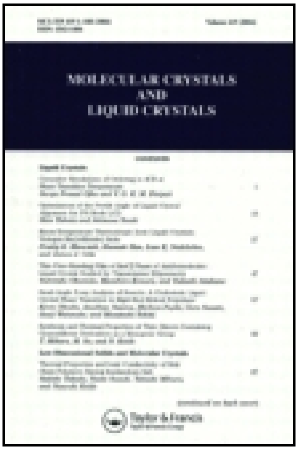

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Comments on Electronic Relaxation Processes in Molecular Crystals‡

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Abstract—A theory of radiationless transitions in isolated molecules is presented, considering the decay of a compound molecular state into a quasi continuum of zero order vibronic levels. The theory is then applied to electronic relaxation processes in molecular crystals with an emphasis on the implications of level shifts in solids, and the nature of the decay of metastable exciton states located above the direct threshold to the conduction band.

1. General Remarks on Electronic Relaxation Processes in Molecules

In the quantum theory of relaxation processes,[1] it is customary to consider the interaction between two (zero order) components of a physical system: a dynamic part which is characterized by a finite number of degrees of freedom and discrete energy levels, and a dissipative part which consists of an infinite number of degrees of freedom and is characterized by a continuous spectrum. A relaxation process in an atom, in a molecule or in a solid takes place when compound state of the total system decays into a continuum. Familiar examples of this physical situation are:

(1) The radiative decay of an atom or a molecule,[2] where the radiation field in vacuum which is characterized by a continuous spectrum, acts as the dissipative part of the system.
(2) The α decay of nuclei, where the translation continuum acts on the dissipative part.

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(3) Atomic and molecular autoionization processes,[3] where a one or a two electron excitation overlaps the one electron ionization continuum, the latter playing the role of the dissipative part.

(4) Molecular predissociation processes,[4] where a compound molecular state interacts with a dissociative continuum.

(5) Unimolecular dissociation processes of polyatomic molecules can be described in terms of a decay of a compound state (the activated state) into a translational continuum.[5] This approach adopted by Mies and Kraus[5] is formally equivalent to Fano's treatment of autoionization[4] and can be described in terms of the theory of resonant scattering.

Some pedantic comments are now in order. The zero order energy levels of the dynamic and of the dissipative subsystems cannot be considered as proper eigenstates of the physical system. These zero order levels of the two subsystems are degenerate or quasidegenerate, so that extensive configuration mixing will be induced by the (small) interaction terms which couple the dynamic and the dissipative parts. A proper description of the energy levels of the complete system should involve a superposition of the zero order discrete level (or levels) of the dynamic part and the zero order continuum of states corresponding to the dissipative part. In the cases of autoionization[3] and of molecular predissociation,[4] these compound states have been treated in detail. The zero order states have no real physical significance and the pertinent physical properties of the system such as the level widths, absorption coefficients and relaxation times have to be described in terms of the compound states. An important problem in the theory of quantum relaxation processes involves the question how is an atomic or molecular excited state " prepared ", and under what circumstances it is meaningful to consider the time development of such a compound state. At the risk of triviality, let us point out that an atomic or a molecular system in a stationary state cannot make transitions to other states which are supposed to be induced by " small terms in the molecular Hamiltonian ". A stationary molecular state can make transitions to other states only by the coupling with the radiation field, so that all time dependent transitions between stationary states are radiative in nature. However, this conclusion does not apply if the molecular system is " prepared " in a non-stationary state of the system's Hamiltonian. Thus, for example, in the theory of molecular predissociation[6] it is not justified to " prepare " the physical system in a pure Born-Oppenheimer bound state and to force transitions to the manifold of continuum dissociative states. If, on the other hand, the excitation process produces the system in a " mixed " state consisting of a superposition of proper eigenstates of the system, a relaxation process will take place. Provided that the width is characterized by a Lorentzian line shape, then the relaxation process wlll result in an exponential decay.

The existence of radiationless intramolecular electronic relaxation processes in moderately large molecules even when isolated in the gas phase, is now a well-established phenomenon.[7-10] This problem was recently considered by us from the point of view of the breakdown of the Born-Oppenheimer approximation.[11] The electronic states of a molecule are conventionally classified in the adiabatic representation derived from the Born-Oppenheimer approximate separability conditions for the electronic and for the nuclear motion. Now, it is well known that the Born-Oppenheimer approximation is valid only provided that the energy separation between vibronic statee belonging to different electronic configurations considerably exceeds the vibronic matrix element arising from the kinetic nuclear term connects these levels. The breakdown of the Born-Oppenheimer approximation is well known in the cases of the Jahn-Teller, the pseudo Jahn-Teller and the Renner effects.[12] To consider in some detail the behavior of the excited electronic levels of a complex molecule, we have displayed in Fig. 1 a simple model of the zero order vibronic levels derived in the Born-Oppenheimer approximation.[13] The zero vibronic level φ_s of the second excited state is quasidegenerate with the manifold $\{\varphi_i\}$ of vibronic levels belonging to the first electronic excited state. The density of the latter states increases with the energy gap between the zero vibronic of the two excited states and with increasing the number of the vibrational degrees of freedom. Under these common circumstances, the Born-Oppenheimer separability conditions break down. This situation where a discrete zero order vibronic level is quasidegenerate with a " background " manifold of vibronic states is common for all electronic excited states of large molecules. Hence we may conclude

