THE JOURNAL OF CHEMICAL PHYSICS VOLUME 41, NUMBER 11 1 DECEMBER 1964

# Charge-Transfer Exciton States in Aromatic Molecular Crystals

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

(Received 6 July 1964)

In this paper we consider some of the consequences of the mixing of neutral exciton states (neutral excitation waves or Frenkel excitons) with charge-transfer exciton states (ion-pair excitons) in the oriented gas model of aromatic molecular crystals.

The lowest-energy charge-transfer exciton is described by suitable symmetry-adapted functions built on the basis functions of a near-neighbor positive and negative ion pair. It is then shown that the energy of this state is not greatly different from the $p$ states of anthracene and naphthalene, and therefore that the ion-pair exciton and Frenkel exciton states can mix. For the cases of anthracene and naphthalene, such configuration interaction leads to the following contributions to the Davydov splitting of the triplet manifold:

$$\Delta\epsilon = 26/\Delta E \text{ cm}^{-1} \text{ naphthalene,}$$

$$\Delta\epsilon = 31/\Delta E \text{ cm}^{-1} \text{ anthracene,}$$

where $\Delta E$ is the energy difference (in electron volts) between the triplet level and the near-neighbor charge-transfer level. In making the computations, it is necessary to consider carefully the effects of vibronic coupling and of configuration changes in the excited state. It is concluded that charge-transfer excitons can make an important contribution to the Davydov splitting of a triplet manifold. This conclusion is supported by preliminary estimates of the interaction matrix elements for crystalline benzene.

## I. INTRODUCTION

INTEREST in the excited electronic states of crystals of aromatic compounds has grown considerably in the last 15 years. Following the pioneering theoretical work of Davydov,[1] McClure,[2] Craig,[3] and others have accumulated considerable experimental data concerned with the polarization of transitions, energy transfer, and spectroscopic splittings in these crystals. Although many of the data are explicable in terms of the original Davydov theory or its extensions, there remain a number of observations which cannot be accommodated within that theory. We mention only one of the problems, the one which was responsible for the theoretical development contained herein. It is observed that the lowest $\pi \rightarrow \pi^*$ transitions in benzene and naphthalene give rise in the crystal to Davydov splittings of the order of 100 to 200 cm$^{-1}$.[2–5] It is impossible to explain these splittings on the basis of the very small vibronically induced free-molecule transition-dipole moments, and the octopole moment which must be attributed to the molecule to fit the splitting is one order-of-magnitude larger than that calculated from molecular wavefunctions.[4–6] Since octopole moments are ordinarily overestimated by molecular orbital calculations,[4] this is a very serious discrepancy.

Crystals of aromatic compounds are particularly attractive systems from the point of view of solid-state theory. The units of the molecular crystal are bound together by weak London dispersion forces which have only a small effect on the ground-state charge distribution of the molecule. Further, crystals of aromatic molecules are unique, in the sense that the electronic overlap between neighboring molecules is relatively small, both in the ground state and in the lower excited states (overlap integrals are of the order of magnitude of $10^{-2}$ to $10^{-3}$). Because of the small overlap, it is possible to use the Heitler–London scheme to construct zero-order crystal wavefunctions based on free-molecule wavefunctions. Previous treatments of the singlet and triplet exciton states of aromatic crystals have, therefore, used the framework of the tight-binding approximation following closely the original work of Frenkel.[7]

Frenkel's theory was extended by Slater and Shockley[8a] and by Wannier[8b] who considered the excitation waves

$$E(\boldsymbol{\kappa}, \mathbf{R}) = (A/N^{\frac{1}{2}}) \sum_m \exp(i\boldsymbol{\kappa}\cdot\mathbf{R}_m) \mid \mathbf{R}_m - \tfrac{1}{2}\mathbf{R}, \mathbf{R}_m + \tfrac{1}{2}\mathbf{R} \rangle,$$

where $\mid \mathbf{R}_m, \mathbf{R}_n \rangle$ represent a crystal state in which an electron is removed from the molecule at $\mathbf{R}_m$ and

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* National Science Foundation Cooperative Fellow.

[1] (a) A. S. Davydov, *Theory of Molecular Excitons*, translated by M. Kasha and M. Oppenheimer (McGraw-Hill Book Company, Inc., New York, 1962). (b) J. Tanaka, Progr. Theoret. Phys. (Kyoto) Suppl. **12,** 183 (1959).

[2] D. S. McClure, Solid State Phys. **8,** 1 (1962).

[3] D. P. Craig and S. H. Walmsley, in *The Physics and Chemistry of the Organic Solid State,* edited by D. Fox, M. Labes, and A. Weissberger (Interscience Publishers, Inc., New York, 1963).

[4] D. Fox and O. Schnepp, J. Chem. Phys. **23,** 767 (1955).

[5] D. P. Craig and S. H. Walmsley, Mol. Phys. **4,** 113 (1961).

[6] O. Schnepp, Ann. Rev. Phys. Chem. **14,** 35 (1963).

[7] J. Frenkel, Phys. Rev. **37,** 17 (1931).

[8] (a) J. C. Slater and W. S. Shockley, Phys. Rev. **50,** 705 (1936). (b) G. Wannier, *ibid.* **52,** 191 (1937).

placed on the molecule at $\mathbf{R}_n$.[9] Such an excitation wave may be considered to describe the coherent motion of the center of mass of the electron and the associated hole with relative-position vector $\mathbf{R}$ fixed. By expanding the wavefunction in terms of the excitation waves, $E(\boldsymbol{\kappa}, \mathbf{R})$, an effective wave equation for the relative motion of the electron and its hole was derived by Wannier.[8b] Under certain conditions, the effective wave equation becomes identical to the Schrödinger equation for the hydrogen atom. The hydrogenlike equation is correct only if the energy eigenvalue corresponding to the relative electron–hole motion is close to the ionization continuum. Wannier excitons have been observed experimentally in inorganic semiconductors[10] and in rare-gas solids.[11]

As already mentioned, because of the close relation between the vapor and crystal spectra of aromatic compounds, the Frenkel exciton states [i.e., the $E(\boldsymbol{\kappa}, \mathbf{0})$ states] have been used to describe the exciton states of such crystals. Clearly, a better approximation must include the effect of excitation waves[12] with $\mathbf{R} \neq 0$ (charge-transfer excitons, or ion-pair excitons). The mixing of ion-pair excitons with neutral exciton states has been previously considered.[13,14] However, there has been no systematic discussion of the configuration interaction between neutral and ion-pair excitons and its effect on the factor-group (Davydov) splittings in aromatic crystals.

Ion-pair exciton states may be of considerable importance when questions connected with transition probabilities to excited states or Davydov splittings are under analysis. A tight-binding approximation based on free-molecule excited states may not be completely satisfactory in all cases, and configuration interaction with ion-pair exciton states may be of considerable importance under some conditions. For example, it is likely that ion-pair exciton states will make a considerable contribution to the bandwidth of some "neutral" exciton states. The neutral exciton states expected to be most effectively mixed with the ion-pair exciton states are those characterized by a relatively small bandwidth, i.e., triplet exciton states (because intermolecular exchange interactions are weak and the bandwidths are of the order of 10 cm$^{-1}$) and singlet exciton states corresponding to very weak molecular transitions (for example, symmetry-forbidden vibronically induced transitions, such as occur in benzene; or formally allowed but mainly vibronically induced transitions in naphthalene). In the examples cited, configuration mixing of the neutral and ion-pair exciton states can determine the Davydov splitting and other features of the spectrum.

TABLE I. The irreducible representation of the space group $C_{2h}^5$ for $\mathbf{k}=0$.

| | $E$ | $C_2^b$ | $\sigma^{ac}$ | $i$ |
|---|---|---|---|---|
| $A_g$ | 1 | 1 | 1 | 1 |
| $A_u$ | 1 | 1 | $-1$ | $-1$ |
| $B_g$ | 1 | $-1$ | $-1$ | 1 |
| $B_u$ | 1 | $-1$ | 1 | $-1$ |

In the analysis presented herein we derive the crystal wavefunctions and energy levels for charge-transfer exciton states in the limit of vanishing crystal momentum, i.e., $\mathbf{k}=0$. Only these states are of importance if attention is focused on optical excitation. Our analysis will be limited to the case of monoclinic aromatic crystals with two molecules per unit cell. The configuration interaction between triplet charge-transfer states and neutral triplet states is examined within the framework of second-order perturbation theory. Having earlier had some success in accounting for the properties of molecular wavefunctions at large intermolecular separations by using a linear combination of atomic self-consistent field functions, we again adopt these functions and herein also present some numerical calculations concerned with the extent of neutral and ion-pair state mixing. Further work concerned with singlet exciton states will be the subject of a separate publication.

