Dynamic theory of spectral diffusion in optical spectra of impurities

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A dynamic theory describing the time-dependent broadening of spectral lines due to both isolated impurities (homogeneous spectral diffusion) and ensembles of impurities (nonhomogeneous spectral diffusion) has been developed. The homogeneous spectral diffusion is caused by interaction between an impurity and long-lived tunneling excitations (tunnelons) in polymers and glasses and is diagonal with respect to electron indices. The inhomogeneous diffusion is due to off-diagonal interaction. The well-known results of the stochastic theory of spectral diffusion can be derived from the dynamic theory proposed. The effect of the initial nonequilibrium tunnelon distribution on the impurity spectral line broadening is discussed. Experimental data which confirm some conclusions of the dynamic spectral diffusion theory are considered. © *1996 American Institute of Physics.* [S1063-7761(96)00703-9]

1. INTRODUCTION

The effect of spectral diffusion on impurity spectra of polymers and glasses has attracted a lot of attention by both experimenters[1–6] and theorists[7–13] in the recent years. Spectral diffusion has the strongest effect on spontaneous time-dependent broadening of dips in spectra[1,2] and on the dependence of the optical transverse relaxation time T_2 on a characteristic time of an experiment, such as the waiting time t_w between the second and third pulse in experiments with three-pulse optical echos.[4,5]

Spectral diffusion was originally detected in spin echo experiments by measuring T_2 as a function of the pause duration τ.[14] Klauder and Anderson[15] proposed a stochastic theory accounting for the spectral diffusion effect. Their stochastic approach was a cornerstone of most theoretical studies of spectral diffusion.[7,8,11,12,16,17]

According to the stochastic theory, the main contribution to spectral diffusion results from the spontaneous relaxation of two-level systems undergoing a tunneling transition, which exists in polymers and glasses. These spontaneous transitions cause fluctuations of electron transition frequencies in impurity centers that result in the time-dependent broadening of optical spectral lines.

It is common knowledge that the stochastic technique yields a relatively simple theory of optical line broadening, but is absolutely inadequate for an interpretation of the intensity distribution among spectral lines in impurity spectra. A typical spectrum usually contains a narrow zero-phonon line, and a neighboring broad phonon sideband, which sometimes has fine structure and vibronic lines for the molecular *impurity center.* On the other hand, all these features of the impurity spectrum, as well as the zero-phonon line broadening, are easily interpreted in terms of the dynamic theory of optical band shapes.[18]

The dynamic approach based on the impurity system Hamiltonian and the respective density operator is more general than the stochastic method and therefore more useful in interpreting experimental data. Hence spectral diffusion can undoubtedly be described in terms of the dynamic theory. With this end in view, the dynamic theory described in the paper has been developed.

A preliminary study of spectral diffusion using the dynamic approach produced fundamentally new results.[13] It was found that there are two types of the spectral diffusion—homogeneous and inhomogeneous. Homogeneous spectral diffusion is a time-dependent broadening of a homogeneous line, hence it should also affect the line width of an isolated impurity center. Inhomogeneous spectral diffusion affects only line widths of ensembles of molecules because it results not from the broadening of a homogeneous spectral line, but from its shift. This shift is actually observed in experiments with isolated molecules.[3]

This paper demonstrates that the stochastic theory takes into account only homogeneous spectral diffusion and ignores inhomogeneous diffusion. The dynamic approach to spectral diffusion reveals some inconsistencies in the stochastic theory that were overlooked in previous studies. The dynamic theory of spectral diffusion, which is free of these contradictions, predicts a slightly different time dependence of the homogeneous line width. Finally, the dynamic theory reveals a new problem concerning the nature of initial nonequilibrium states of two-level systems undergoing tunneling transitions. The above statements demonstrate the importance of the dynamic approach for studying spectral diffusion.

2. DIAGONAL AND OFF-DIAGONAL INTERACTIONS

Let us consider an impurity center in a polymer or glass. Besides phonons, tunneling excitations responsible for structural changes occur in such materials. The system Hamiltonian can be expressed as

$$H^g=\sum_j \varepsilon_j c_j^+ c_j + H_{\mathrm{rel}}, \tag{1}$$

where c_j^+ and c_j are Fermi creation and annihilation operators of excitation in the jth tunneling system, and ε_j is its excitation energy. The operator H_{rel} describes the relaxation of tunneling excitation. It is known that low-temperature properties of polymers and glasses are controlled by tunneling excitations,[19] which we shall call tunnelons for brevity. This assertion also applies to optical properties, so we shall ignore the phonon contribution to spectral line broadening at low temperatures, and phonons are not included in the Hamiltonian in Eq. (1).

Electronic excitations affect the adiabatic Hamiltonian of the impurity–lattice system, which can be given by

$$H^e=E_0B_0^+B_0+\sum_j E_jB_j^+B_j+H^g+\hat{D}+\hat{M}. \tag{2}$$

Here E_0, B_0^+, B_0, and E_j, B_j^+, B_j are the energies of electronic excitations of the impurity center and of host molecules, and creation and annihilation operators of respective excitations. The electron–tunnelon interaction is described by the operators

$$\hat{D}=B_0^+B_0\sum_j \Delta_jc_j^+c_j, \tag{3}$$

$$\hat{M}=\sum_j M_{0j}(B_0^+B_jc_j+B_0B_j^+c_j^+). \tag{4}$$

The operator $\hat{D}$, which is diagonal with respect to electronic indices, describes the effect of tunnelons on the resonant frequency. Its analog in the phonon system is the quadratic electron–phonon interaction responsible for the thermal broadening of zero-phonon lines.[20] We shall see below that stochastic theories of spectral diffusion take into account the interaction described by $\hat{D}$.

