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Triplet Excitons in Crystals of Aromatic Molecules

JOSHUA JORTNER, STUART A. RICE, AND JOSEPH L. KATZ*
Department of Chemistry and Institute for the Study of Metals, The University of Chicago, Chicago, Illinois
AND
SANG-IL CHOI
Department of Physics, University of North Carolina, Chapel Hill, North Carolina

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In the present paper we consider the band structure and the Davydov splitting of the first triplet exciton states in crystalline naphthalene, anthracene, and biphenyl. It is found that: (a) An important contribution to the triplet exciton bandwidth arises from intermolecular exchange interaction. These interactions are calculated in the molecular orbital π-electron approximation. (b) Excitation exchange effects due to spin-orbit coupling are negligible. (c) Nonorthogonality corrections, considered within the framework of the symmetric orthogonalization procedure, have been found to be small. (d) Crystal-field mixing of triplet states arising from $\pi\rightarrow\pi^*$ excitations has no effect on the triplet bands. (e) An important contribution to the triplet exciton bandwidth may arise from configuration interaction with charge-transfer states.

The dynamics of triplet excitons in aromatic crystals was studied in the two limiting cases of strong and weak scattering. The band model, with the constant mean-free-path approximation, leads to a mean free path of the order of one to two lattice distances and seems to be inappropriate. Triplet-triplet annihilation leading to delayed blue fluorescence in crystalline anthracene can be adequately described in terms of a random-walk diffusion model when the effects of charge-transfer interactions are included.

I. INTRODUCTION

FULL theoretical understanding of the properties of the lowest excited states of crystals of aromatic molecules requires complete description of the manifold of electronic bands of the crystal. Included in this manifold are the singlet and triplet exciton bands and various other crystal states which cannot be constructed from the excited-state wavefunctions of an isolated molecule (i.e., charge-transfer exciton states). Now, crystals of aromatic compounds are unique in the sense that the electronic overlap between neighboring molecules is very small in both the ground state and the lower excited states arising from $\pi\rightarrow\pi^*$ transitions. In this case zero-order crystal wavefunctions may be constructed as product functions based on the states of the free molecule (Heitler-London approximation).[1-3] In the case of other molecular crystals, such as Ne, Ar, Kr, Xe, the interatomic overlap in the excited state is quite large, whereupon there arise serious nonorthogonality corrections to the Heitler-London approximation.[4] In addition, there is considerable mixing of delocalized charge-transfer states and the first neutral excited state.[5]

Following the pioneering work of Davydov,[1] there have been in the last 10 years extensive theoretical and experimental studies of singlet exciton states.[2,3] Despite variations in emphasis, details, and to some extent even experimental results, the extended Davydov theory leads to a moderately accurate description of the singlet exciton states in crystals of aromatic molecules. However, the lowest excited state of most aromatic molecules is a triplet, to which direct optical transition from the ground state is extremely weak because of spin selection rules.[6-8] Although direct observation of the Davydov splitting of a triplet level has not yet been reported,[9] there have been many recent investigations of the dynamical properties of triplet excitons. It has now been unambiguously established that triplet excitons are mobile in aromatic crystals, and various phenomena involving triplet energy transfer have been demonstrated. The following observations are pertinent to the present discussion:

(a) From electron spin resonance studies it has been shown that triplet energy is transferred between widely separated guest molecules in a host crystal.[11] For the case of the guests phenanthrene and naphthalene in the host biphenyl, with the guest molecules oriented with their principal magnetic axes approximately parallel to that of the biphenyl, it has been shown that an important pathway for energy transfer involves a vibrationally excited state of the lowest triplet state

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[*] Present address: North American Aviation Science Center, Canoga Park, California.

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[9] Systems which might be studied include halogen substituted aromatic hydrocarbons (i.e., iodonaphthalene) and heterocyclic compounds. In both cases the singlet-triplet transition probability is enhanced by spin-orbit coupling and is much larger than for the equivalent pure hydrocarbon. One could, in principle, determine factor-group splittings by a modification of the method of Ref. 10 (addition of a polarizer).

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of phenanthrene (with energy matching the triplet band energy of the host crystal).[12]

(b) Optical emission studies of isotopically mixed benzene[13] and naphthalene[14] crystals have shown that trap-to-trap migration of triplet excitation energy occurs in these systems.[15] A recent study of the phosphorescence spectra of isotopically mixed benzene crystals leads to a value of 12 cm^{-1} for the nearest-neighbor pair triplet interaction matrix element.[16] The total triplet electronic matrix element is, therefore, of the order of magnitude of 50 cm^{-1}.[16]

(c) Direct population of the first triplet state of the anthracene crystal is possible using intense light sources. Irradiation of an anthracene crystal with a ruby laser ($h\nu=1.8$ eV) leads to delayed blue fluorescence arising from the transition $^1B_{2u}\rightarrow{}^1A_{1g}$ ($h\nu=3.42$ eV).[17] Now, the single photon absorption at room temperature is from a vibrationally excited level of the ground state to the triplet state (i.e., the $1\rightarrow0^1$, $A_{1g}\rightarrow{}^3B_{2u}$ transition), and the delayed fluorescence (observed on a time scale of milliseconds) depends on the square of the light intensity and follows bimolecular kinetics.[17,18] These results have been interpreted[17] by assuming an annihilation process involving two triplet excitons, with the rate constant for exciton–exciton annihilation estimated to be 2×10^{-11} $\text{cm}^{-3}\cdot\text{sec}^{-1}$. An alternative method[19] for population of the triplet state in the anthracene crystal (population by radiationless transition from the $^1B_{2u}$ singlet state to the triplet state) leads to the same biexciton annihilation mechanism. Other experiments using (incoherent) continuous light sources[10] also lead to similar conclusions regarding the annihilation of triplet excitons by a bimolecular process. Finally, we note that the excitation spectrum (in the region 14 000 to 20 000 cm^{-1}) has been identified with the $^1A_{1g}\rightarrow{}^3B_{2u}$ absorption spectrum.[10]

In the present paper we consider the band structure and Davydov splittings for the first (lowest) triplet exciton states in aromatic crystals. Although our results cannot at present be compared with any optical data, they can be used in the study of triplet exciton dynamics in crystals of aromatic molecules. A preliminary report of this work has already been published.[20,21]

The structure of an exciton band in a molecular crystal is determined by the interaction energy between the molecules of the crystal. In the one electron approximation, the intermolecular interaction energies reduce to a sum of Coulomb (excitation exchange) and exchange (electron and excitation exchange) integrals. It was pointed out by Merrifield[22] that intermolecular electron exchange interactions will contribute to the triplet bandwidth, but an order of magnitude estimate by Sternlicht and McConnell[23] indicated that these intermolecular exchange integrals, as calculated with Slater wavefunctions, are extremely small, and do not lead to a large contribution to the bandwidth. Recently, Nieman and Robinson[13] and the present authors[24] have shown that the use of a single Slater orbital (characterized by an orbital exponent $\xi=1.625$ a.u.) to represent the carbon-atom $2p\pi$ wavefunctions seriously underestimates the magnitude of the tails of the wavefunctions, leading to serious errors in the estimates of overlap and electron exchange interactions at typical intermolecular separations. Of course, the problem of representing atomic and molecular wavefunctions at large distances from the molecule has arisen before in the calculation of atomic polarizabilities,[25] molecular quadrupole moments,[26] interatomic and intermolecular dispersion forces,[27] and charge-transfer interactions in molecular complexes.[28] In all these cases the use of SCF wavefunctions for the construction of molecular orbitals is expected to provide an improved description of the molecular wavefunctions at large distances from the molecule. Moreover, it is important to remark that changes in quantitative detail can lead to changes in qualitative interpretation if, as a result of the quantitative changes, the balance is altered between several competing contributions. It should also be pointed out that the use of a simple scaling procedure, i.e., the use of a single Slater-type atomic wavefunction characterized by a smaller orbital exponent than that obtained by the Slater rules, is not consistent with the SCF wavefunctions. We have found that the basic overlap and exchange integrals involving carbon-atom $2p\pi$ wavefunctions (in the region 6 to 10 a.u.) cannot be reproduced by a single Slater-type function. Hence this scaling procedure is not to be recommended. In the present work we adopt the SCF carbon-atom wavefunctions and use them for numerical calculations of the triplet exciton band structure in aromatic crystals.

II. TRIPLET EXCITON STATES

The triplet exciton states of an aromatic crystal can readily be obtained by a simple extension of conven-

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tional exciton theory.[2,3] As the starting point of this analysis we consider the crystal Hamiltonian for a rigid lattice of nonvibrating molecules

$$H=\sum_{m\alpha}H_{m\alpha}+\sum_{m\alpha<n\beta}V_{m\alpha,n\beta}, \tag{1}$$

where $H_{m\alpha}$ is the Hamiltonian for the mth molecule in the αth unit cell when this molecule is isolated, and $V_{m\alpha,n\beta}$ is the pair-interaction potential. Considering each molecule to be characterized by a framework of σ bonds to which the π electrons are confined defines $H_{m\alpha}$ as the self-consistent-field π-electron Hamiltonian for the isolated molecule, while the pair-interaction potential is the sum of the frame–frame ($V_{\sigma\sigma}$), frame–electron ($V_{\sigma e}$), and π-electron–electron interactions:

$$V_{m\alpha,n\beta}=V_{\sigma\sigma}+V_{\sigma e}+\sum_{\substack{i<j\\ i\epsilon m\alpha\\ j\epsilon n\beta}}r_{ij}^{-1}. \tag{2}$$

The zero-order wavefunctions we use are constructed for the oriented gas model, which assumes that the intermolecular interactions are much smaller than the intramolecular interactions. The ground-state wavefunction is then

$$\Phi^0=\mathcal{A}\prod_{n\beta}\varphi^0{}_{n\beta}, \tag{3}$$

where the $\varphi_{n\beta}{}^0$ are the wavefunctions of the isolated molecules, and $\mathcal{A}$ is the antisymmetrization operator permuting electrons between the molecules

$$\mathcal{A}=[(a!)^{2N}/(hNa)!]^{\frac{1}{2}}\sum_P(-)^P P. \tag{4}$$

In Eq. (4), a is the number of electrons on each molecule, N the number of unit cells in the crystal, and h the number of molecules per unit cell.

The zero-order excited-state wavefunctions are given by

$$\Phi_{m\alpha}{}^f=\mathcal{A}\varphi_{m\alpha}{}^f\prod_{m\alpha\neq n\beta}{}'\varphi_{n\beta}{}^0. \tag{5}$$

The triplet excited state $\varphi_{m\alpha}{}^f$ represents three spin states which are the eigenfunctions of S^2 and S_z (i.e., $S=1$ and $M_s=0, \pm1$). Since the molecular Hamiltonian $H_{m\alpha}$ is assumed to be spin-independent, zero-field splitting of the spin states is neglected and the three spin components will be degenerate.