## II. CONSTRUCTION OF SYMMETRY-ADAPTED FUNCTIONS

The lowest-lying charge-transfer exciton states are those with an electron and a hole on adjacent molecules. Simple arguments based on the magnitude of overlap integrals suggest that, of all possible charge-transfer states, these particular states will interact most strongly with the neutral-exciton states. The procedure employed for the construction of the ion-pair exciton states is essentially that suggested by Slater and Shockley: localized, antisymmetrized charge-transfer states are constructed from the positive- and negative-ion wavefunctions. As in the case of neutral excitons, the states so defined are not eigenstates of the tight-binding Hamiltonian, and the localized functions must be transformed to construct charge-transfer exciton states which belong to the representation of the crystal-lattice space group.

Consider the class of crystals described by the symmetry $C_{2h}^5 \equiv P_{21/a}$. Such crystals have a monoclinic cell containing two molecules, one at the corner and the other in the center of the *ab* face. In this paper we examine those excited states with vanishing crystal momentum. For $\mathbf{k}=0$, the irreducible representation of the space group $C_{2h}^5$ is displayed in Table I. The ground state of the crystal belongs to $A_g$, and optical

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[9] Throughout this paper we use the convention that the wavefunction $|A, B\rangle$ represents a positive ion A and a negative ion B.

[10] R. Knox, *Theory of Excitons* (Academic Press Inc., New York, 1964).

[11] G. Baldini, Phys. Rev. **128**, 1562 (1962).

[12] In order to conform to previous usage, we use the term exciton for excitation wave.

[13] The importance of ion-pair exciton states in the understanding of the electronic states of molecular crystals has been discussed by Lyons,[14] Tanaka,[1b] and Merrifield [J. Chem. Phys. **34**, 1835 (1961)].

[14] L. E. Lyons, J. Chem. Soc. **1957**, 5001.

transitions are allowed to states characterized by $A_u$ and $B_u$. The energy difference between $A_g \rightarrow A_u$ and $A_g \rightarrow B_u$ is the Davydov splitting. Consider now one particular excited molecular state denoted by $\psi_m{}^f$, where $m$ is used to identify the molecule. Corresponding to this molecular state, there are exciton states in the crystal. In this paper we use the oriented gas model, in which description an exciton is considered to be constructed from an isolated molecular excitation which is delocalized throughout the crystal and has crystal momentum $\hbar\mathbf{k}$.

Our first step is to construct the several exciton wavefunctions belonging to $\mathbf{k}=0$. Symmetry-adapted exciton states can be obtained with the use of the Wigner projection operator[15]

$$\mathbf{W}_{ts}{}^i=(l_i/h)\sum_{\mathbf{0}} D^i(\mathbf{0})_{ts}{}^*\mathbf{0}, \qquad (1)$$

where $\mathbf{0}$ is a symmetry operation, $l_i$ is the dimension of the $i$th irreducible representation, $h$ is the order of the group, and $D^i(\mathbf{0})_{ts}$ is the $ts$ element of the matrix which represents $\mathbf{0}$ in the $i$th representation.

We take antisymmetrized products of molecular and ionic wavefunctions for the localized states from which symmetry-adapted functions are formed. Such localized states are denoted as follows:

$$|\,\mathbf{R}_m\rangle = A\psi_{m1}{}^f \prod_{l\alpha\neq m1}{}' \psi_{l\alpha}{}^0; \qquad l=1,\cdots,N_u, \qquad \alpha=1,2; \qquad (2)$$

$$|\,\mathbf{R}_m,\mathbf{R}_n\rangle = A_I\psi_{m1}{}^+\psi_{n1}{}^- \prod_{l\gamma,\,l\gamma\neq m1,\,n1}{}'' \psi_{l\gamma}{}^0. \qquad (3)$$

The superscripts 0, $f$, +, and − refer to the ground state, excited state, positive ion, and negative ion, respectively, and $A$ and $A_1$ are the antisymmetrizing operators

$$A=[(a\,!)^{2N_u}/(2N_ua)\,!]^{\frac{1}{2}}\sum_P(-1)^PP, \qquad (4)$$

$$A_1=[(a\,!)^{2N_u-2}(a+1)\,!(a-1)\,!/(2N_ua)\,!]^{\frac{1}{2}}\sum_P(-1)^PP.$$

The operator $P$ interchanges electrons only between molecules, since the molecular and ionic wavefunctions are already antisymmetrized with respect to their electron coordinates. As usual, $N_u$ is the total number of unit cells, and $a$ is the number of electrons on each neutral molecule. The second subscript on $\psi_{m\alpha}$ labels a particular molecule in the $m$th unit cell, while the $\psi_{m\alpha}{}^0$ refer to ground-state wavefunctions. We use $\mathbf{R}_m$ for the vector with components equal to the coordinates of the center of Molecule $m$.

On application of the Wigner projection operator (1) to the localized states defined in Eqs. (2) and (3), there are obtained linear combinations of all the localized states which form the basis sets of the irreducible representations. From Eq. (2) we obtain the well-known neutral-exciton functions

$$\Psi_{A_u}=\frac{1}{(2N_u)^{\frac{1}{2}}}\sum_m^{N_u}[\,|\,\mathbf{R}_m\rangle-|\,\mathbf{R}_m+\boldsymbol{\tau}\rangle], \qquad (5)$$

$$\Psi_{B_u}=\frac{1}{(2N_u)^{\frac{1}{2}}}\sum_m^{N_u}[\,|\,\mathbf{R}_m\rangle+|\,\mathbf{R}_m+\boldsymbol{\tau}\rangle], \qquad (6)$$

where $\boldsymbol{\tau}$ is the vector extending from the corner nearest to the origin to the center of the second molecule in the unit cell, i.e., $\boldsymbol{\tau}=\frac{1}{2}(\mathbf{a}+\mathbf{b})$. The functions $\Psi_{A_u}$ and $\Psi_{B_u}$ are those used earlier for the calculation of the Davydov splitting. Now, the coupling between the neutral and ion-pair excitons decreases exponentially with the distance between the centers of the positive ion and the negative ion. For this reason, we consider only those ion-pair excitons where the electron and the hole are located on adjacent molecules, corresponding to the limitation to nearest-neighbor interactions. It will be shown herein that the coupling between the neutral and ion-pair excitons is determined by overlap, hybrid, and exchange integrals, all of which fall off exponentially with increasing distance. Because of this, the approximation of considering only the mixing of near-neighbor ion-pair excitons and neutral excitons may be seen to be valid.

With the above simplification, we need consider only the following localized states:

$$\begin{aligned}
&|\,\mathbf{R}_m,\mathbf{R}_m+\mathbf{c}\rangle, && |\,\mathbf{R}_m+\mathbf{c},\mathbf{R}_m\rangle;\\
&|\,\mathbf{R}_m,\mathbf{R}_m+\tau\rangle, && |\,\mathbf{R}_m+\boldsymbol{\tau},\mathbf{R}_m\rangle;\\
&|\,\mathbf{R}_m,\mathbf{R}_m+\mathbf{b}\rangle, && |\,\mathbf{R}_m+\mathbf{b},\mathbf{R}_m\rangle;\\
&|\,\mathbf{R}_m,\mathbf{R}_m+\mathbf{a}+\mathbf{c}\rangle, && |\,\mathbf{R}_m+\mathbf{a}+\mathbf{c},\mathbf{R}_m\rangle;\\
&|\,\mathbf{R}_m,\mathbf{R}_m+\mathbf{c}+\boldsymbol{\tau}\rangle, && |\,\mathbf{R}_m+\mathbf{c}+\boldsymbol{\tau},\mathbf{R}_m\rangle. \qquad (7)
\end{aligned}$$