The operator $\hat{M}$, which is off-diagonal with respect to electronic indices, describes the transmission of an excitation from an impurity center to a host molecule and back, which is accompanied by the creation and annihilation of a tunnelon. This interaction was ignored by the stochastic theories of spectral diffusion.

Since spectral diffusion is due to long-lived tunnelons, the tunnelon density matrix is nonequilibrium and, hence, it is time-dependent:

$$\hat{\rho}(t,T)=\prod_j \hat{\rho}_j(t,T), \tag{5}$$

where

$$\hat{\rho}_j(t,T)=(1-\rho_j(t,T))c_jc_j^+ +\rho_j(t,T)c_j^+c_j, \tag{6}$$

$$\rho_j(t,T)=f_j(T)+(\rho_j(0)-f_j(T))\exp(-R_jt). \tag{7}$$

Here R_j^{-1} is the tunnelon lifetime. By defining a model of the tunnelon–phonon interaction, i.e., the operator H_{rel}, we can derive an expression for R_j^{-1}. In this paper, we presume that R_j are unknown constants, and $\rho_j(0)$ and $f_i(T)=[\exp(\varepsilon_i/kT)+1]^{-1}$ determine the initial and final probabilities that there is a tunnelon in the sample.

The shape of an optical absorption band is described by the formula

$$I(\omega)=\int_{-\infty}^{\infty} dx\, e^{i\omega x}I(x,t), \tag{8}$$

where

$$I(x,t)=\mathrm{Tr}[\hat{\rho}(t,T)(\mathbf{dE})e^{-iH^ex}(\mathbf{dE})e^{iH^gx}]. \tag{9}$$

Here

$$(\mathbf{dE})=-i\Lambda(B_0-B_0^+) \tag{10}$$

is the interaction operator between an impurity center and an incident light wave. Equations (8)–(10) are similar to those used in calculations of shapes of electron–phonon spectral bands. There are only two fundamental differences, namely, the Hamiltonians $H^{e,g}$ contain tunnelon operators, and the density operator $\hat{\rho}(t,T)$ is time-dependent.

3. DERIVATION OF STOCHASTIC THEORY FORMULAS USING THE DYNAMIC APPROACH

The results of the stochastic theory can be derived from Eq. (9) if we assume that

$$H_{\text{rel}}=\hat{M}=0. \tag{11}$$

In this approximation, the operators H^g and H^e commute and the expression on the right side of Eq. (9) can be easily calculated:

$$I(x,t)=e^{-iE_0x}\prod_j [1-\rho_j(t,T)(1-e^{-i\Delta_jx})]. \tag{12}$$

We shall see below that basic results of the stochastic theory can be derived from Eq. (12). Note, however, that the model in which $H_{\text{rel}}=0$ and $\rho_j(t,T)$ is time-dependent is not self-consistent since at $H_{\text{rel}}=0$ the constant R_j also have to be zero and $\rho_j(t,T)$ will be constant with time. Since the basic equations of the stochastic theory can be derived from Eq. (12), this inconsistency is also present in the stochastic theory, but is more difficult to find.

Let us introduce the distribution function

$$Q(\Delta,\varepsilon,R)=\frac{1}{N_0}\sum_{j=1}^{N_0} \delta(\Delta-\Delta_j)\delta(\varepsilon-\varepsilon_j)\delta(R-R_j), \tag{13}$$

where N_0 is the total number of tunneling systems, and the partially reduced functions

$$N_0(\Delta)=\int Qd\varepsilon\, dR=\frac{1}{N_0}\sum_j \delta(\Delta-\Delta_j), \tag{14}$$

$$N(\varepsilon,R)=\int Q\, d\Delta=\frac{1}{N_0}\sum_j \delta(\varepsilon-\varepsilon_j)\delta(R-R_j). \tag{15}$$

The shift $\Delta_j\equiv\Delta(\mathbf{r}_{0j})$ is a function of the vector $\mathbf{r}_{0j}$ connecting the impurity to the jth tunneling system. Since ε_j and R_j are independent of $\mathbf{r}_{0j}$, the distributions $N_0(\Delta)$ and $N(\varepsilon,R)$ can be treated as statistically independent, i.e.,

$$Q(\Delta,\varepsilon,R)=N_0(\Delta)N(\varepsilon,R). \tag{16}$$

Using Eqs. (13) and (14) and assuming that Eq. (16) is valid, we can transform Eq. (12) to

$$I(x,t,T)=\exp[-iE_0x+\varphi(x,t,T)], \tag{17}$$

where

$$\varphi(x,t,T)=\int N(\varepsilon,R)J(\varepsilon,R,x)dRd\varepsilon, \tag{18}$$

$$J(\varepsilon,R,x)=\sum_j \ln[1-\rho(\varepsilon,R)(1-e^{-i\Delta_j x})]. \tag{19}$$

The total number N of lattice sites is larger than the number N_0 of tunneling systems. Using the ratio N_0/N, we can replace the summation over the tunneling systems with a summation over lattice sites and then with an integration over the coordinates. After that Eq. (19) is transformed to

$$J(\varepsilon,R,x)=\frac{N_0}{V}\int_V dV\,\ln[1-\rho(\varepsilon,R)(1-e^{-i\Delta(\mathbf{r})x})], \tag{20}$$

where $V=N\Delta V$ is the sample volume.