The single excitation wavefunctions $\Phi_{m\alpha}{}^f$ are not eigenfunctions of the crystal Hamiltonian, but can be used to form proper symmetry-adapted wavefunctions. To be more specific, we only consider molecular crystals belonging to the $C_{2h}{}^5$ space group of monoclinic crystals with two molecules in the unit cell, e.g., naphthalene, anthracene, and biphenyl. The triplet exciton wavefunction is then given by

$$\Psi_\pm{}^f(\mathbf{k})=\frac{1}{(2N)^{\frac{1}{2}}}\sum_{n=1}^{N}\exp(i\mathbf{k}\cdot\mathbf{r}_n)\Big[\mathcal{A}\varphi_{n1}{}^f\prod{}'\varphi_{mj}{}^0 \pm\exp(i\mathbf{k}\cdot\boldsymbol{\tau})\mathcal{A}\varphi_{n2}{}^f\prod{}'\varphi_{mj}{}^0\Big], \tag{6}$$

where $\boldsymbol{\tau}=(\frac{1}{2})(\mathbf{a}+\mathbf{b})$, and $\mathbf{k}$ is the crystal momentum vector, whose values are limited within the first Brillouin zone. For $\mathbf{k}=\mathbf{0}$, $\Psi_+{}^f$ and $\Psi_-{}^f$ correspond to the B_u and A_u representations of the factor group $C_{2h}{}^5$.

The Davydov components of the excited state of the crystal relative to the ground state of the crystal are given by

$$E_f{}^i=E_f{}^0+D_f+E_f{}^\pm(\mathbf{k}),\qquad i=1,2, \tag{7}$$

where $E_f{}^0$ is the excitation energy of the free molecule, and D_f represents the energy shift of the center of gravity of the band. The exciton band structure is determined by

$$E_f{}^\pm(\mathbf{k})=\sum_{m1;m\neq n}(J^f{}_{m1,n1}+K^f{}_{m1,n1})\cos(\mathbf{k}\cdot\mathbf{r}_{m1}) \pm\sum_{m2;m\neq n}(J^f{}_{m2,n1}+K^f{}_{m2,n1})\cos(\mathbf{k}\cdot\mathbf{r}_{m2}), \tag{8}$$

where the excitation-transfer and electron-exchange matrix elements are

$$J^f{}_{m\mu,n1}=\langle\varphi^f{}_{n1}\varphi_{m\mu}{}^0\,|\,V_{n1,m\mu}\,|\,\varphi_{n1}{}^0\varphi^f{}_{m\mu}\rangle, \tag{9}$$

$$K^f{}_{m\mu,n1}=\langle[\sum_P(-)^P P-1]\varphi^f{}_{n1}\varphi^0{}_{m\mu}\,|\,V_{n1,m\mu}\,|\,\varphi^0{}_{n1}\varphi^f{}_{m\mu}\rangle. \tag{10}$$

By definition, the Davydov splitting is

$$\Delta E^f=E_f{}^+(\mathbf{k})-E_f{}^-(\mathbf{k}). \tag{11}$$

Conservation of crystal momentum requires that $\mathbf{k}=\mathbf{q}$, where $\mathbf{q}$ is the wave vector of the incident light. In the case under consideration (triplet exciton states) the dominant interactions are of short range, and the magnitude of the ratio of $|\mathbf{q}|$ to the reciprocal lattice vectors is of the order of 10^{-3}, so that the approximation $\mathbf{q}=\mathbf{0}$ may be used. It should be noted that this approximation is not valid in the case of singlet exciton states where the modulation of the lattice sums by the term $\exp(i\mathbf{q}\cdot\mathbf{r})$ is of considerable importance.[29,30] For triplet exciton states the Davydov splitting is therefore seen to be

$$\Delta E^f=2\sum_{m2}(J^f{}_{m2,n1}+K^f{}_{m2,n1}). \tag{12}$$

Before closing this discussion it is worthwhile mentioning that the tight binding approximation to exciton theory must be extended to include crystal-field mixing of other excited states into the state f. The off-diagonal matrix elements, $H_{fg}{}^\pm=\langle\Psi_\pm{}^f\,|\,H\,|\,\Psi_\pm{}^g\rangle$, are of considerable importance in determining the splitting and the intensity ratios of the Davydov components of singlet exciton states. When the off-diagonal terms are small compared to the energy separation between the states (E_f-E_g), perturbation theory may be used. The revised Davydov splitting is found to be

$$\Delta E^f=2\sum_{m2}(J^f{}_{m2,n1}+K^f{}_{m2,n1}) +\sum_g\frac{|\langle\Psi_+{}^f\,|\,H\,|\,\Psi_+{}^g\rangle|^2-|\langle\Psi_-{}^f\,|\,H\,|\,\Psi_-{}^g\rangle|^2}{E_f-E_g}. \tag{13}$$

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All classifications of the lowest triplet states of alternate aromatic hydrocarbons have to date been based primarily on energy-level calculations. The Pariser–Parr SCF semiempirical calculations,[31] the Ham–Rudenberg free-electron model,[32] and the Moffit perimeter-model[33,34] calculations all indicate that the lowest triplet state of linear polyacenes (characterized by D_{2h} symmetry) corresponds to the $^3B_{2u}$ state (i.e., the *p* state in Clar's notation, or ^3L_a in Platt's notation). ESR measurements lead to confirmation of this prediction in the sense that the observed hyperfine structure and zero-field splitting of the lowest naphthalene triplet agree with the corresponding computed quantities for the $^3B_{2u}$ state.[35] We thus consider the triplet excited state to arise from a one-electron excitation from the highest filled orbital to the lowest antibonding orbital.

III. NUMERICAL CALCULATIONS

We turn now to the calculation of the J and K integrals for the triplet states of aromatic crystals. As long as spin–orbit coupling is neglected, the excitation exchange matrix element vanishes (spin orthogonality). An estimate of the integral J can be obtained by considering the spin–orbit coupling between the triplet state of interest and the perturbing singlet states. Application of perturbation theory leads to

$$(\varphi^f{}_{m\mu})_1=(\varphi^f{}_{m\mu})_0+\sum_s[(H_{s0})_{fs}/(E_f-E_s)]\varphi^s{}_{m\mu}, \qquad (14)$$

where $(\varphi^f{}_{m\mu})_1$ is the perturbed triplet wavefunction, $\varphi^s{}_{m\mu}$ an unperturbed excited singlet state, E_f and E_s the triplet and singlet energies, and $(H_{s0})_{fs}$ the spin–orbit coupling matrix element combining the two states. Equation (9) is then reduced to the form

$$J^f{}_{m\mu,n1}=\left\langle\sum_s\frac{(H_{s0})_{fs}}{E_f-E_s}\varphi^s{}_{n1}\varphi^0{}_{m\mu}\;\middle|\;V_{n1,m\mu}\;\middle|\;\varphi^0{}_{n1}\sum_{s'}\frac{(H_{s0})_{fs'}}{E_f-E_{s'}}\varphi^{s'}{}_{m\mu}\right\rangle. \qquad (15)$$

In this expression the interaction of the ground-state wavefunction with excited triplet states by spin–orbit coupling is not taken into account. For approximate numerical estimates, this omission is not serious.

Spin–orbit coupling in aromatic hydrocarbons has been studied by several investigators.[6–8] McClure[6] has shown that when only coupling between $\pi\rightarrow\pi^*$ transitions is considered, one and two center contributions to the spin–orbit coupling matrix elements vanish, and three center contributions have to be included. Mizushima and Koida[7] considered the possibility of spin–orbit coupling between a triplet $\pi\rightarrow\pi^*$ state and a singlet $\sigma\rightarrow\pi^*$ state, where one center contributions do not vanish.[36] In any case, the spin–orbit coupling is extremely weak in these systems, leading to long radiative (phosphorescence) lifetimes. Following McClure,[6] we assume that $(H_{s0})_{fs}\approx 1$ cm^{-1}, and to make a rough estimate of the excitation exchange integral we consider just one perturbing singlet state. Then taking $E_s-E_f=20\,000$ cm^{-1}, the triplet-state Coulomb integral J^f is related to the perturbing singlet-state Coulomb integral J^s by

$$J^f{}_{m\mu,n1}\approx[|(H_{s0})_{fs}|^2/(E_f-E_s)^2]J^s{}_{m\mu,n1}. \qquad (16)$$

The contribution of these Coulomb-type integrals to the Davydov splitting can be estimated by summing over all translationally inequivalent molecules. For strongly allowed singlet–singlet transitions, $\sum_{m2}J^f{}_{m2,n1}\approx 10^3$–$10^5$ cm^{-1}, so that the contribution of the Coulomb integrals to the Davydov splitting of the triplet state is of the order of 10^{-3} cm^{-1}, and is therefore negligibly small. We conclude that, within the tight binding approximation, the triplet exciton bandwidth arises from intermolecular electron exchange interactions.

We now examine the magnitude of the exchange interaction. Three types of molecular wavefunctions were used for the calculation of the required exchange integrals: antisymmetrized products of Hückel orbitals, antisymmetrized products of π-electron SCF orbitals calculated by Hoyland and Goodman,[37] and π-electron configuration interaction wavefunctions computed by Pariser.[38] When the excited state is represented by a single electronic configuration, i.e., for the case of the Hückel and the Hoyland–Goodman wavefunctions, the electron exchange integrals for the first triplet state can be represented in the form

$$\begin{aligned}&K^f{}_{n1,m\mu}\\&=-\langle u_{m\mu}{}^{N/2}(1)u_{n1}{}^{N/2}(1)\mid r_{12}{}^{-1}\mid u_{m\mu}{}^{N/2+1}(2)u_{n1}{}^{N/2+1}(2)\rangle,\end{aligned} \qquad (17)$$

where $u_a{}^{N/2}$ and $u_a{}^{N/2+1}$ are the highest bonding and the lowest antibonding molecular orbitals located on Molecule *a*. In the derivation of this expression, it is assumed that the molecular orbitals located on adjacent molecules are orthogonal. The overlap integrals between adjacent molecules in an aromatic crystal are quite small, being of the order of magnitude of 10^{-3}, whereupon Löwdin's symmetric orthogonalization[39] procedure may be used to construct new functions. The orthog-

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onalized set $U_a{}^i$ is expanded in the form

$$U_a{}^i = u_a{}^i - \tfrac{1}{2}\sum_{b,b\neq a}\sum_{k}\langle u_a{}^i \mid u_b{}^k\rangle u_b{}^k + \mathcal{O}(S^2), \quad (18)$$

where the first sum is taken over all the molecules, while the second sum involves the molecular orbitals with the same spin as $u_a{}^i$. The convergence condition $\sum_{b,k}\langle u_a{}^i \mid u_b{}^k\rangle < 1$ is expected to be satisfied. The electron exchange integrals $(K^f)_L$, calculated using the orthogonalized set (18), take the form

$$\begin{aligned}(K^f{}_{n1,m\mu})_L = {} & K^f{}_{n1,m\mu}\\ & +\tfrac{1}{2}\sum_{\substack{b\\ b\neq m\mu}}\sum_{k}\langle u_{m\mu}{}^{N/2} \mid u_b{}^k\rangle\langle u_b{}^k u_{n1}{}^{N/2} \mid r_{12}{}^{-1} \mid u_{m\mu}{}^{N/2+1}u_{n1}{}^{N/2+1}\rangle\\ & +\tfrac{1}{2}\sum_{\substack{b\\ b\neq n1}}\sum_{k}\langle u_{n1}{}^{N/2} \mid u_b{}^k\rangle\langle u_{m\mu}{}^{N/2}u_b{}^k \mid r_{12}{}^{-1} \mid u_{m\mu}{}^{N/2+1}u_{n1}{}^{N/2-1}\rangle\\ & +\tfrac{1}{2}\sum_{\substack{b\\ b\neq m\mu}}\sum_{k}\langle u_{n1}{}^{N/2+1} \mid u_b{}^k\rangle\langle u_{m\mu}{}^{N/2}u_{n1}{}^{N/2} \mid r_{12}{}^{-1} \mid u_b{}^k u_{n1}{}^{N/2+1}\rangle\\ & +\tfrac{1}{2}\sum_{\substack{b\\ b\neq n1}}\sum_{k}\langle u_{m\mu}{}^{N/2+1} \mid u_b{}^k\rangle\langle u_{m\mu}{}^{N/2}u_{n1}{}^{N/2} \mid r_{12}{}^{-1} \mid u_{m\mu}{}^{N/2+1}u_b{}^k\rangle\\ & +\mathcal{O}(S^2). \quad (19)\end{aligned}$$

Calculation of the nonorthogonality corrections is considerably simplified by neglecting the terms involving three different molecular centers. In view of the large intermolecular spacing, these three center exchange terms will be negligibly small.

