Femtosecond Non-Markovian Optical Dynamics in Solution

Erik T. J. Nibbering, Douwe A. Wiersma, and Koos Duppen
Ultrafast Laser and Spectroscopy Laboratory, Materials Science Center, University of Groningen,
Nijenborgh 16, 9747 AG Groningen, The Netherlands

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Femtosecond photon-echo experiments on sodium resorufin in dimethylsulfoxide at room temperature show that optical dephasing in solution is of non-Markovian character. A single Gauss-Markov stochastic modulation process is used to interpret both the femtosecond light-scattering results and the steady-state absorption spectrum. The optical dynamics of this system appears to fall in the *intermediate modulation* regime. No evidence was found for contributions of slower dynamical processes to the absorption line breadth.

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In the past decade optical dynamics of molecules in solution has been studied intensively by a variety of nonlinear optical techniques such as resonance Rayleigh scattering,[1,2] polarization spectroscopy,[3] time-resolved hole burning,[4] and recently by femtosecond photon echoes.[5] From the Rayleigh scattering experiments it was inferred that, next to pure dephasing, spectral diffusion gives a separate contribution to the line breadth of the optical spectrum.[1,2] Polarization spectroscopy[3] and transient hole burning[4] confirmed that optical dynamics of molecules in solution is ultrafast. The photon-echo experiments by Becker *et al.*[5] provided the first conclusive evidence, in a real-time experiment, that optical dephasing of a dye molecule in solution proceeds on a femtosecond time scale.

In the analysis of all these experiments[1-5] it was assumed that the optical Bloch equations provide a correct physical basis for a description of the system dynamics. The Bloch equations, however, are only valid if the system-bath interactions can be separated into fast fluctuations, causing *homogeneous* broadening, and slow fluctuations, giving rise to *inhomogeneous* broadening of the relevant transition frequencies. Recently, it was argued[6-8] that optical dynamics in solution cannot be described by the use of the Bloch equations, since the evolution of the system and surrounding bath states may occur on the same time scale. In these circumstances the dynamics of the system is expected to be non-Markovian, which can be modeled by a stochastic approach to the frequency fluctuations of the system.

In this Letter results of femtosecond two-pulse scattering experiments on the molecule sodium resorufin in a solution of dimethylsulfoxide (DMSO) are reported. The experiments are analyzed with a stochastic model for optical dephasing. It is shown that the dynamics of the system falls in the so-called intermediate modulation regime, and that the signal detected may be characterized as a photon echo. From the fact that the absorption spectrum of resorufin can be simulated by the same stochastic model, with the same values for the stochastic parameters, it can be concluded that dephasing is the dominant cause for the breadth of the optical spectrum.

The room-temperature absorption spectrum of resorufin in DMSO is displayed in Fig. 1. It is clear that many vibronic transitions contribute to this spectrum. It has been shown[5] that the optical dynamics of such a system can be explored in a femtosecond transient-grating-type experiment. In these experiments two short optical pulses with wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ excite the system, which responds by emission of a coherent transient in the momentum-matched direction $2\mathbf{k}_2-\mathbf{k}_1$. The timing of the excitation pulses and the signal is shown in Fig. 2. When the Bloch equations hold, the interpretation is straightforward: A photon echo is generated with a maximum in its temporal profile at time $t=t_1$ after the second pulse. In the stochastic case, interferences between fluctuations during times t_1 and t may also cause a rephasing of coherences. The temporal profile of the coherent transient then depends on the parameter values

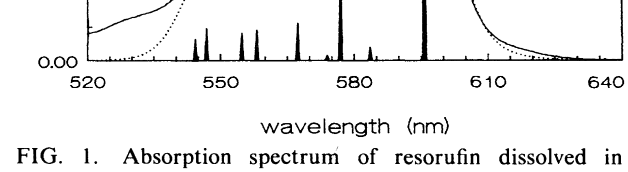

FIG. 1. Absorption spectrum of resorufin dissolved in DMSO (solid line). The dotted line is a fit based on the level structure and transition moments shown below the curve, in black. The line shape is based on Gauss-Markov dynamics with $\Delta=41$ THz and $\Lambda=27$ THz.

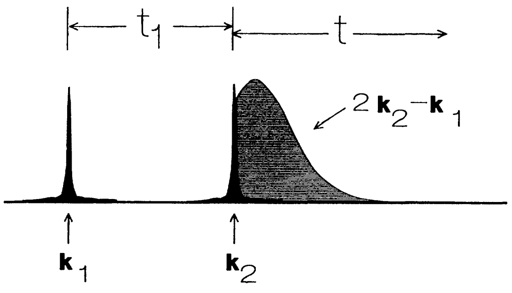

FIG. 2. Timing sequence in a two-pulse transient-grating experiment. The signal scattered in the direction $2\mathbf{k}_2-\mathbf{k}_1$ (shaded area) is a photon echo, calculated using the Gauss-Markov stochastic modulation model with parameter values given in the text.

of the stochastic model.

