

## OPTICAL SPECTRA AND EXCITON COHERENCE \*

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The overlap of donor emission and acceptor absorption spectra has long been known as a determining factor in the rate of excitation transfer. Memory functions capable of providing short time information can be obtained in an equally direct way from spectra. We present several examples derived from both real and model systems to illustrate the effect of spectral linewidth and splitting on the coherence of excitation undergoing transfer.

### 1. Introduction

In many materials exciton motion may be described most appropriately in terms of diffusion, as in Förster's [1] well-known treatment of resonance transfer. Wave-like motion of the exciton has been observed indirectly through the magnetostark effect in CdS [2]. The question naturally arises: when does one kind of motion give way to the other? More precisely, what criteria are available for predicting *coherence* of the exciton? The present paper advocates monomer spectra as a source of information, with particular reference to molecular systems.

### 2. Theory

Many [3] have studied exciton coherence on the basis of models, and we have developed [4] a unified picture based on the generalized master equation (GME). Coherence is described by a memory  $\phi(t)$ , essentially the kernel of the GME, obtained directly from the absorption cross section  $\sigma(\omega)$  and emission probability  $I(\omega)$  of the molecules:

$$\phi(t) = \text{const Re } \mathcal{D}^e(t) \mathcal{D}^a(t)^* , \quad (1)$$

where  $\mathcal{D}^a(t)$  and  $\mathcal{D}^e(t)$  are the Fourier transforms of  $\omega^{-1}\sigma(\omega)$  and  $\omega^{-3}I(\omega)$ , respectively. This result follows [4e] from an extension [4b] of Förster's theory retaining many of its assumptions (dipole–dipole interaction, no exchange, weak interaction)

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but not utilizing ordinary time-dependent perturbation theory. It has been shown [4c] how the fast and slow excitation transfer limits emerge from this unified picture, and how it relates to other theories [4d,4e,5].

The memory, eq. (1), acquires elementary forms when simple spectral features are assumed. Thus, when  $\omega^{-3}I(\omega)$  and  $\omega^{-1}\sigma(\omega)$  are  $\delta$ -functions, lorentzians of half-widths  $\alpha$  and  $\beta$ , or corresponding gaussians, and are separated by  $\Delta$ ,  $\phi(t)$  is proportional to  $\cos \Delta t$ ,  $\{\exp[-(\alpha + \beta)t]\} \cos \Delta t$ , or  $\{\exp[-\frac{1}{2}(\alpha^2 + \beta^2)t^2]\} \cos \Delta t$ , respectively. For an unshifted lorentzian (half-width  $\alpha$ ) and symmetrically located gaussians (half-width  $\beta$  and separation  $\Delta$ ), as in fig. 2a below, we have

$$\phi(t) \propto A^2 e^{-\alpha t} + B^2 e^{-\beta^2 t^2} \cos \Delta t + 2AB e^{-(\alpha t + \beta^2 t^2)} \cos \frac{1}{2} \Delta t, \quad (2)$$

where  $A$  and  $B$  are the relative areas under the lorentzian and gaussian, respectively. Modeling of observed spectra may be done with  $\delta$ -functions and lorentzians representing singular and broadened zero-phonon lines, respectively, and gaussians representing multi-phonon bands. Alternatively, direct numerical computation using eq. (1) yields  $\phi(t)$ .

### 3. Results for real systems

We consider singlet states of typical organic molecules at 300 K and crystal defects showing zero-phonon lines, and assume homogeneous broadening.

Fig. 1 shows room temperature spectra [6] and  $\phi(t)$ 's for anthracene, bacteriochlorophyll (BChl), and adenosine monophosphate (AMP). The main feature of the memories is their fall-off in 0.01–0.03 ps, showing that all coherence is lost well before the picosecond spectroscopy region. A vibrational relaxation time of  $10^{-12}$  s is clearly not the appropriate measure of exciton coherence times here. For systems having spectra similar to those in fig. 1, any effects due to exciton motion currently susceptible to observation may safely be described in terms of diffusion.

Fig. 2 shows  $\phi(t)$  and the low-temperature spectra [7] of the  $F_3^+$  center in NaF, to illustrate effects of zero-phonon lines. The absorption spectrum has been assumed mirror symmetric, since only the excitation spectrum is known in the multiphonon region. During the first 20–30 fs the memory behaves exactly as for high-temperature organics, but it contains a small part (proportional to the square of the relative zero-phonon line intensity [4e]) persisting to relatively long times: 0.8 ps. The decay time of this component is inversely proportional to the zero-phonon line width [see eq. (2)]. Coherence in pairwise excitation transfer among these centers therefore has a long-lived component, but its magnitude is *very* small, despite the zero-phonon line being “visible”.

