Non-Markovian Dephasing of Molecules in Solution Measured with Three-Pulse Femtosecond Photon Echoes

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The electronic dephasing of large molecules in solution is investigated with three-pulse photon echoes generated by 6-fs optical pulses. The observed dephasing behavior, which is analyzed with a model based on a stochastic coupling of the molecules with their heat bath, is clearly shown to be non-Markovian. Moreover, the correlation function of the fluctuations asymptotically approaches an exponential with characteristic times varying from 20 to 80 fs, depending on the solvent environment.

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Ultrafast spectroscopy performed with femtosecond optical pulses has provided important new information on the nature of the optical absorption of large dye molecules in solution. Spectral hole-burning and coherent transient measurements have been used to determine the degree of inhomogeneity of the optical-absorption spectrum and the appropriate statistical description of the molecule in its solvent environment. Hole-burning experiments[1] and two-pulse photon-echo experiments[2] have clearly shown the large molecules Nile Blue and Malachite Green to be inhomogeneously broadened. In this paper we present experimental results and analysis which go beyond the interpretation of the data in terms of a relaxation-time approximation to directly measure the frequency fluctuation correlation function with a three-pulse photon-echo technique using 6-fs optical pulses.

Weiner, Silvestri, and Ippen[3] have previously attempted to measure a three-pulse photon echo using pulses an order of magnitude longer than those used in this experiment, but were unable to resolve the polarization dephasing. Rosker, Wise, and Tang[4] and Chesnoy and Mokhtari[5] have observed what they term "quantum beats" using transient absorption spectroscopy. Although these experiments were originally interpreted in terms of coherence between electronic levels in the dye molecules, recent measurements[6] and theory[7] have shown that the observed oscillations are the result of wave-packet motion brought about by the coherent excitation of the manifold of vibrational levels. Most recently, Nibbering, Duppen, and Wiersma[8] studied optical dephasing in solution using line-shape analysis and resonance light-scattering measurements.

We use femtosecond optical techniques to study the interactions of the dye molecule with its environment and the mechanisms responsible for the loss of electronic coherence. Such interactions may be explicitly analyzed by molecular-dynamic simulations, but usual tractable models collect all the degrees of freedom of the solute and solvent into a coupling with a thermal bath. With this type of description, the dephasing behavior of the molecules is determined by the statistical properties of the molecule–heat-bath coupling. The simplest model of a dephasing process assumes that the correlation time τ_c of the fluctuations of the molecule electronic gap is much shorter than T_2 (the limit $\tau_c = 0$ corresponds to the particular Markovian case of a δ-correlation function). In general, the statistics are more complicated and may or may not show memory effects in the heat bath.[9] These concepts have been explored extensively in the magnetic-resonance literature.[10,11]

In this paper, we use three-pulse photon-echo measurements to directly extract the shape and amplitude of the correlation function of Nile Blue molecules in solution. The results show that the underlying dynamics are non-Markovian, with correlation times on the order of 100 fs. Furthermore, the dephasing dynamics are shown to be solvent dependent. We first develop a theoretical model based on stationary Gaussian-correlated fluctuations between the molecules and their heat bath. We then describe the experimental configuration and discuss the results.

Following Kubo's spectral line-shape theory,[12] we model the random force exerted on the molecules as a stochastic modulation of the frequency difference between two inhomogeneously broadened levels (the ground and excited potential surfaces of the molecule):

$$\omega_0(t) = \omega_0 + \delta\omega(t)\,, \tag{1}$$

where ω_0 is the static resonant frequency and $\delta\omega(t)$ a stochastic modulation. Related descriptions have been used previously to describe the hole-burning process of molecules in solution.[13] For the sake of simplicity, we assume[14] that the heat bath is affecting the molecular system but not the reverse and that it does not perturb the coherent vibronic motion of the molecule. The time dependence of the electronic polarization $P(t)$ of the two-level system is described by the density matrix and the Bloch equations, assuming a dipole interaction with an electric field of amplitude $E(t,r)$ and frequency ω.

