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# Effects of spectral diffusion in incoherent photon-echo experiments

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The application of the incoherent photon-echo experiment to complex systems is analyzed. In systems in which spectral diffusion occurs, incoherent echo measurements do not yield the same optical dephasing rate as conventional two-pulse photon-echo measurements. The difference can be of major significance. To make the calculations explicit, optical dephasing in a glass is considered using the tunneling two-level system model.

Since first being observed in 1983,[1-3] the incoherent photon echo has been generating a great deal of interest as a new technique for the study of ultrafast optical dephasing phenomena.[4] In an incoherent photon-echo experiment, the laser field is purposely made to be non-Fourier-transform-limited. The time resolution is determined by the correlation time of the light source, $\tau_c$, i.e., the inverse of its frequency bandwidth. Thus ultrahigh time resolution can be achieved by increasing the laser frequency bandwidth. It is frequently mentioned in the literature that as long as $\tau_c$ is much shorter than the sample's phenomenological dephasing constant $T_2$ the incoherent photon echo measurement will yield the same dephasing time as that measured by the two-pulse photon echo[5] using ultrashort coherent laser pulses.

While a good deal of attention has been focused on the excellent time resolution of the new technique, little effort has been made to clarify what this technique actually measures when performed on complex systems. A central feature has been overlooked. Since the method is essentially an accumulated echo technique,[6] it is inevitably associated with a long characteristic time scale. The time scale is long compared to the delay time between the two laser beams, which is usually considered the time scale of the experiment. This makes the incoherent photon echo sensitive to spectral diffusion, i.e., slow frequency modulations which appear static to and are rephased by a two-pulse photon echo.

Spectral diffusion is induced by relatively slow environmental fluctuations, such as the spin flips in a crystal lattice[7,8] or two-level system dynamics in an atomic or molecular glass.[9,10] The rates of these fluctuations are comparable to or slower than what is generally defined as the homogeneous dephasing rate $1/T_2$. The effects of spectral diffusion on the two-pulse echo and the three-pulse stimulated echo are drastically different.[7-10]

Here we discuss the dephasing of an ensemble of chromophores embedded in a glassy system where, at very low temperatures, the environmental fluctuations are attributed to tunneling between levels of the glass's two-level systems[11,12] (TLS). Previous investigations have shown that in such systems spectral diffusion plays an important rule in optical dephasing.[13-16] A significant difference between the dephasing rates measured with photon-echo and hole-burning experiments has been observed.[17] (Similar observations were made in doped crystals.[18]) By considering the dynamic properties of the TLS and their interactions with the chromophores in some detail, it will be proven that the incoherent photon-echo measurement generally results in an optical dephasing rate differing from that given by the two-pulse photon-echo measurement. The incoherent echo dephasing rate can be considerably faster than that measured by a photon echo.

In an incoherent photon-echo experiment, an input laser field is split into two beams which are crossed in the sample. The second beam is delayed from the first by a time interval $\tau$ so that $E_1(t)=E(t)$, $E_2(t)=E(t-\tau)$, and $\mathbf{k}_2\neq\mathbf{k}_1$. The echo signal is detected along a direction $\mathbf{k}_s=2\mathbf{k}_2-\mathbf{k}_1$. To the third order in the input field strength, the echo polarization can be written as[19]

$$P(k_s,t)\propto -i\int_0^\infty dt_1\int_0^\infty dt_2\mathcal{R}(t_1,t_2)E^*(t-t_2-2t_1)\times E(t-t_2-t_1-\tau)E(t-t_1-\tau)\,, \tag{1}$$

where $\mathcal{R}$ is the nonlinear response function that contains the necessary information about the sample.

The chromophore is modeled as having three levels. Level $a$ represents the ground electronic state and level $b$ the excited electronic state. Level $b$ decays to levels $a$ and and $c$ at rates $\gamma_{ba}$ and $\gamma_{bc}$, respectively. Its total decay rate is $\gamma_b=\gamma_{ba}+\gamma_{bc}$. Level $c$ is a triplet or other transient intermediate state which decays to the ground state at a rate $\gamma_{ca}$. Optical transitions only occur between levels $a$ and $b$. The transition frequency of the chromophore outside the glassy matrix is $\omega_{ab}$. The matrix causes a shift in the transition frequency $\Delta$ that can be split into two parts, $\Delta=\Delta_0(S)+\Delta(t)$. $\Delta_0(S)$ is caused by a set of coordinates $S$ that are static on all relevant time scales and can be treated as inhomogeneous broadening of the system. The time-dependent detuning $\Delta(t)$, however, is caused by the set of coordinates $D$ that fluctuate within the time scale of the experiment. The distribution of the fluctuation rates can span a very wide temporal range. In the problem considered here, $D$ is a set of TLS in the glass.

