ELSEVIER

25 February 1994

Chemical Physics Letters 218 (1994) 445–453

CHEMICAL PHYSICS LETTERS

Low-temperature dynamics in glasses and the stochastic sudden-jump model

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Received 5 November 1993

Abstract

Non-linear optical experiments in glasses exhibiting spectral diffusion give strong support for the importance of two-level system excitations (TLS). The difference in the line widths measured by these experiments and fast two-pulse photon echo experiments has been ascribed to slowly relaxing TLS. The sudden jump model is found to be an appropriate description of the dynamics; within this model, we derive new analytical results for three-pulse experiments at all temperatures. These experiments and the dynamics of TLS in glasses are discussed within the context of these results.

1. Introduction

The standard description of a glass as a random array of two-level systems (TLSs), proposed by Phillips [1] and Anderson et al. [2] to explain low-temperature acoustic and thermal properties of disordered materials, has recently received some support from optical experiments. Several groups [3–6] have reported the presence of spectral diffusion, detected by hole-burning spectroscopy (HB) and three-pulse photon echo (3PE) experiments performed on a chromophore embedded in a glassy matrix. For some glasses, these experiments yield an effective homogeneous linewidth that is larger than the "true" homogeneous linewidth obtained, for instance, by a two-pulse photon echo (2PE) experiment. These two different results can be explained by arguing that the 2PE experiment is a one time scale experiment (namely, the time scale given by the delay between the two pulses, which is of the order of nanoseconds, the order the inverse of the linewidth measured), whereas both HB and 3PE experiments possess a second time scale (the delay between the burning and the reading pulse – from microseconds to hours – in HB, and the delay between the second and the third pulses – from nanoseconds to seconds – in the 3PE experiment). The effective linewidth measured in the latter experiments has contributions from dynamical processes occurring in the surrounding media during this second time scale. These processes induce fluctuations in the frequency of the chromophore and lead to dephasing [7].

It is now widely believed that the fluctuations of the media can be described in terms of the dynamics of a random array of TLSs, which are coupled to the chromophore via the phonon field.

In this Letter, we shall investigate a model where the frequency of chromophore contains a fluctuating part made up of contributions from each TLS, assuming that the distribution of TLSs is uniform throughout the glass and that they interact with the chromophore via multipolar forces. Instead of examining the exact dynamics of

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SSDI 0009-2614(94)00033-M

the TLSs, a sudden-jump stochastic process is assumed for the interaction term. We then obtain expressions for the observable quantities measured in HB, 2PE and 3PE experiments and proceed to analyze the results of these experiments.

2. Non-linear optical experiments: hole-burning and three-pulse photon echoes

In a first approach, we can assume that the chromophore embedded in a glass can be described by a simple Hamiltonian which contains stochastic terms,

$$H=\tfrac{1}{2}\omega_0\sigma_z+\sum_{i=1}^{N}\tfrac{1}{2}\Delta\omega_i(t)\sigma_z\,, \tag{1}$$

where $\sigma_z=|g\rangle\langle g|-|e\rangle\langle e|$, and $|g\rangle$, $|e\rangle$ are the ground and excited states of the chromophore, respectively; ω_0 is the static absorption frequency in absence of interactions with the surrounding glass. The second term of the above equation reflects the effects of the time evolution of the environment on the absorption frequency of the optical impurity (that is, it contains the fluctuation of the chromophore's frequency due to the coupling to N perturbers).

The relevant quantity to calculate for the discussion of the non-linear optical experiments is the following correlation function [8–10]:

$$C_{3PE}(\tau,T_w)=\left\langle\!\!\left\langle \exp\left(-\mathrm{i}\int_0^t \mathrm{d}\tau'\, s(\tau')\sum_{j=1}^{N}\Delta\omega_j(\tau')\right)\right\rangle\!\!\right\rangle, \tag{2}$$

where the choice of $s(t)$ is

$$s(t)=1\,,\qquad 0<t<\tau\,,$$
$$s(t)=0\,,\qquad \tau<t<T_w+\tau\,,$$
$$s(t)=-1\,,\qquad T_w+\tau<t<T_w+2\tau\,,$$

for a 3PE experiment.