From these states are obtained seven independent, symmetry-adapted states for the $A_u$ and $B_u$ representations. These are

$$\begin{aligned}
|\,0,\mathbf{c};\mp\rangle=\frac{1}{(4N_u)^{\frac{1}{2}}}\sum_m^{N_u}\{|\,\mathbf{R}_m,\mathbf{R}_m+\mathbf{c}\rangle &\mp|\,\mathbf{R}_m-\mathbf{b}+\boldsymbol{\tau},\mathbf{R}_m-\mathbf{b}-\mathbf{c}+\boldsymbol{\tau}\rangle\\
&\mp|\,\mathbf{R}_m-\mathbf{a}+\boldsymbol{\tau},\mathbf{R}_m-\mathbf{a}+\mathbf{c}+\tau\rangle+|\,\mathbf{R}_m,\mathbf{R}_m-\mathbf{c}\rangle\}, \qquad (8)
\end{aligned}$$

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[15] E. Wigner, *Group Theory*, translated by J. J. Griffin (Academic Press Inc., New York, 1959).

$$|0,\mathbf{b};\mp\rangle=\frac{1}{(4N_u)^{\frac{1}{2}}}\sum_{m}^{Nu}\{|\mathbf{R}_m,\mathbf{R}_m+\mathbf{b}\rangle\mp|\mathbf{R}_m-\mathbf{b}+\boldsymbol{\tau},\mathbf{R}_m+\boldsymbol{\tau}\rangle \mp|\mathbf{R}_m-\mathbf{a}+\boldsymbol{\tau},\mathbf{R}_m-\mathbf{a}-\mathbf{b}+\boldsymbol{\tau}\rangle+|\mathbf{R}_m,\mathbf{R}_m-\mathbf{b}\rangle\}, \quad (9)$$

$$|0,\mathbf{a}+\mathbf{c};\mp\rangle=\frac{1}{(4N_u)^{\frac{1}{2}}}\sum_{m}^{Nu}\{|\mathbf{R}_m,\mathbf{R}_m+\mathbf{a}+\mathbf{c}\rangle\mp|\mathbf{R}_m-\mathbf{b}+\boldsymbol{\tau},\mathbf{R}_m-\mathbf{a}-\mathbf{b}-\mathbf{c}+\boldsymbol{\tau}\rangle \mp|\mathbf{R}_m-\mathbf{a}+\boldsymbol{\tau},\mathbf{R}_m+\mathbf{c}+\boldsymbol{\tau}\rangle+|\mathbf{R}_m,\mathbf{R}_m-\mathbf{a}-\mathbf{c}\rangle\}, \quad (10)$$

$$|0,\boldsymbol{\tau};\mp\rangle=\frac{1}{(4N_u)^{\frac{1}{2}}}\sum_{m}^{Nu}\{|\mathbf{R}_m,\mathbf{R}_m+\boldsymbol{\tau}\rangle\mp|\mathbf{R}_m-\mathbf{b}+\boldsymbol{\tau};\mathbf{R}_m\rangle\mp|\mathbf{R}_m-\mathbf{a}+\boldsymbol{\tau},\mathbf{R}_m\rangle+|\mathbf{R}_m,\mathbf{R}_m-\mathbf{a}-\mathbf{b}+\boldsymbol{\tau}\rangle\}, \quad (11)$$

$$|0,\mathbf{c}+\boldsymbol{\tau};\mp\rangle=\frac{1}{(4N_u)^{\frac{1}{2}}}\sum_{m}^{Nu}\{|\mathbf{R}_m,\mathbf{R}_m+\mathbf{c}+\boldsymbol{\tau}\rangle\mp|\mathbf{R}_m-\mathbf{b}+\boldsymbol{\tau},\mathbf{R}_m-\mathbf{c}\rangle \mp|\mathbf{R}_m-\mathbf{a}+\boldsymbol{\tau},\mathbf{R}_m+\mathbf{c}\rangle+|\mathbf{R}_m,\mathbf{R}_m-\mathbf{c}-\boldsymbol{\tau}\rangle\}, \quad (12)$$

$$|\boldsymbol{\tau},0;\mp\rangle=\frac{1}{(4N_c)^{\frac{1}{2}}}\sum_{m}^{Nu}\{|\mathbf{R}_m+\boldsymbol{\tau},\mathbf{R}_m\rangle\mp|\mathbf{R}_m,\mathbf{R}_m-\mathbf{b}+\boldsymbol{\tau}\rangle\mp|\mathbf{R}_m,\mathbf{R}_m-\mathbf{a}+\boldsymbol{\tau}\rangle+|\mathbf{R}_m-\mathbf{a}-\mathbf{b}+\boldsymbol{\tau},\mathbf{R}_m\rangle\}, \quad (13)$$

$$|\mathbf{c}+\boldsymbol{\tau},0;\mp\rangle=\frac{1}{(4N_u)^{\frac{1}{2}}}\sum_{m}^{Nu}\{|\mathbf{R}_m+\mathbf{c}+\boldsymbol{\tau},\mathbf{R}_m\rangle\mp|\mathbf{R}_m-\mathbf{c},\mathbf{R}_m-\mathbf{b}+\boldsymbol{\tau}\rangle \mp|\mathbf{R}_m+\mathbf{c},\mathbf{R}_m-\mathbf{a}+\boldsymbol{\tau}\rangle+|\mathbf{R}_m-\mathbf{c}-\boldsymbol{\tau},\mathbf{R}_m\rangle\}. \quad (14)$$

The negative and positive signs on the right-hand side of Eqs. (8) through (14) refer to the $A_u$ and $B_u$ states, respectively. In the above functions we have neglected the overlap integral in the normalization factors.

## III. CONFIGURATION-INTERACTION SCHEME

We consider now the configuration interaction between the neutral and charge-transfer states (in the oriented gas scheme), and its effect on the Davydov splitting. As long as the mixing matrix elements are small compared with the separation between the two exciton states, the application of perturbation theory is legitimate. Now, our basis functions are not orthogonal functions, but rather than employ an orthogonalization procedure (i.e., the Schmidt or the symmetric orthogonalization method) we prefer to apply second-order perturbation theory for a nonorthogonal set of unperturbed basis functions. Our calculations show that the effects of the nonorthogonality corrections are relatively small. A further error is introduced into the second-order perturbation term by the use of only a limited number of ion-pair exciton wavefunctions. However, this error is negligibly small. The energy, to the second order, is given by

$$E\langle\mathbf{0},\mathbf{0};\mp|\mathbf{1}|\mathbf{0},\mathbf{0};\mp\rangle=\langle\mathbf{0},\mathbf{0};\mp|H|\mathbf{0},\mathbf{0};\mp\rangle +\sum_{i,j}\frac{|\langle\mathbf{0},\mathbf{0};\mp|H|\mathbf{R}_i,\mathbf{R}_j;\mp\rangle-\langle\mathbf{0},\mathbf{0};\mp|H|\mathbf{0},\mathbf{0};\mp\rangle\langle\mathbf{0},\mathbf{0};\mp|\mathbf{1}|R_i,R_j;\mp\rangle|^2}{\langle\mathbf{0},\mathbf{0},\mp|H|\mathbf{0},\mathbf{0};\mp\rangle\langle R_i,R_j\mp|\mathbf{1}|R_i,R_j;\mp\rangle-\langle R_i,R_j\mp|H|R_i,R_j;\mp\rangle}, \quad (15)$$

where $H$ is the Hamiltonian for the system, $\mathbf{1}$ is the unit operator, and $|\mathbf{0},\mathbf{0};\mp\rangle$ denotes the neutral exciton state, Eqs. (5) and (6). The summation over the charge-transfer states $|\mathbf{R}_i,\mathbf{R}_j;\mp\rangle$ implies, in our approximation, a sum over the states listed in Eqs. (8) through (14). The problem reduces now to the computation of the appropriate matrix elements.

