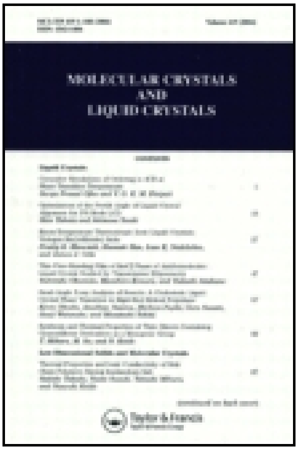

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DYNAMICAL THEORY FOR TEMPORAL AND TEMPERATURE - INDUCED BROADENING OF SINGLE MOLECULE LINES

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Abstract Temporal and temperature-induced broadening of zero-phonon hole associated with electronic impurity transitions in amorphous solids are described using an expression based on a dynamical theory for homogeneous spectral diffusion. Normal thermal broadening and broadening produced in thermal cycling are discussed. It is suggested that the proposed theoretical model is subject to testing by single molecule experiments.

INTRODUCTION

Spontaneous temporal broadening of zero-phonon holes [1,2] and a residual irreversible holewidth measured in temperature cycling experiments [3,4] result from the interaction of a chromophore with slowly relaxing two-level systems (TLS) existing in polymers and glasses.

A theory proposed here is able to explain with the help of a single formula the following experimental facts: 1. linear low temperature broadening of spectral holes [5]; 2. logarithmic temporal hole broadening [3]; 3. appearance of a residual irreversible holewidth γ_{irr} in the course of temperature cycling experiments and its linear dependence on cycling temperature ΔT [3]; 4. the conclusion that there is no change in γ_{irr} after repetitions of the temperature cycles with the same ΔT [3].

BASIC FORMULAE

The basic formula

$$\gamma_{SD}(t,T) = \gamma_0 \int d\varepsilon N_1(\varepsilon) \int dR N_2(R) \rho(1-\rho) \tag{1}$$

for the homogeneous linewidth which results from the chromophore-TLS interaction was derived in the dynamical theory for homogeneous spectral diffusion [6,7]. Here the functions N_1 and N_2 describe distributions with respect to the TLS splitting ε and the rate constant R for TLS relaxation, respectively. The function

$$\rho(t,T) = f(T) + (\rho_0 - f(T))\exp(-Rt) \tag{2}$$

is the probability of finding the TLS in the upper (excited) state. Here ρ_0 and $f(T) = (1+\exp(\varepsilon/kT))^{-1}$ are the initial and final probabilities, respectively. In deriving eq.(1) a dipolar interaction, $F(\theta,\phi)\mu^2/r^3$, between the chromophore and TLS was assumed. A constant $\gamma_0 = \mu^2\pi<|F|>n_0/3$ determines the strength of the chromophore-TLS interaction. Here <...> means the integration with respect to angles and n_0 is the concentration of TLS .

Since $\rho \leq 1$ one can neglect the term with ρ^2 in eq.(1) for simplicity. The analysis reveals that the final results do not change considerably if this term is taken into account. Taking a rectangular shape for the distribution function $N_1(\varepsilon)$ we find

$$\gamma_{SD}(t,T) = \gamma_0 \int_0^{\varepsilon_m} \frac{d\varepsilon}{\varepsilon_m} \int dR N_2(R)\rho(t,T), \tag{3}$$

where ε_m is an upper boundary of the rectangular distribution. Eqs. (3) and (2) enable us to explain all the experimental facts discussed in the introduction.

TEMPORAL AND THERMAL LINE BROADENING

If the distribution with respect to R is of a hyperbolic type

$$N_2(R) = \begin{cases} [R\ln(R_2/R_1)]^{-1}, & R_1 \leq R \leq R_2, \\ 0, & elsewhere. \end{cases} , \tag{4}$$

one can easily find that

$$I = \int dR N_2(R) e^{-Rt} \cong [\ln(R_2/R_1)]^{-1} \int_{R_1}^{1/t} \frac{dR}{R} = -\frac{\ln(R_1 t)}{\ln(R_2/R_1)} \tag{5}$$

Taking eq.(5) into account and carrying out the integration with respect to ε we can rewrite eq.(3) as follows:

$$\gamma_{SD}(t,T) \simeq \frac{\gamma_0}{\ln(R_2/R_1)}[0.7\frac{kT}{\varepsilon_m}\ln(R_2 t) - \rho_0 \ln(R_1 t)]. \tag{6}$$

Here we used that

$$\int_0^{\varepsilon_m/kT} \frac{dx}{1+\exp(x)} = 0.693 \cong 0.7 \tag{7}$$

at $kT/\varepsilon_m << 1$. Eq.(6) describes the temporal and low temperature line broadening. The temperature broadening comes from $f(T)$. Eq.(6) shows that there is a residual halfwidth $\gamma_{SD}(t,0)$. It results from the interaction with nonthermalized TLS which can be considered as defects. The residual halfwidth decreases logarithmically with time. The temporal dependence in eq.(6) emerges because $\rho_0 \neq f(T)$.