 

With this model, the nonlinear response function can be calculated.[17,19] After an average over the inhomogeneous broadening, the response function becomes

$$\mathcal{R}(t_1,t_2)=\mu^4\rho A(t_2)\exp(-\gamma t_1)C(t_1,t_2,t_1)\ , \tag{2}$$

$$A(t_2)=2e^{-\gamma_b t_2}+\phi_c(e^{-\gamma_{ca}t_2}-e^{-\gamma_b t_2})\ , \tag{2a}$$

$$C(t_1,t_2,t_1)=\left\langle \exp\left[i\int_0^{t_1}\Delta(t')dt'-i\int_{t_2+t_1}^{t_2+2t_1}\Delta(t')dt'\right]\right\rangle_D\ , \tag{2b}$$

where $\langle\rangle$ denotes an ensemble average over the TLS. In averaging over the inhomogeneous broadening, we have assumed that $\Delta_0(S)$ is uncorrelated with $\Delta(t)$. The number of chromophores is taken to be uniformly distributed with a density $\rho$ over the laser frequency bandwidth. This is a reasonable assumption for the very broad inhomogeneous lines encountered in chromophore-glass systems.

The first term in Eq. (2a) describes the effect of the excited-state population decay on the echo signal. The second term describes the accumulation of a population grating in the ground state from a net transfer of population from the ground state to the triplet state, the "bottleneck" state. This term decays with the triplet lifetime $1/\gamma_{ca}$ and has an amplitude given by the triplet yield $\phi_c=\gamma_{ca}/\gamma_b$. A population grating will also accumulate in the ground state due to transfer of population to the excited state $b$ if the dephasing is rapid compared to the excited-state lifetime $1/\gamma_b$. This component of the accumulated grating will decay with the excited-state lifetime. If the grating is accumulated only by transfer of population to the excited state $b$ the excited-state lifetime is the sample's "memory time." If the grating is accumulated in a bottleneck state, then the lifetime of the bottleneck state is the sample's memory time.

The four-point correlation function (Refs. 17 and 19), $C(t_1,t_2,t_1)$, describes the dephasing measured by a stimulated photon echo if we take $t_1$ as the time delay between the second and the first pulse, $t_{21}$, and $t_2$ the time delay between the third and the second pulse, $t_{32}$. The limit $t_2=0$ gives the two-pulse photon-echo correlation function.

To resolve the optical dephasing in an incoherent photon-echo experiment, the correlation time of the laser field must be very short compared to the temporal variation of $\mathcal{R}(t_1,t_2)$, $|\mathcal{R}/\tau_c|\gg|d\mathcal{R}/dt_2|$, $|d\mathcal{R}/dt_1|$. In this case the correlation function of the laser field can be replaced by a $\delta$ function,

$$g(t_1-\tau)=\tau_c\delta(t_1-\tau)\ . \tag{3}$$

By substituting Eqs. (2) and (3) into Eq. (1), we can rewrite Eq. (1) as

$$P(k_s,t)\propto -i\mu^4\rho\tau_c E(t-2\tau)\exp(-\gamma_b\tau)\times\int_0^\infty dt_2\langle|E(t-t_2-2\tau)|^2\rangle A(t_2)C(\tau,t_2,\tau)\ . \tag{4}$$

Equation (4) demonstrates that the incoherent photon echo is the sum of a series of stimulated photon echoes with a constant $t_{21}=\tau$, and variable $t_{32}$'s, $0<t_{32}<t_{\max}$, where $t_{\max}$ is given either by the laser pulse duration or by the memory time of the sample, whichever is shorter.

To evaluate the correlation function $C(\tau,t_2,\tau)$, we follow Refs. 15, 17, and 19. The fluctuations of the TLS are modeled by a Gaussian-Markoffian stochastic process[17] so that the transition frequency perturbation of the chromophores induced by the fluctuations obeys

$$\langle\delta\Delta(t)\delta\Delta(t')\rangle=\langle\delta\Delta^2\rangle\exp(-R|t'-t|)\ ,$$

where $\delta\Delta=\Delta-\langle\Delta\rangle$ is the deviation of the perturbation from its equilibrium value, and $R$ is the fluctuation rate which is distributed over a broad range. Theoretical analysis of photon-echo experiments and optical hole-burning experiments in glasses, which yield exponential decays and Lorentzian lines, respectively, demonstrates that the amplitude of the perturbation of a chromophore induced by a single fluctuating TLS is proportional to the cube of the inverse of the distance between the chromophore and the TLS.[15,17] This is consistent with either a strain-dipole or an electric-dipole coupling mechanism. Thus the averages over the stochastic histories of the perturbation and the spatial positions of the TLS yields