## IV. DAVYDOV SPLITTING

We now proceed to evaluate the contribution of the ion-pair exciton states to the Davydov splitting. The matrix elements connecting the various exciton states can be represented in terms of matrix elements between localized charge transfer and neutral excited states. Thus, the nondiagonal matrix element between the states 5, 6, and 8 is given by

$$\begin{aligned}\langle\mathbf{0},\mathbf{0};\mp|H|\mathbf{0},\boldsymbol{\tau};\mp\rangle &=(1/2\sqrt{2}N_u)\sum_{m,n}[\langle\mathbf{R}_n|H|\mathbf{R}_m,\mathbf{R}_m+\boldsymbol{\tau}\rangle\\ &+\langle\mathbf{R}_n|H|\mathbf{R}_m,\mathbf{R}_m-\boldsymbol{\tau}\rangle\\ &+\langle\mathbf{R}_n+\boldsymbol{\tau}|H|\mathbf{R}_m-\mathbf{b}+\boldsymbol{\tau},\mathbf{R}_m\rangle\\ &+\langle\mathbf{R}_n+\boldsymbol{\tau}|H|\mathbf{R}_m-\mathbf{a}+\boldsymbol{\tau},\mathbf{R}_m\rangle\\ &\mp\langle\mathbf{R}_n|H|\mathbf{R}_m-\mathbf{b}+\boldsymbol{\tau},\mathbf{R}_m\rangle\\ &\mp\langle\mathbf{R}_n|H|\mathbf{R}_m-\mathbf{a}+\boldsymbol{\tau},\mathbf{R}_m\rangle\\ &\mp\langle\mathbf{R}_n+\boldsymbol{\tau}|H|\mathbf{R}_m,\mathbf{R}_m+\boldsymbol{\tau}\rangle\\ &\mp\langle\mathbf{R}_n+\boldsymbol{\tau}|H|\mathbf{R}_m,\mathbf{R}_m-\boldsymbol{\tau}\rangle]. \quad (16)\end{aligned}$$

From symmetry considerations,

$$\langle \mathbf{0},\mathbf{0};\mp \mid H \mid \mathbf{0},\boldsymbol{\tau};\pm\rangle=0.$$

Similar expressions can be readily derived for the other matrix elements.

The largest contribution to these matrix elements arises from terms of the form $\langle \mathbf{R}_p \mid H \mid \mathbf{R}_q\mathbf{R}_s\rangle$ when $p=q$ or $p=s$. Terms which do not satisfy one of these conditions yield three-center integrals with the centers located on different molecules. These are small terms, and they are neglected herein. The same consideration applies, of course, to the calculation of the overlap integrals. We therefore consider only those matrix elements where the molecular excitation and the negative (or positive) ion are located on the same molecule.

The diagonal matrix element can readily be written in the simple form

$$\langle \mathbf{0},\mathbf{0};\mp \mid H \mid \mathbf{0},\mathbf{0};\mp\rangle=\langle \mathbf{R}_m \mid H \mid \mathbf{R}_m\rangle + \sum_{n\neq m}\langle \mathbf{R}_m \mid H \mid \mathbf{R}_n\rangle \mp \sum_{n}\langle \mathbf{R}_m \mid H \mid \mathbf{R}_n+\boldsymbol{\tau}\rangle. \tag{17}$$

The leading term on the right-hand side of Eq. (17) is the self-energy of the excited molecule; for the purpose of estimating the nonorthogonality corrections we may therefore set

$$\langle \mathbf{0} \mid H \mid \mathbf{0}\rangle\equiv\langle \mathbf{0},\mathbf{0};\mp \mid H \mid \mathbf{0},\mathbf{0}\mp\rangle\approx\langle \mathbf{R}_m \mid H \mid \mathbf{R}_m\rangle. \tag{18}$$

With these rules, it is apparent that only the following four ion-pair exciton wavefunctions $\mid \mathbf{0},\boldsymbol{\tau};\mp\rangle$, $\mid \boldsymbol{\tau},\mathbf{0};\mp\rangle$, $\mid \mathbf{0},\mathbf{c}+\boldsymbol{\tau};\mp\rangle$, and $\mid \mathbf{c}+\boldsymbol{\tau},0;\mp\rangle$ have different mixing coefficients for the states of $A_u$ and $B_u$ symmetry, and only these four states will contribute to the Davydov splittings. We consider, then, the terms

$$\begin{aligned}
K_1^{\mp}&=\langle \mathbf{0},\mathbf{0};\mp \mid H \mid \mathbf{0},\boldsymbol{\tau};\mp\rangle-\langle \mathbf{0} \mid H \mid \mathbf{0}\rangle\langle \mathbf{0},\mathbf{0};\mp \mid \mathbf{1} \mid \mathbf{0},\boldsymbol{\tau}:\mp\rangle,\\
K_2^{\mp}&=\langle \mathbf{0},\mathbf{0};\mp \mid H \mid \boldsymbol{\tau},\mathbf{0};\mp\rangle-\langle \mathbf{0} \mid H \mid \mathbf{0}\rangle\langle \mathbf{0},\mathbf{0};\mp \mid \mathbf{1} \mid \boldsymbol{\tau},\mathbf{0};\mp\rangle,\\
K_3^{\mp}&=\langle \mathbf{0},\mathbf{0};\mp \mid H \mid \mathbf{0},\mathbf{c}+\boldsymbol{\tau};\mp\rangle-\langle \mathbf{0} \mid H \mid \mathbf{0}\rangle\langle \mathbf{0},\mathbf{0};\mp \mid \mathbf{1} \mid \mathbf{0},\mathbf{c}+\boldsymbol{\tau};\mp\rangle,\\
K_4^{\mp}&=\langle \mathbf{0},\mathbf{0};\mp \mid H \mid \mathbf{c}+\boldsymbol{\tau},0;\mp\rangle-\langle \mathbf{0} \mid H \mid \mathbf{0}\rangle\langle \mathbf{0},\mathbf{0};\mp \mid \mathbf{1} \mid \mathbf{c}+\boldsymbol{\tau};\mp\rangle.
\end{aligned} \tag{19}$$

Off-diagonal matrix elements between a localized excitation and a charge-transfer state may be represented in the form

$$\begin{aligned}
B(i,j)&=\langle \mathbf{R}_i \mid H \mid \mathbf{R}_i,\mathbf{R}_j\rangle-\langle \mathbf{R}_i \mid \mathbf{R}_i,\mathbf{R}_j\rangle\langle \mathbf{R}_i \mid H \mid \mathbf{R}_i\rangle,\\
C(i,j)&=\langle \mathbf{R}_i \mid H \mid \mathbf{R}_j,\mathbf{R}_i\rangle-\langle \mathbf{R}_i \mid \mathbf{R}_j,\mathbf{R}_i\rangle\langle \mathbf{R}_i \mid H \mid \mathbf{R}_i\rangle,
\end{aligned} \tag{20}$$

whereupon the matrix elements (19) become

$$\begin{aligned}
K_1^{\mp}&=\sqrt{2}\{[B(\mathbf{0},\boldsymbol{\tau})+B(\boldsymbol{\tau},\mathbf{0})]\mp[C(\mathbf{0},\boldsymbol{\tau})+C(\boldsymbol{\tau},\mathbf{0})]\}/2,\\
K_2^{\mp}&=\sqrt{2}\{[C(\mathbf{0},\boldsymbol{\tau})+C(\boldsymbol{\tau},\mathbf{0})]\mp[B(\mathbf{0},\boldsymbol{\tau})+B(\boldsymbol{\tau},\mathbf{0})]\}/2,\\
K_3^{\mp}&=\sqrt{2}\{[B(\mathbf{0},\mathbf{c}+\boldsymbol{\tau})+B(\mathbf{c}+\boldsymbol{\tau},\mathbf{0})]\mp[C(\mathbf{0},\boldsymbol{\tau}+\mathbf{c})+C(\boldsymbol{\tau}+\mathbf{c},\mathbf{0})]\}/2,\\
K_4^{\mp}&=\sqrt{2}\{[C(\mathbf{0},\mathbf{c}+\boldsymbol{\tau})+C(\mathbf{c}+\boldsymbol{\tau},\mathbf{0})]\mp[B(\mathbf{0},\mathbf{c}+\boldsymbol{\tau})+B(\mathbf{c}+\boldsymbol{\tau},\mathbf{0})]\}/2.
\end{aligned} \tag{21}$$

By definition, the Davydov splitting is

$$\Delta\epsilon=E(B_u)-E(A_u), \tag{22}$$

and the contribution of the ion-pair exciton states to this splitting is readily obtained from Eq. (15):

$$\Delta\epsilon=\sum_{i=1}^{4}\frac{[(K_i^{+})^2-(K_i^{-})^2]}{\Delta E}$$

$$=\frac{16[\bar{C}(\mathbf{0},\boldsymbol{\tau})\bar{B}(\mathbf{0},\boldsymbol{\tau})+\bar{C}(\mathbf{0},\mathbf{c}+\boldsymbol{\tau})\bar{B}(\mathbf{0},\mathbf{c}+\boldsymbol{\tau})]}{\Delta E},$$

$$\bar{C}(\mathbf{0},\boldsymbol{\tau})=\tfrac{1}{2}[C(\mathbf{0},\boldsymbol{\tau})+C(\boldsymbol{\tau},\mathbf{0})]. \tag{22a}$$

In Eq. (22a), $\Delta E$ is the energy difference between the charge-transfer and the neutral exciton states.