Within the rotating-wave approximation up to third order in time, we get

$$P^{(3)}(t) \propto \int_{-\infty}^{t} dt'\, E(t')\, e^{i[\Omega(t)-\Omega(t')]} \int_{-\infty}^{t'} dt'' \left[E^*(t'') \int_{-\infty}^{t''} dt'''\, E(t''')\, e^{i[\Omega(t'')-\Omega(t''')]} + \text{c.c.} \right] e^{-(t'-t'')/\tau_1}\,, \tag{2}$$

with

$$\Omega(t)=(\omega_0-\omega)t+\int_0^t \delta\omega(u)du\,.$$

The population lifetime τ_1 is much longer than the time scale of the random fluctuations of the resonant frequency $\omega_0(t)$ and will be neglected in the following.

The energy S radiated by the dipoles, for which we assume an inhomogeneous distribution $g(\omega_0)$ of their central frequency ω_0, is finally given by[14]

$$S=\int_0^\infty dt\left|\int_{-\infty}^{\infty} d\omega_0 g(\omega_0)\langle P^{(3)}(t)\rangle\right|^2, \qquad (3)$$

where $\langle P^{(3)}(t)\rangle$ is the statistical ensemble average of the third-order polarization.

In order to evaluate the influence of the heat bath one has to average the polarization over the statistical ensemble in which $\delta\omega(t)$ is distributed. If we assume a stationary Gaussian stochastic process, not necessarily Markovian, we can carry out analytical calculations using the fact that only the second-order correlation function of the stochastic variable is different from zero with

$$C^{(2)}(t+t',t')=\langle\delta\omega(t+t')\delta\omega(t')\rangle=C(t)\,. \qquad (4)$$

The Gaussian nature of the modulation, in the case of interactions in a liquid, is well justified by the central-limit theorem since there are many degrees of freedom in the system. In the case of photon echoes produced by three δ-function pulses, the polarization in the direction $k_1+k_3-k_2$ is given by

$$\langle P^{(3)}(t)\rangle \propto e^{-i(\omega_0-\omega)(t-T-\tau)}M(t)\,, \qquad (5)$$

where τ is the temporal delay between pulses 1 and 2 ($\tau<0$) and T is the delay between pulses 1 and 3 ($T>0$). The total moment[10] $M(t)$ is found to be

$$M(t)=\frac{\Phi(|\tau|)\Phi(T-\tau)\Phi(t)\Phi(t-T)}{\Phi(T)\Phi(t-\tau)}\,, \qquad (6)$$

with

$$\Phi(t)=\exp\left[-\tfrac{1}{2}\int_0^t dt_1\int_0^t dt_2 C(t_2-t_1)\right]$$
$$=\exp\left[-\int_0^t (t-\tau)C(\tau)d\tau\right]\equiv\exp[-\Psi(t)]\,. \qquad (7)$$

The function $\Psi(t)$ defined in Eq. (7) contains the quantities of interest for the photon-echo experiment and is simply related to $C(t)$ through $d^2\Psi/dt^2=C(t)$. In the following we will assume that $C(t)$ converges fast enough to zero when $t\to\infty$ so that $\int_0^\infty C(t)dt=\Gamma$ is defined [then $\tau_c=\Gamma/C(0)$ is the usual definition of the correlation time]. In the case when the correlation is a δ function, Γ is equal to the inverse of the polarization dephasing time T_2.

If we assume infinite inhomogeneous broadening, i.e., $g(\omega_0)=1$, we obtain using Eqs. (6), (7), and (3) the dependence of the logarithm of the photon-echo signal on the different delays $\tau<0$ and $T>0$:

$$\ln S(\tau,T)=\ln K^2-4\Psi(-\tau)$$
$$+2[\Psi(T)+\Psi(T-2\tau)-2\Psi(T-\tau)]\,, \qquad (8)$$

where K is constant. Note that, due to time ordering in Eq. (2) and the assumption $g(\omega_0)=1$, the signal S is equal to zero for $\tau>0$. Before we discuss further the physical information contained in Eq. (8), let us describe the experimental setup.