In terms of this quantity, the amplitude for the 3PE signal is

$$A_{3PE}(\tau,T_w)=A(T_w)C_{3PE}(\tau,T_w)\exp(-\gamma_e\tau)\,,$$

where $A(T_w)$ contains the effect of the population relaxation to the ground state, and γ_e is the homogeneous linewidth in the absence of media fluctuations of the type described above.

The hole-burning signal (see Fig. 2 for a graphical description of the experiment) is proportional to

$$I_{HB}\propto E_B^2\int_{t-T_B}^{t}\mathrm{d}\theta\, A(\theta)\int_0^\infty \mathrm{d}\tau\exp(\mathrm{i}\delta\tau)\exp(-\gamma_e\tau)\,C_{3PE}(\tau;\theta)\,,$$

where δ is the detuning from the burning frequency. Physically, one can think of the HB experiment as the Fourier transform of a collection of 3PE experiments, where the delay between the second and third pulses range from $t-T_B$ to t.

We note that, experimentally, the dependence of $C_{3PE}(\tau,\theta)$ on θ is rather weak (usually logarithmic), so that we can approximate the above expression (especially if $t\gg T_B$) by

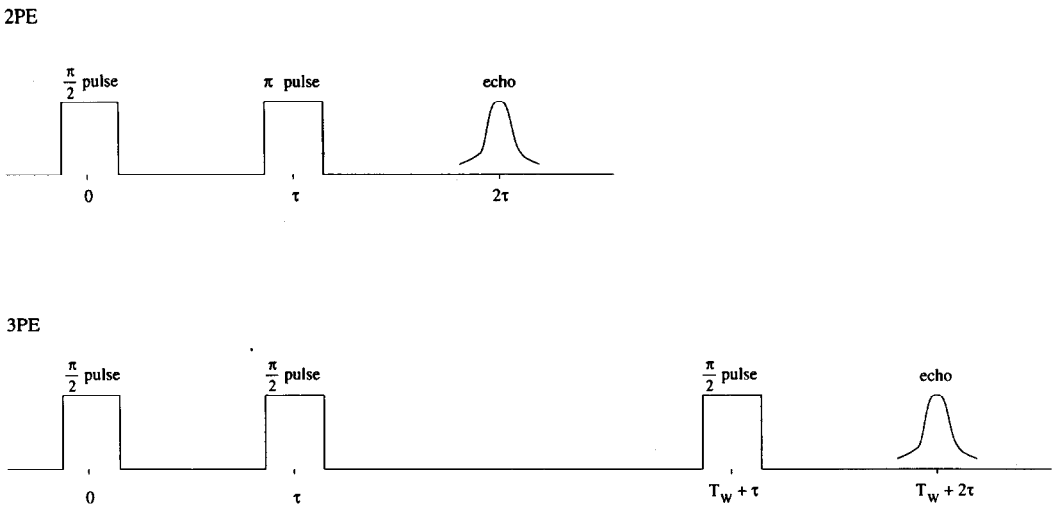

Fig. 1. Photon-echo experiments.