Since the calculations of the intermolecular interactions contributing to the triplet exciton bandwidth are performed within the framework of the π-electron approximation, the molecular orbitals are conveniently represented in terms of a linear combination of carbon-atom $2p_z$ wavefunctions, w^i,

$$u^m = \sum_i C_i{}^m w^i,$$

where the $C_i{}^m$ are Hückel coefficients without overlap or the Hoyland–Goodman SCF coefficients. Using these functions the electron exchange integrals are reduced to the form

$$\begin{aligned}K^f{}_{n1,m\mu} = {} & -\sum_{i,j,k,l} C_i{}^{N/2}C_j{}^{N/2}C_k{}^{N/2+1}C_l{}^{N/2+1}\\ & +\langle w^i{}_{m\mu}(1)w^j{}_{n1}(2) \mid r_{12}{}^{-1} \mid w^k{}_{m\mu}(2)w^l{}_{n1}(2)\rangle. \quad (20)\end{aligned}$$

In the calculation reported herein three and four center integrals are neglected, whereupon,

$$\begin{aligned}K^f{}_{n1,m\mu} = {} & -\sum_{i,j} C_i{}^{N/2}C_j{}^{N/2}C_i{}^{N/2+1}C_j{}^{N/2+1}\\ & +\langle w^i{}_{m\mu}(1)w^j{}_{n1}(2) \mid r_{12}{}^{-1} \mid w^i{}_{m\mu}(2)w^j{}_{n1}(2)\rangle. \quad (20')\end{aligned}$$

The Mulliken approximation is not adequate for the evaluation of intermolecular exchange integrals, and it is quite difficult to estimate the magnitude of these terms. Previous experience in the calculation of one electron–intermolecular exchange integral leads us to believe that the contribution of these many center terms will not exceed 25% to 50% of the total computed interaction.

The exchange integrals are extremely sensitive to the detailed form of the wavefunction at large distance from the carbon-atom nucleus. In these calculations we have represented the carbon-atom wavefunction in terms of the SCF orbitals calculated for the neutral carbon atom [in the electronic configuration ^3P, $(2s)^2(2p)^2$]. These orbitals are represented in the form of a linear combination of Slater functions,[40]

$$w^i = r\cos\theta\sum_j a_j(\alpha_j/\pi)^{\frac{1}{2}}\exp(-\alpha_j r_j). \quad (21)$$

Several carbon-atom wavefunctions with a varying basis set size have been calculated by Roothaan, Clementi, Gilbert, and Cohen[41]; the $2p_z$ orbital is reproduced in Table I. The electronic exchange integrals in the region of interest calculated using these several different functions do not differ from one another by more than 5% (Table II). In the calculations reported herein, Wavefunction B.R. II was employed. The details of the exchange integral calculations are given in Appendix I.

As indicated earlier, calculations were performed only for the several aromatic crystals characterized by a monoclinic unit cell containing two molecules per unit cell. The experimental crystal structure data for anthracene, naphthalene, and biphenyl are accurate within 0.02 Å, as can be inferred from the reported standard deviations in the atomic coordinates.[42] In our calculations we have included the exchange interactions between the reference molecule located at the center of a unit cell and 13 nearest-neighbor molecules at the corners and the side centers of a unit cell. The locations and numbering of these molecules are presented in Table III, where we also display the intermolecular electron exchange interactions. These exchange integrals were computed neglecting the nonorthogonality corrections. We find that the largest values of K are for the molecules located at $\boldsymbol{\tau} = (\frac{1}{2})(\mathbf{a}+\mathbf{b})$ and at $\mathbf{b}$.

TABLE I. Ground-state carbon-atom $(2s^22p^2\,{}^3P)$ SCF wavefunctions.

	C.R.[a]		B.R. I[b]		B.R. II[b]	
i	α_i	a_i	α_i	a_i	α_i	a_i
1	6.3438	0.01090	5.152	0.02472	6.827	0.00847
2	2.5873	0.23563	2.117	0.39516	2.779	0.17442
3	1.4209	0.57773	1.150	0.64975	1.625	0.45191
4	0.9554	0.24756	···	···	1.054	0.43645

[a] Reference 40.

[b] Reference 41.

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[40] E. Clementi and C. C. J. Roothaan, Phys. Rev. **127**, 1618 (1962).

[41] C. C. J. Roothaan, E. Clementi, T. Gilbert, and H. Cohen (private communication).

[42] (a) D. W. J. Cruickshank, Acta Cryst. **10**, 504 (1957). (b) V. C. Sinclair, J. M. Robertson, and A. M. Mathieson, *ibid.* **3**, 251 (1950). (c) A. Hargreaves and S. Hasan Rizvi, *ibid.* **15**, 365 (1962).

TABLE II. Exchange integrals at large separations for SCF $2p$ carbon-atom wavefunctions (all quantities in atomic units).

R	Atomic wavefunction	$\langle p_+p_- \mid p_-p_+\rangle$	$\langle p_+p_+ \mid p_+p_+\rangle$	$\langle p_zp_z \mid p_zp_z\rangle$	$\langle p_zp_+ \mid p_+p_z\rangle$	$\langle p_zp_z \mid p_+p_+\rangle$	$\langle p_zp_+ \mid p_zp_-\rangle$
6.00	C.R.	0.19668×10^{-4}	0.20342×10^{-3}	0.48644×10^{-2}	0.170994×10^{-3}	0.100518×10^{-2}	...
6.00	B.R.I.	0.18914×10^{-4}	0.19208×10^{-3}	0.49125×10^{-2}	0.17476×10^{-3}	0.94428×10^{-3}	0.25532×10^{-3}
6.00	B.R.II	0.19514×10^{-4}	0.20086×10^{-3}	0.48864×10^{-2}	0.17327×10^{-3}	0.989108×10^{-3}	0.26436×10^{-3}
8.00	C.R.	0.65563×10^{-6}	0.70778×10^{-5}	0.33055×10^{-3}	0.78988×10^{-5}	0.48739×10^{-9}	0.12369×10^{-4}
8.00	B.R.I	0.53742×10^{-6}	0.55923×10^{-5}	0.30252×10^{-3}	0.70824×10^{-5}	0.39682×10^{-4}	0.99347×10^{-5}
8.00	B.R.II	0.62078×10^{-6}	0.66088×10^{-5}	0.32518×10^{-3}	0.77896×10^{-5}	0.45945×10^{-4}	0.11597×10^{-4}

The nonorthogonality corrections involve overlap and hybrid (ionic) intramolecular integrals, the computation of which have been previously described: The corrections calculated from Eq. (19) are listed in Table IV. It is apparent that the nonorthogonality corrections to the intermolecular exchange interactions do not exceed 10% to 20% and can therefore be neglected in view of other approximations inherent in the calculations.

IV. BAND STRUCTURE

We have constructed the triplet exciton states in several aromatic crystals in terms of states which involve the symmetric and antisymmetric combinations of molecular wavefunctions corresponding to the two molecules in the unit cell. The corresponding $\mathbf{k}$-dependent eigenvalues give the two energy bands (only $\mathbf{k}$-dependent terms are displayed).

$$\begin{aligned} E_+'(\mathbf{k}) &= 2K_2\cos(\mathbf{k}\cdot\mathbf{c})+2K_3\cos(\mathbf{k}\cdot\mathbf{b}) \\ &+2K_4[\cos\mathbf{k}\cdot(\mathbf{b}+\mathbf{c})+\cos\mathbf{k}\cdot(\mathbf{b}-\mathbf{c})] \\ &+2K_5\cos(\mathbf{k}\cdot\mathbf{a})+2K_6\cos\mathbf{k}\cdot(\mathbf{c}+\mathbf{a}) \\ &+2K_7[\cos\mathbf{k}\cdot(\mathbf{a}+\mathbf{b})+\cos\mathbf{k}\cdot(\mathbf{a}-\mathbf{b})] \\ &+2K_8[\cos\mathbf{k}\cdot(\mathbf{a}+\mathbf{b}+\mathbf{c})+\cos\mathbf{k}\cdot(\mathbf{a}-\mathbf{b}+\mathbf{c})] \\ &\pm2K_9[\cos\mathbf{k}\cdot(\tfrac{1}{2}\mathbf{a}+\mathbf{b})+\cos\mathbf{k}\cdot(\tfrac{1}{2}\mathbf{a}-\mathbf{b})] \\ &\pm2K_{10}[\cos\mathbf{k}\cdot(\tfrac{1}{2}\mathbf{a}+\mathbf{b}+\mathbf{c})+\cos\mathbf{k}\cdot(\tfrac{1}{2}\mathbf{a}-\mathbf{b}+\mathbf{c})], \end{aligned} \quad (22)$$

and the 10 K_i are the electron exchange integrals between the reference molecules 1 and i. The band can be readily visualized if we consider now the special cases when $\mathbf{k}$ is parallel to a reciprocal lattice vector, $\mathbf{a}^{-1}$, $\mathbf{b}^{-1}$, or $\mathbf{c}^{-1}$:

$$E_\pm'(\mathbf{k}\,\|\,\mathbf{a}^{-1})=A+B\cos(\mathbf{k}\cdot\mathbf{a})\pm C\cos(\mathbf{k}\cdot\tfrac{1}{2}\mathbf{a}), \quad (23)$$

$$\begin{aligned} E_\pm'(\mathbf{k}\,\|\,\mathbf{b}^{-1}) &= D+E\cos(\mathbf{k}\cdot\mathbf{b}) \\ &\pm F\cos(\mathbf{k}\cdot\tfrac{1}{2}\mathbf{b})\pm E_{14}\cos(\mathbf{k}\cdot\tfrac{3}{2}\mathbf{b}), \end{aligned} \quad (24)$$

$$\begin{aligned} E_+'(\mathbf{k}\,\|\,\mathbf{c}^{-1}) &= G+H\cos(\mathbf{k}\cdot\mathbf{c}), \\ E_-'(\mathbf{k}\,\|\,\mathbf{c}^{-1}) &= I+L\cos(\mathbf{k}\cdot\mathbf{c}), \end{aligned} \quad (25)$$

where we define A through L by the relations

$$\begin{aligned} A&=2(K_2+K_3+2K_4), \\ B&=2(K_5+K_6+2K_7+2K_8), \\ C&=4(K_9+K_{10}), \\ D&=2(K_2+K_5+K_6), \\ E&=2(K_3+2K_4+2K_7+2K_8), \\ F&=4(K_9+K_{10}), \\ G&=2(K_3+K_5+2K_7+2K_9), \\ H&=2(K_2+2K_4+K_6+2K_8+2K_{10}), \\ I&=2(K_3+K_5+2K_7-2K_9), \\ L&=2(K_2+2K_4+K_6+2K_8-2K_{10}). \end{aligned} \quad (26)$$