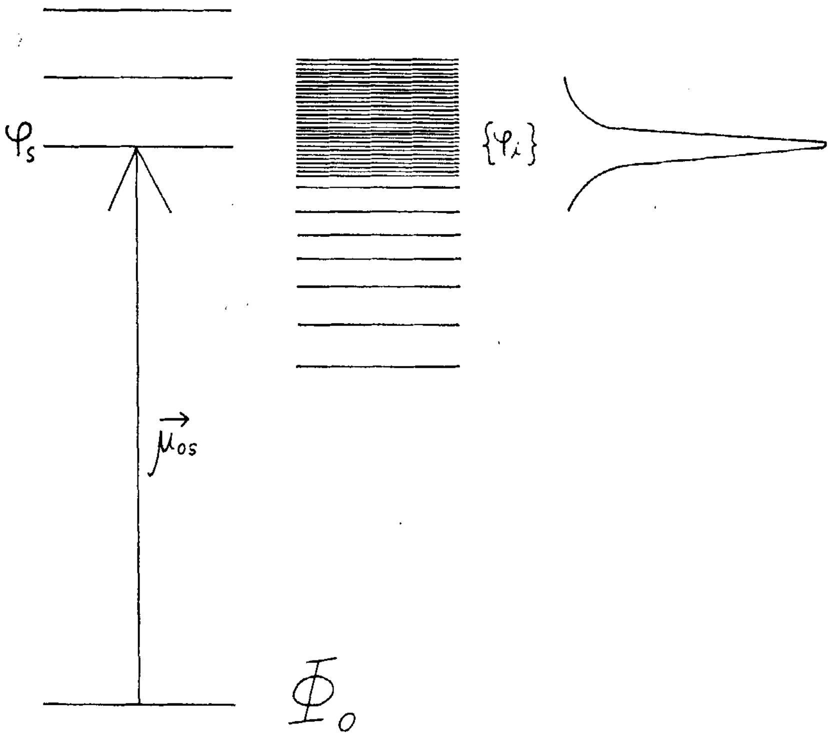

Figure 1. A schematic energy levels diagram of a polyatomic molecule.

that all excited electronic states in large molecules cannot be considered as pure Born-Oppenheimer states.

A proper representation of the molecular eigenstates, ψ_n, involves a superposition of zero order Born-Oppenheimer states, which is displayed in the form[13]

$$\psi_n = a_s^n\phi_s + \sum_i b_i^n\phi_i \qquad (1)$$

This situation of near degeneracy resembles the situation encountered in the treatment of the pseudo Jahn-Teller effect, however, in the present case, the coupling between a large number of quasidegenerate zero order states has to be considered. The configuration interaction scheme employed herein is similar to the treatments employed many years ago by Rice[4a] for the case of predissociation and by Fano[3] for the case of autoionization. However, it should be stressed that unlike the cases of autoionization and predissociation, in the present case the manifold $\{\varphi_i\}$ is discrete. The pertinent question now is under what conditions the manifold of densely spaced discrete levels $\{\varphi_i\}$ can be considered as a dissipative subsystem, so that an intramolecular electronic relaxation process will occur in the isolated molecule. This problem was recently considered by us[13] applying a model based on the following simplifying assumptions:

(1) The manifold of the zero order levels $\{\varphi_i\}$ is characterized by uniformly spaced levels with a separation of ρ^{-1}, where ρ is the (constant) density of states. The zero order energies are

$$E_i = E_s + \alpha + i\rho^{-1} \; ; \quad i = 0, \pm 1, \pm 2, \ldots \tag{2}$$

where E_s is the energy of the state φ_s and $\alpha = E_s - E_0$.

(2) The vibronic coupling matrix elements, v_j, are constant, so that

$$v_j = <\phi_s | H | \phi_j> = v \tag{3}$$

for all v_j. Here H is the complete molecular Hamiltonian. Now, the relevant energy matrix elements are

$$\begin{aligned} \langle \varphi_s | H | \varphi_s \rangle &= E_s \\ \langle \varphi_j | H | \varphi_j' \rangle &= E_j \delta_{jj}' \\ \langle \varphi_j | H | \varphi_s \rangle &= v \end{aligned} \tag{4}$$

The energy levels E_n corresponding to the molecular eigenstates are now obtained from the solution of the eigenvalue problem

$$\begin{pmatrix} E_s - E & v & v\ldots \\ v & E_0 - E & 0\ldots \\ v & 0 & E_1 - E\ldots \\ \vdots & \vdots & \vdots \end{pmatrix} \begin{pmatrix} a_s^n \\ b_0^n \\ b_1^n \\ \vdots \end{pmatrix} = 0 \tag{5}$$

The resulting eigenvalue equation for the energy levels E_n is

$$E_s - E_n = \pi v^2 \rho \operatorname{cotg} [\pi\rho(E_n - E_s + \alpha)] \tag{6}$$

An important feature of the solutions of this equation is the applicability of the separation theorem, which is characteristic of all generalized perturbation expansions. Each new eigenvalue, E_n, is located between a pair of zero order Born-Oppenheimer levels.

The expansion coefficients representing the weight of the zero order state φ_s in the molecular eigenstate ψ_n can be displayed in the form[13,14]

$$|a_s^n|^2 = \frac{v^2}{(E_n - E_s)^2 + (\pi v^2 \rho)^2 + v^2} \tag{7}$$

We are interested in the case where the zero order manifold is characterized by a high density of state so that $v\rho \gg 1$, under these conditions

$$|a_s^n|^2 = \frac{v^2}{(E_n - E_s)^2 + (\pi v^2 \rho)^2} \tag{7a}$$

Equation (7a) exhibits a Lorentzian distribution of the weight factors $|a_s^n|^2$ as a function of E_n. We shall now turn our attention to the absorption coefficient and to the optical line shape resulting from optical excitation from the ground state to the manifold of the molecular eigenstates E_n. In most cases of physical interest, only the transition from the ground state Φ_0 to zero order state φ_s carries oscillator strength, while the transitions from the ground state to the manifold $\{\varphi_i\}$ carry no oscillator strength. If the manifold of Born-Oppenheimer states is triplet while φ_s is a singlet, spin selection rules are sufficient to make this assumption adequate. On the other hand, if the manifold $\{\varphi_i\}$ is singlet and the lowest Born-Oppenheimer vibronic level of φ_s and $\{\varphi_i\}$ are well separated in energy, then the Franck-Condon factors for excitation of the states which are quasi-degenerate with φ_s, are expected to be vanishingly small. We thus set

$$|\langle \Phi_0 | \underset{\sim}{\mu} | \varphi_s \rangle| \gg |\langle \Phi_0 | \underset{\sim}{\mu} | \varphi_i \rangle| \tag{8}$$

where $\underset{\sim}{\mu}$ is the transition moment operator. Under these circumstances, the absorption coefficient for optical excitation to a state ψ_n belonging to the manifold of the molecular eigenstates is just proportional to $|a_s^n|^2$. From the results we conclude that:

(a) The breakdown of the Born-Oppenheimer approximation for the case of a sufficiently dense background of zero order vibronic states results in an inhomogenous line broadening. The inhomogenous broadening arises from a differential distribution of the zero order Born-Oppenheimer component φ_s among the dense manifold

$\{\varphi_i\}$, which all together constitute the representation of the exact molecular eigenstates $\{\psi_n\}$.