## V. VIBRONIC COUPLING PROBLEM

In the study of the electronic exciton spectra of molecular crystals, it is convenient to consider two limiting cases of behavior: these are the strong and the weak coupling limits. In the strong coupling limit, the electronic exciton-transfer matrix elements are larger than the width of the vibronic band envelope of an isolated molecule, and the pattern of vibronic levels is determined only by the electronic interactions. In the weak coupling limit the electronic coupling is small, and the Davydov splitting has to be considered separately for each vibronic band.

The configuration-interaction scheme presented in Secs. III and IV considered the total electronic interaction. We have, however, to consider the common case of electronic bands where the intensity is spread over several vibronic components. We are interested in the configuration interaction between charge-transfer excitons and some triplet and singlet neutral exciton states, both characterized by relatively small intermolecular electronic-coupling matrix elements. Under these circumstances, the application of the weak coupling scheme is legitimate, and in the following we consider configuration interaction between the individual vibronic components of the charge-transfer and the neutral exciton states.

In the weak coupling limit, the wavefunctions for the neutral excited molecule and for the positive and negative ions are represented as a product of electronic and vibrational wavefunctions. The localized excitation and charge-transfer states are taken to be the vibronic components

$$|\mathbf{R}_m\rangle\chi_{m1}{}^{fp}\prod_{l\alpha\neq m1}{}'\chi_{l\alpha}{}^{0q} \tag{23}$$

and

$$|\mathbf{R}_m,\mathbf{R}_n\rangle\chi_{m1}{}^{+k}\chi_{n2}{}^{-l}\prod_{l\gamma\neq m\alpha,n\beta}{}''\chi_{l\gamma}{}^{0q}. \tag{24}$$

The indices $p$, $q$, $k$, and $l$ refer to the quantum states of the molecular vibrations. We consider the system to be at a relatively low temperature so that the ground-state molecules are in the zeroth vibrational state, and $q=0$ for all $l\alpha$ and $l\gamma$. The electronic integrals (21) are now replaced by integrals over both the vibrational and the electronic coordinates. The off-diagonal matrix elements $B$ and $C$ [Eq. (20)] take the form

$$\begin{aligned}C(i,j)V^{plk}=[&\langle\mathbf{R}_i|H|\mathbf{R}_j,\mathbf{R}_i\rangle\\&-\langle\mathbf{R}_i|\mathbf{1}|\mathbf{R}_j,\mathbf{R}_i\rangle\langle\mathbf{R}_i|H|\mathbf{R}_i\rangle]\\&\times\langle\chi_i{}^{fp}|\chi_i{}^{-l}\rangle\langle\chi_l{}^{00}|\chi_j{}^{+k}\rangle,\end{aligned} \tag{25}$$

$$\begin{aligned}B(i,j)V^{pkl}=[&\langle\mathbf{R}_i|H|\mathbf{R}_i,\mathbf{R}_j\rangle\\&-\langle\mathbf{R}_i|\mathbf{1}|\mathbf{R}_i,\mathbf{R}_j\rangle\langle\mathbf{R}_i|H|\mathbf{R}_i\rangle]\\&\times\langle\chi_i{}^{fp}|\chi_i{}^{+k}\rangle\langle\chi_j{}^{00}|\chi_j{}^{-l}\rangle,\end{aligned} \tag{26}$$

where the coefficients $V^{pkl}$ and $V^{plk}$ are the vibrational overlap factors. It is necessary to examine the effect of the $k$ and $l$ positive and negative ion vibronic states on the $fp$ neutral exciton vibronic state. For the sake of simplicity, we consider only one progression in the $fp$ neutral exciton state, the totally symmetric vibrational mode. Furthermore, only the totally symmetric progressions will be considered in the vibronic states $k$, $l$ of the ions. This is a serious approximation. However, the vibrational overlap integrals $V^{pkl}$ and $V^{plk}$ cannot be obtained from experimental spectroscopic data, and our approximate treatment should lead to a reasonable estimate of the vibronic coupling.

The contribution to the Davydov splitting of a given vibronic band of a neutral exciton by configuration interaction will be

$$\Delta\epsilon^{00\rightarrow fp}=\sum_k\sum_l\frac{16\{\bar{B}(\mathbf{0},\boldsymbol{\tau})\bar{C}(\mathbf{0},\boldsymbol{\tau})+\bar{B}(\mathbf{0},\mathbf{c}+\boldsymbol{\tau})\bar{C}(\mathbf{0},\mathbf{c}+\boldsymbol{\tau})\}V_C{}^{plk}V_B{}^{pkl}}{E(fi)-E(+k,-l)}, \tag{27}$$

where $E(fi)$ is the energy of the neutral exciton vibronic state, while $E(+k,-l)$ is the energy of the vibronic charge-transfer state with the positive and negative ions in the vibrational states $k$ and $l$.

If the energy denominator is large enough not to be strongly dependent on the vibronic charge-transfer state, it may be replaced by a mean-energy difference $\Delta E$, so that

$$\Delta\epsilon^{00\rightarrow fp}=\Delta\epsilon\sum_{k,l}V^{plk}V^{pkl}; \tag{28}$$

whereupon the total electronic contribution $\Delta\epsilon$ given by Eq. (22a) is just modified by multiplying by the vibrational overlap integrals.

The summation appearing in Eq. (28), taken over all the vibronic charge-transfer states, can be considerably simplified by writing

$$\begin{aligned}\sum_{k,l}V^{pkl}V^{plk}=&\sum_k\langle\chi_i{}^{fp}|\chi_i{}^{+k}\rangle\langle\chi_j{}^{00}|\chi_j{}^{+k}\rangle\\&\times\sum_l\langle\chi_i{}^{fp}|\chi_i{}^{-l}\rangle\langle\chi_j{}^{00}|\chi_j{}^{-l}\rangle.\end{aligned} \tag{29}$$

The intramolecular vibrational overlap integrals are, of course, independent of the labeling of the particular molecule, so that the subscripts $i$ and $j$ can be omitted. Hence the sums in Eq. (29) reduce to

$$\sum_k\langle\chi^{fp}|\chi^{+k}\rangle\langle\chi^{+k}|\chi^{00}\rangle=\langle\chi^{fp}|\chi^{00}\rangle, \tag{30}$$

so that

$$\sum_{k,l}V^{pkl}V^{plk}=\langle\chi^{00}|\chi^{fp}\rangle^2, \tag{31}$$

and the contribution of the charge-transfer states to the Davydov splitting in any vibronic band is just given by

$$\Delta\epsilon^{00\rightarrow fp}=\Delta\epsilon\langle\chi^{00}|\chi^{fp}\rangle^2. \tag{32}$$

We have therefore demonstrated that, when the separation between the charge-transfer and the neutral exciton states is large compared to the vibronic spread of the individual electronic states, the total configuration-interaction matrix element is multiplied by a vibrational overlap factor specifying the transition probability of the isolated molecule to the particular excited vibronic state. This is the same result as obtained for the weak coupling case for neutral exciton states.

The vibrational overlap integrals were estimated using a treatment due to Ross and McCoy,[16,17] who were able to account for the intensity distribution in the excited singlet and triplet states of aromatic molecules with good accuracy. The application of the Ross–McCoy procedure to the computation of the vibrational overlap between states of the neutral molecule and the corresponding ions is based on the following assumptions:

(1) Only a single normal coordinate need be used to account for the change of the molecular shape in an excited or in an ionized state.