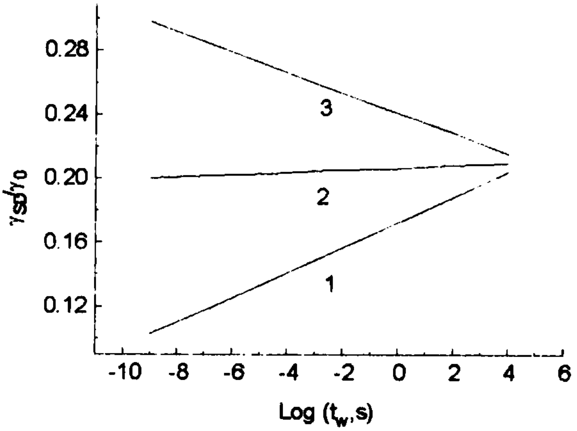

FIGURE 1. Logarithmic temporal behavior of a linewidth calculated with the help of eq.(6) at $R_2 = 10^9\ s^{-1}$, $R_1 = 10^{-5}\ s^{-1}$, $\rho_0 = 0.1$ (1), 0.2 (2), 0.3 (3) and at $kT/\varepsilon_m = 0.3$.

Figure 1 shows that halfwidth increases logarithmically at $\rho_0 = 0.1$ and decreases at $\rho_0 = 0.3$. To the best of my knowledge, temporal hole narrowing has yet to be observed. This narrowing results from the residual halfwidth $\gamma_{SD}(t,0)$.

TEMPERATURE CYCLING REGIME

Let T_0 and T_1 be the initial and excursion temperatures. We shall take $\rho_0 = f(T_0)$. With eq.(2) one can show that

$$\Delta\rho_1(t_1,t_2) = \rho(t_1,t_2) - f(T_0) = (f(T_1) - f(T_0))(1 - e^{-R't_1})e^{-Rt_2} \tag{8}$$

For the rate constants we choose a model which allows for transitions crossing TLS barriers:

$$R = R_0 e^{-\frac{U}{kT_0}}, \qquad R' = R_0 e^{-\frac{U}{kT_1}} . \tag{9}$$

The difference of the two halfwidths is expressed via $\Delta\rho_l$:

$$\Delta\gamma = \gamma_{SD}(t_1, t_2, T_0', T_1') - \gamma_{SD}(0, T_0') = \gamma_0 \int_0^{\varepsilon_m} \frac{d\varepsilon}{\varepsilon_m} \int dR N_2(R) \Delta\rho_1 . \tag{10}$$

The function $\Delta\rho_l$ approaches zero after the temperature cycle is over. It is shown in figure 2.

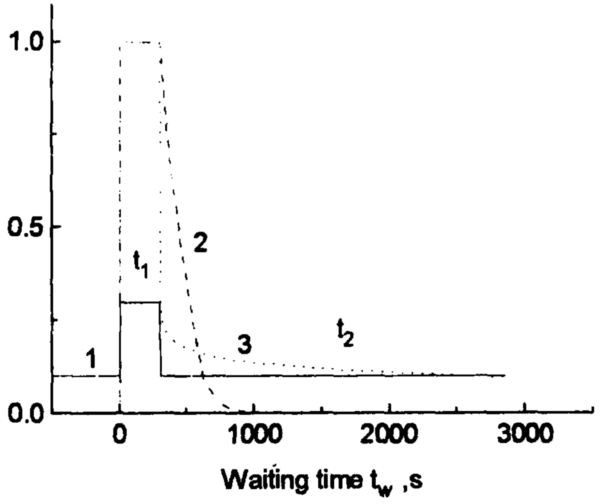

FIGURE 2. Temporal behavior of the functions *f(T)* – 1, $\Delta\rho_l$ – 2 and $I(t_1,t_2)$ – 3 in temperature cycling regime. Values of the parameters are: $R_0 = R_2 = 10^9$ s^{-1}, $R_1 = 10^{-5}$ s^{-1}, $U/kT_0 = 26$, $T_1/T_0 = 2$.

