

# Two mechanisms for spectral diffusion in optical spectra of impurity centers

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A study has been made of how the interaction of an impurity center with tunneling excitations of the solvent affects the time evolution of the spectral lines of pentacene molecules in a para-terphenyl crystal. Interactions diagonal and nondiagonal in terms of electron indices are considered; they are manifested in different ways in the spectral diffusion. © 1995 American Institute of Physics.

1. Spectral diffusion is usually manifested as a spontaneous broadening, over time, of spectral holes burned in inhomogeneously broadened optical bands of impurity centers.<sup>1,2</sup> Spectral diffusion is usually linked with a change in the resonant frequency  $\omega_0$  of the chromophore as the result of a relaxation of two-level systems of polymers and glasses.

Changes in the resonant frequency of an impurity have recently been studied at the monomolecular level.<sup>3</sup> Three types of time variations have been observed in the spectral lines of various impurity centers for the case of a pentacene molecule in a para-terphenyl crystal:<sup>3</sup> a) jumps of the line with  $\lambda = 592.404$  nm between two spectral positions, b) jumps of the line with  $\lambda = 592.582$  nm among many spectral positions; c) creep of the line with  $\lambda = 592.544$  nm along the frequency scale, over 0.6 GHz in 1.6 h (Fig. 1).

A theory was offered in Refs. 4–6 in an effort to explain effects a) and b). That theory assumes that phenyl rings of the para-terphenyl molecule can undergo a tunneling accompanied by a change in their orientation. The theory of Refs. 4–6 does not, on the other hand, explain effect c).

In the present letter we show that there are two mechanisms for spectral diffusion. One of them was taken into account in Refs. 4–6; it is manifested by “hops” of a spectral line. The second mechanism, not considered in Refs. 4–6, leads to a monotonic shift of the resonant frequency  $\omega_0$  as time elapses.

2. We adopt the Hamiltonian of an electronically unexcited, impure crystal in the following form:

$$H^g = \sum_n \epsilon_n C_n^+ C_n + H_{\text{rel}}, \quad (1)$$

where the Fermi operators  $C_n^+$  and  $C_n$  describe the creation and annihilation of an excitation in the  $n$ th two-level system. We refer to this excitation below as a “tunnelon.” Here  $\epsilon_n$  is the tunnelon energy, and  $H_{\text{rel}}$  determines the tunnelon relaxation mechanism.

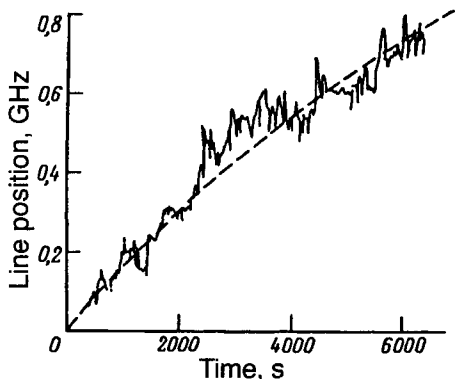


FIG. 1. Creep in the violet direction of the pentacene-molecule line with  $\lambda=592.544$  nm (Ref. 3), along with results calculated from Eqs. (6) and (13) (the dashed curve).

We adopt the adiabatic Hamiltonian of the impure crystal in the following form, which incorporates electronic excitations:

$$H^e = E_0 B_0^+ B_0 + \sum_n E_n B_n^+ B_n + \hat{D} + \hat{M} + H^g. \quad (2)$$

Here  $E_0$ ,  $B_0^+$ ,  $B_0$  and  $E_n$ ,  $B_n^+$ ,  $B_n$  are the energies of the electronic excitation and the operators which create and annihilate an electronic excitation in the impurity and in the solvent molecule, respectively. The electron-tunnelon interaction has a component which is diagonal ( $\hat{D}$ ) and one which is not diagonal ( $\hat{M}$ ) in terms of the electron indices. In the diagonal interaction  $\hat{D}$  we incorporate the interaction of only the impurity center with tunnelons:

$$\hat{D} = B_0^+ B_0 \sum_{n=1}^N \Delta_n C_n^+ C_n. \quad (3)$$

Here  $\Delta_n$  describes the increment in the tunnelon energy  $\epsilon_n$  upon electronic excitation of the impurity.

We write the nondiagonal interaction  $\hat{M}$  as follows:

$$\hat{M} = \sum_{n=1}^N M_{0n} (B_0^+ B_n C_n + B_0 B_n^+ C_n^+). \quad (4)$$

Although this interaction has not previously been considered in the work on spectral diffusion, it generates effect c). Let us take a closer look at this question.