TABLE III. Electron exchange intermolecular integrals in some aromatic crystals. (Energies in units of 10^{-4} eV).

i	Location of molecule	Naphthalene H–G[a] 300°K[c]	Naphthalene Hückel[b] 300°K[c]	Anthracene Hückel[b] 300°K[c]	Anthracene H–G[a] 300°K[c]	Anthracene H–G[a] 77°K[d]	Biphenyl Hückel[b] 300°K[c]
2	c	−0.0019	−0.0035	−0.0113	−0.0046	−0.0176	0.9949
3	b	9.4476	8.4811	7.2857	9.1194	7.6299	−1.3089
4	$c+b$	0.0041	0.0035	0.0	0.0	0.0	0.0
5	a	0.0002	0.0	0.0002	0.0001	0.0003	−0.0001
6	$c+a$	−0.0006	−0.0043	−0.0018	−0.0009	−0.0043	0.0040
7	$a+b$	0.0001	0.0001	0.0001	0.0001	0.0002	0.0
8	$a+b+c$	0.0	0.0001	0.0	0.0	0.0	0.0
9	$\frac{1}{2}(a+b)$	−5.6956	−4.9109	−5.4043	−5.4126	−6.1133	−0.4628
10	$c+\frac{1}{2}(a+b)$	0.0018	−0.0199	−0.0173	−0.0052	−0.0203	0.0182

[a] Hoyland–Goodman molecular wavefunctions from Ref. 37.
[b] Hückel molecular wavefunctions from C. A. Coulson and R. Daudel, *The Dictionary of Values of Molecular Constants* (privately printed).
[c] Room-temperature crystal data from Ref. 42.
[d] Anthracene crystal structure at 77°K from V. M. Kozhin and A. I. Kitaĭgorodskiĭ, Zh. Fiz. Khim. **27**, 1676 (1953).

TABLE IV. Nonorthogonality corrections for intermolecular exchange integrals (in units of 10^{-4} eV).[a]

i	Naphthalene	Anthracene
2	0.001	···
3	0.748	0.400
6	−0.005	−0.001
9	−0.708	0.147
10	0.070	−0.001

[a] Contributions for molecules not listed were found to be smaller than 10^{-7} eV.

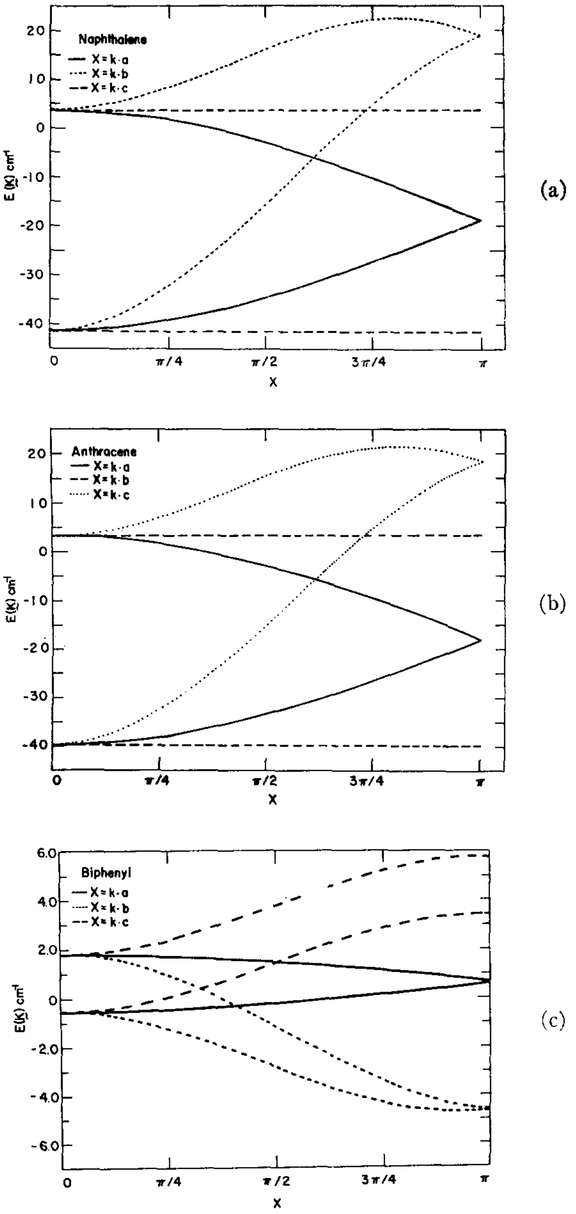

FIG. 1. Electron exchange contributions to the shape of the triplet exciton bands in (a) naphthalene, (b) anthracene, and (c) biphenyl.

TABLE V. Electron-exchange contribution to triplet exciton bandwidths (energy in units of 10^{-4} eV).

	Naphthalene	Anthracene	Biphenyl
$(a^{-1})_+$	22.78	21.67	1.762
$(a^{-1})_-$	22.77	21.67	1.794
$(b^{-1})_+$	18.41	17.97	7.014
$(b^{-1})_-$	60.60	58.15	3.609
$(c^{-1})_+$	0.038	0.064	4.142
$(c^{-1})_-$	0.009	0.020	3.850

The symmetry properties of these energy bands have previously been discussed. For the cases when $\mathbf{k}$ is parallel to the reciprocal lattice vectors $\mathbf{a}^{-1}$ and $\mathbf{b}^{-1}$, the two bands are degenerate at $\pi\mathbf{a}^{-1}$ and at $\pi\mathbf{b}^{-1}$ and intersect at these points with equal and opposite slopes. This conclusion is a general result of the effect of time reversal symmetry on the energy bands of crystals. The energy bands are expected to stick together in pairs on the boundary plane of the Brillouin zone that is perpendicular to a twofold screw axis of the reciprocal lattice.

The first triplet exciton band structure of anthracene, naphthalene, and biphenyl is displayed in Fig. 1. The band structure has been plotted in the three principal reciprocal lattice directions. In Table V we display the values of the widths of the bands in the $\mathbf{a}^{-1}$, $\mathbf{b}^{-1}$, and $\mathbf{c}^{-1}$ directions. These results are of interest in the study, of triplet exciton dynamics.

V. DAVYDOV SPLITTING

Since the triplet exciton band structure is determined entirely by short-range interactions, the Davydov splitting is

$$\Delta E^f = 8(K_9 + K_{10}). \tag{27}$$

The term K_9, involving electron exchange interactions between the two molecules in the unit cell leads to the major contribution to the Davydov splitting. The total electronic contributions to the Davydov splittings are summarized in Table VI. To proceed further, the vibronic coupling problem must be examined.

For the case of triplet exciton states the Davydov

TABLE VI. Electron-exchange contribution to the Davydov splitting of the first triplet state in some aromatic crystals (energy units in cm^{-1}).

Crystal	Molecular wavefunctions	ΔE
Naphthalene, 300°K	Hückel	−31.7
	Hoyland–Goodman	−36.8
	Pariser	−29.6
Anthracene, 300°K	Hückel	−34.9
	Hoyland–Goodman	−34.9
Anthracene, 77°K	Hoyland–Goodman	−39.4
Biphenyl 300°K	Hückel	−3.0

splitting is small relative to the vibrational spacing ($\sim$1000 cm^{-1}), and the weak coupling scheme is obviously appropriate. In the weak coupling limit,[43,44] the Davydov splitting is considered separately for each vibronic band. The molecular wavefunctions are constructed from the vibronic functions

$$\varphi_n^{fi} = \varphi_n^{f} \chi_n^{fi}, \tag{28}$$

where χ_n^{fi} is a vibrational wavefunction for the nth molecule in the f electronic and the ith vibrational states. When the vibronic wavefunctions are used as the basis for calculation of the matrix elements of the pair potential, the splitting of a vibronic component arising from the transition $00 \rightarrow fi$ is

$$\Delta E^{f} = 8(K_9 + K_{10}) \langle \chi^{00} \mid \chi^{fi} \rangle^2, \tag{29}$$

i.e., the electronic matrix elements are modified by a vibrational overlap factor. The vibrational overlap integrals $\langle \chi^{00} \mid \chi^{fi} \rangle$ can be estimated from the relative intensities of the vibronic components of the phosphorescence spectrum of the aromatic molecule in a rigid glass.[45] The vibrational overlap integrals for the totally symmetric a_g vibrational mode also can be estimated theoretically using the Ross–McCoy procedure.[46] For the 1400-cm^{-1} a_g progression in the ${}^1A_{1g} \rightarrow {}^3B_{2u}$ transition in anthracene we get from the calculated bond-order changes: $\langle \chi^{00} \mid \chi^{f0} \rangle^2 = 0.26$ (exptl., 0.27), $\langle \chi^{00} \mid \chi^{f1} \rangle^2 = 0.35$ (exptl., 0.30), $\langle \chi^{00} \mid \chi^{f2} \rangle^2 = 0.24$ (exptl., 0.26). It may therefore be concluded that the Davydov splitting of the 0–0 vibronic component of the ${}^3B_{2u}$ state of anthracene would be about -8 cm^{-1} if only neutral exciton states were to be considered. The intensity of the 0–0 vibronic component in the aromatic crystals of interest is usually of order 0.20 to 0.25 of the total band intensity, so that in general the Davydov splitting of the 0–0 component of the triplet state is given by the total electronic matrix element reduced by a numerical factor of $\frac{1}{4}$ to $\frac{1}{5}$.

Finally, it is necessary to consider the effect of crystal-field mixing between the first triplet state and higher triplet states. Our calculations show this mixing to be extremely small. For the anthracene crystal, the second triplet state is expected to have symmetry ${}^3B_{3u}$. The off-diagonal matrix elements $\langle ({}^3B_{2u}) \mid H \mid ({}^3B_{3u}{}^{+}) \rangle$ were found to be of the order of 10 cm^{-1} for the A_u and the B_u representations of the factor group, while the energy separation between these states is about 12 000 cm^{-1}.[38] Therefore, the contribution of second-order crystal-field mixing is of the order of magnitude of 0.01 cm^{-1} and can be safely neglected. In general, in triplet exciton states where the off-diagonal matrix elements of the crystal Hamiltonian are of the same order of magnitude as the diagonal elements and the energy separation between the first and other triplet states of the order of 10^4 cm^{-1}, the effect of crystal-field mixing is negligible.

