Exciton Line Shapes at Finite Temperatures

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Equations of motion for excitons in molecular aggregates obtained from stochastic Hamiltonian models are known to be applicable only at infinite temperatures. It is argued that the problem lies in the omission of dissipative contributions that must be present if the excitons are to achieve thermal equilibrium. Stochastic equations of motion are constructed that are applicable at finite temperatures. As an application of the model optical line shapes are considered.

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One of the most useful theories of energy transfer in molecular crystals is originally due to Haken and Strobl[1,2] and has since been used and extended by other authors.[3-6] In this theory, the exciton-phonon coupling is treated phenomenologically and semiclassically via the introduction of a stochastic term in the Hamiltonian. The Hamiltonian is assumed to have the form

$$H=\sum_k E_k a_k{}^\dagger a_k + \sum_{n,m} V_{nm}(t) a_n{}^\dagger a_m . \qquad (1)$$

Here $a_k{}^\dagger$ and a_k are respectively creation and annihilation operators of an exciton with momentum k and energy E_k. The operators $a_n{}^\dagger$ and a_n create and destroy an exciton localized at the nth site of the lattice and are discrete Fourier transforms of the operators $a_k{}^\dagger$ and a_k. The fluctuating functions $V_{nm}(t)$ model the fluctuations in the site energy $(n=m)$ and in the interactions $(n\neq m)$ of localized excitons due to the scattering of excitons by phonons. The fluctuations are assumed to be zero-centered, Gaussian, and delta-correlated in time.[1,2] This model is formulated for rapidly relaxing fluctuations and is hence appropriate only for a small exciton bandwidth relative to the phonon bandwidth. The results obtained from the Haken-Strobl model are well known to be valid only in the infinite-temperature limit. Thus the temperature dependence of transport coefficients and line shapes cannot be determined from this model.

The Haken-Strobl model has been generalized in a number of useful ways. Sumi[4] and Blumen and Silbey[5] considered nondelta-correlated site energy fluctuations, with

$$\langle V_{nn}(t) V_{mm}(t')\rangle = D^2 \exp(-\gamma|t-t'|)\delta_{nm} . \qquad (2)$$

Nondelta-correlated transfer integrals have been dealt with by Jackson and Silbey.[6] The parameter γ in (2) is a measure of the phonon bandwidth, and D is the average amplitude of the potential fluctuations at each lattice site. We note that this generalization (and in fact any generalization of the stochastic model to date) does not *per se* introduce a temperature.

In spite of the restriction of these models to infinite temperatures, their tractability has engendered their widespread use. These models are assumed to be capable of representing a gamut of exciton-phonon interactions from weak to strong and from local to nonlocal. The variety of possible interactions is manifest in different statistical properties chosen for $V_{nm}(t)$. It would therefore be highly desirable to have available a phenomenological model built on premises similar to those adopted by Haken and Strobl but applicable at finite temperatures. Such a model would enable one to calculate the temperature dependence of transport and spectral properties. In this paper we propose such a model.[7] We note that the problem of exciton dynamics at finite temperatures has been approached by means of fully dynamical models.[8,9] However, this approach has been limited by the technical difficulties in calculating physical observables.

The exciton operators are assumed to obey Bose-Einstein commutation relations, an approximation which is valid at low exciton density. The equations of motion of the exciton operators are then

$$\mathring{a}_k(t) = i[H, a_k] = -iE_k a_k(t) - i\sum_{k_1} F_{kk_1}(t) a_{k_1}(t), \qquad (3)$$

where the fluctuating coefficient F_{kk_1} is a Fourier transform of the Hamiltonian potential fluctuations in (1). The model with which we propose to replace the Haken-Strobl–type models is described by the equations of motion

$$\dot{a}_k(t) = -iE_k a_k(t) - i\sum_{k_1} F_{kk_1}(t)a_{k_1}(t) - \sum_{k_1}\sum_{k_2}\sum_{k_3}(E_{k_3}-E_{k_2})\int_0^t d\tau\, K_{k_2k_3}{}^{kk_1}(t-\tau)a_{k_2}{}^\dagger(\tau)a_{k_3}(\tau)a_{k_1}(t) \quad (4)$$

and its Hermitian conjugate for each k. The new contribution appearing in our model is the last term in (4). We identify this as a *dissipative* contribution which has been absent in all prior stochastic formulations of the exciton transport problem. The crux of the model lies in the choice of the dissipative kernel $K_{k_2k_3}{}^{kk_1}(t)$, which must satisfy the physical constraints described below.