Stochastic theories are usually based on the dipole–dipole interaction model, in which

$$\Delta(\mathbf{r})=\frac{\mu}{r^3}F(\vartheta,\psi)=\Delta(r)F(\vartheta,\psi). \tag{21}$$

Substituting Eq. (21) to Eq. (20) and using a spherical coordinate system, we obtain

$$J(\varepsilon,R,x)=\frac{\mu n_0}{3}\left\langle \int_0^\infty \frac{d\Delta}{\Delta^2}\ln[1-\rho(1-e^{-i\Delta F x})]\right\rangle, \tag{22}$$

where $n_0=N_0/V$ is the density of tunneling systems and $\langle\dots\rangle$ denotes integration with respect to the angles ϑ and ψ. It is proved in the Appendix that

$$\left\langle \int_0^\infty \frac{d\Delta}{\Delta^2}\ln[1-\rho(1-e^{-i\Delta F x})]\right\rangle = -\left\langle \int_0^\infty \frac{d\Delta}{\Delta^2}\ln[\rho(1-e^{-i\Delta F x})]\right\rangle. \tag{23}$$

According to Eq. (21), the minimum radius r corresponds to the maximum shift Δ and vice versa. Therefore Eq. (22), with due account of Eq. (23), can be transformed to

$$J(\varepsilon,R,x)=-\rho(\varepsilon,R)\frac{\mu n_0}{3}\left\langle \int_{\Delta_{\min}}^{\Delta_{\max}} \frac{d\Delta}{\Delta^2}(1-e^{-i\Delta F x})\right\rangle \simeq -\frac{\rho\mu n_0}{3}\left[i\left\langle F\ln\frac{\pi}{\Delta_{\min}Fx}\right\rangle x+\pi\langle|F|\rangle|x|\right]. \tag{24}$$

Here we have replaced ∞ and 0 by $\Delta_{\max}=\mu/\Delta V$ and $\Delta_{\min}=\Delta_{\max}/N$. It is obvious that $\Delta_{\max}$ is the energy of the dipole–dipole interaction between an impurity and its nearest tunneling system. Presently we know nothing about its value, but it is quite plausible that it is larger than all R, i.e., $\Delta_{\max}/R>1$.

The logarithmic function is slower than the linear one, hence we may replace x in the argument of the logarithm with the constant γ^{-1}, where γ is the FWHM of the zero-phonon line. The parameter $a=\ln(\pi\gamma/\Delta_{\min}F)$ is about one order of magnitude larger than π. Substituting Eq. (24) into Eq. (18), we obtain

$$\varphi(x,t,T)=-i\delta(t,T)x-\frac{\gamma(t,T)}{2}|x|, \tag{25}$$

where

$$\delta(t,T)=\frac{\mu n_0 a}{3}\langle F\rangle\Psi(t,T),$$

$$\gamma(t,T)=\frac{\mu n_0 2\pi}{3}\langle|F|\rangle\Psi(t,T), \tag{26}$$

$$\Psi(t,T)=\int N(\varepsilon,R)\rho(\varepsilon,R)\,d\varepsilon\,dR. \tag{27}$$

One can easily find that Eqs. (17) and (25) substituted into Eq. (8) lead to a Lorentzian line shape:

$$I(\omega,t,T)=\frac{\gamma(t,T)}{(\omega-E_0-\delta(t,T))^2+(\gamma(t,T)/2)^2}. \tag{28}$$

Stochastic theories also predict this line shape. Unlike equations of the stochastic theories,[11,12,15–17] Eq. (26) is temperature-dependent. Well-known results of the stochastic theory can be derived for special cases from Eq. (26).

If we assume like Klauder and Anderson[15] that $\rho(0)=0$, then at a small time t we have

$$\Psi(t,T)\cong f(T)Rt. \tag{29}$$

Substituting Eq. (29) into (26) and taking $F=1$, we find the equation derived by Klauder and Anderson:

$$\frac{\gamma}{2}=mt=\frac{2\pi^2}{3}n_0\mu f(T)Rt. \tag{30}$$

The expression for the constant m coincides with Eq. (1.13) in Ref. 15, but in our theory the constant m is temperature-dependent.

If all the dipoles are parallel to each other, then $F=1-3\cos^2\theta$, hence $\langle F\rangle=\delta=0$ and $\langle|F|\rangle=16\pi/3^{3/2}$. Substituting the latter formula into Eq. (26) for γ, we obtain

$$\frac{\gamma}{2}=\frac{16\pi^2}{3^{5/2}}n_0\mu\Psi(t,T). \tag{31}$$

Here the function $\Psi(t,T)$ is multiplied by a factor which is identical to the expression for $\Delta\omega_{1/2}$ derived by Hu and Hartmann,[16] whereas the function Ψ in Refs. 16 and 17 is different and constant with temperature, since it was calculated by the random-jump method.

Using the approximation of statistical independence expressed by the equation

$$N(\varepsilon,R)=N_1(R)N_2(\varepsilon), \tag{32}$$

and taking a step function for $N_2(\varepsilon)$, which equals unity over the range of 0 to $\varepsilon_{\max}$ we obtain the following expression for Ψ at $\rho(0)=0$:

$$\Psi(t,T)=\frac{kT}{\varepsilon_{\max}}\int_0^{\varepsilon_{\max}/kT}dx\,f(x)\int_0^\infty dR\,N_1(R)(1-e^{-Rt}), \tag{33}$$

where $f(x)=(e^x+1)^{-1}$. The function Ψ is linear with temperature if $kT\ll\varepsilon_{\max}$. This temperature dependence was actually observed in the millikelvin region.[21] The time dependence of Ψ is identical to that derived by Littau *et al.*[2]

Thus we can see that under the condition $H_{\mathrm{rel}}=0$ the dynamic theory including only the diagonal interaction yields results identical to those of the stochastic theories of spectral diffusion.