VI. HOPPING MODEL FOR TRIPLET EXCITON MIGRATION

We have demonstrated that in the first excited triplet state of some typical aromatic crystals the electron exchange interactions between adjacent molecules are of the order of 5 to 10 cm^{-1}. These relatively small interactions determine the rate of migration of triplet excitons. Clearly, the frequency of transfer of triplet excitation will be of the order of magnitude of the frequency of intermolecular lattice vibrations, and much smaller than the frequency of intramolecular vibrations. Under these conditions there will be appreciable scattering of the triplet exciton by the lattice phonons. Two models are useful for the description of the triplet exciton motion. First, we may assume that the scattering of the triplet excitation wave is so strong that the mean free path is of the order of magnitude of the intermolecular separation in the crystal. The motion of the excitation can then be described as a random walk, i.e., a diffusion process. Alternatively, the triplet exciton motion can be described within the framework of the band model, where the limiting case of narrow bands is considered.

The hopping model for triplet exciton motion has previously been considered in some detail,[21] and we limit ourselves to the basic results. In describing the incoherent motion of the triplet excitation, the transition probability W_{1i} for energy transfer from the reference molecule 1 to Molecule i is given by

$$W_{1i} = \frac{2\pi}{\hbar} \mid K_{1i} \mid^2 \int F(E) f(E) dE, \tag{30}$$

where $F(E)$ and $f(E)$ are the singlet–triplet absorption function and the triplet–singlet phosphorescence function, respectively, each normalized to unity on the energy scale. The integral $\int F(E)f(E)dE$ corresponds to a vibrational overlap factor, the vibrational spectrum being treated as a continuum. In view of the short range of the exchange integrals K_{1i}, energy transfer only to near neighbors need be considered. The mean lifetime of the triplet excitation on the reference molecule 1, τ_1, is given by

$$\tau_1^{-1} = \sum_i W_{1i}, \tag{31}$$

and the mean diffusion coefficient of the triplet excitation is

$$D = \tfrac{1}{6} \sum_i W_{1i} R_{1i}^2, \tag{32}$$

where R_{1i} is the distance between Molecules 1 and i. The diagonal elements of the diffusion tensor along the

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[43] W. T. Simpson and D. L. Peterson, J. Chem. Phys. **26**, 588 (1957).

[44] A. Witkowski and W. Moffitt, J. Chem. Phys. **33**, 872 (1960).

[45] S. P. McGlynn and M. Kasha, J. Chem. Phys. **24**, 588 (1956).

[46] E. F. McCoy and I. G. Ross, Australian J. Chem. **4**, 573 (1962).

crystal axes are

$$D_{aa}=a^2/2(\tau_1)_a,$$
$$D_{bb}=b^2/2(\tau_1)_b,$$
$$D_{cc}=c^2/2(\tau_1)_c. \qquad (33)$$

The vibrational overlap integral $\int F(E)f(E)dE$ for anthracene was estimated from the phosphorescence spectrum in EPA glass[45] and from the reaction spectrum of the anthracene-crystal laser-induced blue fluorescence.[10] We find $\int F(E)f(E)dE=0.2$ eV^{-1}, whereupon, for the anthracene crystal, $1/\tau_1=6\times10^9$ sec^{-1} and $D=6.2\times10^{-6}$ cm^2 sec^{-1}. It is worthwhile noting that when electron exchange interactions are considered, only interactions within the *ab* plane are of appreciable magnitude.

The diffusion length for a triplet excitation in the anthracene crystal in the limiting case of small exciton concentration is given by $l=(2D\tau_0)^{\frac{1}{2}}$, where $\tau_0=10^{-2}$ sec is the triplet lifetime in anthracene.[17,18] Hence, $l=3.5\times10^{-4}$ cm, which is of the same order of magnitude as the diffusion length of singlet excitons. It should be noted that the diffusion length under actual experimental conditions will be decreased by triplet–triplet exciton–exciton annihilation.

An estimate of the rate of encounter of two triplet excitons is of considerable interest with respect to the study of biexcitonic annihilation. Within the framework of the random-walk model, the rate of collision of two excitons is[47]

$$\Gamma=8\pi D\langle R\rangle n_T^2, \qquad (34)$$

where $\langle R\rangle$ is an average crystal spacing and n_T the number of triplet excitons per unit volume. An alternative formalism sets

$$\Gamma=(z/2\rho\tau_1)n_T^2, \qquad (34')$$

where z is the number of nearest neighbors to a molecule and ρ the number of molecules per unit volume. A comparison between the predictions of (34) and (34′) sets bounds on the reliability of Γ. The main features of the triplet–triplet annihilation mechanism leading to the formation of an excited singlet can be described in terms of the simple kinetic scheme[48]:

$$T+T\underset{k-1}{\overset{k_1}{\rightleftarrows}}T_iT_j\overset{k_2}{\longrightarrow}S_1\overset{k_3}{\longrightarrow}G+h\nu, \qquad (35)$$

where G, S_1, and T refer to the ground state, first excited singlet, and first excited triplet, respectively. The T_iT_j refers to a state where the two triplets are located on adjacent molecules. The annihilation process may involve some intermediate steps and is further discussed later. Under steady-state conditions the rate of fluorescence emission is given by

$$\mathcal{R}=\frac{k_1n_T^2}{[(k_{-1}/k_2)+1]}. \qquad (36)$$

Two limiting cases are of interest:

(a) When the rate of dissociation of the triplet pair is large compared with the annihilation rate, i.e., $k_{-1}\gg k_2$, the annihilation reaction is expected to be determined by the transition rate k_2 to the final state, $\mathcal{R}=(k_1k_2/k_{-1})n_T^2$.

(b) If the transition to the final singlet state is fast on the time scale of triplet exciton migration, i.e., $k_{-1}<k_2$, then the annihilation reaction is diffusion controlled. In this case the rate is $\mathcal{R}=k_1n_T^2$, being determined by the rate of collision of the triplet excitons.

As we show later, in the case of triplet–triplet annihilation the rate determining step involves the production of two adjacent excited molecules. It should be noted that if spin conservation is maintained, the conversion of the triplet pair to a singlet state is modified by the probability for the formation of the pair T_iT_j in the singlet state. This leads to a statistical factor of $w=\frac{1}{9}$ (since two triplet excitons may form a singlet, triplet, and a quintet pair). For the case of the diffusion controlled triplet–triplet annihilation, the rate is thus given by

$$\mathcal{R}=w\Gamma. \qquad (37)$$

The random-walk model just considered may underestimate the mean free path, i.e., the mean free path may be larger than the intermolecular spacing. In this case the exciton motion is better described within the framework of the band scheme.

Before numerical calculations can be made there is another important contribution to the intermolecular interactions in the triplet state which must be considered. We refer to intermolecular charge-transfer interactions, which are not contained in the Heitler–London scheme, and which lead to an increase of the interactions, thereby enhancing the rate of migration of the triplet excitation. The role of ion-pair excitons is considered in Sec. VIII.

VII. BAND MODEL FOR TRIPLET EXCITON MIGRATION[49]

The band structure calculations reported in Sec. IV can be used to estimate the diffusion coefficient of the triplet exciton within the framework of the band model. We adopt the conventional assumption that the rate of exciton migration is limited by scattering arising from interaction with lattice phonons. The most difficult problem faced concerns the treatment of the scattering mechanism. We adopt a phenomenological approach and assume that exciton scattering can be described in the constant relaxation time approximation.

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[47] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).

[48] We consider here the limiting case of high exciton concentration where the bimolecular mechanism predominates over monomolecular decay processes.

[49] The band model was considered independently by R. G. Kepler and by W. Siebrand (private communication) using somewhat simplified models for the triplet exciton band structure.

In this approximation, the components of the diffusion tensor are expressed in the form

$$D_{ij}=\tau_s\langle v_iv_j\rangle, \qquad (38)$$

where τ_s is a constant isotropic relaxation time, independent of $\mathbf{k}$, and v_i, v_j are the components of the group velocity, $\mathbf{V}(\mathbf{k})$,

$$\mathbf{V}(\mathbf{k})=(1/\hbar)\nabla_{\mathbf{k}}E(\mathbf{k}). \qquad (39)$$

The diffusion tensor can also be related to an isotropic constant mean free path, $\Lambda=\tau_s\langle\,|\mathbf{V}(\mathbf{k})\,|\,\rangle$, by

$$D_{ij}=\Lambda\langle v_iv_j/|\,\mathbf{V}(\mathbf{k})\,|\,\rangle. \qquad (40)$$

In the following, we employ an orthogonal coordinate system with axes parallel to **a**, **b**, and **c**′ ($\mathbf{c}'\cdot\mathbf{a}=\mathbf{c}'\cdot\mathbf{b}=\mathbf{0}$)

In Eqs. (38) and (40), the angular brackets represent an average over the Boltzmann distribution of excitons in the band,

$$\langle v_iv_j\rangle=\int\left[\frac{\partial E_+}{\partial k_i}\frac{\partial E_+}{\partial k_j}g(E_+)+\frac{\partial E_-}{\partial k_i}\frac{\partial E_-}{\partial k_j}g(E_-)\right]d^3k\Big/\hbar^2\int[g(E_+)+g(E_-)]d^3k, \qquad (41)$$

where $g(E_i)=\exp(-E_i/k_BT)$ is the Boltzmann factor. In the present case the triplet exciton bandwidth W is smaller than k_BT (at room temperature), the band states are almost equally populated, and the effective mass approximation cannot be used.

The components of the velocity tensor in the constant-free-time and constant-free-path approximations were calculated using the electron exchange interactions displayed in Table VII. In this description, the anisotropy of the velocity components along the crystal axes arises only from the anisotropy in the energy bands. Since the off-diagonal components of the velocity tensor are small, the mean diffusion coefficient is approximately

$$D\approx\tfrac{1}{3}(D_{aa}+D_{bb}+D_{cc}) \qquad (42)$$

or

$$D\approx\frac{\Lambda}{3}\left[\left\langle\frac{V_a^2}{|\,\mathbf{V}(\mathbf{k})\,|}\right\rangle+\left\langle\frac{V_b^2}{|\,\mathbf{V}(\mathbf{k})\,|}\right\rangle+\left\langle\frac{V_c^2}{|\,\mathbf{V}(\mathbf{k})\,|}\right\rangle\right]. \qquad (43)$$

Now, the existence of a scattering mechanism implies the presence of molecular vibrations. When the band structure in the tight binding approximation is based on the vibronic states of the constituent molecules, the band corresponding to the rigid lattice separates into a number of subbands, each determined by the total interaction matrix element multiplied by the vibrational overlap factor $\langle\chi^{00}\,|\,\chi^{fi}\rangle^2$. For all aromatic molecules of interest, the intramolecular vibrational quanta exceed k_BT at room temperature, so that for our study only the 0–0 vibronic band need be considered. Provided that the triplet bandwidth is smaller than k_BT, the diffusion-controlled exciton–exciton annihilation rate now assumes the form

$$\Gamma=\tfrac{8}{3}\pi w\langle R\rangle\Lambda\langle|\,\mathbf{V}(\mathbf{k})\,|\,\rangle\langle\chi^{00}\,|\,\chi^{fi}\rangle^2n_T^2. \qquad (44)$$

In order to reproduce the observed annihilation rate, it is necessary that the mean free path be between 6 and 12 Å, corresponding to the two limits of the observed annihilation rate. In this calculation we have used $\langle|\,\mathbf{V}(\mathbf{k})\,|\,\rangle\approx1.3\times10^5$ cm/sec as determined from the band structure, and $\langle\chi^{00}\,|\,\chi^{fi}\rangle^2=0.20$, all for the case of crystalline anthracene. From the mean-free path we obtain the mean scattering time. Corresponding to the limits on Λ, we find τ_s to be between 0.8×10^{-11} and 1.6×10^{-11} sec.