The choice of the kernel is dictated by the fact that the last term in (4) results from the average interaction of the exciton with the heat bath. Contrary to the usual statements,[3-6] this average interaction *cannot* be included in E_k because it is irreversible and can therefore not be incorporated into a purely excitonic Hamiltonian. The combined exciton-phonon system is thermodynamically isolated, and the exciton system is thermodynamically closed. It then follows that the kernel and the fluctuations $F_{kk_1}(t)$ must be connected by a *fluctuation-dissipation relation.* This relation depends on the temperature and on the nature of the interactions between the excitons and phonons, and can generally be expressed as[7,10]

$$\Phi \equiv \tfrac{1}{2}\langle F_{kk_1}(t)F_{k_2k_3}(t+\tau)F_{k_2k_3}(t)\rangle = \int_0^\infty d\tau\, g(\beta,t,\tau)K_{k_2k_2}{}^{kk_1}(\tau), \quad (5)$$

where $g(\beta, t, \tau)$ is a scalar function of the temperature. We note that (5) is unusual in that the fluctuations are not dissipated instantaneously.[7,11,12] The correlation time of the fluctuations is thus temperature dependent.

The physical properties of the fluctuations and of the dissipative kernel can be derived from fully dynamical models of the exciton–heat-bath system. The differences among models manifest themselves in $g(\beta, t, \tau)$. For instance, consider the "linear coupling model"[3,7,9]

$$H = \sum_k E_k a_k{}^\dagger a_k + \sum_{q,\alpha}\omega_{q\alpha} b_{q\alpha}{}^\dagger b_{q\alpha} + \sum_{k,q,\alpha}\Gamma_{kq\alpha}(b_{q\alpha}{}^\dagger + b_{-q\alpha})a_k{}^\dagger a_{k+q}. \quad (6)$$

The operators $b_{q\alpha}{}^\dagger$ and $b_{q\alpha}$ respectively create and annihilate a phonon of wave vector q in branch α. The last term in (6) expresses the exciton-phonon interactions. The exciton equation of motion obtained after explicit integration of the phonon equations is precisely (4) with[7]

$$K_{k_2k_3}{}^{kk_1}(t) = \sum_\alpha \frac{\Gamma_{kq\alpha}\Gamma_{k_2,-q,\alpha}}{\omega_{q\alpha}}\cos\omega_{q\alpha}t\,\delta_{k_3,k_2-q}\,\delta_{k_1,k+q}, \quad (7)$$

$$F_{kk_1}(t) = \sum_\alpha \Gamma_{kq\alpha}[b_{q\alpha}{}^\dagger(0)\exp(i\omega_{q\alpha}t) + b_{-q\alpha}(0)\exp(-i\omega_{q\alpha}t)]\,\delta_{k_1,k+q}, \quad (8)$$

and

$$g(\beta,t,\tau) = \frac{\pi}{2\beta}\left[\operatorname{csch}^2\frac{\pi}{\beta}(t+\tau) + \operatorname{csch}^2\frac{\pi}{\beta}(t-\tau)\right], \quad (9)$$

where $\beta \equiv (k_B T)^{-1}$. Equation (8) is interpreted as a fluctuating energy because the initial phonon operators are chosen from a canonical ensemble. The fluctuation-dissipation relation dictates that one must retain terms only to $O(\Gamma)$ in the fluctuations if one retains terms to $O(\Gamma^2)$ in the dissipation. This has been done above.

The function $g(\beta, t, \tau)$ of Eq. (11) decays on a time scale $t-\tau \sim \beta$. We believe this to be a general (Hamiltonian-insensitive) feature.[11] The relation (5) then implies that the decay rate of Φ either is the same as that of K (high-T limit) or is k_BT, whichever is shorter. When γ is the shorter of the two, then the dissipative response of the bath is instantaneous so that $g(\beta, t, \tau) \simeq g_0(\beta)\delta(t-\tau)$ (this result does *not* imply delta-correlated fluctuations).[7,11] This limit yields a classical fluctuation-dissipation relation and is independent of the detailed dynamical model.[11] For the linear coupling model $g_0(\beta) \sim \beta^{-1}$ so that the fluctuation level D^2 is proportional to temperature.[4]