The case of  $V^{2+}$  in MgO [8] provides another possible example of relatively long coherence times. The transition involved is magnetic-dipole and the sidebands may be of a different type [9]. Moreover, the sidebands are due to lattice phonons and a factored transition rate is not possible under these conditions [10]. Despite these

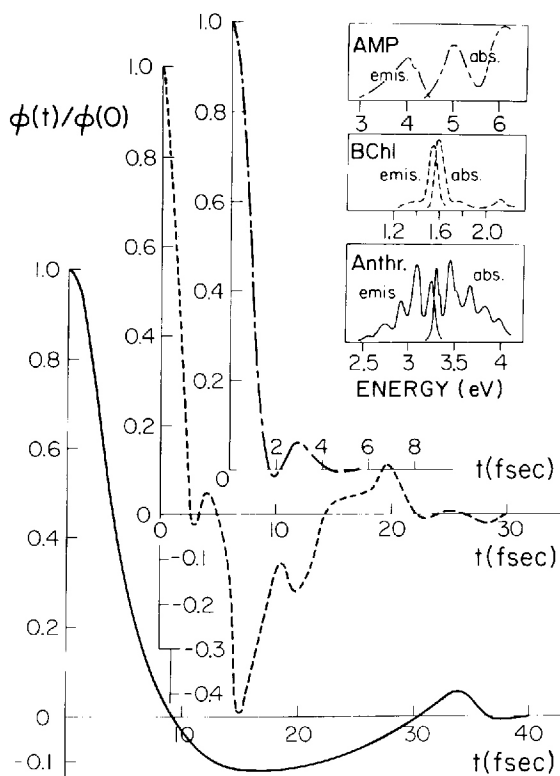


Fig. 1. Memory functions and spectra (inserts for anthracene (—), bacteriochlorophyll (---) and adenosine monophosphate (AMP) (-.-.-)). Ordinate scales normalized such that  $\phi(0) = 1$ . Spectra, with arbitrary ordinate units, from refs. [6a-c].

problems (important when completely quantitative results are required), we have computed  $\phi(t)$  from the fluorescence spectrum and a mirror-symmetric absorption spectrum. The very narrow phonon line ( $\hbar\alpha \sim 0.1 \text{ cm}^{-1}$ ) produces a tail in  $\phi(t)$  with a lifetime of 53 ps; the interplay of the relatively narrow sidebands with the zero-phonon line and with themselves produces oscillations until almost 1 ps. Despite the enormous height of the emission peak, its area is only  $\approx 21\%$  of the total, producing a quasi-coherent memory amplitude reaching only 4.4% of  $\phi(0)$ .

#### 4. Discussion of approximations and assumptions

We comment on three aspects of the theory: (1) evaluation of memories in second order, (2) initial exciton localization and (3) the assumption of homogeneous broadening.

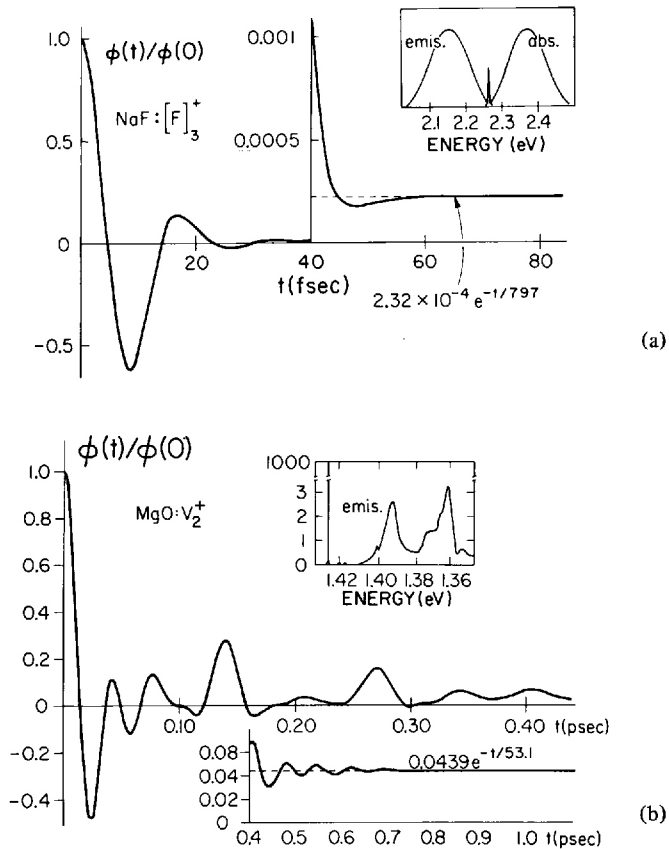


Fig. 2. Memory functions and spectra (inserts) for (a)  $F_3^+$  centers in NaF and (b)  $MgO:V_2^+$ . Ordinates as in fig. 1, with indicated changes of scale. Spectra from (a) ref. [8], (b) ref. [9].

The second-order approximation is involved as well in Förster's theory and in one form or another in all recent theories of exciton motion. While its elimination is desirable for systems with strong intermolecular interaction, the mathematical difficulties for a complex system are known to be considerable.