It is the opinion of the authors that when the mean-free path of the excitation wave is as short as one or two lattice distances, as is the case in anthracene, then the use of a band scheme is inappropriate. Moreover, the assumption of a constant scattering time, or constant mean free path is so uninformative and so fraught with conceptual difficulties that, before the difficult problem of the nature of exciton scattering is solved for the cases under discussion, no meaningful comparison of band theory and experiment can be made. The very short mean free path leads us to prefer the limiting case of strong scattering, wherein the localized states are dominant and the exciton motion is diffusive.

VIII. EFFECT OF CHARGE-TRANSFER STATES ON TRIPLET EXCITON MIGRATION

In the discussion of triplet exciton states we have thus far limited attention to neutral exciton states, constructed from the isolated molecule wavefunctions within the framework of the oriented gas model. As pointed out elsewhere,[50] a tight binding approximation based on only the free molecule excited states is not completely satisfactory, and configuration interaction between neutral exciton states and charge-transfer exciton states may be important. Indeed, ion-pair

TABLE VII. Components of the triplet exciton velocity tensor in the constant mean-free-path approximation[a] (energy units 10^4 cm/sec).

	Naphthalene	Anthracene	Biphenyl
$\langle V_a^2/\lvert\mathbf{V}\rvert\rangle$	3.592	3.570	0.147
$\langle V_b^2/\lvert\mathbf{V}\rvert\rangle$	10.246	9.904	0.977
$\langle V_{c'}^2/\lvert\mathbf{V}\rvert\rangle$	0.000	0.000	1.432
$\langle\lvert\mathbf{V}\rvert\rangle$	13.839	13.474	2.556

[a] Electron-exchange contributions only are included. The molecular wavefunctions for naphthalene and anthracene are the Hoyland–Goodman functions, while for biphenyl Hückel functions were used. The crystal data are for 300°K. These results apply to a rigid lattice consisting of rigid molecules. The actual triplet velocity has to be modified by a vibrational overlap factor.

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[50] S. Choi, J. Jortner, S. A. Rice, and R. Silbey, J. Chem. Phys. **41**, 3294 (1964).

states with an electron and hole located on adjacent molecules may mix efficiently with neutral exciton states characterized by small bandwidths, thereby considerably affecting the bandwidths and the Davydov splittings.[50] The effect of configuration interaction between triplet ion-pair exciton states and neutral triplet exciton states has been examined,[50] and it is found that for crystalline, anthracene, and naphthalene the Davydov splitting of the triplet is increased by about 50%. Clearly, the contribution of charge-transfer states will also increase the rate of migration of triplet excitons in these systems.

We proceed now to examine the effect of charge-transfer states on the triplet excitation hopping probability, within the framework of the random-walk model. In this case we limit ourselves to consideration of a localized neutral excitation mixing with a localized charge-transfer state. For estimation of the transition probability W_{1i} we consider the following initial and final states:

$$\Psi_I = |\, R_1{}^f, R_i{}^0 \rangle + \lambda_i \,|\, R_1{}^+, R_i{}^- \rangle + \mu_i \,|\, R_i{}^+, R_1{}^- \rangle,$$

$$\Psi_F = |\, R_1{}^0, R_i{}^f \rangle + \eta_i \,|\, R_1{}^+, R_i{}^- \rangle + \nu_i \,|\, R_i{}^+, R_i{}^- \rangle, \qquad (45)$$

where R^0, R^f, R^+, and R^- represent molecular wavefunctions corresponding to the ground state, first triplet state, positive ions, and negative ions, respectively. The states $|\, R^f R^0 \rangle$, $|\, R^+ R^- \rangle$, and $|\, R^- R^+ \rangle$ correspond to excited triplet and triplet ion-pair states, while λ, μ, η, and ν are the mixing coefficients between the neutral and charge-transfer states. It should be noted that the present formulation is identical with Mulliken's charge-transfer description of molecular complexes.

Since the off-diagonal elements of the crystal Hamiltonian are small compared with the energy separation between the neutral and charge-transfer states, the mixing coefficients are obtained from first-order perturbation theory:

$$\lambda_i = \langle R_1{}^f R_i{}^0 \,|\, H \,|\, R_1{}^+ R_i{}^- \rangle / \Delta E,$$

$$\eta_i = \langle R_1{}^0 R_i{}^f \,|\, H \,|\, R_1{}^+ R_i{}^- \rangle / \Delta E,$$

$$\mu_i = \langle R_1{}^f E_i{}^0 \,|\, H \,|\, R_i{}^+ R_1{}^- \rangle / \Delta E,$$

$$\nu_i = \langle R_1{}^0 R_i{}^f \,|\, H \,|\, R_i{}^+ R_1{}^- \rangle / \Delta E. \qquad (46)$$

We do not introduce the nonorthogonality corrections to the electronic matrix elements in Eq. (46). A study of these terms shows that the nonorthogonality corrections would not affect our results by more than 20%.

The electronic matrix element determining the transition probability W_{1i} can be expanded to first order in the mixing coefficients, with the result that

$$\begin{aligned} \langle \Psi_I \,|\, H \,|\, \Psi_F \rangle &= K_{1i} + \lambda_i \langle R_1{}^0 R_i{}^f \,|\, H \,|\, R_1{}^+ R_i{}^- \rangle \\ &\quad + \mu_i \langle R_1{}^0 R_i{}^f \,|\, H \,|\, R_i{}^+ R_1{}^- \rangle \\ &\quad + \eta_i \langle R_1{}^f R_i{}^0 \,|\, H \,|\, R_1{}^+ R_i{}^- \rangle \\ &\quad + \nu_i \langle R_1{}^f R_i{}^0 \,|\, H \,|\, R_i{}^+ R_1{}^- \rangle \\ &= K_{1i} + 2(\lambda_i \eta_i + \mu_i \nu_i) \Delta E. \end{aligned} \qquad (47)$$

For the anthracene crystal, the charge-transfer state has been estimated to be 3.4±0.5 eV above the ground state,[50] so that $\Delta E = -1.5 \pm 0.5$ eV. The matrix elements determining the mixing coefficients have previously been evaluated and, when nonorthogonality effects are neglected, are given by

$$\langle R_m{}^f R_n{}^0 \,|\, H \,|\, R_m{}^+ R_n{}^- \rangle = \langle u_m{}^{N/2+1} \,|\, V_n{}^{\mathrm{GMS}} \,|\, u_n{}^{N/2} \rangle - \sum_{i=1}^{N/2} [\langle u_m{}^{N/2+1} u_n{}^i \,|\, r^{-1} \,|\, u_n{}^i u_n{}^{N/2+1} \rangle + \langle u_m{}^{N/2+1} u_m{}^i \,|\, r^{-1} \,|\, u_m{}^i u_n{}^{N/2+1} \rangle],$$

$$\langle R_m{}^f R_n{}^0 \,|\, H \,|\, R_n{}^+ R_m{}^- \rangle = -\langle u_m{}^{N/2} \,|\, V_n{}^{\mathrm{GMS}} \,|\, u_n{}^{N/2} \rangle$$

$$+ \sum_{i=1}^{N/2} \langle u_n{}^{N/2} u_n{}^i \,|\, r^{-1} \,|\, u_n{}^i u_m{}^{N/2} \rangle - \langle u_n{}^{N/2} u_m{}^{N/2} \,|\, r^{-1} \,|\, u_m{}^{N/2+1} u_m{}^{N/2+1} \rangle + 2 \langle u_m{}^{N/2} u_m{}^{N/2+1} \,|\, r^{-1} \,|\, u_m{}^{N/2+1} u_m{}^{N/2} \rangle. \qquad (48)$$

In Eq. (48), V^{GMS} is the Goeppert-Mayer–Sklar potential of the molecule, which involves the screening of the nuclear charge by the Hartree field. These potentials and the hybrid integrals have been evaluated in other work.[50] In Table VIII we display the results of the calculation of the contribution of the charge transfer states to the electronic matrix elements determing the transition probability for triplet exciton transfer in anthracene.

TABLE VIII. The contribution of charge-transfer states to the triplet excitation transfer matrix elements in anthracene crystal.

Molecule	Charge-transfer contribution to $\langle \Psi_I \,|\, H \,|\, \Psi_F \rangle$ (10^{-4} eV)
2	3.03
3	11.7
9	−8.82
10	+2.36

It is apparent that the triplet exciton transfer time is decreased by including charge-transfer states; we find $1/\tau_1 = 3 \times 10^{10}$ sec, increasing the triplet exciton diffusion coefficient and the diffusion length.[50a] The rate constant for triplet–triplet annihilation in the anthracene crystal can now be obtained from Eqs. (32), (34),

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[50a] *Note added in proof*: P. Avakian and R. E. Merrifield [Phys. Rev. Letters **13**, 541 (1964)] have shown that the diffusion length for triplet excitons is $10 \pm 5 \times 10^4$ Å, in agreement with our estimate of 8×10^4 Å [obtained from $l_{CT} = l(\tau \,|\, \tau_{CT})^{\frac{1}{2}}$ and using the values cited in Sec. VI].

and (37). In Eq. (34′) counting all the nearest neighbors to a given molecule leads to $z=42$. When only electron-exchange interactions are included, $\Gamma=0.9\times 10^{-11}n_T^2$ cm$^{-3}\cdot$sec^{-1} from (34) and $\Gamma=3\times10^{-11}\ n_T^2$ cm$^{-3}\cdot$sec^{-1} from (34′), whereupon $0.1\times10^{-11}<\mathcal{R}<0.3\times10^{-11}$ cm$^{-3}\cdot$sec^{-1}. When the effect of electron-transfer states on the triplet mobility is also included, the triplet–triplet annihilation rate is determined by an exciton–exciton collision rate $\Gamma=4.5\times10^{-11}n_T^2$ cm$^{-3}\cdot$sec^{-1} from (34) and $15\times10^{-11}n_T^2$ cm$^{-3}\cdot$sec^{-1} from (34′) so that $0.5\times10^{-11}<\mathcal{R}<1.5\times10^{-11}n_T^2$ cm$^{-3}\cdot$sec^{-1}. In view of the uncertainties in the calculated electronic matrix elements and the overlap factor $\int F(E)f(E)dE$, our theoretical estimate is uncertain to one order of magnitude. The experimental triplet–triplet[17,18] annihilation rate constant in the anthracene crystal is $(2\text{–}6)\times10^{-11}n_T^2$ cm$^{-3}\cdot$sec^{-1}, which is in good agreement with the theoretical value.[51]

The mixing of charge-transfer states alters the model for triplet exciton migration in one important quantitative way: When only electron-exchange interactions are important, the triplet exciton motion is restricted to the *ab* plane. However, the mixing of charge-transfer states into the neutral exciton states leads to an appreciable transition probability from the reference molecule to the one located at $\mathbf{c}+\boldsymbol{\tau}$, and the motion of the exciton is not confined to a single molecular plane.