(2) The force constants and vibrational frequencies of the molecule are the same in the ground, excited, and ionized states. This approximation is reasonable for the neutral-molecule states. Analysis of the Rydberg states of benzene[18] (which should show vibrational progressions similar to those of the positive ion) indicates that the changes in the vibrational frequencies are small compared to the frequencies of the neutral molecule.

(3) The molecular vibrations are harmonic.

(4) The change in molecular shape is characterized by a single length $Z$ (representing a normal displacement), and the shift of the origin of the configuration coordinate is expressible in terms of the bond-length changes $\Delta R_{ij}$:

$$Z=(\sum_{i<j}\Delta R_{ij}^2)^{\frac{1}{2}}. \tag{33}$$

The bond-length changes may be related to the changes of the bond orders $B_{ij}$ by Coulson's formula,[16]

$$0.20\Delta B_{ij}=\Delta R_{ij}(\text{Å}). \tag{34}$$

The general expression for the vibrational overlap in the harmonic oscillator approximation was derived by Hutchisson.[17] In our simplified treatment, the frequency difference between the two states is neglected, so that the vibrational overlap between the electronic states $\omega$ and $\epsilon$ characterized by the vibrational quantum numbers $n'$ and $n''$, the force constant $k$, and the frequency $\nu$ is given by

$$\langle\chi^{\omega n'}\mid\chi^{\epsilon n''}\rangle=(n'!n''!)^{\frac{1}{2}}\exp(-\delta_{\omega\epsilon}{}^2/4)$$
$$\times\sum_{l=0}\frac{(-1)^{n'-l}(\delta_{\omega\epsilon}/\sqrt{2})^{n'+n''-2l}}{l!(n'-l)!(n''-l)!}, \tag{35}$$

where the limit for the sum is the smaller of $n'$ and $n''$. The difference between the minimum position of the potential-energy curve of State $\epsilon$, relative to $\omega$, is $Z$. The parameter $\delta_{\omega\epsilon}$ is related to $Z$ by

$$\delta_{\omega\epsilon}=(k/h\nu)^{\frac{1}{2}}Z=\sqrt{2}\times158.9(k''/\nu'')^{\frac{1}{2}}Z, \tag{36}$$

where $k$ is given in dynes per angstrom unit, $\nu$ in reciprocal centimeters, and $Z$ in angstrom units.

The general expressions for the vibrational overlap become very simple for $n'=0$. We require these integrals for the computation of $\langle\chi^{00}\mid\chi^{+k}\rangle$ and $\langle\chi^{00}\mid\chi^{-l}\rangle$ and also for the study of the effect of the ion-pair states on the origin (the 0–0 transition) of the exciton absorption band. For our simple case, Eq. (28) reduces to

$$\langle\chi^{\omega0}\mid\chi^{\epsilon n}\rangle=[1/(n!)^{\frac{1}{2}}](\delta_{\omega\epsilon}/\sqrt{2})^n\exp-(\delta_{\omega\epsilon}{}^2/4). \tag{35a}$$

The reader should note that these integrals obey the vibrational sum rule

$$\sum_n\langle\chi^{\omega0}\mid\chi^{\epsilon n}\rangle^2=1.$$

A difficulty arising in the determination of the vibrational overlap factors in the present case involves the absolute sign of $Z$. This problem was not encountered in the previous computations of the vibronic band intensities. We have used the convention that the sign of $Z$ is the same as that corresponding to $\sum_{i<j}\Delta B_{ij}$, hence $Z$ (negative triplet) $=Z$ (positive triplet) $=$ 0.082 Å, $Z$ (negative ground) $=Z$ (positive ground) $=$ $-0.060$ Å, and $Z$ (triplet ground) $=0.131$ Å.

The results for the vibrational overlap integrals for anthracene are displayed in Table II. The vibrational

TABLE II. Vibrational overlap data for anthracene.

(a) Bond orders calculated from the Hoyland and Goodman SCF wavefunctions.[a]

| Bond[b] | Ground state | Positive ion | Negative ion | Triplet |
|---|---|---|---|---|
| 1–2 | 0.8125 | 0.7228 | 0.7224 | 0.6837 |
| 2–3 | 0.4937 | 0.5730 | 0.5726 | 0.6267 |
| 1–11 | 0.4533 | 0.5243 | 0.5244 | 0.6035 |
| 9–11 | 0.6298 | 0.5617 | 0.5615 | 0.3861 |
| 11–12 | 0.5190 | 0.5128 | 0.5135 | 0.5804 |

(b) $Z$ values for anthracene.

| | Calc. (Å) | Obs. (Å) |
|---|---|---|
| Positive triplet | 0.082 | |
| Negative triplet | 0.082 | |
| Positive neutral | 0.060 | |
| Negative neutral | 0.061 | |
| Triplet ground | 0.131 | 0.12[c] |

(c) Vibrational overlap integrals for anthracene.

| $k$ | $\langle\chi_i{}^{f0}\mid\chi^{+k}\rangle$[d] | $\langle\chi_i{}^{00}\mid\chi_i{}^{+k}\rangle$[e] |
|---|---|---|
| 0 | 0.6346 | 0.7775 |
| 1 | 0.6052 | −0.5516 |
| 2 | 0.4082 | 0.2767 |
| 3 | 0.2247 | −0.1133 |
| 4 | 0.1072 | 0.0402 |
| 5 | 0.0457 | −0.0127 |

[a] J. R. Hoyland, Thesis No. 61–6790, University Microfilms, Ann Arbor, Michigan (1961).

[b] The notation is that given in *The Dictionary of Values of Molecular Constants*, edited by C. A. Coulson and R. Daudel. (The Mathematical Institute, Oxford, England, 1952).

[c] Derived in Ref. 16 from the phosphorescence spectrum of anthracene.

[d] $\chi^{f0}$ represents the zeroth vibrational state of the triplet state.

[e] $\chi^{00}$ represents the zeroth vibrational state of the ground state.

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

[17] E. Hutchisson, Phys. Rev. **36**, 410 (1930).

[18] P. G. Wilkinson, Can. J. Phys. **34**, 596 (1956).

overlap contribution to the 0−0 $^1A_{1g}\to{}^3B_{2u}$ transition due to configuration interaction with charge-transfer states, assuming a constant energy denominator, is calculated to be $\sum_{k,l}V^{ikl}V^{lik}=0.25$, which is in reasonable agreement with the analysis of the experimental spectroscopic data for this transition in the isolated molecule.[16] The present discussion has just demonstrated that vibronic overlap factors can be estimated without referring to experimental data. This treatment will be much more important in the case when the separation between neutral and charge-transfer excitons is small and the assumption of a constant energy denominator is not applicable.

## VI. LOCATION OF THE CHARGE-TRANSFER STATES

In order to proceed with the configuration-interaction scheme outlined in the previous sections, the position of the charge-transfer exciton band must be determined. To date, charge-transfer states in aromatic crystals have not been observed. However, the experimental spectroscopic data for the naphthalene crystal $^1B_{2u}(p)$ state show some peculiarities which are not understood. Only a wide absorption band is observed in the $a$ and $b$ directions of polarization, and most of the vibrational structure seems to be washed out. The unusual shape of this exciton absorption band may be due[19] to overlapping between the charge-transfer exciton state and the neutral exciton state. It should be noted that the intensity of the optical transition to the charge-transfer exciton state should be very low,[20,21] and overlap between charge-transfer and neutral exciton absorption bands will make impossible the observation of the former states. The approximate location of the charge-transfer exciton state relative to the ground state of the crystal can be estimated from the simple expression

$$E(CT)=I+EA+G+P, \qquad (37)$$

where $I$ and $EA$ are the ionization potential and the electron affinity of the free molecule, $G$ is the Coulomb interaction between the positive and negative ion, and $P$ represents the polarization energy of the lattice due to the ion pair.

The ionization potentials of aromatic molecules are well known, but the electron affinities are not known. It has recently been demonstrated, by Hoyland and Goodman [see Table II(a)], that previous calculations of the electron affinities are seriously in error. The direction of the error in the earlier calculations is such as to overestimate the electron affinity. The treatment of Hoyland and Goodman takes into account the effects on the molecular framework of $\pi$-electron capture and the changes of the $\pi$ basis functions upon electron capture. The electron affinities were calculated in the $\pi$-electron SCF scheme, including orbital deformation effects. These electron affinities are used in the present discussion.