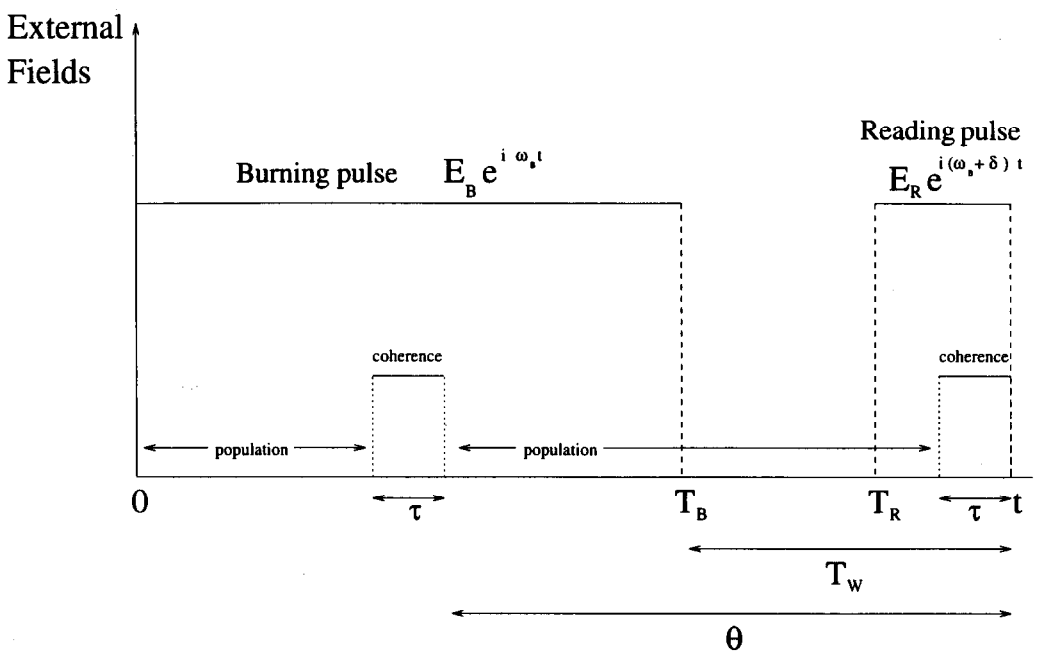

Fig. 2. Hole-burning experiment.

$$I_{\mathrm{HB}} \propto F_{\mathrm{B}} A(T_{\mathrm{w}}) \int_0^\infty \mathrm{d}\tau \exp(\mathrm{i}\delta\tau) \exp(-\gamma_{\mathrm{e}}\tau)\, C_{3\mathrm{PE}}(\tau, T_{\mathrm{w}}) ,$$

where $F_{\mathrm{B}} = E_{\mathrm{B}}^2 T_{\mathrm{B}}$ is the burning fluence and $T_{\mathrm{w}} = t - T_{\mathrm{B}}$. Hence, the small fluence limit of the hole-burning spectrum is approximately the Fourier transform of the 3PE signal.

3. Results in the sudden-jump model

In summary, the relevant quantity to evaluate in HB and 3PE experiments is $C_{3PE}(\tau, T_w)$ (Eq. (2)) where the double angular brackets stand for a series of averages that define the measurable quantity: first, we have to calculate the average over an ensemble of chromophores. By making use of the ergodic hypothesis, this can be evaluated as a temporal average over the history of the environment fluctuations. The second one is an average over all the different environments in which the optical impurity can be found. This second average can be separated into an average over the positions of the TLSs, which we shall call configurational average, and an average over the TLS parameters.

The configurational average is easily evaluated in the thermodynamic limit ($N \to \infty$), for the case of low density [8], and for a uniform distribution of the TLSs in the glass (which, presumably, are the actual conditions in these experiments)

$$\left\langle\left\langle \exp\left(-\mathrm{i}\int_0^t \mathrm{d}\tau'\, s(\tau') \sum_{j=1}^{N} \Delta\omega_j(\tau')\right)\right\rangle\right\rangle = \exp\left\{\rho \int \mathrm{d}\boldsymbol{r}\left[\left\langle \exp\left(-\mathrm{i}\int_0^t \Delta\omega(\tau') s(\tau')\, \mathrm{d}\tau'\right)\right\rangle - 1\right]\right\}. \tag{3}$$

In the previous expression, $\Delta\omega(\tau)$ is the frequency fluctuation due to a two-level system situated at a position $\boldsymbol{r}$ (with the chromophore at the origin), and ρ is the density of TLSs. The remaining brackets stand for the history average and for the average over the TLS parameters.