(b) The line shape in optical absorption is Lorentzian. The line shape is

$$L(E) \propto \rho \,|\, a_s^n \,|^2 = \frac{v^2 \rho}{(E_s - E)^2 + (\pi v^2 \rho)^2} \tag{9}$$

(c) The line width is given by

$$\Delta = \pi v^2 \rho \tag{9a}$$

(d) No Fano type antiresonances[3] are expected to be observed in the optical spectrum. This conclusion is a direct consequence of condition (8). Interference effects between the discrete state and the background continuuim (or quasicontinuum) are expected to be manifested in the line shape only provided that the zero order background levels carry oscillator strength.

2. Intramolecular non Radiative Decay

The state mixing in large molecules leads to the distribution of intensity over a moderately large energy region, this effect occurs entirely as an intramolecular phenomenon. This limiting case was referred to by Berry and Jortner as the statistical limit.[15] The validity conditions for statistical mixing were obtained by us[13] from the consideration of the time development of coherently excited states. The molecule in the ground state is subjected to a radiative perturbation, which in the dipole approximation is

$$H'(t) = \mu \cdot \underset{\sim}{\epsilon}(t) \;; \quad 0 \leqslant t \leqslant t_1 \tag{10}$$

where $\epsilon(t)$ is the electric field acting on the molecule at time t. The excited state at time t can be described in terms of a superposition of molecular eigenstates:

$$\Psi(t) = \sum_n |\, \psi_n > \underset{\sim}{\mu}_{n0} \exp\left(\frac{-iE_s t}{\hbar}\right) \times \int_0^{t_1} \exp\left(\frac{iEt'}{\hbar}\, \underset{\sim}{\epsilon}(t') dt'\right) \tag{11}$$

where

$$\mu_{n0} = \langle\, \psi_n \,|\, \underset{\sim}{\mu} \,|\, \Phi_0 \rangle \tag{12}$$

is the transition dipole moment to the molecular eigenstate ψ_n, which by the use of Eq. (8) can be displayed in the form

$$\underset{\sim}{\mu}_{n0} = a_s^n\langle\phi_s|\underset{\sim}{\mu}|\Phi_0\rangle = a_s^n\underset{\sim}{\mu}_{s0} \tag{12a}$$

Consider now the time development of the amplitude of the zero order state φ_s in the excited state, which is given by

$$\langle\varphi_s|\Psi(t)\rangle = -\frac{i}{\hbar}\underset{\sim}{\mu}_{s0}\int_0^{t_1} S(t,t')\underset{\sim}{\epsilon}(t')dt' \tag{13}$$

where the kernel $S(t,t')$ is given by

$$S(t,t') = \sum_n |a_s^n|^2 \exp\left(-\frac{i}{\hbar}E_n(t-t')\right) \tag{13a}$$

Now, using Eq. (7) one obtains:

$$S(t,t') = \sum_{n=\infty}^{\infty}\left[1 + (\pi v\rho)^2 + \left(\frac{E_n - E_s}{v}\right)^2\right]^{-1} \times \exp\left[-\frac{i}{\hbar}E_n(t-t')\right] \tag{14}$$

Now, assuming that the energy levels E_n are equidistant so that $E_n - E_s = n\rho^{-1}$ where $n = 0, \pm 1 \pm 2$ etc. we can write

$$S(t,t') = \exp\left[-\frac{i}{\hbar}E_s(t-t')\right]\sum_{n=-\infty}^{\infty}\left[1 + (\pi v\rho)^2 + n^2(v\rho)^{-2}\right]^{-1} \times \exp\left[\frac{in}{\hbar\rho}(t-t')\right] \tag{14a}$$

This infinite sum can be evaluated using the series summation:[16]

$$\sum_{n=1}^{\infty}\frac{\cos n\theta}{n^2 + a^2} = \frac{1}{2a}\left[\frac{\pi\cosh[a(\pi - \theta)]}{\sinh(\pi a)} - \frac{1}{a}\right] \quad (0 < \theta < 2\pi) \tag{15}$$

leading to the result

$$S(t,t') = \frac{\pi v\rho}{\sqrt{1 + (\pi v\rho)^2}} \times \frac{\cosh[v\rho\sqrt{1 + (\pi v\rho)^2}\{\pi - (t-t')/\hbar\rho\}]}{\sinh[\pi v\rho\sqrt{1 + (\pi v\rho)^2}]} \times \exp -\left[\frac{i}{\hbar}E_s(t-t')\right] \tag{16}$$

Now, under the limiting conditions[13]

$$v\rho \gg 1 \tag{17a}$$

$$t - t' \ll \hbar\rho \tag{17b}$$

Equation (16) is reduced to the simple form

$$S(t,t') = \exp\Bigl[-\frac{i}{\hbar}E_s(t-t')\Bigr]\exp\Bigl[-\frac{\pi v^2\rho}{\hbar}(t-t')\Bigr] \tag{18}$$

At this stage, it will be useful to define a non-radiative decay time τ, in the form

$$\tau = \frac{\hbar}{2\pi v^2\rho} \tag{19}$$

so that the exponential time decay of the kernel $S(t,t')$ can be displayed in the form

$$S(t,t') = \exp\Bigl[-\frac{i}{\hbar}E_s(t-t')\Bigr]\exp\Bigl[-\frac{t-t'}{2\tau}\Bigr] \tag{18a}$$

Now, the average time dependent probability, $\overline{W}_s$, for locating the component φ_s in $\overline{\psi}(t)$ can be obtained by taking the square of the amplitude (13) and averaging over the phases and amplitudes of the electric field, so that

$$\begin{aligned}\overline{W}_s = |\langle\varphi_s\,|\,\Psi(t)\rangle\,|^2 &= \frac{\mu_{s0}^2}{\hbar}\exp\Bigl[-\frac{t-t_1}{\tau}\Bigr]\int_0^{t_1}\int_0^{t_1} dt'dt'' \\ &\times \exp\Bigl[-\frac{t'+t''-2t_1}{2\tau}\Bigr]\exp\Bigl[\frac{i}{\hbar}(t'-t'')\Bigr]\langle\underset{\sim}{\epsilon}(t')\underset{\sim}{\epsilon}(t'')\rangle\end{aligned} \tag{20}$$

Here $\langle\underset{\sim}{\epsilon}(t')\underset{\sim}{\epsilon}(t'')\rangle$ corresponds to the second order auto-correlation function of the field. Considering now an excitation by a conventional light source, where the amplitudes and the phases of the field are subjected to random fluctuations, which are determined by the width, $\delta\nu$, of the exciting spectral band. The field autocorrelation function differs from zero for time intervals shorter than the reciprocal width of the exciting source. In the limit $\delta\nu \gg \Delta$, that is the width 4ν exceeds the inhomogenously broadened line width, the field autocorrelation function can be expressed in terms of a delta function.