We measure three-pulse photon echoes from Nile Blue dye molecules in solution. The echoes are produced using 6–8-fs optical pulses generated in a manner described previously.[15] The beam is split into three parts which are focused in a thin jet of solvent in which the Nile Blue molecule has been dissolved. Measurements are made with different solvents, as discussed below, and in each case the solute concentration was adjusted to give a 30% transmittance at the peak absorption wavelength. The total pulse bandwidth (160 nm centered at 620 nm) covers the dye absorption spectrum. The photon-echo signal is detected in the direction $k_1+k_3-k_2$ as a function of the relative delay τ between pulses 1 and 2 or as a function of the relative delay T (>0) between pulses 1 and 3. In all measurements the pulse energy is such that the echoes can be described in the perturbation limit, and we observe no intensity dependence of the decay times. Two types of measurements are performed which we detail in the following.

In a first set of measurements, the delay τ is varied, while T is kept constant. Under these conditions, it is possible to determine the asymptotic value Γ defined previously. It is easily shown that when $t\to\infty$, and for any delay T, the expression (8) converges asymptotically towards

$$\ln S(\tau,T)=4\Gamma\tau+\text{const},\quad \tau<0\,. \qquad (9)$$

In Fig. 1 we show the logarithm of the echo signal obtained from the molecule Nile Blue in ethylene glycol, measured in the direction $k_1+k_3-k_2$ for different fixed delays T of 0, 40, and 90 fs. In each case the long-delay behavior displays the same 15-fs slope, as expected from Eq. (9). In order to compare this result with the case of two-pulse photon echoes,[2] we checked that the signal observed in the direction $2k_1-k_2$ was identical to the case $T=0$. We therefore deduce a constant $1/\Gamma$ of 60 fs. This value (which as previously stated would strictly correspond to the dephasing time T_2 for a δ-correlated Markovian process) is on the order of the inverse homogeneous linewidth deduced from hole-burning experiments performed in a similar oxazine dye.[1]

It is worth pointing out that when T is increased in Eq. (8) one obtains a family of curves $\ln S(\tau,T)$, which converge to a curve given by

$$\lim_{T\to\infty}\ln S(\tau,T)=\ln K^2-4\Psi(-\tau),\quad \tau<0\,, \qquad (10)$$

whose linear asymptotic behavior is in contrast with a spectral cross-relaxation model as described in Ref. 3. Additional information is contained in Fig. 1. As stated earlier the asymmetry of the three-pulse echo signal is a clear signature of the inhomogeneous broadening of the

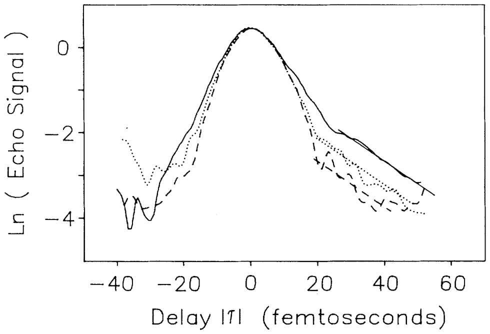

FIG. 1. Logarithm of the photon-echo signal from the molecule Nile Blue dissolved in ethylene glycol as function of the relative delay τ for different delays T. Solid line, $T=0$ fs; dotted line, $T=40$ fs; dashed line, $T=90$ fs.