3. Spectral diffusion results from the interaction of an impurity center with nonequilibrium tunnelons, which tend toward equilibrium over the entire duration of the experiment. A phase relaxation has obviously already occurred in a system of such tunnelons, so the density matrix of the tunnelons has only diagonal elements. Incorporating the statistical independence of the tunnelons, we can write their density matrix as  $\hat{\rho}(t, T) = \prod_n \hat{\rho}_n(t, T)$ , where

$$\hat{\rho}_n(t, T) = [1 - \rho_n(t, T)] C_n C_n^+ + \rho_n(t, T) C_n^+ C_n, \quad (5)$$

$$\rho_n(t, T) = f_n(T) + [\rho_n(0) - f_n(T)] e^{-R_n t}. \quad (6)$$

Here  $R_n$  is the relaxation constant of the  $n$ th tunnelon. We can find an explicit expression for this constant once we have determined  $H_{\text{rel}}$ . Here also,  $\rho_n(0)$  is the initial value of the element of the density matrix, and  $f_n(T) = [\exp(\epsilon_n/kT) + 1]^{-1}$  is its final value. If  $R_n t \gg 1$ , the matrix  $\hat{\rho}_n$  becomes the equilibrium density matrix.

We denote by  $\epsilon_\alpha$ ,  $|\alpha\rangle$  and  $\epsilon_\beta$ ,  $|\beta\rangle$  eigenvalues and eigenvectors of the operators  $H^s$  and  $H^e$ . We can then write the following expression for the optical band of the impurity center ( $\hbar = 1$ ):

$$I(\omega) = 2\pi \sum_{\alpha, \beta} \langle \alpha | \hat{\rho}(t, T)(\mathbf{dE}) | \beta \rangle \langle \beta | (\mathbf{dE}) | \alpha \rangle \delta(\omega + \epsilon_\alpha - \epsilon_\beta), \quad (7)$$

where  $\hat{\rho}(t, T)$  is the density matrix of the nonequilibrium tunnelons, and the operator

$$(\mathbf{dE}) = -i\Lambda(B_0 - B_0^\dagger) \quad (8)$$

incorporates the interaction of only the impurity center with the light.

The shape function  $I(\omega)$  can be calculated exactly in the zeroth approximation in  $\hat{M}$  (Refs. 7-9). These calculations show that the diagonal interaction  $\hat{D}$  does lead to a broadening and shift of a purely electronic line of an impurity, but the half-width and shift of the line are proportional to the reciprocal of the tunneling lifetime,  $R$ . Accordingly, for the long-lived tunnelons which cause the spectral diffusion, this half-width  $\gamma$  and this shift  $\delta$  are vanishingly small (for  $R^{-1} \equiv 200$  s, we would have  $\gamma \propto \delta < 10^{-3}$  Hz). With  $\hat{M} = 0$  but  $\hat{D} \neq 0$ , the following result is found for the shape function of the band<sup>4,7-9</sup> ( $\omega_0 = E_0/\hbar$ ):

$$I(\omega, t) = \Lambda^2 \int_{-\infty}^{\infty} dx \cdot e^{i(\omega - \omega_0)x} I_D(x), \quad (9)$$

where

$$I_D(x) = \prod_{n=1}^N [1 + \rho_n(t, T)(e^{-i\Delta_n x} - 1)]. \quad (10)$$

The shape of an electron-tunnelon optical band has been calculated from Eqs. (9) and (10) for both equilibrium<sup>7,9</sup> and nonequilibrium<sup>4,8</sup> tunnelons.

The Reilly-Skinner theory<sup>4-6</sup> for spectral diffusion is based on Eqs. (9) and (10). If  $\Delta_n$  falls off with distance from the impurity as  $1/r^3$ , we have

$$I_D(x) \approx \exp[-a(t, T)|x|]. \quad (11)$$

This expression leads to a spectral line of Lorentzian shape whose width depends on the time. In other words, it leads to a Lorentzian spectral diffusion.