4. HOMOGENEOUS SPECTRAL DIFFUSION

If $H_{\mathrm{rel}}\neq 0$, the operators H^g and H^e do not commute and the calculation of the right-hand side in Eq. (9) becomes very cumbersome. This calculation was performed by Zaitsev *et al.*,[22,23] and technical details were given in those references. We shall use the final formulas derived in Refs. 22 and 23 to develop the dynamic theory of spectral diffusion. One of those formulas is

$$\exp\varphi(x,t,T)=\exp\left[i\sum_j\left(\Omega_{0j}-\frac{\Delta_j}{2}\right)x+\sum_j\left(\gamma_{0j}-\frac{R_j}{2}\right)|x|\right]\times\prod_j\left[1-F_j(1-\exp(-i2\Omega_{0j}x-2\gamma_{0j}|x|))\right]. \quad (34)$$

By omitting the index j and taking into account that $F=1-A-iB$ and $\gamma=R/2$, we can transform Eqs. (41), (43), and (44) from Ref. 22 to

$$F=\frac{\Omega_0(f\Delta+\Omega_0-\Delta/2)+\gamma_0(\gamma_0-R/2)+i[\gamma_0(f\Delta-\Delta/2)+\Omega_0R/2]}{2(\Omega_0^2+\gamma_0^2)}, \quad (35)$$

$$\Omega_0=\pm\frac{1}{2\sqrt{2}}\sqrt{\sqrt{(\Delta^2+R^2)^2-16\Delta^2R^2(1-f)f}+\Delta^2-R^2}, \quad (36)$$

$$\gamma_0=\frac{1}{2\sqrt{2}}\sqrt{\sqrt{(\Delta^2+R^2)^2-16\Delta^2R^2(1-f)f}-\Delta^2+R^2}, \quad (37)$$

where $f=[\exp(\varepsilon/kT)+1]^{-1}$, and ε and $\varepsilon+\Delta$ are the tunnelon energies when the impurity is in the ground and excited states, respectively. Equations (34)–(37) may be used in a numerical calculation of the spectral line shape.[22,23] But these equations are too complicated and, at first view, it seems that they cannot compete with simpler formulas of the stochastic theory. Fortunately, Eqs. (34)–(37) may be considerably simplified and the formulas of the dynamic theory may be comparable in simplicity with those of the stochastic theory.

Let us take account of the fact that

$$\xi=\frac{16\Delta^2R^2(1-f)f}{(\Delta^2+R^2)^2}\leq 1, \quad (38)$$

and $\xi=1$ only in the specific case in which $R=\Delta$ and the temperature is infinite. In the most interesting case of low temperature the strong inequality $\xi\ll 1$ holds. Then expanding the right-hand sides of Eqs. (36) and (37) in powers of ξ and retaining the lowest-order nonvanishing terms, we obtain

$$\Omega_0=\frac{\Delta}{2}-\delta, \quad \gamma_0=\frac{R}{2}-\frac{\Gamma}{2}, \quad (39)$$

where

$$\delta=\frac{R^2\Delta}{\Delta^2+R^2}f(1-f), \quad \frac{\Gamma}{2}=\frac{R\Delta^2}{\Delta^2+R^2}f(1-f). \quad (40)$$

It follows from Eq. (40) that $\delta<\Delta/2$ and $\Gamma<R$. Therefore we may substitute

$$\Omega_0\to\Delta/2, \quad \gamma_0\to R/2 \quad (41)$$

in Eq. (35) and easily find that

$$F=\frac{\Delta}{\Delta-iR}f. \quad (42)$$

Using Eq. (39) and the substitution (41) in the product on the right side of Eq. (34), we obtain

$$\exp\varphi=\exp\left[-ix\sum_j\delta_j-|x|\sum_j\Gamma_j/2\right]\prod_j\left[1-F_j(1-\exp(-i\Delta_jx-R_j|x|))\right]. \quad (43)$$

Equation (43) can serve as the basic formula for the analysis of spectral diffusion. If we take into account not only equilibrium tunnelons, but also nonequilibrium ones, we can substitute the equilibrium tunnelon distribution function $f(T)$ in Eqs. (40) and (42) with the nonequilibrium function $\rho(t,T)$ described by Eq. (7), i.e.,

$$F_j=\frac{\Delta_j}{\Delta_j-iR_j}\rho_j(t,T), \quad (44)$$

$$\delta_j=\frac{R_j^2\Delta_j}{\Delta_j^2+R_j^2}\rho_j(1-\rho_j), \quad \frac{\Gamma_j}{2}=\frac{R_j\Delta_j^2}{\Delta_j^2+R_j^2}\rho_j(1-\rho_j). \quad (45)$$

Equations(43)–(45) adequately describe spectral diffusion.

Let us first consider the product over j in Eq. (43). It resembles the product in Eq. (12), which was used to derive formulas for the line width and shift identical to those of the stochastic theory. It is obvious that at $R_j=0$ the two products are identical. But in real solids $H_{\mathrm{rel}}\neq 0$, hence $R_j\neq 0$, so the real situation is quite different. Most tunneling systems are far from an impurity, so their coupling constants Δ_j are small. But at $R_j\neq 0$ the function F_j tends to zero at $\Delta_j\to 0$, and distant tunneling systems do not contribute to the product in Eq. (43). Only tunnelons with $\Delta_j>R_j$, i.e., those strongly interacting with the impurity, contribute to the product. But such tunnelons must be close to the impurity, hence they are relatively scarce. If the number of tunneling systems is small, the transition from the product in Eq. (19) to the integral with respect to the coordinates in Eq. (20) is not justified. Hence all the formulas derived from Eq. (20) in Section 3 are not valid. This means that if we eliminate the inconsistency of the approximation described by Eq. (11), which was discussed in Section 3, we conclude that the product over j in Eq. (43) does not contribute to spectral diffusion.