The history average of $\langle \exp[-\mathrm{i}\int_0^t \mathrm{d}\tau'\, \Delta\omega(\tau') s(\tau')]\rangle$ will be evaluated assuming that the fluctuating part of the optical frequency takes the form: $\Delta\omega(t) = ah(t)$, where a measures the interaction of the chromophore and the TLS in question (it depends on the distance and orientation relative to the chromophore and on intrinsic parameters of the TLS, such as the energy splitting E and the tunneling matrix element Δ) and $h(t)$ is a random telegraph function taking values -1 and $+1$ with the following properties: the probability of being in the state -1 at time t and in the state $+1$ at $t+\mathrm{d}t$ is given by $W(+1, t+\mathrm{d}t|-1, t) = W_2\, \mathrm{d}t$. Similarly, the probability of being in the state $+1$ at time t and in the state -1 at $t+\mathrm{d}t$ is given by $W(-1, t+\mathrm{d}t|+1, t) = W_1\, \mathrm{d}t$. We have allowed for different upward and downward rates in order to account for detailed balance at every temperature,

$$W_2/W_1 = \mathrm{e}^{-\beta E}, \qquad \text{at a temperature } T = 1/k_B\beta .$$

This is called the sudden-jump model and can be derived from a microscopic description. The following definitions shall be useful:

$$R = \tfrac{1}{2}(W_1 + W_2), \qquad W_- = \tfrac{1}{2}(W_1 - W_2), \qquad (Y^{\pm})^2 = a^2 - R^2 \pm 2\mathrm{i}aW_-, \qquad \theta = a + \mathrm{i}W_- .$$

It is possible to derive within this stochastic model a series of "weights" of the form $P^k_{\mathrm{if}}(t)$ for the path where i is the initial state, f is the final state (i, f $= \pm 1$) and k is the sign of $s(\tau')$ in the interval of length t that we are considering (e.g. $P^-_{+\,+}(t)$ is the value of $\langle \exp[\mathrm{i}\int_0^t \mathrm{d}\tau'\, \Delta\omega(\tau')]\rangle$ for a path which is restricted to have $h(0) = h(t) = +1$; $s(\tau') = -1$ for $0 < \tau' < t$). The importance of these weights is that the history average relevant to a series of optical experiments such as free-induction decay, two- and three-pulse echoes, can be expressed in terms of them. For this reason, we shall now tabulate these quantities:

$$P^{+}_{++}(t)=\mathrm{e}^{-Rt}\left(\cos(Y^{+}t)+(\mathrm{i}a-W_{-})\frac{\sin(Y^{+}t)}{Y^{+}}\right),$$

$$P^{+}_{--}(t)=\mathrm{e}^{-Rt}\left(\cos(Y^{+}t)-(\mathrm{i}a-W_{-})\frac{\sin(Y^{+}t)}{Y^{+}}\right),$$

$$P^{+}_{+-}(t)=\mathrm{e}^{-Rt}\,W_1\frac{\sin(Y^{+}t)}{Y^{+}},\qquad P^{+}_{-+}(t)=\mathrm{e}^{-Rt}\,W_2\frac{\sin(Y^{+}t)}{Y^{+}},$$

$$P^{-}_{++}(t)=\mathrm{e}^{-Rt}\left(\cos(Y^{-}t)-(\mathrm{i}a+W_{-})\frac{\sin Y^{-}t)}{Y^{-}}\right),$$

$$P^{-}_{--}(t)=\mathrm{e}^{-Rt}\left(\cos(Y^{-}t)+(\mathrm{i}a+W_{-})\frac{\sin(Y^{-}t)}{Y^{-}}\right),$$

$$P^{-}_{+-}(t)=\mathrm{e}^{-Rt}\,W_1\frac{\sin(Y^{-}t)}{Y^{-}},\qquad P^{-}_{-+}(t)=\mathrm{e}^{-Rt}\,W_2\frac{\sin(Y^{-}t)}{Y^{-}},$$

$$P^{0}_{++}(t)=\frac{1}{2R}\,(W_2+W_1\,\mathrm{e}^{-2Rt}),\qquad P^{0}_{--}(t)=\frac{1}{2R}\,(W_1+W_2\,\mathrm{e}^{-2Rt}),$$

$$P^{0}_{+-}(t)=\frac{W_1}{2R}\,(1-\mathrm{e}^{-2Rt}),\qquad P^{0}_{-+}(t)=\frac{W_2}{2R}\,(1-\mathrm{e}^{-2Rt}). \tag{4}$$