$$\langle\underset{\sim}{\epsilon}(t')\underset{\sim}{\epsilon}(t'')\rangle = \frac{8\pi I_0}{c}\,\delta(t'-t'') \tag{21}$$

where I_0 is the intensity of the source and c the velocity of light. Inserting this result into Eq. (20) we obtain

$$\overline{W}_s = \frac{8\pi I_0\mu_{s0}^2\tau}{\hbar c}\exp\Bigl(\frac{t-t_1}{\tau} \times \Bigl[1-\exp\Bigl(-\frac{t_1}{\tau}\Bigr)\Bigr] \tag{22}$$

Thus, Eqs. (20) and (22) exhibit the proper kinetic behavior. The radiationless decay of the probability amplitude of the zero order state φ_s, is exponential, characterized by the nonradiative lifetime τ. Several comments should be made at this point:

(a) The energetic condition (17a) provides a necessary condition for the inhomogenous line broadening and for the occurrence of the intramolecular radiationless process. Thus, the density of states has to be large enough, so that the vibronic coupling matrix element has to exceed the reciprocal separation of levels in dense vibronic manifold $\{\varphi_i\}$.

(b) The relation (17b) establishes the time scale for the occurrence of the nonradiative decay. In fact, $\hbar\rho$ represents the recurrence time for the decay of the zero order level φ_s into the quasi continuum. For times longer than this recurrence time, the amplitude of φ_s in $\psi(t)$ will increase again. However, for large molecules these times considerably exceed the time scale of any experiment.

(c) The definition of the recurrence time introduces the notion of irreversibility for the intramolecular radiationless process. An irreversible relaxation process will occur when a compound state of the system decays into a real continuum, as encountered in the cases of autoionization or predissociation. However, the representation of the dissipative system in terms of a continuum or of a quasi continuum depends solely on what boundary conditions are applied at large distances from the compound system. The intramolecular radiationless process in the case of sufficiently large density of vibronic levels which satisfy relations (17a) and (17b) corresponds to an irreversible process on the time scale which is shorter than the recurrence time $\hbar\rho$.

(d) The expression (19) for the non-radiative lifetime can be exhibited in the form

$$\tau = \frac{\hbar\rho}{2\rho\Delta} \tag{19a}$$

Now $n = \rho\Delta$ is just the average number of levels within that half-width of the inhomogenously broadened line, so that

$$\tau = \frac{\hbar\rho}{2n} \tag{19b}$$

Hence, the non radiative lifetime can be displayed as the recurrence time " diluted " by the factor n.

(e) In the case of sufficiently large molecules such as naphthalene and anthracene, both the density of states is sufficiently large and the recurrence time is sufficiently long so that the validity conditions (17a) and (17b) for the occurrence of the radiationless process are satisfied, as evident from the results presented in Table 1. On the other hand, the benzene molecule provides a border line case, where where $v\rho \sim 1$ and the recurrence time is of the order of the radiative decay. A small molecule like SO_2 is characterized by a low value of ρ, but by a relatively large vibronic coupling term. In this case, $v\rho \sim 1 - 10$ (if the ground state vibronic manifold is also included), however, the recurrence time is extremely short. The behavior of this system can reveal a Poincare cycle, so that recurrence will occur faster than collisions on any other external source of irreversibility. This behavior leads to interesting conclusions concerning the radiative decay of such a small molecule which will be characterized by a large radiative lifetime than expected on the basis of the integrated oscillator strength. Such a situation may indeed be experimentally encountered in the case of SO_2 and of NO_2.[8]

TABLE 1 Radiationless Transitions in Large Molecules

System	τ sec	v cm^{-1}	ρ cm	$v\rho$	$\hbar\rho$ sec
Anthracene $^1B_{2u} \rightarrow {}^3B_{2u}$ $\Delta E = 12000$ cm^{-1}	5×10^{-9}	6×10^{-7}	5×10^{10}	3×10^4	0.25
Naphthalene $^1B_{2u} \rightarrow {}^1B_{3u}$ $\Delta E = 34000$ cm^{-1}	$\sim 10^{-12}$	6×10^{-2}	2×10^3	10^2	10^{-8}
Naphthalene $^3B_{2u} \rightarrow {}^1A_{1g}$ $\Delta E = 20000$ cm^{-1}	2	10^{-14}	8×10^{15}	80	4×10^4
Azulene $^1B_1 \rightarrow {}^1A_1$ $\Delta E = 14,000$ cm^{-1}	$\sim 10^{-11}$	7.10^{-5}	10^{11}	7.10^4	0.5
Benzene $^1B_{2u} \rightarrow {}^3B_{1u}$	10^{-6}	1.5×10^{-5}	8×10^4	1.5	4×10^{-7}

(f) We shall consider now the life story of the electronically-vibrationally excited state resulting from an intermolecular radiationless transition in an isolated large molecule. The pertinent time scale is again assumed to be shorter than the recurrence time $\hbar\rho$. In the case of internal conversion, the dense manifold of the zero order vibronic levels is connected by nonvanishing radiative coupling to high vibronic levels of the ground state, although, of course, restriction (8) still holds. In the case of internal conversion, in an isolated molecule, fluorescence will then take place from a vibrationally excited level of the lowest excited state, which can decay radiatively to high vibrational levels of the ground state. Thus, fluorescence will result from transitions between two vibrationally excited states, resulting in a molecule in a vibrationally excited ground state. If the molecule stays free, it will emit its excess energy as infrared radiation, however, in view of the long radiative lifetimes for vibrational transitions, vibrational relaxation by collisions may also take place.

(g) The results pertaining to the observation of a Lorentzian line shape whose time Fourier transform corresponds to an exponential decay, are expected to hold only for the case of an isolated resonance. Sometimes, two (or more) zero order levels say (φ_s and $\varphi_{s'}$) which interact with the same quasi continuum have to be considered. Such a situation is indeed encountered in the case of two (or more) low vibronic components of a second higher excited singlet state, both carrying oscillator strength. Two compound states of the system result in this case. If the widths of the two states exceed their separation, the line shapes show deviation from a Lorentzian shape and the nonradiative decay rate is nonexponential.