TABLE III. The location of charge-transfer states in some aromatic crystals (all energies in electron volts).

| | Naphthalene | Anthracene |
|---|---|---|
| $I$ | 8.3 | 7.4 |
| $EA$ | −0.2 | −0.5 |
| $G(\mathbf{0},\boldsymbol{\tau})$[a] | −2.65(−2.83) | −2.50(−2.75) |
| $G(\mathbf{0},\mathbf{c}+\boldsymbol{\tau})$ | −1.90(−1.83) | −1.56(−1.46) |
| $P$ | (−1.0) | (−1.0) |
| $E(CT)$ | 4.4±0.5 | 3.4±0.5 |

[a] $G(\mathbf{0},\boldsymbol{\tau})$ and $G(\mathbf{0},\mathbf{c}+\boldsymbol{\tau})$ refer to the Coulomb interactions in the exciton states $|\mathbf{0},\boldsymbol{\tau}\rangle$ and $|\mathbf{0},\mathbf{c}+\boldsymbol{\tau}\rangle$, respectively, calculated by the distributed charge approximation. Numbers in parentheses are calculated from the point-charge approximation.

The Coulomb interaction energy was estimated using two different approximations: (a) Following Lyons,[14] the ion-pair interaction energy is computed as that between two charges located at the centers of the molecules. (b) The charges on the positive and negative ions were assumed to be distributed on the ring carbons with densities determined by Hückel-type wavefunctions. It is surprising that the difference between the point charge and the distributed charge approximation to $G$ is only 10%. The polarization energy $P$ was estimated by Lyons,[14] assuming that the ion pair constitutes a dipole with magnitude determined by the distance between neighboring sites. This treatment leads to $P=-0.8$ eV for anthracene and $P=-0.6$ eV for naphthalene. A more recent evaluation of these polarization energies, again using a classical ion-pair model but taking into account the anisotropic polarizability of the aromatic molecule,[22] leads to a value of $P=-1.7$ eV for anthracene. The cited classical calculation of the polarization energy raises questions similar to those previously encountered in the study of the exciton states in alkali halides on the basis of the electron-transfer model.[23] The ion pair does not represent a stationary state, and the charge distribution in the true excited state is characterized by a multipole moment higher than a dipole, thus leading to a decrease of the polarization energy arising from long-range interactions.[24] In view of these uncertainties, we take for the calculation of $\Delta E$, $P\approx-1$ eV for both anthracene and naphthalene. Since the value of $\Delta E$ for the configuration interaction between triplet and charge-transfer states is large, this is not expected to cause any serious error.

The calculated positions of the charge-transfer states for naphthalene and anthracene crystals are displayed in Table III. From our estimates, these states are

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[19] We are grateful to D. S. McClure for drawing our attention to this effect.

[20] The main source of intensity of the charge-transfer transition may be intensity borrowing (or stealing, depending on one's morals) from the neutral-exciton states. This situation is similar to the encountered in contact charge-transfer complex.[21]

[21] (a) L. E. Orgel and R. S. Mulliken, J. Am. Chem. Soc. **79,** 4839 (1957). (b) J. L. Murrell, *ibid.* **81,** 5037 (1959).

[22] R. S. Berry, J. Jortner, J. Mackie, E. Pysh, and S. A. Rice (to be published).

[23] R. Hilsch and R. W. Pohl, Z. Physik **48,** 384 (1928); **57,** 145 (1929); **59,** 812 (1930).

[24] I. M. Dykman, Zh. Eksperim. i Teor. Fiz. **26,** 307 (1954).

located in the vicinity of the $p$ band of the aromatic crystal. Since exchange interactions between the component ions and the ion pair are expected to be quite small (probably of the order of 10 cm$^{-1}$), the energy difference between the singlet and triplet charge-transfer exciton states may be taken to be negligible for our purposes.

From the known locations of the first naphthalene and anthracene triplet states, we estimate the energy denominators as $\Delta E=-1.7$ eV for naphthalene and $\Delta E=-1.5$ eV for anthracene.

## VII. EVALUATION OF THE ELECTRONIC MATRIX ELEMENTS

The calculation of the electronic matrix elements $\langle\mathbf{R}_m\,|\,H\,|\,\mathbf{R}_m\mathbf{R}_n\rangle$ and $\langle\mathbf{R}_m\,|\,H\,|\,\mathbf{R}_m\mathbf{R}_n\rangle$ is straightforward although somewhat lengthy.[25] Unlike some more conventional treatments within the framework of perturbation theory, the matrix elements contributing to charge-transfer interactions cannot be expressed in powers of some perturbation parameter. Instead, they consist of molecular integrals involving the excited molecule and the positive- and negative-ion wavefunctions. The wavefunctions of the isolated molecule, and of the ion pair, are assumed to be represented in the SCF $\pi$-electron approximation. Extensive theoretical work has established that Hückel orbitals are a reasonable approximation to the SCF wavefunctions. Thus, the molecular orbitals $u_n$ are approximated as a linear combination of carbon atom $2p_z$ wavefunctions[26] $\omega_i$

$$u^n=\sum_i\omega_iC_{in}, \qquad (38)$$

where the $C_{in}$ are Hückel coefficients without overlap. Our calculation involves long-range intermolecular interaction, where the behavior of the wavefunctions at large distances is crucial. Approximating the carbon atomic orbitals by a single Slater-type orbital characterized by an orbital exponent $\xi=1.625$ a.u. is clearly inadequate, as it seriously underestimates the magnitude of the tails of the wavefunctions. In the present case, we have followed our previous procedure and represented the $\pi$-type molecular orbital in the forms of a linear combination of Slater-type orbitals (LCSTO), with the best available carbon-atom wavefunctions also represented by a LCSTO:

$$\omega_j=r\cos\theta\sum_i a_i(\alpha_i^5/\pi)^{\frac{1}{2}}\exp(-\alpha_i r_j).$$

Further details can be found in previous work.[27]

The molecular wavefunction for a pair of identical neutral aromatic molecules, one of them excited to the first triplet state, can be represented in the form

$$\begin{aligned}|\,\mathbf{R}_m^f,\mathbf{R}_n^0\rangle\\ &=\mathcal{A}[u_m^1(1)\bar{u}_m^1(2)\cdots\bar{u}_m^{N/2}(N-1)\bar{u}_m^{(N/2)+1}(N)\\ &\times u_n^1(N+1)\bar{u}_n^1(N+2)\cdots u_n^{N/2}(2N-1)\bar{u}_n^{N/2}(2N)]. \qquad (39)\end{aligned}$$

The subscript refers to the molecule, while the superscript labels the particular MO. The bar refers to spin $\beta$, while the absence of a bar refers to spin $\alpha$. $N$ is the number of atoms in the molecule. The lowest-lying triplet state of the aromatic molecules of interest involves the excitation $u^{N/2}\rightarrow u^{(N/2)+1}$. The triplet state represented in Eq. (39) corresponds to the spin components $S=1$, $S_z=-1$. $\mathcal{A}$ represents the antisymmetrization operator $\sum_P(-1)^PP$ permuting all the electrons of the system.

The triplet ion-pair wavefunction for the same spin components, $S=1$, $S_z=-1$, is given by

$$\begin{aligned}|\,\mathbf{R}_m,\mathbf{R}_n\rangle\\ &=\mathcal{A}[u_m^1(1)\bar{u}_m^1(2)\cdots\bar{u}_m^{N/2}(N-1)\bar{u}_n^{(N/2)+1}(N)\\ &\times u_n^1(N+1)\bar{u}_n^1(N+2)\cdots u_n^{N/2}(2N-1)\bar{u}_n^{N/2}(2N)]. \qquad (40)\end{aligned}$$

The total Hamiltonian for the two molecules is taken in the form $H=H_m+H_n+H_{mn}$, where $H_m$ and $H_n$ are the Hamiltonian operators for the isolated molecules $m$ and $n$, while $H_{mn}$ is the intermolecular interaction potential.