Thus, for the 3PE experiment,

$$\begin{aligned}\left\langle\exp\left(\mathrm{i}\int_0^t \mathrm{d}\tau'\,\Delta\omega(\tau')s(\tau')\right)\right\rangle_{3\mathrm{PE}}=&\left(\frac{W_2}{2R}P^{+}_{++}(\tau)+\frac{W_1}{2R}P^{+}_{-+}(\tau)\right)P^{0}_{++}(T_{\mathrm{w}})\,[P^{-}_{++}(\tau)+P^{-}_{+-}(\tau)]\\
&+\left(\frac{W_2}{2R}P^{+}_{+-}(\tau)+\frac{W_1}{2R}P^{+}_{--}(\tau)\right)P^{0}_{--}(T_{\mathrm{w}})\,[P^{-}_{-+}(\tau)+P^{-}_{--}(\tau)]\\
&+\left(\frac{W_2}{2R}P^{+}_{++}(\tau)+\frac{W_1}{2R}P^{+}_{-+}(\tau)\right)P^{0}_{+-}(T_{\mathrm{w}})\,[P^{-}_{-+}(\tau)+P^{-}_{--}(\tau)]\\
&+\left(\frac{W_2}{2R}P^{+}_{+-}(\tau)+\frac{W_1}{2R}P^{+}_{--}(\tau)\right)P^{0}_{-+}(T_{\mathrm{w}})\,[P^{-}_{++}(\tau)+P^{-}_{+-}(\tau)].\end{aligned} \tag{5}$$

Evaluating this last expression, we obtain

$$\left\langle\exp\left[\mathrm{i}\left(\int_0^{\tau}\mathrm{d}t\,\Delta\omega(t)-\int_{\tau}^{2\tau+T_{\mathrm{w}}}\mathrm{d}t\,\Delta\omega(t)\right)\right]\right\rangle=1-\{F_1(\tau)+[1-\exp(-2RT_{\mathrm{w}})]F_2(\tau)\}, \tag{6}$$

where

$$F_2(\tau)=\frac{a^2}{R^2}W_1W_2\,\mathrm{e}^{-2R\tau}\frac{\sin(Y^{+}\tau)}{Y^{+}}\frac{\sin(Y^{-}\tau)}{Y^{-}},\qquad\text{and}\qquad F_1(\tau)=4R\int_0^{\tau}\mathrm{d}\tau'\,F_2(\tau'). \tag{7}$$

Hence,

$$C_{3\mathrm{PE}}(\tau,T_{\mathrm{w}})=\exp\left(-\rho\int_{\mathrm{glass}}\mathrm{d}\boldsymbol{r}\,\{F_1(\tau)+[1-\exp(-2RT_{\mathrm{w}})]F_2(\tau)\}\right).$$

We remark that for $T_w=0$ we obtain the two-pulse echo experiment results. For $a \gg R$ the expression for F_2 simplifies to $F_2(\tau)=\operatorname{sech}^2(\frac{1}{2}\beta E)\sin^2(a\tau)$, which is the result quoted by Bai and Fayer [3].

