

a more flexible 100-term wave function. Finally, in the last six rows one can see the energies obtained by varying the internuclear distance, R , around the equilibrium value. The energy has also been computed for other values of R .

The above results show clearly that the previous single-precision energy for the equilibrium internuclear distance was accurate up to the eighth figure. They also strongly suggest, especially in connection with the previous results,² that a calculation with a still more flexible wave function would not lower the energy by more than a small fraction of a reciprocal centimeter.

The diagonal corrections for nuclear motion^{2,4} computed previously with a 54-term wave function have now been recomputed in double precision and using a different algorithm. They fully agree with the single-precision results, and an extension of the expansion length to 66 terms (for $R = 1.4011$ and $R = 2.2$ a.u.) decreased the nuclear motion corrections by only 0.01 cm^{-1} .

Using for $1.0 \leq R \leq 3.2$ the energies calculated in double precision, and for $R < 1.0$ as well as for $R > 3.2$ the previously calculated values, and also the previously computed corrections for nuclear motion, the vibrational equation was solved and for the ground state the dissociation energy $D_0 = 36\,118.1 \text{ cm}^{-1}$ was obtained. The above value of D_0 can easily be corrected for the relativistic and radiative effects. Using^{2,5} $\Delta D_{\text{rel}} = 0.5 \text{ cm}^{-1}$ and⁶ $\Delta D_{\text{rad}} = -0.2 \text{ cm}^{-1}$ one gets the final ground-state dissociation energy $D_0 = 36\,117.4 \text{ cm}^{-1}$, and hence the final theoretical total energy of the molecule is 3.8

cm^{-1} lower than the experimental value. The discrepancy is one order of magnitude larger than the experimental error and any improvement of the adiabatic energy would increase the discrepancy.

Since all known effects of non-negligible magnitude have been included in the theoretical calculation, and since we see no reason to doubt the accuracy of the experimental value, the explanation of the discrepancy remains to be found.

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COLLISIONS OF SINGLET EXCITONS IN MOLECULAR CRYSTALS

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The recent publication of an experimental study of singlet-singlet exciton annihilation in crystalline anthracene¹ has been followed by two communications^{2,3} attempting to provide a theoretical analysis of these experimental data. This Letter presents a study of the metastable exciton states resulting from singlet-exciton collisions in molecular crystals. Any coherent theoretical analysis of the collision annihilation¹⁻¹⁰ of singlet excitons in crystal-

line anthracene has to be consistent with the following experimental facts.

(a) Kinetic data.—The rate constants for singlet-singlet annihilation γ_S , and for the production of charge carriers by exciton-exciton annihilation γ_i , can be expressed in terms of the exciton density n_E and the charge carrier density n_e :

$$\gamma_S = n_E^{-2}(-dn_E/dt); \quad \gamma_i = n_E^{-2}(dn_e/dt). \quad (1)$$

The previously reported value² $\gamma_S = (4 \pm 3) \times 10^{-8}$ cm³ sec⁻¹ was recently confirmed¹¹ by measurements of the fluorescence yield from crystalline anthracene [excited by the second harmonic ($\lambda = 3470$ Å) of a ruby laser]. On the other hand, $\gamma_i \leq 5 \times 10^{-12}$ cm³ sec⁻¹, as inferred from recent studies of laser-induced photoconductivity^{12,13} and photoconductivity induced by weakly absorbed light.^{6,13} In this system the major pathway for the intrinsic photogeneration of charge carriers involves the photoionization of singlet excitons.^{12,13}

(b) Cross sections and quantum yields.—The quantum yield for the intrinsic generation of charge carriers by excitation from the valence band (i.e., the ground state) to the conduction band is 10^{-4} .^{14,15} The cross section for the photoionization of singlet excitons is 10^{-19} cm².^{12,13}

(c) Line shapes in the optical spectrum.—The absorption bands in the spectrum of a single anthracene molecule in heptane solution in the region of 5–6 eV have a linewidth of $\Delta = 0.5$ eV.¹⁶ The line broadening arises mainly from intramolecular radiationless transitions,^{17,18} the internal conversion rate being $\hbar/\Delta = 5 \times 10^{14}$ sec⁻¹. The linewidths in crystalline anthracene in the same spectral region are comparable with those of the isolated molecule.¹⁶ The spectrum reveals no evidence of Fano-type antiresonances^{19,20} in the intense \bar{b} -polarized crystal spectrum.¹⁶