Now let us discuss the exponential factor in Eq. (43). The stochastic theories do not contain such expressions. After substituting the functions δ_j and Γ_j defined by Eq. (45), we obtain the following expressions for the spectral linewidth and shift:

$$\delta(t,T)=\sum_j \frac{R_j^2\Delta_j}{\Delta_j^2+R_j^2}\rho_j(1-\rho_j),$$

$$\frac{\Gamma(t,T)}{2}=\sum_j \frac{R_j\Delta_j^2}{\Delta_j^2+R_j^2}\rho_j(1-\rho_j). \tag{46}$$

Tunneling systems in close proximity to an impurity have the largest coupling constants Δ_j. Therefore only the coupling constants of the tunnelons from the immediate neighborhood of the impurity satisfy the inequality

$$\Delta_j>\Gamma_m, \tag{47}$$

where Γ_m is the total electronic transition line width determined by all broadening mechanisms. We shall calculate the contribution of these tunnelons separately by dividing the sum over j into two parts:

$$\sum_j=\sum_{l=1}^{n}+\sum_{j=n+1}^{N_0}, \tag{48}$$

where n is most likely somewhat greater than unity, and N_0 is approximately the total number of tunneling systems. By separating the sums in Eq. (46) according to Eq. (48), we obtain

$$\delta(t,T)=\delta_L(T)+\delta_{\mathrm{hom}}(t,T),$$

$$\Gamma(t,T)=\Gamma_L(T)+\Gamma_{\mathrm{hom}}(t,T), \tag{49}$$

where δ_L, Γ_L and δ_{hom}, Γ_{hom} are described by sums over l and $s=j-n$, respectively.

It is obvious that δ_L and Γ_L describe the spectral line shift and width due to the tunneling systems from the nearest impurity environment. This environment is different around different impurities, hence the parameters δ_L and Γ_L for different impurities are also quite different. The distributions $\Gamma(t,T)$ found in experiments with isolated terrylene molecules in polyethylene[24] are likely due to the inhomogeneity of Γ_L. Long-lived tunnelons with $1/R_j\rightarrow 0$, whose coupling constants do not satisfy the condition (47), do not contribute to δ_L and Γ_L, so the number n in the sum of Eq. (48) includes only short-lived tunnelons, which satisfy the condition (47). But the short-lived tunnelons have enough time to thermalize by the start of an optical experiment and their distribution function $\rho_j=f_j(T)$. Therefore δ_L and Γ_L are described by the following equations:

$$\delta_L(T)=\sum_{l=1}^{n} \frac{R_l^2\Delta_l}{\Delta_l^2+R_l^2}f_l(1-f_l),$$

$$\frac{\Gamma_L(T)}{2}=\sum_{l=1}^{n} \frac{R_l\Delta_l^2}{\Delta_l^2+R_l^2}f_l(1-f_l). \tag{50}$$

These are the formulas which were previously studied in the dynamic theory of the thermal broadening and shift of spectral lines.[20]

In contrast to the expressions for δ_L and Γ_L in Eq. (50), those for δ_{hom} and Γ_{hom} include sums over the enormous number N_0 of tunneling systems in the sample. The parameters δ_{hom} and Γ_{hom} are obviously independent of the immediate environment of the impurity center, i.e., they are equal for all impurity centers. Although the contribution of each tunnelon to δ_{hom} and Γ_{hom} is vanishingly small, their total number is very large and their resulting contribution is quite sizable. Therefore δ_{hom} and Γ_{hom} may be time-dependent.

As in Eq. (12), integrals with respect to coordinates may be introduced into the expression for δ_{hom} and Γ_{hom}. Now the distribution function defined by Eq. (16) depends on the initial condition $\rho_0=\rho(0)$:

$$Q(\Delta,\varepsilon,R,\rho_0)=N_0(\Delta)N(\varepsilon,R,\rho_0). \tag{51}$$

Using the same transformations as in the derivation of Eq. (18) from Eq. (12), we derive from Eq. (46) the following formulas:

$$\delta_{\mathrm{hom}}=N_0\int d\varepsilon\, dR d\rho_0 N(\varepsilon,R,\rho_0)\rho(1-\rho)R^2\sum_{s=1}^{N_0}\frac{\Delta_s}{\Delta_s^2+R^2}, \tag{52}$$

$$\Gamma_{\mathrm{hom}}=2N_0\int d\varepsilon\, dR d\rho_0 N(\varepsilon,R,\rho_0)\rho(1-\rho)R\sum_{s=1}^{N_0}\frac{\Delta_s^2}{\Delta_s^2+R^2}. \tag{53}$$