Let us carry out the average of $F_2(\tau)$ over the position of the TLS,

$$\bar{F}_2(\tau)=\int_{\text{glass}} \mathrm{d}\boldsymbol{r}\, F_2(\tau)\,.$$

The only quantity that depends on $\boldsymbol{r}$ in the integrand is a, which measures the strength of the TLS–chromophore interaction. Assuming that this interaction is multipolar

$$a=A(\theta,\phi)/r^n\,,$$

the average is

$$\bar{F}_2(\tau)=\frac{\pi^{3/2}}{4n}\left|\frac{\bar{A}}{R}\right|^{3/n}\frac{W_1W_2}{R^2}\,\mathrm{e}^{-x}\,2^w\Gamma(\tfrac{1}{2}+w)\int_0^x \mathrm{d}x'\,(x')^{-w}I_{-w}(x')\;{}_1F_2[\tfrac{1}{2}+w;\tfrac{1}{2},1;\tfrac{1}{4}\xi^2(x-x')^2]\,, \tag{8}$$

with the definitions

$$|A|^{3/n}=\int \mathrm{d}\Omega\,|A(\theta,\phi)|^{3/n}\,,\qquad w=\tfrac{1}{2}(1-3/n)\,,\qquad x=2R\tau\,,\qquad \text{and}\qquad \xi=\tanh(\tfrac{1}{2}\beta E)\,.$$

The generalized hypergeometric function is defined by its Taylor series,

$${}_1F_2[a;b,c;z]=\sum_{n=0}^{\infty}\frac{(a)_n}{(b)_n(c)_n}\frac{z^n}{n!}\,.$$

Eq. (8) is an extension of Huber's results [10] to 3PE and low-temperature experiments. It is straightforward to check that the high-temperature limit ($\xi\to 0$) of $\bar{F}_1(\tau)$ coincides with Huber's result for 2PE experiments.

The experimental evidence is that in glasses, the interaction between the TLSs and the chromophore is mediated by phonons. Once the phonon field is eliminated, this interaction can be shown to be of the dipole–dipole type. For this case ($n=3$) the expression for the configurational average is given by

$$\bar{F}_2(\tau)=\frac{\pi}{12}\bar{A}\frac{W_1W_2}{R^3}\,\mathrm{e}^{-x}\int_0^x \mathrm{d}x'\,I_0(x')I_0(\xi(x-x'))\,. \tag{9}$$

This result for dipolar interactions was already derived by Hu and Walker [11] by performing the history and configurational averages in the opposite order from our derivation.

The only remaining average is over the parameters of the two-level systems. In particular, assuming that the TLSs relax via phonon emission, a process that seems to be confirmed by recent experimental data [12] the relaxation rate has the following functional dependence [9,13]:

$$R=cf(E)\exp(-2\Delta\lambda)\coth(\tfrac{1}{2}\beta E)\,, \tag{10}$$

where c is a constant, $f(E)$ is a function of the asymmetry, whose particular form depends on the spectral strength of the perturbation (it could also contain some residual dependence on the tunneling matrix element Δ) and the last factor comes from detailed balance. The most important term is the exponential dependence on $\Delta\lambda=\lambda-\lambda_{\min}$, where λ is the overlap between two wavefunctions localized on either side of the double-well potential corresponding to the TLS in question (note that the tunneling matrix element is $\Delta\propto\mathrm{e}^{-\lambda}$). In order to carry out the averages over E and λ, we shall assume a constant density function $\rho(E,\lambda)=\text{const.}$ for $\lambda_{\min}\leqslant\lambda\leqslant\lambda_{\max}$ and $0\leqslant E\leqslant E_{\max}$. This is the standard model used to explain the low-temperature acoustic and optical properties of glasses. It has been confirmed, at least partially, by numerical simulations (see Heuer and Silbey [14]). In most cases the experimental temperatures are low, so that $\beta E_{\max}\ll 1$ and the width of the distribution in λ is fairly large $\Delta\lambda_{\max}\approx 5$–20. The $\{E,\lambda\}$ average can be transformed into a $\{E,R\}$ average,

$$\int_0^{E_{\max}} \mathrm{d}E \int_{\lambda_{\min}}^{\lambda_{\max}} \mathrm{d}\lambda\, \rho(E,\lambda)\ldots = \int_0^{E_{\max}} \mathrm{d}E \int_{R_{\min}(E)}^{R_{\max}(E)} \frac{\mathrm{d}R}{R}\ldots ,$$

where

$$R = R_{\max}(E)\exp(-2\,\Delta\lambda)\,, \qquad R_{\min}(E) = R_{\max}(E)\exp(-2\,\Delta\lambda_{\max})\,, \qquad R_{\max}(E) = cf(E)\coth(\tfrac{1}{2}\beta E)\,.$$