The initial-random-phase assumption, which allows [4b] the exclusion of an "initial term" from the GME, is also necessary for the derivation of the Pauli Master Equation, the basis of the Förster theory. It is built into the definition of transport quantities in treatments like ref. [3a]. This assumption, particularly in the form of an initial localization, is often unjustified unless nonstationary localized states are excited by appropriate bandwidth and polarization. Descriptions of situations in which the absorption process prepares a momentum state, in terms of equations de-

rived under the localization assumption, clearly involve a contradiction. A tractable treatment of the "initial term" or the development of GME's in momentum space will provide the correct solution to this problem.

An extension of our arguments will be necessary for systems in which broadening is primarily inhomogeneous, which implies random rates of pairwise transfer. It could well lead to incoherence in a way again related to the spectral width.

## 5. Commentary and conclusions

Our approach to the question posed at the outset is based on the intimate interrelation of two separate effects of a bath on isolated molecules: the broadening of the monomer spectral  $\delta$ -functions and the destruction of the pure coherent character of exciton motion. We believe the answer lies largely in *experimentally accessible* spectra and we provide a prescription [eq. (1)] for its *quantitative* extraction.

The inverse of the spectral line width, closely connected to the decay time of  $\phi(t)$ , provides a rough measure of the period of coherence before Förster-like transfer prevails. This coherence time, infinite in the absence of phonons or other baths and zero in treatments employing Förster theory for all times, is predicted to vary from 10 fs to 53 ps (figs. 1, 2) in diverse systems.

Other treatments of the coherence question involve formalisms based on stochastic-Liouville equations (SLE's). Recent work [4d,4e] concerning their relation to our approach has established a quasi-equivalence and shown that careful application of those theories to systems with broadened spectra results in precisely the same predictions as ours. The approaches have been shown [4e] identical in content except for an additional coherence in the SLE theories, which, however, is governed by the same parameter which measures the strength of the zero-phonon singularity in the monomer spectrum and which is, therefore, zero for systems with broadened spectra. Disagreement can occur only for extremely narrow zero-phonon peaks and we thus conclude that, for systems with broadened spectra, even the SLE analyses reestablish diffusion theory as adequate for currently accessible times.

We propose that (i) localizing excitation conditions, (ii) time resolved spectroscopy in the range of the inverse width of strong narrow lines, and (iii) a homogeneous system would make possible definitive observation of the coherent part of spatial excitation transfer. These may be realized by pulse excitation spanning all components of a Davydov multiplet (to localize on one set of dipoles) in a crystal (for a large homogeneous density of absorbers) and observation of the fluorescence in polarization perpendicular to that of the excitation. Generally, steady-state experiments cannot reveal coherent behavior [11].

## Acknowledgement

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## Discussion

R. Silbey: In the Kenkre–Knox theory, the zeroth order hamiltonian is taken to be that containing no intermolecular interaction,  $J$ ; therefore, since the second order perturbation theory is used to compute the memory function, secular terms in  $J$  arise in particular for the systems with more than two molecules. This will lead to a failure of the theory for times larger than  $J^{-1}\hbar$ . It is straightforward to take an  $H_0$  containing  $J$  and avoid this problem (as was done in the Haken–Reinecker or Grover–Silbey theories) but this modifies the approximate memory function in the GME. Have you taken this into consideration, in particular with respect to the relation of the memory function to the spectrum?

R.S. Knox: We recognize the problem posed by using second order perturbation theory, but our expansion parameter is more closely related to your  $\tilde{J}$  than to  $J$  ( $\tilde{J}$  is usually much smaller than  $J$  because of Franck–Condon factors). In answer to the question: a very detailed analysis of these issues has been made by Kenkre in refs. [4d] and [4e]. He shows that under certain conditions, especially when zero-phonon lines are absent,  $\tilde{J} \equiv 0$ . In those cases where  $\tilde{J}$  is not taken to be zero, one must weigh the validity of making an expansion in the full interaction (as we do) as against its fluctuations around  $\tilde{J}$  (as you do). We believe the problem of the secular terms is actually common to both theories.

R. Kopelman: What predictions can you make for the exciton coherence length and its anisotropy in molecular crystals?

R.S. Knox: For a packet initially localized, the coherence length  $l_c$  can be defined as the distance at which  $\langle x^2 \rangle$  changes from a  $t^2$  dependence (wave-like) to a  $t$  dependence (diffusion-like). This can be calculated for a given memory by the method of ref. [4a]. For a simple memory  $\alpha e^{-\alpha t}$  and coupling matrix element  $J$ , this leads to  $l_c \approx aJ/\alpha$ , where  $a$  is the nearest neighbor distance. Taking  $J \approx 300 \text{ cm}^{-1}$ ,  $\alpha \approx 10^{12} \text{ s}^{-1}$ , we have  $l_c \approx 9a$ . The anisotropy in  $l_c$  would come in as usual through  $J$ , probably very little through  $\alpha$ .