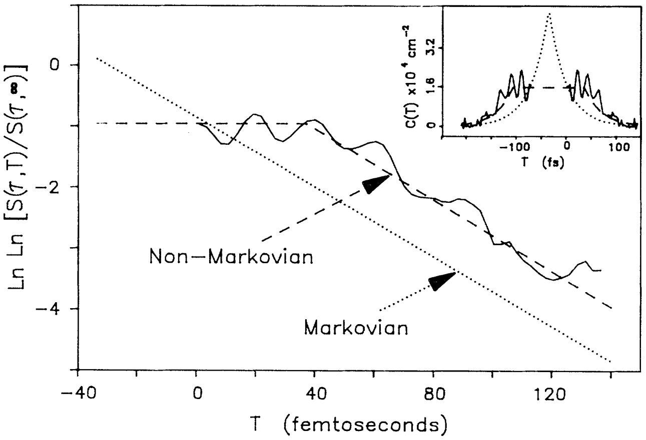

FIG. 2. Experimental correlation function measured for times longer than 35 fs (solid line) obtained for the solvent ethylene glycol. The measured signal as a function of delay T between pulses 1 and 3 is processed following Eq. (12) and plotted on a logarithmic scale. The dotted line corresponds to the Ornstein-Uhlenbeck correlation function and the dashed line represents the best fit using Eq. (13). Inset: The correlation function $C(T)$ obtained by symmetrizing the signal around $T=-35$ fs. The plateau corresponds to a frequency excursion of 400 cm^{-1}. All the theoretical curves follow the requirement that their integral over $-\infty$ to $+\infty$ is equal to 2Γ.

Nile Blue molecule in solution, confirming our initial assumption $[g(\omega_0)=1]$. The same signal would be symmetric (for $|\tau|<T$) if the entire absorption line were homogeneously broadened. This distinction between homogeneous and inhomogeneous broadening cannot be made with two-pulse photon echoes since in this case both signals are asymmetric with respect to τ.[3,16]

In a second set of measurements, the delay T is varied, τ being kept constant. While varying τ yields only the integral Γ, we find that varying T provides additional information about the correlation function $C(t)$. This is obtained by noticing that, for a given correlation function, the quantity

$$\ln S(\tau,T)-\ln S(\tau,\infty)$$
$$=2[\Psi(T)+\Psi(T-2\tau)-2\Psi(T-\tau)] \qquad (11)$$

is fixed with no free parameters. Using a Taylor-series expansion we obtain

$$\ln S(\tau,T)-\ln S(\tau,\infty)$$
$$=2\tau^2 C(T-\tau)+O((\tau/\tau_c)^4)\,. \qquad (12)$$

In Fig. 2, we show the echo signal from Nile Blue processed according to the right-hand side of expression (11) and taking the logarithm as a function of the delay T and for a delay τ set at -35 fs. The coherent part of the signal at time $T=0$ has been removed from these experimental data. Using Eq. (12) we see that the measured signal divided by $2\tau^2$ is strictly equal to the correlation function shifted in time by the quantity τ. $C(t)$ is undetermined only in a small region of time $[0,\tau]$ but can, however, be estimated in this domain because we know from Eq. (9) the total area Γ under $C(t)$. As seen in Fig. 2 for delays T longer than 30 fs the decay is exponential with a corresponding slope $\tau_a=35\pm5$ fs. This shows that $C(t)$ asymptotically approaches an exponential, $\exp(-t/\tau_a)$. The measured correlation function (inset to Fig. 2) also shows oscillations with periods of 20 and 60 fs, which are related to the coherent motion of the molecule. These vibronic modes, which we neglected in the theoretical model, have been extensively studied before.[2,6,7] They do not affect the main properties of the correlation function in which we are interested in this work.

The experimentally deduced correlation function shown in Fig. 2 clearly reveals that the coupling between the molecules and their heat bath is not δ correlated. The next simplest model could assume the stochastic frequency modulations to be Markovian. As is well known, the Ornstein-Uhlenbeck process[17] is the only one-variable stationary Gaussian-Markov process for which the asymptotic decay time τ_a is equal to the correlation time τ_c. The corresponding correlation function $\Gamma\tau_c^{-1}\times\exp(-t/\tau_c)$ would then be given by the dotted curve in Fig. 2 which clearly does not fit the experimental results. In order to fit the experimental correlation function, one must therefore assume that the modulation is non-Markovian. A very simple correlation function which fits the data (dashed line in Fig. 2) is a truncated exponential,