To compare our results to those of the Haken-Strobl–type models we choose the dissipative kernel to be local and site diagonal with a simple exponential correlation function, so that

$$K_{k_2k_3}{}^{kk_1}(t) = \epsilon e^{-\gamma|t|}\,\delta_{k_3,k_2-q}\,\delta_{k_1,k+q}. \quad (10)$$

We note that it is physically more reasonable to choose the dissipative kernel phenomenologically and then use the fluctuation-dissipation relation (5) to specify Φ rather than the reverse.[11] The coefficient ϵ has dimensions of energy and constitutes an *additional parameter*, previously unrecognized in stochastic Hamiltonian formulations, that plays an important role in exciton dynamics. The linear coupling model provides an interpretation of this parameter in terms of microscopic quantities: $\epsilon \sim \Gamma^2/\Omega_{\text{ph}}$, where Γ is a typical exciton-phonon coupling energy and Ω_{ph} is a typical phonon energy. From (10) and (5) we conclude that the correlation function Φ of the fluctuations decays on a time scale γ^{-1} at high temperatures and $(k_BT)^{-1}$ at low temperatures.

Sumi[4] and Silbey *et al.*[5,6,8,13] have emphasized the importance of considering the exciton bandwidth (B), the phonon bandwidth (γ), and the fluctuation level (D) in the transport and spectral behavior of the excitons. In the spirit of their discussion we are now able to introduce the two additional energy parameters that affect exciton dynamics, namely, the temperature k_BT and the exciton-phonon coupling strength ϵ. Heretofore the former has been assumed to be infinite (i.e., much larger than γ and B) and consequently the latter has been assumed to vanish. Let us now consider what happens when k_BT is finite and ϵ is nonvanishing. Since Eq. (4) is nonlinear, its detailed analysis is difficult. We therefore restrict our investigation here to a set of approximations that are often made (in other mode-coupling contexts)[14] without more justification than their physical plausibility. We make the following approximations within the integrand in (4): (1) We retain only diagonal terms. (2) We approximate the evolution of $a_{k_2}^\dagger$ and a_{k_3} by their evolution in the absence of the heat bath. (3) We replace the diagonal quadratic terms in the symmetrized product by unity (low-exciton-density approximation). The resulting equation is

$$\dot{a}_k(t) = -iE_k a_k(t) - i\sum_{k_1} F_{kk_1}(t) a_{k_1}(t) - \lambda_k(t) a_k(t). \tag{11}$$

In terms of the exciton density of states $g_{\text{ex}}(\omega)$, the dissipative coefficient $\lambda_k(t)$ is given by

$$\lambda_k(t) = \epsilon \int d\omega\, g_{\text{ex}}(\omega)\, \frac{(E_k-\omega)[\gamma + i(E_k-\omega)]}{(E_k-\omega)^2+\gamma^2} \{1 - \exp[i(E_k - \omega + i\gamma)t]\}. \tag{12}$$

The exciton line shape obtained from the solution to (11) up to the second cumulant,[5,15] with $\Lambda_k(t) \equiv \int_0^t \lambda_k(t')dt'$, is

$$I_k(\omega) = \frac{1}{\pi} \operatorname{Re} \int_0^\infty d\tau \exp[i(\omega - E_k)\tau - \Lambda_k(\tau)] \exp\left[-\int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2\, \varphi(\tau_1-\tau_2) G_k(\tau_1,\tau_2)\right]. \tag{13}$$

Here $\Lambda(\omega, t)$ is $\Lambda_k(t)$ with E_k replaced by ω, $\varphi(t) \equiv \epsilon \int_0^\infty f(\beta, t, \tau) e^{-\gamma\tau} d\tau$, and

$$G_k(t_1, t_2) = \exp[iE_k(t_1-t_2)] \exp[\Lambda_k(t_1) - \Lambda_k(t_2)] \int d\omega\, g_{\text{ex}}(\omega) \exp[-i\omega(t_1-t_2)] \times \exp\{-[\Lambda(\omega,t_1) - \Lambda(\omega,t_2)]\}. \tag{14}$$