Therefore an irreversible halfwidth cannot be expected in the case when a broad distribution with respect to R is absent. In the case of hyperbolic distribution we find:

$$\Delta\gamma = \gamma_0 0.7 \frac{k\Delta T}{\varepsilon_m} I(t_1, t_2), \tag{11}$$

where $\Delta T = T_1 - T_0$ is cycling temperature and

$$I(t_1, t_2) = [\ln(R_2 / R_1)]^{-1} \int_{R_1}^{R_2} (1 - e^{-R' t_1}) e^{-R t_2} \frac{dR}{R} \tag{12}$$

The temporal behavior of this integral differs considerably from that for $\Delta\rho_l$ because its value decreases very slowly after completion of the temperature cycle, figure 2. The value of the integral at waiting time $t_w = t_1+t_2$ is I_{irr}. It is obvious that an irreversible residual linewidth appears in this case. One can find with the help of eq.(11) the following expression for the irreversible residual linewidth:

$$\gamma_{irr}(t_2,\Delta T)=\gamma_0 0.7\frac{k\Delta T}{\varepsilon_m}I_{irr} \tag{13}$$

The integral $I(t_1,t_2)$ almost does not depend on t_1 at $T_1 > 2T_0$. For this temperature range it equals the integral I defined by eq.(5). Inserting eq.(5) instead of I_{irr} we find

$$\gamma_{irr}(t_2,\Delta T)=-\gamma_0 0.7\frac{k\Delta T}{\varepsilon_m}\frac{\ln(R_1t_2)}{\ln(R_2/R_1)}. \tag{14}$$

The irreversible linewidth is a linear function of cycling temperature and is decreasing logarithmically after temperature cycle is over.

We can easily find the irreversible line width after a second temperature cycle with the same cycling temperature. In this case we have to substitute $\Delta\rho_l$ in eq.(9) by

$$\Delta\rho_2(t_1,t_2,t_3,t_4)=\Delta\rho_1(t_3,t_4)+\Delta\rho_1(t_1,t_2)e^{-R't_3}e^{-Rt_4}, \tag{15}$$

where the times t_3, t_4 in the second cycle play the role of the respective times t_1, t_2 in the first cycle. Eq.(15) was derived with the help of the basic eq.(2). The function $\exp(-R't_3)$ rapidly approaches zero at $T_1 > 2T_0$ Therefore, the contribution to γ_{irr} from the second term in eq.(15) rapidly approaches zero as well. Its contribution is already negligible on the time scale of seconds . Therefore, the irreversible line width does not change after a second cycle in accordance with the experimental observations [3].

MORE GENERAL CASE

It was shown that there are at least two mechanisms for an irreversible change in linewidth. One stems from nonthermalized initial conditions for TLS. This type of an nonequilibrium appears in the course of sample preparation and one is expressed with the help of the inequality $\rho_0 \neq f(T)$. This type of the nonnequilibrium yields eq.(6).

The second mechanism has to do with a nonequilibrated TLS distribution produced during the course of a temperature cycle. In this case we find eq.(13). With the help of eq.(2) one can easily find that contributions to $\Delta\rho_l$ from both sources of the nonequilibrium are additive:

$$\Delta\rho_1(t_1,t_2)=(f(T_0)-\rho_0)(1-e^{-R't_1}e^{-Rt_2})+(f(T_1)-f(T_0))(1-e^{-R't_1})e^{-Rt_2}. \tag{16}$$

This equation can be easily found with the help of eq.(2). By inserting eq.(16) into eq.(10) we find

$$\gamma_{irr}(t_2,T_0)+\gamma_{irr}(t_2,\Delta T)=$$

$$=\frac{\gamma_0}{\ln(R_2/R_1)}\left[(0.7\frac{kT_0}{\varepsilon_m}-\rho_0)\ln(R_2t_2)-0.7\frac{k\Delta T}{\varepsilon_m}\ln(R_1t_2)\right]. \qquad (17)$$

Eq.(17) for irreversible width allows for both types of nonequilibrium conditions which can exist in a sample.

CONCLUSION

All the four experimental facts for spectral holes mentioned in the introduction can be explained with the help of eqs.(6) and (13). Both equations relate to the width of a single molecule line. This conclusion is of great importance because if this explanation is correct all these effects must manifest themselves in experiments with single molecules. Therefore, experiments with single molecules can play a decisive role to test this explanation.

To the best of my knowledge, none of the four temporal and temperature phenomena discussed in the introduction have not yet detected in single molecule experiments. If they will not be found in single molecule experiments undertaken specially to search them, this fact will unambiguously prove an inhomogeneous character of spectral diffusion. Then the theory for inhomogeneous spectral diffusion [8,9] must be invoked to explain the above mentioned experimental facts.

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