(d) Singlet-exciton migration mechanism.—The diffusion coefficient for singlet excitons in crystalline anthracene is $D = 5 \times 10^{-3}$ cm² sec⁻¹,²¹ while the exciton group velocity determined from the Davydov splitting is $\langle v \rangle = 3 \times 10^6$ cm sec⁻¹. The exciton linewidths at room temperature exceed the Davydov splitting. These data are consistent with the strong-scattering random-walk model for singlet-exciton migration.^{2,8,10}

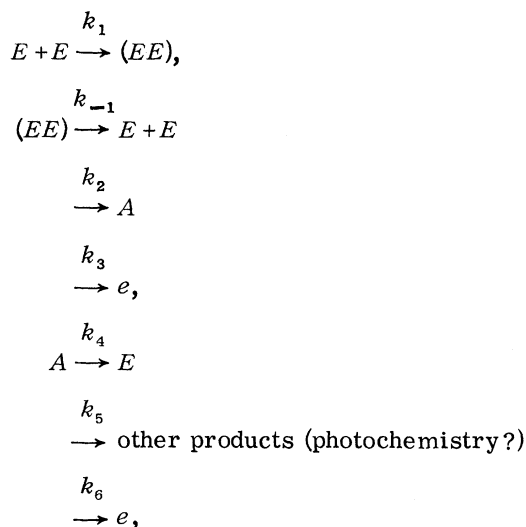
It was recently pointed out that an understanding of the intrinsic photogeneration of charge carriers¹² and of singlet-exciton collision processes^{2,3} requires the inclusion of metastable states described by the interference of bound states φ_A with the conduction-band states $\{\varphi_E\}$.^{19,20} In this scheme the metastable exciton state decays by an elastic, energy-conserving, autoionization process involving a two-electron dynamical resonance overlapping the one-electron scattering continuum.^{19,20} However, the interaction of a bound state in a closed channel with a single open channel ordinarily leads to a high ionization yield. In molecular crys-

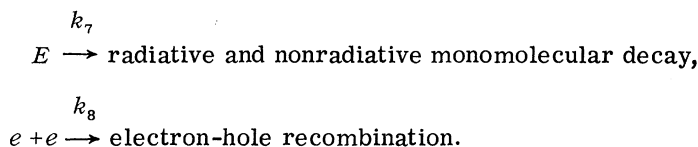
tals of polyatomic molecules, a new feature is introduced by the existence of intramolecular radiationless transitions.^{17,18} The latter processes can be adequately described in terms of configuration interaction between the localized state φ_A and the manifold of densely spaced vibronic states $\{\varphi_i\}$. The wave function for the metastable state can be then written²² by a straightforward modification of Fano's theory:

$$\psi = a(E)\varphi_A + \sum_i b_i \varphi_i + \int C_{E'} \varphi_{E'} dE'. \quad (2)$$

The coupling matrix elements $W_i = \langle \varphi_i | H | \varphi_A \rangle$ (or rather the interaction per unit energy, $W_E = W_i^2 \rho$, where ρ is the density of vibronic states) determine the role of intramolecular radiationless decay, while $V_E = \langle \varphi_E | H | \varphi_A \rangle$ determines the role of the autoionization process.²³ In view of small vibrational-overlap Franck-Condon factors,¹⁷ the coupling terms $\langle \varphi_E | H | \varphi_i \rangle$ are expected to be small. Therefore, the metastable state in a molecular crystal should be considered to be an effectively closed channel interacting with two open channels. In view of the small cross section for photogeneration of charge carriers and the linewidth data, it is proposed that the radiationless transition process dominates the autoionization process.

We proceed now to the analysis of the experiment of Bergman, Levine, and Jortner.¹ Choi and Sharma¹⁰ have demonstrated that the transition probability for a pair of singlets to the conduction band and to the metastable state (where only the autoionization channel was explicitly considered) is dominated by nearest-neighbor interactions. Using the random-walk model for singlet-exciton migration the following kinetic scheme has to be considered:





Here E , (EE) , and e correspond to the singlet exciton, to an exciton pair on adjacent molecules, and to the charge carriers, respectively. Adopting the steady-state approximation for the densities of (EE) and of A , the following equations result:

$$\frac{dn_E}{dt} = -k_1 n_E^2 \left\{ 1 - \left(1 + \frac{k_2 + k_3}{k_{-1}} \right)^{-1} - \left[\left(1 + \frac{k_5 + k_6}{k_4} \right) \left(1 + \frac{k_{-1} + k_3}{k_2} \right) \right]^{-1} \right\} - k_7 n_E, \quad (3)$$

$$\frac{dn_e}{dt} = k_1 n_E^2 \left\{ \left(1 + \frac{k_{-1} + k_2}{k_3} \right)^{-1} + \left[\left(1 + \frac{k_{-1} + k_3}{k_2} \right) \left(1 + \frac{k_4 + k_5}{k_6} \right) \right]^{-1} \right\} - k_8 n_e^2. \quad (4)$$