The experimental setup employed to generate the two-pulse sequence of Fig. 2 consisted of an argon-laser-pumped, colliding-pulse mode-locked laser, amplified by a copper laser at a repetition rate of 8.3 kHz. The amplified pulses were chirped in a fiber and compressed by a set of gratings and four prisms as described by Fork *et al.*[9] The width of the compressed optical pulse was measured in an autocorrelation experiment, using a 150-μm-thick potassium dihydrogen phosphate (KDP) crystal. The pulses crossed at an angle of 4.5° by focusing two parallel beams with a 75-mm lens. With the assumption of a hyperbolic-secant shape, a pulse width (FWHM) of 9 fs was obtained. The spectrum of this pulse, centered at 620 nm, is so broad that its blue side overlaps quite well with the absorption spectrum of resorufin. Below 570 nm the intensity falls rapidly, so the molecular states in that region will be coupled more weakly to the radiation field.

In the femtosecond photon-echo-type experiment, the KDP crystal was replaced by a flowing jet stream of DMSO with a thickness of 60 μm, containing resorufin at a concentration of 10^{-3} mol/liter. The signal in the direction $2\mathbf{k}_2-\mathbf{k}_1$ was detected as a function of the delay between the excitation pulses by a photomultiplier at a considerable distance from the dye jet, to reduce stray light. The current from the photomultiplier was processed by a lock-in amplifier operating at 1.2 kHz.

The result of this femtosecond two-pulse transient-grating scattering experiment on resorufin in DMSO, at room temperature is shown in Fig. 3. The solid line is a fit to the data, which is based on a stochastic model (the stationary Gauss-Markov process) for optical dephasing.[10,11] In this model, the transition frequency between two states of the system is assumed to fluctuate randomly, with excursion $\delta\omega(t)$, around a central frequency ω_0. The correlation function of frequency fluctuations is defined by

$$\langle \delta\omega(t_1)\delta\omega(t_2)\rangle = \Delta^2 \exp\{-\Lambda|t_1-t_2|\} . \qquad (1)$$

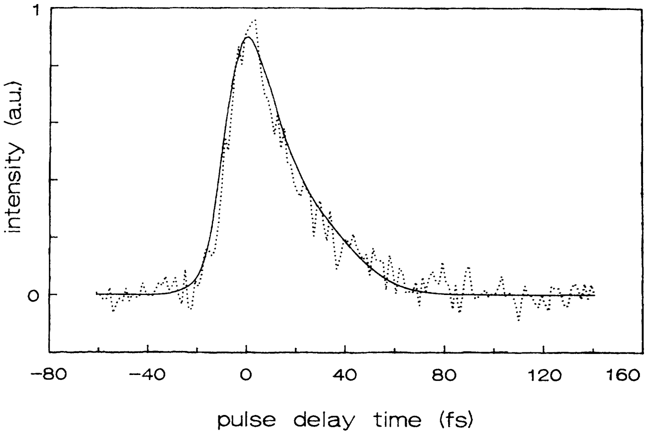

FIG. 3. Photon-echo signal for resorufin dissolved in DMSO (dotted trace). The solid line is a fit based on the Gauss-Markov stochastic modulation model for dephasing, with parameters $\Delta = 41$ THz and $\Lambda = 27$ THz.

Here, Δ is the root-mean-square amplitude of the fluctuations and $\Lambda = \tau_c^{-1}$ is the inverse of the correlation time of the interaction between the system quantum states and the levels of the bath. Loring and Mukamel showed[10] that the time evolution of the macroscopic polarization with wave vector $2\mathbf{k}_2-\mathbf{k}_1$, formed by two ultrashort optical pulses separated by time t_1, is governed by the relaxation function

$$R(t,t_1) = \left\langle \exp\left[-i\left(\int_{t_1}^{t+t_1} \delta\omega(\tau)d\tau - \int_0^{t_1} \delta\omega(\tau)d\tau \right) \right] \right\rangle , \qquad (2)$$

where the angular brackets denote an average over the ensemble of molecules that participate in the superposition state. Equation (2) can be evaluated by the use of a cumulant expansion[10]:

$$R(t,t_1) = \exp[-2g(t) - 2g(t_1) + g(t+t_1)] , \qquad (3)$$

where

$$g(x) = (\Delta^2/\Lambda^2)[\exp(-\Lambda x) + \Lambda x - 1] . \qquad (4)$$

In the fit to the data of Fig. 3, only two transitions of the entire vibronic manifold were taken into account: the 0-0 transition at 16795 cm^{-1} and the vibronic transition at 17340 cm^{-1}. The neglect of all other, less intense, vibronic transitions is permitted because of the nonlinear character of the molecular response. The signal amplitude scales as the fourth power of the transition moment and the third power of the pulse spectral amplitude. Because of the smaller Franck-Condon factors and the spectral distribution of the short pulses, the contribution from all other vibronic transitions is negligible on any part of the decay curve of Fig. 3. Thus, the signal consists of two components which in principle exhibit quantum beats due to interference of the coherences.

