on the level structure and transition moments shown below the curve. The enlarged view of the origin region clearly shows that the steady-state Stokes shift of 114 cm^{-1} is correctly predicted.

only describe the absorption and emission spectra very well, but also, within 10% accuracy, the steady-state Stokes shift. The Brownian oscillator model further predicts that the time-dependent Stokes shift occurs typically in about the correlation time Λ^{-1}. The time scale of solvation for resorufin in DMSO is therefore 37 fs. This fast reorientation of the solvent shells agrees with recent results of molecular dynamics simulations [Maroncelli, 1991].

Stimulated photon echo experiments

In the previous section we showed that a single Brownian solvent oscillator provides an excellent description of the optical dynamics on *all* time scales. Two-pulse photon echo and chirped four-wave mixing experiments on the system pinacyanol in ethylene glycol, however, showed that the dynamics in this solvent cannot be modelled by one Brownian oscillator. The question arises whether this different dynamical behaviour is due to hydrogen bonding effects in this solvent.

In order to obtain greater insight in this question we performed stimulated photon echo experiments.

Fig. 5 shows that the echo decay of pinacyanol in ethylene glycol extends over a couple of hundred femtoseconds with oscillatory structure superimposed on it. The very fast beating is due to coherent excitation of the vibronic structure in the absorption spectrum. The initial fast and slower decays must be due to different overdamped solvent oscillators. The observed low-frequency modulation may be due to a solvent librational mode. To analyze this complex echo decay we need an expression for the stimulated photon echo (3PSE). In the MBO model for the three pulse photon echo intensity the following expression is obtained:

$$I_{3PSE}(\tau, T) \propto \int_0^\infty |[R_1(t, T, \tau) + R_2(t, T, \tau)]|^2 \, dt$$
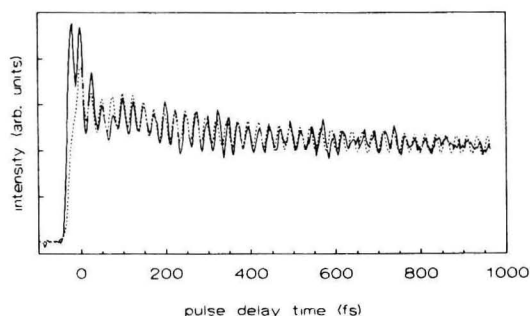
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Fig. 5. Fits to a three pulse stimulated photon echo on pinacyanol in ethylene glycol using three Brownian solvent oscillators. The delay between beams 2 and 1 is 10 fs.

where the explicit forms of $R_1(t, T, \tau)$ and $R_2(t, T, \tau)$ are:

$$R_1(t, T, \tau) \equiv \exp[-g^*(t) - g^*(\tau) + g(T) - g(T+t) - g^*(\tau+T) + g^*(\tau+T+t)]$$

$$R_2(t, T, \tau) \equiv \exp[-g(t) - g^*(\tau) + g^*(T) - g^*(T+t) - g^*(\tau+T) + g^*(\tau+T+t)]$$

with $g(t) \equiv \sum_j g_j(t)$, and $g_j(t)$ is given by Eq. (2) for the overdamped modes.

To simulate the 3PSE echo decay for pinacyanol in ethylene glycol we took the following approach: first we determined from the absorption spectrum the high-frequency mode (1360 cm^{-1}) to fix the fast beating pattern; then the ultra-fast component in the echo decay (tens of fs) was generated by varying the parameters Δ and Λ of one oscillator; in the third step we followed the same procedure to generate the long component (few hundred fs) in the echo decay; finally we made an educated guess about the underdamped solvent mode from the experimental echo trace. When all these independent simulations were judged to be satisfactorily, calculations were performed including all three Brownian oscillators. Our best result at this time is shown as the dotted curve in Fig. 5. While the simulated echo signal does not provide an excellent fit to the experimental
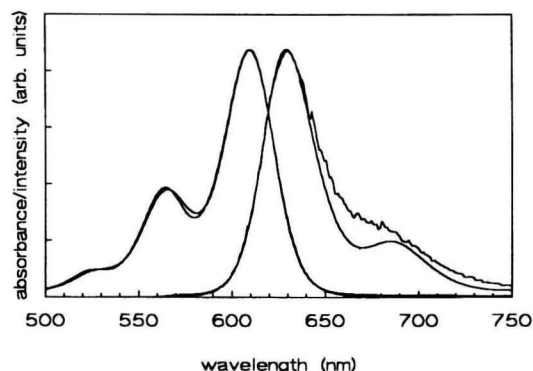