(h) A common situation is encountered when a zero order level ϕ_s, which carries oscillator strength, interacts with two or more quasi-continua, say $\{\varphi_i\}$ and $\{\varphi_i'\}$. This situation occurs, for example, in the case of the first singlet state which interacts with the vibronic manifolds of the lowest triplet and of the ground state. When the vibronic manifolds are sufficiently dense, this situation can be considered as a closed channel interacting with two open channels. The line shape is again Lorentzian and given in the form[3]

$$L(E) \alpha \frac{\sum_i v_i^2 \rho_i}{(E - E_s)^2 + (\pi \sum_i v_i^2 \rho_i)^2} \tag{23}$$

where $v_i = \langle \varphi_s | H | \varphi_i \rangle$ for all φ_i and ρ_i the density of zero order vibronic states in the manifold $\{\varphi_i\}$. This result is a generalization of the previous simple case represented by Eq. (9).

3. Comments on Radiationless Transitions in Molecular Crystals

We start this discussion by observing that in general the rates of radiationless transition between excited states of aromatic molecules in a dense medium, such as a solution or a rigid glass, are of the same order of magnitude as the rates observed for the isolated molecules in the gas phase. We may therefore conclude that the same mechanism which operates in the isolated molecule must be also responsible for the gross features of the radiationless transition process in a dense medium. Considering a supermolecule consisting of the molecule of interest and the surrounding solvent molecules, one has to consider the contribution to the coupling matrix elements, v, arising both from intermolecular and intramolecular vibrations. These vibronic matrix elements between the zero order Born-Oppenheimer states $\varphi m(q_1Q)\chi_{mn}(Q)$ and $\varphi_n(q_1Q)\chi_{ns}(Q)$ (where φ and χ correspond to the electronic and nuclear functions, respectively) can be displayed in the form[13,17]

$$v \approx -\hbar^2 \sum_k \langle \varphi_m(q_1 Q) | \frac{\partial}{\partial Q_k} | \varphi(q_1 Q) \rangle \times \int \chi_{mn}(Q) \frac{\partial}{\partial Q_k} \chi_{ns}(Q) d\alpha \qquad (24)$$

where the set $\{Q\kappa\}$ corresponds to the normal coordinates of the system under consideration.

Now, it is well known from previous work on vibronic coupling[18] in aromatic hydrocarbons that intramolecular skeleton vibrations rather than C-H vibrations lead to an appreciable vibronic coupling contribution to the term $\langle \varphi_m(q_1 Q) | \frac{\partial}{\partial Q_k} | \varphi_n(q_1 Q) \rangle$. It is thus expected that intermolecular vibrations will have a negligible effect on the coupling of electronic states of interest. Hence, for internal conversion processes, where the matrix elements are solely determined by vibronic coupling, no appreciable medium effect on the nonradiative lifetime is expected. On the other hand, intersystem crossing processes are enchanced by the external heavy atom effect, which leads to a contribution to the electronic coupling term.

The effect of coupling between the molecular electronic states and the lattice phonons is manifested by the rôle of the medium as a 'heat bath' which enables thermal excitations between molecular eigenstates constructed from different zero order vibronic components φ_s and $\varphi_{s'}$ corresponding to two (or more) compound states of the system. A similar situation may, of course, be encountered in the gas phase where collisions lead to vibrational excitation. Considering the simple case when the separation of these states exceeds their widths, each state decays exponentially into the common quasi continuum. However, the nonradiative decay rates of two states (say φ_s and $\varphi_{s'}$) are by no means equal. We expect faster radiationless decay rates in the higher excited vibronic state, in view of the increase of the coupling term v for such a state. This enhancement effect may arise from two sources: (a) thermal excitation of a nontotally symmetric vibration may lead to larger vibronic coupling matrix elements, in view of selection rules for vibronic coupling. (b) A more favorable Franck Condon vibrational overlap factor may be encountered in a higher vibronic level.[21,15] We believe that the first mechanism is more important in this case.

Now, let $\Delta\epsilon$ be the energy gap between the zero order states φ_s and $\varphi_{s'}$ (which is of the order of an intermolecular vibrational frequency) and let k and k' ($k < k'$) be the radiationless transition decay rates of these two states. Provided that vibrational excitation and vibrational relaxation rates are fast on the time scale of the radiationless decay, the effective radiationless rate constant is:

$$R = \frac{k + k'e^{-\ \epsilon/kT}}{1 + e^{-\Delta\epsilon/kT}} \tag{25}$$

The observed temperature effect of the intersystem crossing rate of deuteronaphthalene in some solid solutions,[19] seems to fit Eq. (25) quite well. For this system, one gets $\Delta\epsilon \simeq 600\ \mathrm{cm}^{-1}$ (which is of the order of a low frequency out of plane molecular vibration) and $k'/_k = 15$.

Turning now our attention to radiationless transitions in "pure" molecular crystals of aromatic molecules, one has to consider crystal field effects which may lead to the inversion of the order of the triplet and singlet exciton levels relative to the corresponding molecular states.[21] Davydov's tight binding approximation leads to the manifold of (optically accessible $\underset{\sim}{k} = 0$) crystal energy levels which can be displayed in the form[22]

$$E_i = \Delta E^f + D^f + I_{\mathrm{eq}}(\underset{\sim}{k} = 0) + I_i(\underset{\sim}{k} = 0) \quad i = 1, 2, \ldots, 6 \qquad (26)$$

where ΔE^f is the gas phase excitation energy, D^f is the medium (solvent) shift, I_{eq} $(\underset{\sim}{k} = 0)$ corresponds to the sum of excitation transfer interactions between translationally equivalent molecules, $I_i(k = 0)$ is a linear combinations of the interaction terms between the reference molecule and translationally inequivalently molecules, which occupy 6 different sites in the unit cell. The molecular states split into 6 exciton branches. Now, the shift of the centre of gravity of the Davydov components in the crystal is given by $D^f + I_{\mathrm{eq}}(\underset{\sim}{k} = 0)$, so that crystal field induces an additional spectral shift which is given by $I_{\mathrm{eq}}(\underset{\sim}{k} = 0)$. The implications of this well known result are as follows: for allowed singlet states (i.e. the first singlet state of anthracene) an important contribution to the intermolecular interactions arises from long range dipole–dipole coupling and $I_{\mathrm{eq}} \sim 500\ \mathrm{cm}^{-1}$, on the other hand for triplet states where the intermolecular interactions are dominated by short range electron exchange terms $I_{\mathrm{eq}} \sim 1\ \mathrm{cm}^{-1}$.[23] Such shifts of the energy levels may change the relative location of the first singlet and the second excited triplet state in the crystal. Now, the role of the second excited triplet may be crucial in the radiationless transition, as it sometimes happens that more than two levels are involved in the process. This effect is manifested in the enhancement of intersystem crossing when the second triplet state is located very close to the excited singlet.[13] It is meaningless to consider intersystem crossing between the excited singlet and the second triplet as an isolated process, as the density of the vibronic levels corresponding to this second triplet is extremely low. However, the presence of the second triplet may greatly enhance the coupling matrix element between the zero order singlet state and the quasi continuum of the first triplet state. We have demonstrated that under these circumstances, the enhancement of the coupling matrix element, v, can be expressed in the form:[13]