The decay curve of the transient-grating scattering signal can now be constructed by (a) summing the two spectral components at frequencies ω_i with a ratio derived from the transition moments μ_i (see discussion on the optical spectrum below); (b) integrating the square of Eq. (3) over t, since the signal is observed at all times; and (c) convoluting (designated by $\otimes$) this signal with the time resolution $T(t_1)$ derived from the autocorrelation. The expression for the signal intensity is thus

$$I(t_1)=\int_0^\infty \left|\sum_{i=1,2}\mu_i^4 e^{i\omega_i t}R(t,t_1)\right|^2 dt\otimes T(t_1)\,. \tag{5}$$

With this equation the parameters Δ and Λ of the correlation function of frequency fluctuations, defined in Eq. (1), were optimized to the decay of Fig. 3: $\Delta=41$ THz and $\Lambda=27$ THz ($\tau_c=37$ fs). These values put the dynamics clearly in the non-Markovian or intermediate modulation regime. Note that it was assumed here that other relaxation processes such as vibrational dephasing or energy relaxation are not effective on the ultrafast time scale of the electronic fluctuations. These assumptions are certainly warranted for resorufin.

The character of the generated coherent transient will now be discussed. By taking the derivative of $R(t,t_1)$ in Eq. (3) with respect to t, one finds that a maximum occurs at $t=\Lambda^{-1}\ln(2-\exp\{-\Lambda t_1\})$. With the parameter values for resorufin the signal profile thus has a distinct maximum for a given value of pulse separation t_1, outside the pulse amplitude itself. It can therefore be classified as a photon echo. As an illustration, the photon-echo profile that was calculated with the parameter values for Δ and Λ from above is displayed schematically in Fig. 2.

Another point worth to be mentioned is that the photon-echo signal, integrated over all t, decays faster than exponential as a function of pulse delay t_1. This is a consequence of the fact that the echo cannot occur for a time delay greater than the correlation time after the second pulse. This illustrates an important aspect of photon-echo formation in the intermediate modulation regime. Rephasing of the macroscopic coherence induced by the second excitation pulse is not due to a static component in the interactions, but is a consequence of interfering fluctuations during times t_1 and t, which is made possible by a finite correlation time between the evolution of the system and the bath.

A description of the optical absorption spectrum of resorufin will be given next. The spectral line shape is the Fourier transform of the impulsive response which, for a single resonance, can be expressed as[12]

$$R(t)=\left\langle \exp\left[-i\int_0^t \delta\omega(\tau)d\tau\right]\right\rangle . \tag{6}$$

Using the cumulant expansion for Eq. (6), one obtains

$$R(t)=\exp\{-g(t)\}\,, \tag{7}$$

with $g(t)$ given by Eq. (4). The envelope of an absorption spectrum consisting of many overlapping vibronic transitions is thus given by the expression

$$I(\omega)=\sum_i \omega\mu_i^2 R(\omega-\omega_i)\,, \tag{8}$$

where $R(\omega)$ is the real part of the Fourier-Laplace transform of $R(t)$ in Eq. (7).

In order to explain the absorption spectrum of resorufin in DMSO with Eq. (8), information concerning vibrational frequencies and Franck-Condon factors is needed. Using the reported vibrational frequencies of resorufin in a glass,[13] an attempt was made to simulate the absorption spectrum with the same values for Δ and Λ as in the photon-echo decay. The only fit parameters were the relative intensities of the vibronic transitions. The dotted trace in Fig. 1 results from this procedure. The line positions and relative intensities are indicated by the sharp structure underneath the spectrum. The vibronic intensities thus found agree well with those of Ref. 13. The hot-band structure around $\lambda=620$ nm was not included in the fit. Also, reliable information about high-frequency vibrations is not available ($\lambda<540$ nm) and hence no attempt was made to fit this part of the spectrum. Altogether, however, we consider the simulated spectrum in excellent agreement with the measured one, indicating that the Gauss-Markov model for ultrafast modulations describes the optical dynamics of resorufin in DMSO remarkably well.

Recently, stimulated femtosecond photon echoes were reported by Bigot *et al.*[14] for the dye molecule nile blue in various protic solvents. It was shown that this system displays fast as well as slow dynamics. This contrasts with resorufin in DMSO where no hint was found for inhomogeneous broadening. From resonance light scattering and absorption line-shape analysis[15] it was found that inhomogeneous broadening is negligible for azulene in isopentane and cyclohexane as well. At this moment we can only speculate about the reasons for the presence or absence of slow modulation effects in the different systems. It is possible that hydrogen bonding among solvent molecules, or between solvent and solute molecules, plays an important role in the system dynamics.

In summary, it was shown that optical dephasing of resorufin in DMSO can be described by using a stochastic modulation model. With Gauss-Markov statistics both the femtosecond photon-echo experiment and the steady-state absorption spectrum can be adequately simulated with the same values for the stochastic parameters. In the first case, the time scale of the experiment is that of the fluctuations themselves, which allows for rephasing of coherences; in the second case the effect of all possible fluctuations is sampled in the frequency domain. The dynamics is shown to fall in the intermediate modulation regime. Three-pulse femtosecond-scattering experiments are planned to further explore dephasing, spectral diffusion, and solvation dynamics in optical transitions of molecules in the liquid phase.

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