Taking the function $\Delta_s=\Delta(\mathbf{r}_{0s})$ to be defined by Eq. (21), we obtain

$$N_0\sum_s \frac{\Delta_s}{\Delta_s^2+R^2}=\frac{n_0\mu}{3}\left\langle F\int_{\Delta_{\min}F}^{\Delta_{\max}F}\frac{dy}{y}\frac{1}{y^2+R^2}\right\rangle$$

$$\cong\frac{n_0\mu}{3R^2}\langle F\rangle\ \ln\frac{R}{|\Delta_{\min}F|}, \tag{54}$$

$$N_0\sum_s \frac{\Delta_s^2}{\Delta_s^2+R^2}=\frac{n_0\mu}{3}\left\langle F\int_{\Delta_{\min}F}^{\Delta_{\max}F}dy\frac{1}{y^2+R^2}\right\rangle$$

$$\cong\frac{n_0\mu}{3R}\langle|F|\rangle\frac{\pi}{2}, \tag{55}$$

where angular brackets denote integration with respect to the angles. Here $n_0=N_0/V$ is the density of tunneling systems. Equations (54) and (55) are valid at $R>\Delta_{\min}F$. We may replace R in the logarithm with the effective value R_{eff}. Then $a=\ln(R_{\mathrm{eff}}/|\Delta_{\min}F|)$ is a constant less than 20. The dependence of the sums in Eqs. (54) and (55) on R is eliminated by the factors R^2 and R in Eqs. (52) and (53). The R-dependence is not canceled if the dipole–dipole interaction is replaced with an interaction of shorter range.

After substituting Eqs. (54) and (55) into (52) and (53), we obtain the following expressions for $\delta_{\rm hom}$ and $\Gamma_{\rm hom}$:

$$\delta_{\rm hom}=\frac{n_0\mu a}{3}\langle F\rangle\Psi_D(t,T),\quad \Gamma_{\rm hom}=\frac{n_0\mu\pi}{3}\langle|F|\rangle\Psi_D(t,T), \tag{56}$$

where

$$\Psi_D(t,T)=\int d\varepsilon\; dR d\rho_0 N(\varepsilon,R,\rho_0)\rho(1-\rho). \tag{57}$$

Equations (56) and (57) derived at $H_{\rm rel}\neq 0$ are similar to Eqs. (26) and (27), which were derived at $H_{\rm rel}=0$. The only difference between them is in the shapes of the functions Ψ and Ψ_D, which describe the time dependence of the line shift and width. Thus we have obtained the curious result that the only difference between the "inconsistent" dynamic theory of spectral diffusion, discussed in Section 3, whose results are close to those of the stochastic theories, and the self-consistent dynamic theory described in this section, is in the form of the functions $\Psi(t,T)$ and $\Psi_D(t,T)$.

5. TIME AND TEMPERATURE DEPENDENCES OF THE WIDTH AND SHIFT OF SPECTRAL LINES

Let us consider the case when the physical parameters ε, R, and ρ_0 are statistically independent, i.e.,

$$N(\varepsilon,R,\rho_0)=N_1(R)N_2(\varepsilon)N_3(\rho_0). \tag{58}$$

Assuming as in Section 3 that the distribution $N_2(\varepsilon)$ is a step function, we find

$$\Psi_D(t,T)=\int dRN_1(R)\int_0^{\varepsilon_m}\frac{d\varepsilon}{\varepsilon_m}\langle\langle\rho(1-\rho)\rangle\rangle, \tag{59}$$

where $\langle\langle\ldots\rangle\rangle$ denotes the averaging over the initial conditions, i.e., over the functions ρ_0. In the low-temperature limit, when $kT/\varepsilon_m\ll 1$, we easily find that

$$\int_0^{\varepsilon_m}\frac{d\varepsilon}{\varepsilon_m}\langle\langle\rho(1-\rho)\rangle\rangle=\frac{kT}{\varepsilon_m}A(t)+B(t), \tag{60}$$

where

$$A(t)=0.7[1-2\langle\langle\rho_0\rangle\rangle e^{-Rt}](1-e^{-Rt})-0.2(1-e^{-Rt})^2, \tag{61}$$

$$B(t)=\langle\langle\rho_0\rangle\rangle e^{-Rt}-\langle\langle\rho_0^2\rangle\rangle e^{-2Rt}. \tag{62}$$

Substituting Eqs. (59) and (60) into Eq. (56), we obtain

$$\delta_{\rm hom}=\frac{n_0\mu a}{3}\langle F\rangle\int dRN_1(R)\left[\frac{kT}{\varepsilon_m}A(t)+B(t)\right], \tag{63}$$

$$\Gamma_{\rm hom}=\frac{n_0\mu\pi}{3}\langle|F|\rangle\int dRN_1(R)\left[\frac{kT}{\varepsilon_m}A(t)+B(t)\right]. \tag{64}$$

The shift and width of spectral lines are controlled by the same constants $n_0\mu a\langle F\rangle/3$ and $n_0\mu\pi\langle|F|\rangle/3$ as in the stochastic theories. This is not surprising, since both theories take into account the dipole–dipole interaction of an impurity center with an enormous number of tunneling systems. The temperature dependence is linear as in the stochastic theory.

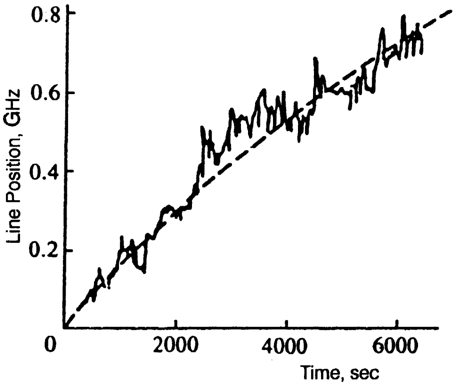

FIG. 1. High-energy shift of the pentacene line maximum[3] ($\lambda=592.544$ nm) and the calculation by (Eq. 66) (dashed line).