$$\left(\frac{v}{v_0}\right)^2 = 1 + 2\frac{v_v}{\delta} + \left(\frac{v_v}{\delta}\right)^2 \qquad (27)$$

where v_0 is the coupling element in the absence of the second triplet, v_v is the vibronic coupling matrix element between the second triplet and the manifold $\{\phi_i\}$ and Δ is the energy gap between the sero order first singlet and the second singlet. Relation (27) is expected to hold when $\delta > v_{s0} \sim 1\ \text{cm}^{-1}$, where v_{s0} is the spin-orbit coupling matrix element between the singlet and the second triplet. Hence, if $\delta < v_v \sim 10^3\ \text{cm}^{-1}$ the rate is enhanced. In the limiting case of degeneracy when $\Delta = 0$, one obtains instead[13]

$$\left(\frac{v}{v_0}\right)^2 = \tfrac{1}{2} + \left(\frac{v_v}{v_{s0}}\right) + \tfrac{1}{2}\left(\frac{v_v}{v_{s0}}\right)^2 \tag{27a}$$

so that in this case $(v/v_0)^2 \simeq 10^6$, and the intersystem crossing rate is appreciably increased.

The effect of level shifts in the crystalline state may be of considerable importance in the enhancement of the rate of radiationless transitions in molecular crystals. Thus, for example, the first excited $^1B_{2u}$ of the anthracene molecule is located about $\simeq 600\ \text{cm}^{-1}$ above the second triplet state.[20] Hence, $\delta < v_v$ and the intersystem crossing process is quite effective at room temperature leading to a fluorescence quantum yield of about 0.3 for this molecule in the gas phase or in solution.[20] In the crystal, the singlet state is red shifted by about 1800 cm^{-1}, while the second triplet state is hardly affected, so that the energy gap δ between those two close lying states increases in the crystal. Hence, the coupling term, v, is smaller in the crystalline state, decreasing the rate of the intersystem crossing, so that the fluorescence yield is close to unity.[20]

Another interesting example of crystal effects is manifested by the behavior of crystalline tetracene,[24,25] which at room temperature is characterized by a very low fluorescence quantum yield of about 0.002, while in mixed crystals the fluorescence yield of tetracene is close to unity. Kazzaz and Zahlan[25] have recently reported that the fluorescence yield of the tetracene crystal is increased by about two orders of magnitude by cooling from 285 °K to 4 °K. The analysis of these data using Eq. (25) leads to $\Delta\epsilon \simeq 1300\ \text{cm}^{-1}$ (which corresponds to the totally symmetric vibration) and $k'/k \sim 2 \times 10^4$. These experimental data were interpreted[25] by assuming a faster radiationless decay in a vibrationally excited state of the first excited singlet. The nature of the enhancement of the radiationless decay in the vibrationally excited level raises some interesting questions:

(a) It is not clear why the same mechanism should not be operating also for the case of the mixed crystal where the fluorescence quantum yield of tetracene is high at room temperature.

(b) The ratio $k'/k \sim 10^4$ is by about three orders of magnitude higher than that observed for the $^3B_{1u} \rightarrow {}^1A_{ig}$ intersystem crossing in deuteronaphthalene.[19]

A way out of this difficulty is to assume that because of level shifts in the pure tetracene crystal, the second triplet state is located close to the $^1B_{2u}(a_{1g})$ vibrationally excited singlet state. In this case, the coupling matrix element for the $^1B_{2u}a_{1g}$ vibronic level and its radiationless decay rate will be appreciably higher than the radiationless decay of the $^1B_{2u}(0)$ vibronic level.

4. Metastable Exciton States in Molecular Crystals

In molecular crystals of aromatic molecules, the conduction band is located at relatively low energies. Thus, for example, intrinsic photoconductivity studies in crystalline anthracene[26,27] have demonstrated that the bottom of the conduction band is located at about 4.1 eV, about 1.0 eV above the first $^1B_{2u}$ singlet exciton state. We shall now turn our attention to the higher states of a molecular crystal, which overlap the conduction band states. Such states can be produced by the following methods: (a) conventional optical excitation from the ground state; (b) optical excitation of a singlet (or triplet) exciton state; (c) singlet exciton–exciton collisions. The line shapes and the decay process of these states are of considerable interest for understanding photoconductivity processes in molecular crystals. Exciton states located above the direct threshold to the conduction band are not stable. In a molecular crystal of polyatomic molecules two modes of decay of the metastable exciton state have to be considered:

(a) *Autoionization process*. In view of the coulomb interaction between the exciton state and the valence and conduction bands state, the exciton may decay by an energy conserving autoionization process.[28] Such a situation corresponds to a closed channel interacing with an open channel, the latter corresponds to the conduction band continuum. Such a situation is encountered in monoatomic solids, such as the rare gas crystals.[28] To consider this physical situation, one can immediately adopt Fano's treatment,[3] which we have already used before for the interaction of a discrete state φ_s with a quasicontinuum. The stationary wavefunction of the system can be described as a superposition of the zero order bound (exciton) state and the continuum (conduction band) states. Let φ_s be the exciton state and the set $\{\varphi_E\}$ correspond to the conduction band states, then the proper eigenfunctions of the system are

$$\psi_E = a(E)\varphi_s + \int dE' C_{E'}\phi_{E'} \tag{28}$$

The matrix elements of the Hamiltonian are

$$\begin{aligned} \langle\varphi_s|H|\varphi_s\rangle &= E_s \\ \langle\varphi_s|H|\phi_{E'}\rangle &= V_{E'} \\ \langle\phi_{E'}|H|\phi_{E''}\rangle &= E'\delta(E'' - E') \end{aligned} \tag{29}$$

It is assumed that the submatrix in the subset of the continuum states $\{\phi_E\}$ has been previously diagonalized. The energy matrix (29) is now diagonalized in the new representation (28).[3] Fano's theory leads to the resonance width for the autoionization process:

$$\Gamma = 2\pi|V_E|^2 \tag{30}$$

which in fact is analogous to Eq. (9a) obtained by us for the radiationless process, as here the continuum states $\{\phi_E\}$ are normalized per unit energy scale. The absorption line shape is in this case given by[3]

$$L(E) = \frac{\left(q + \dfrac{E - E_s - \delta_0}{\Gamma}\right)^2}{1 + \left(\dfrac{E - E_s - \delta_0}{\Gamma}\right)^2} \tag{31}$$

where δ_0 is the level shift and q is the line profile index determined by the relative oscillator amplitude of the resonant state f_ϕ and the continuum state f_c, that is $q = 2f_\phi f_c \Gamma$. This general theory first developed for atomic autoionization process can be applied to exciton states in crystal consisting of atomic solids.[28] In molecular crystals of polyatomic molecules, a new feature is introduced arising from intramolecular electronic relaxation processes.