IX. COMMENTS ON THE MECHANISM OF TRIPLET–TRIPLET ANNIHILATION

Thus far in our analysis of triplet–triplet annihilation we have examined only the consequences of the assumption that the rate of annihilation is diffusion controlled. We now turn to an examination of the mechanism of annihilation, in the sense of studying possible intermediate states along the reaction path.

The singlet electronic state involving two triplet excitations on adjacent molecules (a and b) can be constructed using the Wigner angular-momentum coupling coefficients[52]:

$$\Psi_{TT}=(1/\sqrt{3})\sum_{m=0,\pm1}(-)^{m+1}\,|\,T_a{}^mT_b{}^{-m}\rangle. \tag{49}$$

The simplest wavefunctions usable in the present discussion involve four electrons occupying the highest bonding and lowest antibonding orbitals on the molecules a and b. These are

$$\begin{aligned}
|\,T_a{}^1T_b{}^{-1}\rangle&=\mathcal{A}[u_a{}^{N/2+1}\alpha(1)u_a{}^{N/2}\alpha(2)u_b{}^{N/2+1}\beta(3)u_b{}^{N/2}\beta(4)],\\
|\,T_a{}^{-1}T_b{}^1\rangle&=\mathcal{A}[u_a{}^{N/2+1}\beta(1)u_a{}^{N/2}\beta(2)u_b{}^{N/2+1}\alpha(3)u_b{}^{N/2}\alpha(4)],\\
2\,|\,T_a{}^0T_b{}^0\rangle&=\mathcal{A}[u_a{}^{N/2+1}\alpha(1)u_a{}^{N/2}\beta(2)+u_a{}^{N/2+1}\beta(1)u_a{}^{N/2}\alpha(2)][u_b{}^{N/2+1}\alpha(3)u_b{}^{N/2}\beta(4)+u_b{}^{N/2+1}\beta(3)u_b{}^{N/2}\alpha(4)],
\end{aligned} \tag{50}$$

with α and β the usual spin functions. Now, the functions displayed in (50) do not represent a stationary state. If the annihilation process leads to the direct formation of the ${}^1B_{2u}$ singlet excited state (Ψ_{GS_1}), the matrix element which determines the transition probability is

$$\begin{aligned}
\langle\Psi_{TT}\,|\,H\,|\,\Psi_{GS_1}\rangle=(\tfrac{3}{2})^{\frac12}[\langle u_a{}^{N/2+1}(1)u_b{}^{N/2}(1)\,|\,r^{-1}\,|\,u_a{}^{N/2+1}(2)u_b{}^{N/2+1}(2)\rangle\\
-\langle u_a{}^{N/2}(1)u_b{}^{N/2}(1)\,|\,r^{-1}\,|\,u_a{}^{N/2}(2)u_b{}^{N/2+1}(2)\rangle],
\end{aligned} \tag{51}$$

where G and S_1 refer, respectively, to the ground state and first singlet excited state of the molecule. From our preceding analysis, it is seen that (51) is of the order of magnitude of the electron-exchange interaction, i.e., 10^{-4} to 10^{-3} eV.

Now, as already mentioned in Sec. VIII, it has been shown that ion-pair excitons can mix with the neutral triplet exciton band in anthracene and naphthalene.[50] It is to be expected, then, that an important contribution to the transition probability may arise from the charge-transfer state G^+G^- with the electron and hole on adjacent molecules. The wavefunction representing G^+G^- has the form

$$\begin{aligned}
\Psi_{G^+G^-}&\\
=(\mathcal{A}/\sqrt{2})&[u_a{}^{N/2}\alpha(1)u_b{}^{N/2+1}\beta(2)u_b{}^{N/2}\alpha(3)u_b{}^{N/2}\beta(4)\\
&-u_a{}^{N/2}\beta(1)u_b{}^{N/2+1}\alpha(2)u_b{}^{N/2}\alpha(3)u_b{}^{N/2}\beta(4)].
\end{aligned} \tag{52}$$

For the four-electron system under consideration, it is convenient to take the Hamiltonian in the form

$$\begin{aligned}
H&=\sum_{i=1}^{4}[T_i+H_a{}^c(i)+H_b{}^c(i)+\sum_{i<j}(1/r_{ij})],\\
H_a{}^c&=V_a{}^{\text{nucl}}+\sum_{k=1}^{N/2-1}(2J_a{}^s-K_a{}^s),
\end{aligned} \tag{53}$$

where T_i is the kinetic-energy operator, $H_a{}^c$ and $H_b{}^c$ are the core potentials of Molecules a and b, and $V_a{}^{\text{nucl}}$ is the bare nuclear potential of Molecule a. Using (53) the transition matrix elements between the states represented by Ψ_{TT} and $\Psi_{G^+G^-}$ are

$$\begin{aligned}
\langle\Psi_{TT}\,|\,H\,|\,\Psi_{G^+G^-}\rangle\cong\langle u_a{}^{N/2+1}\,|\,V_a{}^{\text{GMS}}\,|\,u_b{}^{N/2}\rangle\\
-\sum_{k=1}^{N/2-1}\langle u_a{}^{N/2+1}u_a{}^k\,|\,r_{ij}{}^{-1}\,|\,u_a{}^ku_b{}^{N/2}\rangle\\
+\langle u_a{}^{N/2+1}u_b{}^{N/2}\,|\,r_{ij}{}^{-1}\,|\,u_b{}^{N/2+1}u_b{}^{N/2}\rangle\\
+\langle u_a{}^{N/2+1}u_b{}^{N/2}\,|\,r_{ij}{}^{-1}\,|\,u_b{}^{N/2}u_b{}^{N/2}\rangle
\end{aligned} \tag{54}$$

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[51] It should also be noted that the reduction by 1/9 may overestimate the effects of spin selection rules, since it is conceivable that radiationless transitions could occur from the compound intermediate state to S_1. All such effects tend to raise $\mathcal{R}$.

[52] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1957), p. 73.

when nonorthogonality corrections are neglected. Here V_a^{GMS} is the Goeppert-Mayer–Sklar potential of the molecule a. Because the final density of states is unknown, direct evaluation of (51) or (54) is not, at present, feasible. However, an order-of-magnitude estimate indicates that $\langle\Psi_{TT}\,|\,H\,|\,\Psi_{G^+G^-}\rangle$ is one to two orders of magnitude larger than $\langle\Psi_{TT}\,|\,H\,|\,\Psi_{GS_1}\rangle$. The reason that the two matrix elements differ so much is that the magnitude of (51) is determined by intermolecular exchange integrals, while the magnitude of (54) is determined by Coulomb hybrid integrals. Thus, if the vibrational overlap factors do not differ greatly in the two cases cited, the transition probability to the ion-pair state will exceed the transition probability to the excited singlet state by a factor of 10^3-10^4.

We have already cited the estimated energy of the charge-transfer state (3.4±0.5 eV). The reader should note that this estimate places the charge-transfer state very close to the first excited singlet state ($^1B_{2u}$) of anthracene. A detailed theoretical study of the spectrum of crystalline anthracene[53] leads to the conclusion that the energy separation between the charge-transfer state and the $^1B_{2u}$ state in anthracene must exceed 500 cm^{-1}. The spectrum is consistent, however, with a limited amount of mixing of the states G^+G^- and GS_1, i.e., a representation of the form $\Psi_{GS_1}+\lambda\Psi_{G^+G^-}$ with $\lambda^2\approx 0.1$ will not noticeably alter the Davydov splitting. Now, it is not necessary that the final state in the triplet–triplet annihilation be a pure charge-transfer state, as previously conjectured by us.[21] If configuration mixing of the limited type previously mentioned occurs, the transition probability to the mixed state will still be of order of magnitude 10–10^2 larger than the transition probability to the pure $^1B_{2u}$ state. Under these conditions the annihilation process is still efficient on the time scale of the triplet migration from site to site in the crystal.

There is one indirect corroboration of the suggestion that ion-pair states play a role in the annihilation process. Lindquist[54] has studied the kinetics of the decay in solution of triplet fluorescein generated by flash excitation. It is found that the kinetics cannot be understood unless the decay mechanism includes the reaction between two triplet fluorescein molecules to give as products the oxidized and reduced forms of fluorescein. This reaction is, of course, the direct analog of the reaction of two triplet excitons to form an ion-pair exciton.

X. DISCUSSION

In this paper an attempt has been made to present a systematic survey of the properties of the first triplet exciton band in some typical crystals of aromatic molecules. Of course, the numerical results of the analysis presented herein depend critically on the molecular wavefunctions employed in the calculations. The procedure employed, namely, the use of a linear combination of carbon-atom SCF wavefunctions to represent the molecular orbitals, is obviously only the first step in obtaining a good representation of the molecular wavefunctions at large distances from the molecule. In support of our procedure, it should be noted that recent *a priori* SCF calculations on diatomic molecules, carried out by Roothaan, Cade, and Wahl,[55] indicate that atomic SCF orbitals are a good starting point for the construction of molecular wavefunctions. The exact nature of the behavior of the molecular wavefunction at large distances from the molecular core will be settled only by advances in the theory of molecular structure. Because approximate wavefunctions have been used in the present analysis, we do not claim that the numerical results reported are accurate to better than a multiplicative factor of 2 or 3. However, we do believe that the present work is useful in providing a reliable order-of-magnitude description of the triplet band structure. It is worthwhile again to point out that in the lowest excited states of crystals of aromatic molecules intermolecular overlap is quite small, whereupon the Heitler–London scheme is useful as a starting point and the distortion of the molecular wavefunctions in the crystal is correctly accounted for by orthogonalization.

It is useful to summarize the importance of the various contributions to the energies of the triplet exciton states in crystals or aromatic molecules:

(a) Excitation exchange effects without electron exchange are negligible, since the influence of spin–orbit coupling on the excited π states of aromatic molecules is small.

(b) An important contribution to the triplet exciton bandwidth and to the Davydov splitting arises from the electron exchange interaction. In studying the triplet p states of crystalline anthracene, naphthalene, and biphenyl only the contribution of two center exchange integrals have been included. Three and four center integrals may change the values of the intermolecular exchange integrals by 25%.

(c) The contribution of electron exchange integrals to the Davydov splitting of the α bands of crystalline naphthalene and benzene (i.e., the B_{3u}^- state of naphthalene and the B_{2u} state of benzene) is expected to be extremely small. From the analysis presented herein, it is seen that the two center integrals and some of the three center integrals vanish. This result is a consequence of the pairing property of Hückel and SCF π-electron wavefunctions, but is not very interesting as far as triplet states are concerned. The $^3B_{3u}^-$ state of crystalline naphthalene and the $^3B_{2u}$ state of crystalline benzene cannot be studied experimentally. It is important to note that electron-exchange interactions will be negligible in the corresponding singlet states.

(d) Nonorthogonality corrections, considered within

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[53] R. Silbey, J. Jortner, and S. A. Rice, "Comments on the Singlet Exciton States of Crystalline Anthracene," J. Chem. Phys. (to be published).

[54] L. Lindquist, Arkiv Kemi **16**, 79 (1961).

[55] C. C. J. Roothaan, P. C. Cade, and C. Wahl (article to be published and private communication).

the framework of the Löwdin orthogonalization procedure, have been expressed in terms of intramolecular hybrid and exchange integrals. The contribution of these terms is found to be small. Terms of the order of S^2 were studied qualitatively by Sternlicht, Nieman, and Robinson[15] and were found to be negligible. It should be pointed out that a study[56] of the interaction between He $^3S(1a2a)$ and ground-state helium ^1S atoms indicates that, for distances larger than 4 a.u., the interatomic interactions arise from electron exchange and nonorthogonality corrections are small.