The most intriguing feature of Eqs. (63) and (64) is the dependence on the initial distribution function ρ_0. If $\langle\langle\rho_0\rangle\rangle=\langle\langle\rho_0^2\rangle\rangle=0$, we find that $B(t)=0$ and $A(t)$ is an increasing function of time. But if these averages are nonzero, the function $B(t)$ is also nonzero. In this case there should be a residual FWHM of an optical line larger than the inverse luminescence decay time T_1. This residual homogeneous FWHM is due to the interaction with nonequilibrium tunnelons, which act as defects in this case.

Note that the effect of the initial condition on the spectral line width in polymers and glasses was essentially completely ignored in previous theoretical studies. This is a new aspect of spectral diffusion problem revealed by the dynamic approach. Presently it is impossible to say which initial conditions prevail place in real solids with impurities. The situation could be clarified by dedicated experiments if measurements are processed using the present dynamic theory.

6. INHOMOGENEOUS SPECTRAL DIFFUSION

The stochastic theories describe spectral diffusion in terms of jumps of the resonant frequency. Recently variations in the resonant frequency with time were studied on the molecular level.[3] Three types of changes in the spectral line position of a pentacene molecule in paraterphenyl were observed: a) jumps of the $\lambda=592.404$-nm line between two spectral positions; b) jumps of the $\lambda=592.582$-nm line among many positions; c) a drift of the $\lambda=529.544$-nm line over 0.6 GHz in 1.6 h (Fig. 1). We shall not discuss physical causes of jumps, but the reasons for the monotonic line drift.

Until now we have ignored the off-diagonal interaction described by the operator M. Since the diagonal interaction D does not give an explanation why lines corresponding to some defects drift with time and lines of other defects do not, we shall take into account the off-diagonal interaction. Its effect on an optical line can be interpreted in terms of perturbation theory with the small parameter $M_{0j}/|E_0-E_j\pm\varepsilon|$. Since $M_{0j}\sim 10$–100 cm^{-1} and $E_0-E_j\sim 10^4$ cm^{-1}, this parameter is very small.

The interaction M, which is nonresonant by its nature, does not directly affect the line width, and its contribution to the line shift in the lowest nonvanishing approximation is described by the formula

$$\Omega(t,T)=\sum_{j=1}^{N}\frac{M_{0j}^2[1-\rho_j(t,T)]}{E_j+\varepsilon_j-E_0}, \tag{65}$$

where $\rho_j(t,T)$ is defined by Eq. (7).

This correction to the resonant frequency ω_0 may be a very slow function of time, nonetheless, its amplitude may be several gigahertz. Let us estimate this addition. Since M_{j0}^2 drops with the distance as r^{-6}, only the tunneling systems closest to the impurity make a sizable contribution to the frequency. Let us assume that

$$\Omega(t,T)=\frac{M^2}{E}[1-\rho(t,T)]. \tag{66}$$

The parameter M for the pentacene impurity in paraterphenyl is not known, so we use in our estimate the parameter $M=20\ \text{cm}^{-1}$ for the interaction between two neighboring molecules in a naphthalene crystal.[25] Since the pentacene impurity in paraterphenyl has $E\sim 10^4\ \text{cm}^{-1}$, we have $\Omega\sim 1$ GHz. The function $\Omega(t,T)$ calculated by Eq. (66) for $R^{-1}=10^4$ s, $M^2 f(T)/E=1.1$ GHz, and $\rho(0)=0$ is plotted in Fig. 1 as a dashed line.

The drift of the line position may lead to a time-dependent broadening of lines of ensembles of impurity molecules. Consider a quasi-homogeneous ensemble whose molecules have the same resonant frequencies ω_0 at $t=0$, but whose neighborhoods include different tunneling systems with $\rho(0)$ ranging from 0 to 1. Therefore the lines of some impurities will drift to the low-energy side, and other lines will drift to the high-energy side. If the numbers of impurities of both types are equal, the optical line of the molecular ensemble can be described by the following equation:

$$J_a(\omega,t)=\int_{-\infty}^{\infty}\frac{d\Omega}{\pi}P(\Omega)\frac{\gamma(T)/2}{[\omega-\omega_0-\Omega\rho(t,T)]^2+[\gamma(T)/2]^2}, \tag{67}$$

where $P(\Omega)$ is the probability that there is an impurity center with the frequency shift $\Omega=M^2/E$, and $\gamma(T)$ is the FWHM of the optical line due to the diagonal quadratic electron–tunnelon and electron–phonon interactions. In Eq. (67) we can take $\rho(t,T)=f(T)[1-\exp(-Rt)]$ which leads to a blueshift at $\Omega>0$. The redshift is also taken into account by virtue of the fact that $p(-\Omega)\neq 0$. Given that the broadened lines have Lorentzian shapes, we may assume that

$$P(\Omega)=\frac{\Gamma/2}{\Omega^2+(\Gamma/2)^2}. \tag{68}$$

In fact, substituting Eq. (68) into (67) and integrating with respect to Ω, we obtain

$$J_a(\omega,t)=\frac{\Delta\omega(t,T)/2}{(\omega-\omega_0)^2+[\Delta\omega(t,T)/2]^2}, \tag{69}$$

where the FWHM of the line in a quasi-homogeneous ensemble,

$$\Delta\omega(t,T)=\Gamma\rho(t,T)+\gamma(T), \tag{70}$$

is a function of both time and temperature. Obviously $\Delta\omega(0,T)=\gamma(T)$ and $\Delta\omega(\infty,T)=\Gamma f(T)+\gamma(T)$. The correction to the homogeneous half-width, $\gamma(T)$, is due to spectral diffusion. Since this type of spectral diffusion only takes place in optical lines of molecular ensembles, it is natural to classify it with inhomogeneous effects.