$$C(\tau,t_2,\tau)=\exp[-\alpha\tau\langle\sigma\Delta\langle f(R\tau,Rt_2)\rangle_R\rangle_\Delta]\ , \tag{5}$$

$$f(R\tau,Rt_2)=(\sqrt{2}/R\tau)\{\exp(-R\tau)-1+R\tau-\exp[-R(t_2+\tau)][\cosh(R\tau)-1]\}^{1/2}\ , \tag{5a}$$

where $\alpha=\frac{4}{3}\pi^{3/2}\rho_G$, $\rho_G$ is the density of the TLS, and $\sigma$ is the relative deviation of the fluctuation, $\sigma^2=\langle(\delta\Delta)^2\rangle/\Delta^2$. The bistable nature of the TLS suggests that $\sigma^2=4p(1-p)$, where $p$ is the probability of finding the TLS in its excited state.

We note that Eq. (5) reflects a general feature of optical dephasing in the presence of spectral diffusion. Since $f(R\tau,Rt_2)$ is essentially a constant between $R=(t_2+\tau)^{-1}$ and $R=\tau^{-1}$,[17] all fluctuations whose rates fall into this range contribute to the dephasing. For different systems, the fluctuation rate distributions can vary, and the dephasing rate can relate to the average in a different manner. However, it remains true that the total optical dephasing rate is governed by a summation over a fluctuation rate distribution with a weight function slowly varying in the range of $((t_2+\tau)^{-1},\tau^{-1})$.

The distributions of the perturbation amplitudes, $\Delta$, and the fluctuation rates, $R$, can be related to the standard TLS model, which is defined by the TLS energy splitting $E$, and the tunneling parameter $\lambda=d(2MV/\hbar)^{1/2}$. $d$ is the distance of the tunneling motion, $M$ is the reduced mass of the tunneling particles, and $V$ is the height of the TLS potential barrier. To make the connection between these parameters, we assume the following: (a) The perturbation amplitude is independent of $E$ and $\lambda$, and (b) the fluctuations of the TLS are caused only by resonant

single phonon assisted tunneling processes.[11,12] The fluctuation rate is equal to the relaxation rate towards equilibrium, $R=\Omega E\coth(E/2kT)e^{-2\lambda}$, where $\Omega$ is a collection of constants describing the coupling of the TLS to the acoustic phonons of the glass.

In equilibrium, the probability of finding the TLS in its excited state is $p=\exp(-E/kT)/[1+\exp(-E/kT)]$, which yields $\sigma=\mathrm{sech}(E/2kT)$. Thus, the average in Eq. (5) becomes

$$\langle\sigma\Delta\langle f\rangle_R\rangle_\Delta=\Delta\int_0^\infty dE\,P(E)\,\mathrm{sech}(E/2kT)\times\int_0^\infty dR\frac{P(\lambda)f}{2R}\ , \tag{6}$$

where $P(E)$ and $P(\lambda)$ are the distributions of $E$ and $\lambda$, respectively. Following the common assumptions that $P(\lambda)=P_\lambda$ is a constant between $\lambda_{\max}\geq\lambda\geq\lambda_{\min}(E)$ (Refs. 11 and 12) and $P(E)=P_EE^\mu$ between $E_{\max}\geq E\geq E_{\min}$,[14] we find that the fluctuation rate distribution function is in the form of $1/R$ over a range $(R_{\min},R_{\max})$, with

$$R_{\min}=\Omega E\coth(E/2kT)\exp(-2\lambda_{\max})\ ,$$

$$R_{\max}=\Omega E\coth(E/2kT)\exp(-2\lambda_{\min})\ .$$

Noting that the dominant part of the first integral in Eq. (6) is within $E\leq 2kT$ and that $R_{\min}$ is insensitive to $E$ in this range, we replace the limits in the second integral by $R_{\min}\rightarrow 2kT\Omega\exp(-2\lambda_{\max})$ and $R_{\max}\rightarrow 2kT\Omega\times\exp[-2\lambda_{\min}(E)]$. If we further assume $R_{\max}(2kT)\gg 1/\tau$, we can treat the two integrals independently,[14]

$$C(\tau,t_2,\tau)=\exp\left[-\beta\tau\int_{R_{\min}}^{R_{\max}}dR\,\frac{f(R\tau,Rt_2)}{R}\right]\ , \tag{7}$$

$$\beta=a\Delta(kT)^{1+\mu}P_\lambda P_E\int_0^\infty dx\,x^\mu\,\mathrm{sech}(x/2)\ , \tag{7a}$$

where $R_{\max}=R_{\max}(2kT)$, $x=E/kT$, and we have assumed $E_{\max}\gg kT\gg E_{\min}$.