Fig. 6. Absorption and fluorescence spectra of pinacyanol chloride in ethylene glycol at room temperature. The smooth curves are fits using a set of three Brownian solvent oscillators.

decay yet, it seems that we have captured the gross features of the bath dynamics. (The discrepancy near zero delay time remains puzzling!) Of the three solvent Brownian oscillators needed to describe the echo decay two are strongly overdamped, while the third one is an underdamped mode with a frequency of about $220 \, cm^{-1}$. We tentatively assign these oscillators to inertial, diffusive and librational solvent molecule motion, respectively. The librational and diffusive components in the dynamics may be due to hydrogen bonding because they are not significant in aprotic solvents. Further analysis of these echo decays, however, is necessary to substantiate these conjectures.

In Fig. 6 we show the absorption and emission spectra of pinacyanol chloride in ethylene glycol at room temperature. As can be seen, reasonable agreement is obtained for the lineshapes in absorption and emission, as well as for the Stokes shift. The noticable discrepancy between theory and experiment in case of the emission spectrum may be due to pinacyanol isomer emission. This is subject of further investigation.

Discussion

In the previous section it was shown that a number of different optical experiments on resorufin in DMSO can all be explained consistently in terms of a rather simple model, based on Brownian nuclear motion. The optical transition, which involves electronic degrees of freedom, is dressed with nuclear motion in harmonic potential wells. It turned out to be sufficient to consider a single overdamped mode for a quantitative explanation of all observed experimental features. Only two parameters are involved that are the same for all calculated (non-) linear optical responses, from the ultrafast photon echo and chirped four wave mixing results to the absorption and emission properties, including the magnitude of the solvation Stokes shift. The modulation strength of the electronic transition is $\Delta = 41 \, THz$ (in angular frequency units), while the inverse correlation time is $\Lambda = 27 \, THz$ ($\tau_c = 37 \, fs$). This indicates that the solute and solvent dynamics occur on similar time scales, and the optical dephasing therefore has a non-Markovian character.

For pinacyanol the situation is more complex; here we need at least three different Brownian solvent oscillators and the fits obtained, especially to the stimulated photon echo decay, are not very satisfactory. As stated, the reason for the different behaviour of the two solvents may be related to the occurrence of hydrogen bonding in ethylene glycol. Further coherent optical studies of different probe molecules in this and other similar solvents are called for.

What remains to be answered is the physical significance of the Brownian oscillator model; in what way should the overdamped mode be interpreted? One way to address this question is to relate the results presented here to recent molecular dynamics simulations of solvation dynamics [Maroncelli, 1991] and of two pulse photon echoes [Fried et al., 1992]. In these simulations it appears that the time dependence of solvation is mainly due to reorientational motions

of solvent molecules. However, the time scale for solvation-energy relaxation is much faster than the times normally associated with single-particle reorientations (typically in the order of pico- to subnanoseconds). The solvation relaxation process apparently is due to a collective effect of the solvent molecules surrounding the solute. Molecular dynamics simulations therefore strongly suggest that the overdamped Brownian oscillator in the case of resorufin describes the collective effect of the inertial motions of individual DMSO molecules around the solute molecules. While the Brownian oscillator is strongly overdamped (which predicts an unphysical exponential behavior of the oscillator at very short times), the underlying single molecule rotational motions could well be underdamped.

Acknowledgment

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