The rate of encounter of a singlet-exciton pair is $k_1 = 8\pi D\langle R \rangle$ or $k_1 = 4\pi\langle R \rangle^2\langle v \rangle$; i.e., $k_1 = (1-3) \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$.¹ The rate of separation of the pair is estimated from the hopping rate of singlet excitons $k_{-1} = 5 \times 10^{12} \text{ sec}^{-1}$. The monomolecular rate for the direct ionization of an exciton pair $k_3 = 10^{11} \text{ sec}^{-1}$ was evaluated by Choi.^{4,7,8} From the linewidths of the energy spectrum of the single molecule we estimate $k_4 + k_5 = 5 \times 10^{14} \text{ sec}^{-1}$. The measurements of the fluorescence yield of liquid benzene²⁴ at 5-6 eV indicate that $k_5 > k_4$. The rate constants $k_7 = 5 \times 10^7 \text{ sec}^{-1}$ and $k_8 = 2 \times 10^{-6} \text{ cm}^3 \text{ sec}^{-1}$ ¹² have been determined experimentally. From the laser-induced photoconductivity data^{12,13} we find that $k_6/(k_4 + k_5) \leq 10^{-4}$, so that $k_6 = 5 \times 10^{10} \text{ sec}^{-1}$. Fano's theory¹⁹ relates this rate constant to the coupling matrix element V_E by $k_6 = 2|V_E|^2\hbar^{-1}$, so that $|V_E|^2 = 2 \times 10^{-16} \text{ erg}$. Obviously, $|V_E|^2 \ll W_E$. Finally, k_2 can be expressed in the form

$$k_2 = (2\pi/\hbar) |a(E)|^2 |\langle \varphi'' | H | \varphi' \varphi' \rangle|^2. \quad (5)$$

Following Choi's³ notation, $|\varphi' \varphi' \rangle$ and $|\varphi'' \rangle$ correspond to the (EE) and A zero-order crystal states, respectively. Now, the amplitude squared can be described by a Lorentzian curve:

$$|a(E)|^2 = \frac{|V_E|^2 + W_E}{(E - E_A)^2 + \pi^2[|V_E|^2 + W_E]^2}$$

$$\approx \frac{W_E}{(E - E_A)^2 + \pi^2 W_E^2}. \quad (6)$$

Application of the dipole approximation³ leads to $k_2 \approx 10^{15} \text{ sec}^{-1}$.

From this analysis we conclude the following: (a) Because $k_2 \gg k_{-1}$, the transition to the final state is fast on the time scale of the singlet-exciton migration, and therefore the rate of singlet-exciton annihilation is determined by the rate of exciton collisions. This result contradicts the conclusions of Choi's work,³ where it was assumed that the annihilation reaction of the pair is slow relative to k_{-1} , and that the rate is determined by the transition rate k_2 to the final state. A similar situation prevails in the case of triplet-triplet annihilation.²⁵ (b) The "dilution" of the localized state is determined by the radiationless decay process rather than by the autoionization decay process. According to Choi's analysis³ $W_E/|V_E|^2 = (k_5 + k_4/k_6) \sim 1$, in contradiction to the photoconductivity data.^{12,13} (c) The experimental rate constants are $\gamma_S = k_1$ and $\gamma_i = k_1[(k_3/k_2) + k_6/(k_5 + k_4)]$, so that $\gamma_i \leq 10^{-4}\gamma_S$. (d) The rate constant determined by Bergman, Levine, and Jortner¹ represents the collision rate of a pair of singlet excitons, and is in good agreement with the theoretical estimate¹ based on the strong-scattering model. (e) The coupling term $|V_E|^2$ in crystalline anthracene is considerably smaller than the $|V_E|^2$ term for the He atom ($2s2p$) configuration. This result is consistent with the line-shape data and implies a high value of the Fano q factor¹⁹ in the molecular crystal. (f) The dominating role of the intramolecular channel for the decay of the metastable states in crystalline anthracene is probably a general phenomenon which prevails in all molecular crystals of organic molecules.

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