4. The function  $I(\omega)$  cannot be calculated exactly when the operator  $\hat{M}$  is taken into account, even in the zeroth approximation in  $\hat{D}$ . However, in the nonresonant case of interest in this letter we have the small parameter  $M_{0n}/|E_0 - E_n - \epsilon_n| \ll 1$ , since we have  $M_{0n} \approx 10-100 \text{ cm}^{-1}$  and  $E_0 - E_n \approx 10^4 \text{ cm}^{-1}$ . We can therefore use a perturbation theory

in the operator  $\hat{M}$ . In the first nonvanishing approximation in  $\hat{M}$ , we find a time-dependent increment in the resonant frequency. In other words, the frequency  $\omega_0$  in Eq. (9) should be replaced by  $\omega_0 - \Omega(t, T)$ , where

$$\Omega(t, T) = \sum_{n=1}^N \frac{M_{0n}^2 [1 - \rho_n(t, T)]}{E_n + \epsilon_n - E_0}. \quad (12)$$

This increment may be a very weak function of the time; nevertheless, its magnitude may be on the order of 1 GHz. Let us estimate this increment. Since  $M_{0n}^2$  falls off spatially as  $1/r^6$ , several terms make significant contributions to  $\Omega$  in Eq. (12). We assume

$$\Omega(t, T) \approx \frac{M^2}{E} [1 - \rho(t, T)]. \quad (13)$$

We do not know the strength of the resonant interaction  $M$  between pentacene and para-terphenyl molecules. For an estimate we accordingly adopt the value  $M = 20 \text{ cm}^{-1}$ , which has been found for an interaction between two neighboring molecules in a naphthalene crystal.<sup>10</sup> In the pentacene-paraterphenyl system we would have  $E = E_1 - E_0 \approx 10^4 \text{ cm}^{-1}$ . Since we have  $\rho(t, T) \approx 1$ , we find  $\Omega(t, T) \approx 1 \text{ GHz}$ . This is the order of magnitude of the line creep in Fig. 1. The dashed line in that figure shows the function  $\Omega(t, T)$  calculated from Eqs. (13) and (6) with the values  $M^2 f(T)/E = 1.1 \text{ GHz}$ ,  $1/R = 10^4 \text{ s}$ , and  $\rho_n(0) = 0$ . Random hops of a spectral line can apparently be described by the theory of Refs. 4–6, which incorporates the diagonal interaction  $\hat{D}$ . The monotonic creep of the line with  $\lambda = 592.544 \text{ nm}$  can be described satisfactorily by simple expression (13). With  $\rho_n(0) = 0$  and  $\rho_n(0) = 1$ , the impurity lines shift in the violet and red directions, respectively, as time elapses.

5. Let us examine the spectral diffusion in the example of an optical absorption line of a quasihomogeneous ensemble of impurity molecules which have a frequency  $\omega_p$  at  $t = 0$ , but in whose local neighborhood there are two-level systems with various values of  $\rho(0)$  on the interval from 0 to 1. As time elapses, the lines of some of the centers shift in the red direction, and those of others shift in the violet direction. If we assume that the two types of centers are present in identical numbers, then the shape of the line of the ensemble of impurities can be described by

$$J(\omega, t) = \int_{-\infty}^{\infty} \frac{d\Omega}{\pi} P(\Omega) \frac{\gamma(T)/2}{[\omega - \omega_p - \Omega \rho(t, T)]^2 + [\gamma(T)/2]^2}, \quad (14)$$

where  $P(\Omega)$  is the probability density for finding an impurity center with a given value of  $\Omega = M^2/E$ , and  $\gamma(T)$  is the half-width set by the electron-phonon interaction. In the expression for  $J(\omega, t)$  we must now consider only the violet shifts, which correspond to the function  $\rho(t, T) = f(T)(1 - e^{-Rt})$ . The possibility of red shifts is taken into account by the circumstance that we have  $P(-\Omega) \neq 0$ . The Lorentzian shape of the holes, which broaden as time elapses, suggests that the distribution  $P(\Omega)$  is Lorentzian:

$$P(\Omega) = \frac{\Gamma/2}{\Omega^2 + (\Gamma/2)^2}. \quad (15)$$

Substituting (15) into (14), we find the following expression for the lineshape of the molecular ensemble,  $J(\omega, t)$ :

$$J(\omega, t) = \frac{\Delta\omega(t, T)/2}{(\omega - \omega_p)^2 + [\Delta\omega(t, T)/2]^2} \cdot \quad (16)$$

The half-width of the Lorentzian,

$$\Delta\omega(t, T) = \Gamma\rho(t, T) + \gamma(T), \quad (17)$$

depends on the time and the temperature. We evidently have  $\Delta\omega(0, T) = \gamma(T)$  and  $\Delta\omega(\infty, T) = \Gamma f(T) + \gamma(T)$ . The increment  $\Gamma f(T)$  in the homogeneous half-width  $\gamma(T)$  is a consequence of spectral diffusion.

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