(b) *Non-radiative decay processes.* The high energy exciton state is degenerate with a dense quasi continuum of vibronic molecular levels corresponding to the lower excited states of the crystal. It is apparent from our previous discussion that we have to consider also configuration interaction between the localized zero order state φ_s and the manifold $\{\varphi_i\}$ of vibronic states (characterized by the density ρ) which leads to an intramolecular radiationless transition process. Hence, the metastable state in a molecular crystal should be considered to be an effectively closed channel interacting with two open channels.[29] The wave function for the metastable state can be written as a straightforward modification of Fano's theory, by considering configuration interaction between the (zero order) exciton state φ_s the conduction band continuum $\{\phi_E\}$ and the vibronic quasi continuum $\{\varphi_i\}$, so that

$$\psi_E = a(E)\varphi_s + \sum_i b_i \varphi_i + \int dE' C_{E'} \phi_{E'} \tag{32}$$

The off diagonal coupling matrix elements are

$$\begin{aligned} v_i &= \langle \varphi_i | H | \varphi_s \rangle \\ V_E &= \langle \varphi_s | H | \phi_E \rangle \end{aligned} \tag{33}$$

which determine the role of intramolecular decay and of the autoionization process respectively. In view of the small vibrational overlap Franck Condon factors we speculate that the coupling terms $\langle \phi_E | H | \varphi_i \rangle$ are small. The physical situation corresponds now to a bond state interacting with two continua. The amplitude squared of the exciton state can be described as a Lorentzian[3]

$$| a(E) |^2 = \frac{| V_E |^2 + v^2\rho}{(E - E_s)^2 + \pi^2(| V_E |^2 + v_i^2\rho)} \tag{34}$$

where a (small) level shift term has been disregarded. From this grand consideration we conclude that the ionization yield of a metastable exciton state in a molecular crystal of polyatomic molecules will be determined by the branching ration, B, between the two channels which is just

$$B = \frac{| V_E |^2}{v_i^2 \rho} \tag{35}$$

We have now to turn to the available experimental data to analyze the relative role of autoionization and of radiationless decay of the metastable exciton states.

5. Singlet Exciton Collisions in Crystalline Anthracene

From recent experimental photoconductivity studies in crystalline anthracene, the following information was obtained concerning generation mechanisms, quantum yields and cross sections:

(a) Direct Population of the Conducting Band

The quantum yield for intrinsic generation of charge carriers (observed at energies above 4.1 eV) from the valence band (i.e. the ground state) to the conduction band[26,27] is about $\eta = 10^{-4}$.

(b) Bulk Photoconductivity

Light absorption into the first singlet exciton state of crystalline anthracene leads to the intrinsic generation of charge carriers. The cardinal question in this case is how does an exciton state at 3.1 eV dissociate into electrons and holes when the conduction band is located at 4.1 eV? To the best of our knowledge, it has never been demonstrated that an isolated excited state can overcome the energy gap of 1.0 eV and dissociate to yield a pair of charge carriers in the bulk of the crystal. The energy balance problem may be resolved by considering non linear effects leading to the intrinsic generation of charge carriers. Two mechanisms should be considered in this context:

(1) *Collision Ionization.* This singlet exciton–exciton interaction mechanism first proposed by Northrop and Simpson[30] was theoretically worked out by Choi and Rice[31] who computed the transition probability for an Auger type autoionization process of a pair of singlet excitons. This theoretical treatment led to a bimolecular rate constant $\gamma_i = 5 \times 10^{-12}\,\text{cm}^3\text{sec}^{-1}$ for the singlet exciton–exciton collision ionization process which leads to charge carrier generation in crystalline anthracene. This treatment may overestimate the actual cross sections, as the theory was applied for a rigid lattice, while intramolecular vibrations may reduce the theoretical γ_i value by a Franck Condon vibrational overlap factor of the order of $10^{-1} - 10^{-2}$.[32]

(2) *Exciton photoionization.* It was proposed by Choi[33] that the first singlet exciton state may be optically excited by a photon of energy $h\nu > 1.$ eV to the conduction band.

Experiments using weakly absorbed light[34] cannot distinguish between these two alternatives as in both cases (provided that under the experimental conditions electron-hole recombination is negligible) the photocurrent is expected to vary as I^2, e.g., the square of the light intensity. On the other hand, the first singlet exciton state can be populated by two photon absorption. Experimental studies[35,36] of photoconductivity in crystalline anthracene induced by a giant pulsed ruby laser ($h\nu = 1.74$ eV) led to photocurrents which are proportional to I^3. These results lead to the conclusion[35] that the dominant mechanism for intrinsic charge carriers generation involves photoionization of two photon excited singlet exciton states. The photoionization cross section, σ, of a single exciton to a conduction band state at 4.8 eV is $\eta\sigma = 10^{-19}$ cm^2. No evidence for a I^4 dependence of the photocurrent (which will be consistent with the collision ionization mechanism) could be detected, leading to an upper limit $\gamma_i \leqslant 10^{-11}$ cm^3 sec^{-1} for the collision ionization cross sections. Charge carrier generation in crystalline anthracene induced by weakly absorbed light[34] also involves a substantial contribution arising from the exciton photoionization process.[35,36] Thus, from results of Silver *et al*[34] we can conclude that $\gamma_i < 5 \times 10^{-12}$ cm^3 sec^{-1}.