7. CONCLUSION

Let us summarize the new results obtained using the dynamic approach to spectral diffusion.

Both diagonal, D, and off-diagonal, M, interactions can contribute to spectral diffusion. The stochastic theories take into account only the diagonal interaction.

The dynamic theory which takes into account only the diagonal interaction D allows us to calculate using a common approach both thermal and time-dependent spectral line-widths, and shifts.

The diagonal interaction with tunnelons in the immediate neighborhood generates the spectral line shift δ_L and the FWHM Γ_L, which are time-independent and different for different molecules.

The diagonal interaction with the bulk of the tunneling systems yields additional contributions to the line shift and halfwidth, δ_{hom} and Γ_{hom}, which are time- and temperature-dependent and equal for all molecules.

The off-diagonal interaction M leads to a time- and temperature-dependent line shift $\Omega(t,T)$ controlled by the immediate neighborhood, which is therefore different for different impurities. This shift may lead to a time-dependence of optical lines due to quasi-homogeneous ensembles of molecules, i.e., inhomogeneous spectral diffusion.

The problem of the initial distribution of nonequilibrium tunnelons arises in the dynamic theory. Different shapes of the initial distribution lead to different effects, such as a residual linewidth larger than the reciprocal luminescence decay time.

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APPENDIX

By expanding the logarithm as a power series, the integral in Eq. (22) can be expressed as

$$\sum_{n=1}^{\infty}\frac{\rho^n}{n}\int_0^{\infty}\frac{d\Delta}{\Delta^2}(1-e^{-i\Delta Fx})^n=-\sum_{n=1}^{\infty}X_n. \tag{A1}$$

Calculating X_n at $n>1$, we find

$$X_n=\frac{\rho^n}{n}\sum_{p=0}^{n}(-1)^p\frac{n!}{(n-p)!p!}p\int_0^{\infty}\frac{d(p\Delta)}{(p\Delta)^2}$$

$$\times\exp(-ip\Delta Fx)=\rho^n J\sum_{q=0}^{n-1}(-1)^{q+1}\frac{(n-1)!}{(n-1-q)!q!}$$

$$=0.$$

This equation proves that only the first term in Eq. (A1) is nonzero, i.e., Eq. (23) is valid.

[1] W. Breinl, J. Friedrich, and D. Haarer, J. Chem. Phys. **81**, 3915 (1984).
[2] K. Littau, Y. S. Bai, and M. D. Fayer, J. Chem. Phys. **92**, 4145 (1990).
[3] W. P. Ambrose, Th. Basche, and W. E. Moerner, J. Chem. Phys. **95**, 7150 (1991).
[4] N. V. Gruzdev, E. G. Sil'kis, V. D. Titov, and Yu. G. Vainer, J. Opt. Soc. Am. B **9**, 941 (1992).
[5] H. C. Meijers and D. A. Wiersma, Phys. Rev. Lett. **68**, 381 (1992); J. Chem. Phys. **101**, 6927 (1994).
[6] P. Tchenio, A. B. Myers, and W. E. Moerner, J. Luminescence **56**, 1 (1993).
[7] W. O. Putikka and D. L. Huber, Phys. Rev. B **36**, 3436 (1987).
[8] Y. S. Bai and M. D. Fayer, Phys. Rev. B **39**, 11066 (1989).
[9] I. S. Osad'ko, in *Persistent Spectral Hole-Burning: Science and Applications. Technical Digest Ser.* **16**, 86 (1991), Monterey, California.
[10] I. S. Osad'ko, Phys. Rep. **206**, 45 (1991).
[11] P. D. Reilly and J. L. Skinner, J. Chem. Phys. **101**, 959, 965 (1994).
[12] A. Suarez and R. Silbey, J. Phys. Chem. **94**, 4145 (1994).
[13] I. S. Osad'ko, JETP Lett. **61**, 270 (1995).
[14] W. B. Mims, K. Nassau, and J. D. McGee, Phys. Rev. **123**, 2059 (1961).
[15] R. Klauder and P. W. Anderson, Phys. Rev. **125**, 912 (1962).
[16] P. Hu and S. B. Hartmann, Phys. Rev. B **9**, 1 (1974).
[17] P. Hu and L. R. Walker, Phys. Rev. B **18**, 1300 (1978).
[18] I. S. Osad'ko, in *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems*, V. Agranovich and R. Hochstrasser (eds), North Holland, Amsterdam (1983).
[19] D. A. Parshin, Fiz. Tverd. Tela **36**, 1809 (1994).
[20] I. S. Osad'ko, Adv. Polym. Sci. **114**, 125 (1994).
[21] K. P. Müller and D. Haarer, Phys. Rev. Lett. **66**, 2344 (1991).
[22] D. I. Donskoi, N. N. Zaitsev, and I. S. Osad'ko, Chem. Phys. **176**, 135 (1993).
[23] N. N. Zaitsev and I. S. Osad'ko, Zh. Éksp. Teor. Fiz. **104**, 4042 (1993).
[24] L. Fleury, A. Zumbusch, M. Orrit, R. Brown, and J. Bernard, J. Luminescence **56**, 15 (1993).
[25] V. L. Broude, É. I. Rashba, and E. F. Sheka, *Spectroscopy of Molecular Excitons* [in Russian], Énergoatomizdat, Moscow (1981), p. 38.

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