We can rewrite the expressions for $\bar{F}_1(\tau)$, $\bar{F}_2(\tau)$ ($x = 2R\tau$, K is a constant),

$$\bar{F}_2(\tau) = \frac{K}{2R}\,[\mathrm{sech}(\tfrac{1}{2}\beta E)]^2 G(\xi, x)\,, \qquad G(\xi, x) = \int_0^x \mathrm{d}x'\, I_0(x') I_0(\xi(x-x'))\,,$$

$$\bar{F}_1(\tau) = \frac{K}{2R}\,[\mathrm{sech}(\tfrac{1}{2}\beta E)]^2 F(\xi, x)\,, \qquad F(\xi, x) = 2\int_0^x \mathrm{d}x'\, G(\xi, x')\,,$$

and evaluate the average of the 2PE portion over the TLS parameters in the standard model,

$$\langle \bar{F}_1(\tau)\rangle_{E,R} = \tfrac{1}{2}K \int_0^{E_{\max}} \mathrm{d}E\,[\mathrm{sech}(\tfrac{1}{2}\beta E)]^2 \int_{R_{\min}}^{R_{\max}} \frac{\mathrm{d}R}{R^2} F(\xi, x) = K\tau \int_0^{E_{\max}} \mathrm{d}E\,[\mathrm{sech}(\tfrac{1}{2}\beta E)]^2 \int_{2R_{\min}\tau}^{2R_{\max}\tau} \frac{\mathrm{d}x}{x^2} F(\xi, x)\,. \tag{11}$$

We remark that the term $[\mathrm{sech}(\frac{1}{2}\beta E)]^2$ provides an upper cutoff for E so that the only TLSs that contribute in a significant way to the spectral diffusion are those with $\beta E \leqslant 2$.

Assuming that the delay between the two pulses in the 2PE experiment (the first two in the 3PE) is such that $R_\tau = 1/\tau$ is well within the interval $[R_{\min}(E), R_{\max}(E)]$ for most contributing TLSs, we can extend both limits of the integral in Eq. (11), and obtain the result:

$$\langle \bar{F}_1(\tau)\rangle_{E,R} = K\tau \int_0^{E_{\max}} \mathrm{d}E\,[\mathrm{sech}(\tfrac{1}{2}\beta E)]^2 \int_0^{\infty} \frac{\mathrm{d}x}{x^2} F(\xi, x)\,. \tag{12}$$

The convergence is not problematic as $F(\xi, x) \sim x^2$ when $x \to 0$ and $F(\xi, x) \sim x^{1/2}$ when $x \to \infty$, which implies that the two-pulse echo decay is exponential. This argument was first presented by Maynard et al. [15] and is supported by experiments: the usual time scale of the 2PE experiment (from a few hundred picoseconds to microseconds) seems to be well within the range of relaxation times for the glass TLSs. The deviations from exponential decay are very small in most cases (see however Macfarlane et al. [16] where very non-exponential decay is found in complex crystals. However we note that in this case the averaging procedure might be different).

The fact that the 3PE signal presents a simple exponential decay is more complex. There are three pieces to consider in the echo amplitude:

$$A_{3\mathrm{PE}} \approx \exp\{-\rho[\langle \bar{F}_1(\tau)\rangle_{E,R} + \langle \bar{F}_2(\tau)\rangle_{E,R} - \langle \exp(-2RT_{\mathrm{w}})\,\bar{F}_2(\tau)\rangle_{E,R}]\}\,. \tag{13}$$