The rate constant for singlet–singlet exciton annihilation can be directly determined by observing the fluorescence decay curves and fluorescence quantum yields. Bergman, Levine and Jortner[37] have observed a fast component of the fluorescence decay at high exciton densities populated by two photon absorption from a giant pulsed ruby laser. These experiments led to the bimolecular rate constant $\gamma_s = 10^{-8}$ cm^3 sec^{-1} for the exciton–exciton annihilation process. Subsequent experiments[38] of the decay curves induced by one photon absorption (the second harmonic of the ruby laser $h\nu = 3.54$ eV) led to the result $\gamma_s = 5 \times 10^{-8}$ cm^3 sec^{-1}. These results were also further confined by the measurement of the fluorescence yield from crystalline anthracene.[38,39] Fluorescence yields induced by the second harmonic of a ruby laser leads to[38] the result $\gamma_s = 2 \times 10^{-9}$ cm^3 sec^{-1}. Excitation by a broad source[39] leads to $\gamma_s = 10^{-8}$ cm^3 sec^{-1} (these experimental results of Tolstoi and Abramov[39] were corrected for the exciton lifetime in the crystal $\tau_0 = 2.0$–2.5×10^{-8} sec in place of the free molecule value $\tau_0 = 4 \times 10^{-9}$ sec used by them). It appears that all the experimental determination of γ_s are self-consistent.

From these experimental results, we thus conclude that $\gamma_s\gamma_i \geqslant 10^{+4}$. This somewhat surprising low efficiency for charge carrier generation can be adequately rationalized by considering the nature of the metastable state resulting from exciton–exciton collisions, which decays by both radiationless decay and via autoionization. The experimental results on singlet–exciton–exciton annihilation can be interpreted[29b] in terms of a kinetic scheme displayed in Table 2, which is based on the strong scattering random walk model for singlet

TABLE 2 Kinetic Analysis of Singlet–Singlet Exciton Annihilation in Crystalline Anthracene

Definitions:
e —excitons; (ee)—exciton pairs; c—charge carriers
A —metastable excitons
D —singlet exciton diffusion coefficient
$\langle R\rangle$—mean molecular separation
Δ —optical line width for single molecule

Process	Estimates of rate constant	Comments
$e + e \xrightarrow{k_1} (ee)$	$k_1 = 4\pi\langle R\rangle D$	Diffusion coefficient from ref (41) $\langle R\rangle = 5 \times 10^{-8}$ cm
$(ee) \xrightarrow{k_{-1}} e + e$	$k_{-1} = \frac{6D}{\langle R\rangle^2} = 5 \times 10^{12}\ \text{sec}^{-1}$	
$(ee) \xrightarrow{k_2} A$	$k_2 = \frac{2\pi}{\hbar} \vert a(E) \vert^2 \langle \varphi_A \vert H \vert \varphi_{ee} \rangle \vert^2$	$a(E)$ from Eq. (34)
	$k_2 \simeq 10^{-15}\ \text{sec}^{-1}$	$vi^2\rho \gg \vert V_E \vert^2$
$(ee) \xrightarrow{k_3} C$	$k_3 = 10^{11}\ \text{sec}^{-1}$	ref (31)
$A \xrightarrow{k_4} e$	$k_5 > k_4$	Benzene emission data ref (42)
$A \xrightarrow{k_5}$ other products (photochemistry)	$k_4 + k_5 = \hbar/\Delta \simeq 5 \times 10^{14}\ \text{sec}^{-1}$	Δ from ref (40)
$A \xrightarrow{k_6} C$	$B = k_6/(k_4 + k_5) \leqslant 10^{-4}$	photoconductivity data ref (26), (27)
	$k_6 \simeq 5 \times 10^{10}\ \text{sec}^{-1}$	
$C \xrightarrow{k_7}$ monomolecular decay	$k_7 \simeq 5 \times 10^7\ \text{sec}^{-1}$	ref (37)
$c + c \xrightarrow{k_8}$ recombination	$k_8 \simeq (0.5 - 2) \times 10^{-8}\ \text{cm}^3\,\text{sec}^{-1}$	ref (35)

exciton migration in crystalline anthracene.[23] The most interesting quantity is the branching ratio $B = {}^{k6}/(k_4 + k_5)$. From the photoconductivity data involving the direct population of the conduction band[26,27] we infer that $B \leqslant 10^{-4}$. Now, as the radiationless decay channel is determined by an intramolecular process, the sum of the rate constants $(k_4 + k_5)$ can be determined from the line shapes in the optical spectrum of a single molecule. The absorption band in the spectrum of anthracene in heptane solution in the region 5–6 eV are characterized by a linewidth of $\Delta\, b\, 0.5$ eV,[40] which as discussed before arises mainly from an intramolecular radiationless transition. Hence, $k_4 + k_5 = 5 \times 10^{14}\,\mathrm{sec}^{-1}$. From these results, we estimate $k_6 \simeq 5 \times 10^{10}\,\mathrm{sec}^{-1}$. Making use of Fano's theory (Eq. (30)), we set $k_6 = 2\,|V_E|^2/\hbar$ and get $|V_E|^2 = 2 \times 10^{-16}\,\mathrm{erg}$. Obviously, we may conclude that $|V_E| \ll \Delta = \pi v_i^2 \rho$, so that the intramolecular radiationless decay process plays a dominating role.

From this analysis, we conclude that:

(a) The experimental bimolecular rate constants are

$$\gamma_s = k_1$$
$$\gamma_i = Bk_1$$

As $k_2 \gg k_{-1}$ the transition of an exciton pair to the metastable exciton state is fast on the time scale of singlet exciton migration, and hence the singlet exciton annihilation process is determined by the rate of excitons collisions. The experimental rate constant γ_s is in good agreement with the theoretical model.[29b]

(b) The " dilution " of the metastable exciton state is determined by the branching ratio $B = |V_E|^2/v_i^2\rho \leqslant 10^{-4}$. The low value of $\gamma_i(\gamma_i \leqslant 10^{-4}\gamma_s)$ arises from the dominating role of radiationless decay.

(c) The autoionization coupling terms $|V_E|^2$ in crystalline anthracene is considerably lower than the $|V_E|^2$ term for a typical atomic case such as the He atom ($2s$ $2p$) configurations.[1] This kinetic result is consistent with optical line shape data, as the line widths in crystalline anthracene in the spectral region 5–6 eV are comparable to those of the isolated molecule.[40] This result implies a relatively high value of the Fano line profile index q in the molecular crystal.

(d) The dominating role of the intramolecular decay channel for metastable exciton states in crystalline anthracene is probably a general phenomenon which prevails in molecular crystals of aromatic molecules.

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