$$C(t)=\frac{\Gamma}{\rho+\tau_a}\times\begin{cases}1 & \text{for } |t|<\rho\,,\\ e^{-(|t|-\rho)/\tau_a} & \text{for } |t|>\rho\,,\end{cases} \qquad (13)$$

with $\rho=70$ fs and $\tau_a=35$ fs and $\tau_c=\rho+\tau_a=105$ fs. In good agreement with the inhomogeneous nature of the absorption line, the frequency excursion $(\Gamma/\tau_c)^{1/2}\sim12$

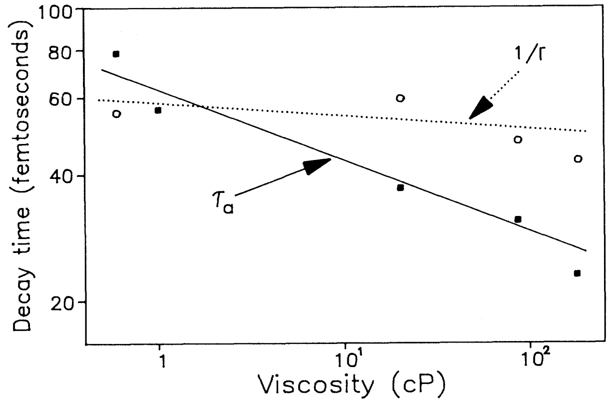

FIG. 3. Asymptotic decay time τ_a (squares and solid line) and exponential decay time $1/\Gamma$ (circles and dotted line) of the molecule Nile Blue as a function of the solvent viscosity on a log-log scale.

THz or 400 cm^{-1} is about 10% of the total absorption bandwidth of the molecule. This frequency excursion is consistent with previously reported spectral hole-burning experiments.[1] Note that in Fig. 2 any smooth function which does not depart too much from the one defined in Eq. (13) will also be suitable. Note also the distinction we make here between the non-Markovian decay of the polarization and the non-Markovian interaction with the heat bath. The former case just implies that the correlation function is not a δ function. The latter case which excludes the generally assumed Ornstein-Uhlenbeck stochastic model[13] corresponds to our observations and implies some memory in the heat bath.[9]

The question arises now to determine the origin of the fluctuations $\delta\omega(t)$, a problem which we partially addressed by changing the solvent environment. We have repeated a set of measurements of the two quantities $1/\Gamma$ and τ_a with the molecule Nile Blue in methanol, water, and two mixtures of glycerol and methanol containing, respectively, 60% and 70% glycerol molecules. In Fig. 3 we have plotted $1/\Gamma$ and τ_a versus the viscosity η of the solvent on a log-log scale. The straight lines indicate that the quantity $1/\Gamma$ (i.e., the area of the correlation function) is nearly constant while the asymptotic decay time τ_a varies as $\eta^{-0.16}$. The shorter asymptotic decay times τ_a, obtained with the more viscous solvents, indicate that the solvent-solute interactions play a fundamental role in perturbing the electronic polarization on a very short time scale. More precisely, a short decay time means that the spectrum of the stochastic perturbation acting on the molecules extends to higher frequencies. Therefore our results suggest that highly viscous solvents transmit high-frequency perturbations better than low viscous solvents. A full description of our measurements would require a microscopic theory of the solute-solvent interactions, or a dynamic molecular simulation, which are beyond the statistical description adopted here.

In conclusion, we have derived a method to directly measure the correlation function of molecules interacting with their solvent based on three-pulse photon echoes and applied it to Nile Blue molecules in solution. Assuming that the fluctuations in the molecule-heat-bath interactions follow stationary Gaussian statistics, we have been able to demonstrate that the stochastic perturbation is non-Markovian. The different decay times ($1/\Gamma$ and τ_a) obtained with different solvents show that the fluctuations are strongly dependent on the liquid environment. We foresee that this method should apply to a great variety of media.

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