The first term is the same as in the 2PE. For the second one, the linear dependence in τ can be derived in a similar fashion as for the first one, except that the extension of the lower integration limit to zero presents special difficulties,

$$\langle \bar{F}_2(\tau)\rangle_{E,R} = K\tau \int_0^{E_{\max}} \mathrm{d}E\,[\mathrm{sech}(\tfrac{1}{2}\beta E)]^2 \int_{2R_{\min}(E)\tau}^{2R_{\max}(E)\tau} \frac{\mathrm{d}x}{x^2} G(\xi, x)\,.$$

Again the asymptotic behavior as $x \to \infty$ is $G(\xi, x) \sim x^{1/2}$. However as $x \to 0$, $G(\xi, x) \sim x$ only. This yields an extra term,

$$\langle \bar{F}_2(\tau)\rangle_{E,R} = K\tau \int_0^{E_{\max}} \mathrm{d}E\,[\mathrm{sech}(\tfrac{1}{2}\beta E)]^2 \left(\int_{\theta(E)}^{\infty} \frac{\mathrm{d}x}{x^2} G(\xi, x) + \int_{2R_{\min}(E)\tau}^{\theta(E)} \frac{\mathrm{d}x}{x^2} G(\xi, x) \right).$$

The factor $\theta(E)$ is small enough at all accessible energies so that $G(\xi, x)$ can be expanded about $x=0$. This extra term is then proportional to $\tau \ln \tau$ and will be very difficult to distinguish from the term linear in τ in actual experiments.

The contribution of the last portion of the exponent in the 3PE amplitude is linear in τ for entirely different reasons: as a general rule $T_w \gg \tau$, which implies that in $\langle \exp(-RT_w)\, \bar{F}_2(\tau)\rangle_{E,R}$ the main contributions will come from $R \leqslant 1/T_w$. This means that $x \approx \tau/T_w \ll 1$ allowing us to expand $G(\xi, x)$ about $x=0$,

$$\langle \exp(-2RT_w)\, \bar{F}_2(\tau)\rangle_{E,R} \approx \int_0^{E_{\max}} \mathrm{d}E\,[\mathrm{sech}(\tfrac{1}{2}\beta E)]^2 \int_{R_{\min}(E)}^{R_{\max}(E)} \frac{\mathrm{d}R}{R^2} G(\xi, x) \exp(-2RT_w)$$

$$\approx \tau \int_0^{E_{\max}} \mathrm{d}E\,[\mathrm{sech}(\tfrac{1}{2}\beta E)]^2 \int_{R_{\min}(E)}^{R_{\max}(E)} \frac{\mathrm{d}R}{R} \exp(-2RT_w)\,, \tag{14}$$

which is indeed linear in τ. Furthermore, this is the only part dependent on T_w.

4. Conclusions

Using the stochastic sudden-jump model, we have discussed the phenomenon of spectral diffusion in glasses, where TLSs induce fluctuations in the frequency of the chromophore whose optical response is being probed. Experiments, such as free-induction decay, and two- and three-pulse echoes require the history average of a quantity like

$$\left\langle \exp\left(-\mathrm{i} \int_0^t \mathrm{d}\tau'\, s(\tau')\, \Delta\omega(\tau') \right) \right\rangle$$

within the sudden-jump model. $s(\tau')$ has a different form in the various experiments: its value is 0 for the interval that the chromophore's *population* is relaxing and ± 1 when its *coherence* is evolving. These averages can be readily calculated by using the series of "weights" tabulated in Eq. (4).

In this Letter, we have extended the sudden-jump model results obtained by Huber for 2PE at high temperature (relative to the TLS splitting), to the more general case of 3PE and arbitrary temperatures. In the limit of dipolar interactions we recover the familiar results given by Hu and Walker [11]. The exponential decay of the three-pulse echo signal (at least for $T_w \gg \tau$) is seen to require a uniform distribution of two-level systems coupled to the chromophore via dipolar interaction, as well as exponentially decaying two-pulse echoes. The particular form for the distribution of relaxation rates for $R\tau \ll 1$ does not have an effect on the exponential character of this decay.

5. Acknowledgement

The authors would like to thank the National Science Foundation for its support.

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