(e) Crystal-field mixing of triplet states has no effect on the triplet bands.

(f) An important contribution to the triplet exciton bandwidth may arise from charge-transfer exciton states, involving the configuration with an electron and a hole located on adjacent molecules. A detailed study[50] of the contribution of charge-transfer states indicates that the Davydov splitting of the first triplet state is increased by 50% in some crystals. This conclusion is in agreement with the proposal of Sternlicht and McConnell[23] regarding the contribution of charge-transfer states to the triplet exciton bandwidth. The relative contributions of intermolecular electron exchange and charge-transfer interactions are not expected to be very sensitive to the wavefunctions used in the calculations.

Direct experimental test of the theoretical predictions of the factor-group splittings of the triplet states in the simple crystals studied in this paper will be extremely difficult since absorption measurements cannot be carried out. However, direct population of the triplet state using a tunable laser may someday be practical. A study of the reaction spectrum of the blue emission induced by a tunable polarized laser might lead to an experimental determination of the factor group splitting of the first triplet state in anthracene and naphthalene. Alternatively, the intramolecular interaction in a triplet state of a molecular crystal may be obtained from phosphorescence measurements on isotopically labeled crystals as proposed by Nieman and Robinson.[15] In the case of the benzene crystal, such studies lead to an intermolecular interaction electronic matrix element of the order of 50 cm^{-1}, while theoretical calculations of the electron exchange matrix elements (without charge transfer) lead to a value of the order of 5 to 10 cm^{-1}.[57] Charge-transfer interactions may be of considerable importance in this system.

Finally, we now examine the temperature dependence of the triplet exciton diffusion coefficient and the exciton–exciton collision rate as predicted by the strong scattering model. The thermal expansion of the anthracene crystal is of the order of magnitude of a few percent over the range 77° to 300°K. The electron-exchange interactions increase on cooling, leading to an increased bandwidth, whereupon D and $\mathbf{V}(\mathbf{k})$ are also expected to be larger at low temperatures than at high temperatures. From our estimates, we expect the diffusion coefficient to increase by about 20% to 50% on cooling the crystal from 300° to 77°K. Within the framework of the band model the same qualitative trend is to be expected. However, in addition to the effect of the thermal expansion, the relaxation time will be temperature dependent (due to the temperature dependence of the phonon population). Hence, $\partial D/\partial T$ is expected to be larger for the band model than for the strong scattering model.[58] It is important to note that both models predict an increase of the triplet exciton migration and biexciton annihilation as the temperature is lowered.

Studies of the temperature dependence of the triplet–triplet annihilation in crystals of aromatic molecules can provide an important test of the applicability of the theory presented herein. Our model is applicable to pure crystals, where only a relatively small temperature dependence of the triplet–triplet annihilation rate is expected. In crystals containing impurities, triplet–triplet annihilation may proceed by long-range trap-to-trap interaction through the virtual states of the host, as proposed by Robinson *et al.*[15] This model predicts a large temperature dependence of the rate of the triplet migration and biexciton annihilation, and in the opposite direction from that predicted by our model. Further experimental studies of the temperature dependence of the triplet–triplet annihilation, taking into account possible changes in the rate of population of the triplet state and the temperature dependence of vibrational relaxation processes (i.e., triplet exciton phonon interactions) will be of considerable importance.

The triplet–triplet annihilation rate in crystalline anthracene can be adequately interpreted as a diffusion controlled reaction. This situation differs from the case of the singlet exciton–exciton bimolecular annihilation,[59] where the encounter rate is of the order of $10^{-7}n_s^2$ $\text{cm}^{-3}\cdot\text{sec}^{-1}$ (i.e., five orders of magnitude larger than the observed rate). The singlet–singlet biexciton annihilation rate is determined by the transition probability to the final state, involving a positive ion and an electron in the conduction band.

A comparative study of triplet–triplet annihilation rates in different aromatic crystals would be of considerable interest. Our results indicate that in naphthalene and anthracene the triplet–triplet annihilation rates are comparable, while in biphenyl the electron exchange integrals are smaller than in anthracene by about one order of magnitude. Hence, the rate of triplet–triplet collision is expected to be smaller in biphenyl by about a factor of 10 to 100. Recent experiments by Hutchison and Hirota[12] show that the rate constant for annihilation of a triplet impurity state and a triplet exciton in the biphenyl crystal is $\sim 3\times10^{-12}$ cm^{-3} sec^{-1}, which is about one order of magnitude

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[56] R. A. Brickingham and A. Dalgarno, Proc. Roy. Soc. (London) **A213**, 327 (1952).

[57] R. Silbey, J. Jortner, and S. A. Rice, "On the Triplet States of Crystalline Benzene" (to be published).

[58] The reader should note that $\int f(E)F(E)dE$ is also a function of T in the strong scattering model so that this deduction must be used carefully.

[59] S. Choi and S. A. Rice, J. Chem. Phys. **38**, 366 (1963).

TABLE IX. Atomic exchange integrals.[a]

R	(P+P-/P-P+)	(P+P+/P+P+)	(PZP+/PZP-)	(PZP+/P+PZ)	(PZPZ/P+P+)	(PZPZ/PZPZ)
6.0	0.1952742E-04	0.2007937E-03	0.2643580E-03	0.1732290E-03	0.9886485E-03	0.4883789E-02
6.4	0.9872253E-05	0.1022642E-03	0.1437886E-03	0.9476338E-04	0.5452546E-03	0.2924110E-02
6.6	0.7008263E-05	0.7285636E-04	0.1056794E-03	0.6983308E-04	0.4032914E-03	0.2248450E-02
6.8	0.4970206E-05	0.5185067E-04	0.7750517E-04	0.5134626E-04	0.2975570E-03	0.1722342E-02
7.0	0.3521377E-05	0.3686407E-04	0.5672772E-04	0.3767369E-04	0.2190388E-03	0.1314652E-02
7.2	0.2492751E-05	0.2618743E-04	0.4144068E-04	0.2758670E-04	0.1608853E-03	0.1000099E-02
7.4	0.1763072E-05	0.1857893E-04	0.3021810E-04	0.2016240E-04	0.1179375E-03	0.7584623E-03
7.6	0.1245878E-05	0.1317165E-04	0.2199604E-04	0.1470945E-04	0.8628525E-04	0.5734943E-03
7.8	0.8796841E-06	0.9329973E-05	0.1598462E-04	0.1071287E-04	0.6301158E-04	0.4324224E-03
8.0	0.6207816E-06	0.6608853E-05	0.1159761E-04	0.7789304E-05	0.4594596E-04	0.3251806E-03
8.3	0.3673091E-06	0.3925339E-05	0.7146854E-05	0.4815292E-05	0.2850300E-04	0.2110772E-03
8.6	0.2170401E-06	0.2329526E-05	0.4389847E-05	0.2966851E-05	0.1762415E-04	0.1362859E-03
8.9	0.1278618E-06	0.1386433E-05	0.2688178E-05	0.1822187E-05	0.1085416E-04	0.8751822E-04
9.2	0.7531847E-07	0.8161229E-06	0.1641674E-05	0.1116519E-05	0.6672953E-05	0.5599969E-04
9.5	0.4429464E-07	0.4819788E-06	0.9991144E-06	0.6812963E-06	0.4087509E-05	0.3565592E-04
9.9	0.2175409E-07	0.2380449E-06	0.5133257E-06	0.3516948E-06	0.2117000E-05	0.1940917E-04
10.3	0.1066878E-07	0.1174428E-06	0.2625996E-06	0.1806048E-06	0.1091458E-05	0.1049317E-04
10.7	0.5220059E-08	0.5769889E-07	0.1338085E-06	0.9250801E-07	0.5602152E-06	0.5636492E-05
11.1	0.2576195E-08	0.2834976E-07	0.6779034E-07	0.4708600E-07	0.2862350E-06	0.3009932E-05
11.5	0.1255621E-08	0.1387064E-07	0.3423233E-07	0.2389567E-07	0.1457617E-06	0.1597702E-05
12.5	0.2044856E-09	0.2289143E-08	0.6097445E-08	0.4323220E-08	0.2657591E-07	0.3205312E-06
13.5	0.3312713E-10	0.3567934E-09	0.1087649E-08	0.7835447E-09	0.4686174E-08	0.6266741E-07
14.5	0.5302359E-11	0.5742557E-10	0.1843553E-09	0.1331682E-09	0.8216653E-09	0.1193791E-07
15.5	0.8391294E-12	0.9133112E-11	0.3115355E-10	0.2267761E-10	0.1324223E-09	0.2201109E-08
17.5	0.2036651E-13	0.2236115E-12	0.8508349E-12	0.6282410E-12	0.3714675E-11	0.6515224E-10
19.5	0.4759682E-15	0.4860013E-14	0.2206445E-13	0.1649956E-13	0.9171548E-13	0.1840158E-11

[a] All quantities are in atomic units.

smaller than the triplet–triplet annihilation rate in crystalline anthracene. This result is consistent with our calculations.

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APPENDIX. CALCULATION OF EXCHANGE INTEGRALS

The two center exchange integrals are

$$I=\langle w_n^{\alpha} w_m^{\beta} \mid r^{-1} \mid w_n^{\alpha} w_m^{\beta} \rangle.$$

These integrals involve interactions between $2p\pi$ orbitals at orientations determined by the crystal structure. The coordinate system used in these calculations is the same as that used by Kotani *et al.* The line joining Atoms α and β defines the z axis, and we may choose the y axis to be perpendicular to one orbital. Defining

$$A=\mathbf{n}\cdot\mathbf{x}_{\alpha},\qquad B=\mathbf{n}\cdot\mathbf{y}_{\alpha}=0,\qquad C=\mathbf{n}\cdot\mathbf{z}_{\alpha},$$
$$D=\mathbf{m}\cdot\mathbf{x}_{\beta},\qquad E=\mathbf{m}\cdot\mathbf{y}_{\beta},\qquad F=\mathbf{m}\cdot\mathbf{z}_{\beta},$$

where $\mathbf{n}$ and $\mathbf{m}$ are unit vectors in the direction of the $2p\pi$ orbitals located on centers α and β, respectively, we find that the atomic exchange integrals may be expressed as

$$\begin{aligned} I={}&A^2D^2\langle p_+p_+ \mid p_-p_-\rangle+A^2(D^2-E^2)\langle p_+p_- \mid p_-p_+\rangle\\ &+[A^2F^2+C^2(D^2+E^2)]\langle p_+p_z \mid p_-p_z\rangle\\ &+2ACDF(\langle p_+p_z \mid p_zp_+\rangle+\langle p_+p_+ \mid p_zp_z\rangle)\\ &+C^2F^2\langle p_zp_z \mid p_zp_z\rangle. \qquad \text{(A1)}\end{aligned}$$

These atomic exchange integrals were calculated on an IBM 7094 computer using an integral program written by A. C. Wahl and P. E. Cade of the Laboratory of Molecular Structure and Spectra, The University of Chicago. The six basic exchange integrals are presented in Table IX.