In the $\ln(R)$ scale, the relaxation distribution function is a constant. Thus one can evaluate the integral simply by examining the behavior of the function $f(R\tau,Rt_2)$ in the $\ln(R)$ scale. For $t_2=0$, $f(R\tau,0)$ is a narrowly peaked function centered about $\ln(R\tau)=0$. If the entire peak lies within the range $(R_{\min},R_{\max})$, we can safely change the integral limits to $(0,\infty)$ and perform the integration. As a result, the two-pulse photon-echo correlation function becomes an exponentially decaying function,

$$C(\tau,0,\tau)=\exp(-\beta\Theta\tau)\ , \tag{8}$$

$$\Theta=\int_0^\infty dx\,\frac{f(x,0)}{x}\simeq 3.6\ . \tag{8a}$$

Experimentally, it is found that two-pulse photon-echo signal decays exponentially in many glasses.[14,17] This indicates that in these systems, the relaxation distribution function is indeed in the form of $1/R$ for $R\gg R_{\min}$, which is consistent with the assumption made following Eq. (6).

In general, we can write

$$C(\tau,t_2,\tau)=C(\tau,0,\tau)C_1(\tau,t_2,\tau)\ , \tag{9}$$

where $C_1$ is the correlation function which describes the dephasing arising from the spectral diffusion.[17] The function $f(R\tau,Rt_2)-f(R\tau,0)$ can be replaced by a step function[17,20]

$$f(R\tau,Rt_2)-f(R\tau,0)\simeq H(R-1/(\tau+t_2))H((1/\tau)-R)\ . \tag{10}$$

Using this approximation and knowing that $R_{\max}>1/\tau$, we can carry out the integral in Eq. (7) letting the limits be 0 to $\infty$. The correlation function $C_1$ then becomes

$$C_1(\tau,t_2,\tau)\simeq\exp[-\beta\tau\ln(t_c/\tau)]\ , \tag{11}$$

where $t_c=\min(\tau+t_2,1/R_{\min})$. Thus the final expression for the incoherent photon-echo polarization becomes

$$P(k_s,t)\propto i\mu^4\rho\tau_cE(t-2\tau)\exp[-(\gamma_b+\beta\Theta)\tau]\times\int_0^\infty dt_2\,\frac{\langle|E(t-t_2-2\tau)|^2\rangle A(t_2)}{(t_c/\tau)^{\beta\tau}}\ , \tag{12}$$

where the integral describes an extra dephasing factor caused by spectral diffusion.

Now we consider a concrete example. Let $\beta\Theta=(2\ \mathrm{ps})^{-1}$, the laser pulse duration, $\Delta t=10$ ns, and $1/\Delta t>\gamma_b$, $\gamma_{ca}$, $R_{\min}$. Substituting these numbers into Eq. (12), we find the extra dephasing factor $\simeq[(1-\beta\tau)(1+\Delta t/\tau)^{\beta\tau}]^{-1}$. Thus the ratio between the dephasing rate measured by the incoherent photon echo and that measured by the two-pulse photon-echo experiment is approximately

$$\{\Theta+[\ln(\Delta t\beta\Theta)-1]\}/\Theta\simeq 3\ .$$

In general, our calculations predict that an incoherent photon-echo experiment always measures a dephasing rate larger than that measured in a two-pulse photon-echo experiment by a factor of $\ln[(\beta\Theta+\gamma_b)t_{\max}]$, where $t_{\max}$ is defined to be the shorter of the laser pulse duration and the sample's memory time. When $t_{\max}>1/R_{\min}$, the factor is given by $\ln[(\beta\Theta+\gamma_b)/R_{\min}]$. These detailed predictions are based on the assumption of a constant tunneling parameter distribution in the TLS model. Although this assumption may not be true in general, the fundamental conclusion that the incoherent photon echo measures larger dephasing rates than a two-pulse photon echo will hold for glasses and other systems with broad relaxation rate distributions such as complex crystals[18] or proteins.[21] Moreover, by varying $t_{\max}$, which could be accomplished by choosing a system with a long "bottleneck" lifetime and varying the laser pulse duration, one can experimentally map out the relaxation rate distribution and the tunneling parameter distribution.

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