The line shape (13) has the same "formal" structure as that for the Haken-Strobl–type models but with two important modifications: (1) We include the new dissipative term $\Lambda_k(t)$ both in the τ integrand and in the modified exciton spectral correlation function $G_k(\tau_1, \tau_2)$; and (2) we take into account the fluctuation-dissipation relation. We examine the line shape in different parametric regimes. When $D^2 \gg B^2 + \gamma^2$ and $D \gg \epsilon$, the absorption line is broadened at each lattice site. For moderate frequencies one obtains a Gaussian,[4,5] i.e.,

$$I_k(\omega \lesssim D') = \frac{1}{\sqrt{2\pi} D'} \exp\left[-\frac{(\omega - E_k)^2}{2D'^2}\right] \tag{15}$$

with width proportional to $D' = [D^2 + c_1 B\epsilon]^{1/2}$ where c_1 is a real constant of order unity. Thus the square of the linewidth is still linear in the temperature (Haken-Strobl–type models with $D^2 \sim k_BT$)[4] but contains corrections dependent on the exciton bandwidth B and the coupling strength ϵ. If $D^2 < \epsilon$ but still $D^2 \gg B^2 + \gamma^2$, then the line shape remains Gaussian but the correction becomes small. If $D^2 \ll B^2 + \gamma^2$ and $\epsilon^2 \ll B^2 + \gamma^2$, then the line shape is approximately Lorentzian with the width given by

$$\Gamma \sim 2\frac{D^2}{B^2}[(B^2+E^2)^{1/2} - E] + c\frac{\epsilon\gamma B}{B^2+\gamma^2}, \tag{16}$$

where $E = \gamma$ if $\gamma < k_BT$ and $E = k_BT$ if $\gamma > k_BT$, and where c is again a real constant of order unity.

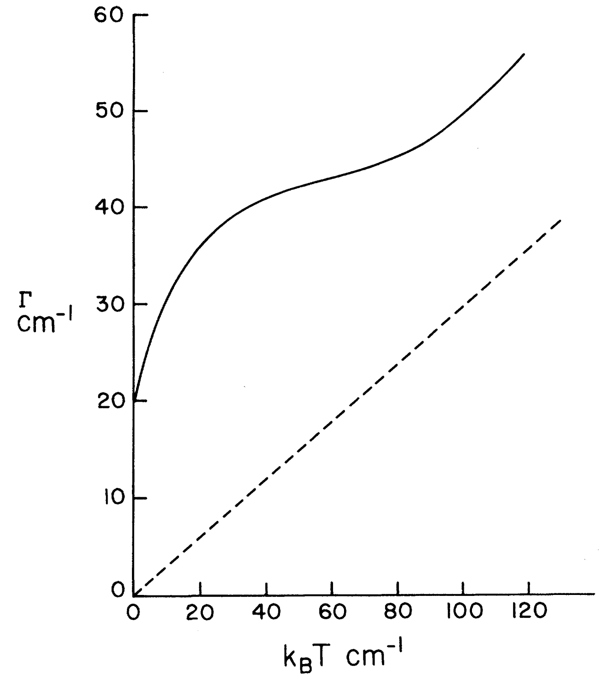

FIG. 1. Sketch of linewidth Γ vs k_BT for typical parameter values in molecular crystals. $B = 40$ cm^{-1}, $\gamma = 80$ cm^{-1}, $\epsilon = 25$ cm^{-1}, and $D^2 = \epsilon k_B T$. Dashed line: Haken-Strobl–type model. Solid line: our model with $c = 2$.

The Haken-Strobl–type models yield $\Gamma \sim (2D^2/B^2)[(B^2+\gamma^2)^{1/2} - \gamma]$.[4,5] The temperature dependence of our results in this regime is quite different from those of the Haken-Strobl–type models. The difference is most pronounced when $B < \gamma$. We have illustrated this in Fig. 1. Furthermore, the additional ϵ-dependent contribution can be appreciable and in fact *larger* than the Haken-Strobl contribution at low temperatures.

Regardless of the particular form of the line shape, the dissipative contribution of our model thus induces a broadening in addition to that obtained in the Haken-Strobl–type models, with a different temperature dependence. An estimate of the magnitude of the corrections shows that they may be appreciable for excitons in molecular crystals even at ordinary and certainly at low temperatures.

We have extended the usual stochastic formulation of exciton transport[1-6] so as to obtain a description valid at finite temperatures. We have shown that the average exciton-phonon interaction leads to an irreversible dissipative contribution in the equations of motion, a contribution that has been absent from previous stochastic models. The dissipative term is related to the fluctuations via a fluctuation-dissipation relation that ensures thermal equilibration of excitons with the phonon bath. The dissipative effects, being irreversible, cannot be built into a purely excitonic Hamiltonian.

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