We have assumed that the molecular orbitals are known, and that the molecular wavefunctions are not distorted by the interaction between the excited- and ground-state molecules, or by the interaction between the positive and the negative ions. The calculation of the matrix elements can then be considerably simplified by the introduction of core potentials. In the configurations of the neutral excited molecular pair and the ion pair, the occupation numbers of orbitals on the two molecules are different, and care must be used in the definition of the core potentials and the interaction potential. The simplest wavefunctions which will allow

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[25] In the evaluation of $\langle R_m\,|\,H\,|\,R_m,R_n\rangle$ we neglect the presence of molecules other than $m$ and $n$.

[26] It is known that atomic wavefunctions are changed in molecular fields by being contracted. Since our calculations depend on the properties of orbitals at large distances from the atomic core, it is necessary to comment on the accuracy of the LCAO assumption. We have compared the computed values of a typical exchange integral and a typical overlap integral, as obtained from two different wavefunctions, at distances of 6 and 7 a.u. The wavefunctions used in this paper are based on SCF $^3P$ carbon-atom functions. Recent work at the Laboratory for Molecular Structure of the University of Chicago enables us to compute integrals based on the SCF orbitals of the molecule $C_2$. It is found that, at 7 a.u., the overlap integrals computed from atomic $^3P$ basis functions differ by only 25% from those computed using "atomic" functions retrieved from either $^1\Sigma$ or $^3\Sigma$ molecular functions. Similarly, even when $d$ and $f$ orbital contributions are neglected, the computed exchange integrals based on $^3P$ atomic functions are only 1.5–1.6 times larger than the exchange integrals computed from $^1\Sigma$ or $^3\Sigma$ molecular functions. Clearly, the difference is further reduced by inclusion of the $d$ and $f$ orbital contributions to the SCF $C_2$ molecular orbitals. We conclude that our numerical calculations are not in serious error by virtue of the use of LCAO functions.

[27] J. L. Katz, S. A. Rice, S. Choi, and J. Jortner, J. Chem. Phys. **39**, 1683 (1963).

us to consider all the interactions pertinent for the present discussion are those involving four electrons, which in the state $|\mathbf{R}_m{}^f\mathbf{R}_n{}^0\rangle$ occupy the highest filled orbital on $n$ and the orbital $u_m{}^{N/2}$ and $u_m{}^{(N/2)+1}$, so that

$$|\mathbf{R}_m{}^f\mathbf{R}_n{}^0\rangle=\mathcal{A}[\bar{u}_m{}^{N/2}(1)\bar{u}_m{}^{(N/2)+1}(2)u_n{}^{N/2}(3)\bar{u}_n{}^{N/2}(4)],$$

$$|\mathbf{R}_m\mathbf{R}_n\rangle=\mathcal{A}[\bar{u}_m{}^{N/2}(1)\bar{u}_n{}^{(N/2)+1}(2)u_n{}^{N/2}(3)\bar{u}_n{}^{N/2}(4)].$$

The core Hamiltonian $H^C$ for the molecules $m$ and $n$ will be defined in the form[28]

$$H_m{}^C=V_m{}^{Nuc}+\sum_{s=1}^{(N/2)-1}(2J_m{}^s-K_m{}^s),$$

$$H_n{}^C=V_n{}^{Nuc}+\sum_{s=1}^{(N/2)-1}(2J_n{}^s-K_n{}^s),\tag{41}$$

where $V_m{}^{Nuc}$ and $V_n{}^{Nuc}$ are the bare nuclear potentials of Molecules $m$ and $n$, and $J^s$ and $K^s$ are the Coulomb and exchange operators defined by the well-known relations

$$J_m{}^su_r{}^i(1)=\int\frac{|u_m{}^s(2)|^2}{r_{12}}d\tau_2u_r{}^i(1),$$

$$K_m{}^su_r{}^i(1)=\int\frac{u_m{}^s(2)u_r{}^i(2)}{r_{12}}d\tau_2u_m{}^s(1),\tag{42}$$

where $r=m$, $n$. The Hamiltonian for the four-electron system may now be recast in the form

$$H=\sum_{i=1}^{4}[T_i+H_m{}^C(i)+H_n{}^C(i)+\sum_{j<i}(r_{ij})^{-1}],\tag{43}$$

where the $T_i$ are the kinetic-energy operators. This scheme can be easily extended including all the non-orthogonality corrections for all the $\pi$ electrons.

Calculation of the configuration-interaction matrix elements leads to the following results:

$$\begin{aligned}B=&\langle\mathbf{R}_m{}^f\mathbf{R}_n{}^0|H|\mathbf{R}_m{}^+\mathbf{R}_n{}^-\rangle-\langle\mathbf{R}_m{}^f\mathbf{R}_n{}^0|\mathbf{R}_m{}^+\mathbf{R}_n{}^-\rangle\langle\mathbf{R}_m{}^f\mathbf{R}_n{}^0|H|\mathbf{R}_m{}^f\mathbf{R}_n{}^0\rangle\\
&=\langle u_m{}^{(N/2)+1}|V_n{}^{\mathrm{GMS}}|u_n{}^{(N/2)+1}\rangle-\langle u_m{}^{(N/2+1)}|u_n{}^{(N/2)+1}\rangle\\
&\times\langle u_m{}^{(N/2)+1}|V_n{}^{\mathrm{GMS}}+2K_m{}^{N/2}-J_m{}^{N/2}|u_m{}^{(N/2)+1}\rangle+\langle u_m{}^{(N/2)+1}|K_m{}^{N/2}-\sum_i^{N/2}K_n{}^i|u_n{}^{(N/2)+1}\rangle\\
&-\langle u_m{}^{(N/2)+1}|u_n{}^{N/2}\rangle\langle u_n{}^{(N/2)+1}|V_m{}^{\mathrm{GMS}}|u_n{}^{N/2}\rangle+\langle u_m{}^{N/2}|u_n{}^{(N/2)+1}\rangle\langle u_m{}^{N/2}|V_n{}^{\mathrm{GMS}}|u_m{}^{(N/2)+1}\rangle\\
&+\langle u_m{}^{(N/2)+1}|u_n{}^{N/2}\rangle\langle u_m{}^{N/2}u_m{}^{(N/2)+1}|u_n{}^{N/2}u_n{}^{N/2}\rangle-\langle u_m{}^{N/2}|u_n{}^{N/2}\rangle\\
&\times\langle u_m{}^{N/2}u_m{}^{(N/2)+1}|u_n{}^{N/2}u_n{}^{(N/2)+1}\rangle-\sum_{i=1}^{(N/2)-1}\{\langle u_m{}^i|u_n{}^{(N/2)+1}\rangle\\
&\times\langle u_m{}^i|V_n{}^{\mathrm{GMS}}|u_m{}^{(N/2)+1}\rangle+\langle u_m{}^i|u_n{}^{(N/2)+1}\rangle\langle u_m{}^i|K_m{}^{N/2}-J_m{}^{N/2}|u_m{}^{(N/2)+1}\rangle\}\\
&-\sum_{i=1}^{(N/2)-1}\{\langle u_n{}^i|V_m{}^{\mathrm{GMS}}-J_m{}^{N/2}+K_n{}^{N/2}|u_n{}^{(N/2)+1}\rangle\langle u_m{}^{(N/2+1}|u_n{}^i\rangle\\
&-\langle u_m{}^{N/2}|u_n{}^i\rangle\langle u_m{}^{(N/2)+1}u_m{}^{N/2}|u_n{}^{(N/2)+1}u_n{}^i\rangle-\langle u_m{}^{(N/2)+1}|u_n{}^{(N/2)+1}\rangle\langle u_m{}^{(N/2)+1}u_n{}^i|u_n{}^iu_m{}^{(N/2)+1}\rangle\}\end{aligned}\tag{44a}$$

and

$$\begin{aligned}C=&\langle\mathbf{R}_m{}^f\mathbf{R}_n{}^0|H|\mathbf{R}_m{}^-\mathbf{R}_n{}^+\rangle-\langle\mathbf{R}_m{}^f\mathbf{R}_n{}^0|\mathbf{R}_m{}^-\mathbf{R}_n{}^+\rangle\langle\mathbf{R}_m{}^f\mathbf{R}_n{}^0|H|\mathbf{R}_m{}^f\mathbf{R}_n{}^0\rangle\\
&=-\langle u_m{}^{N/2}|V_n{}^{\mathrm{GMS}}|u_n{}^{N/2}\rangle+\sum_{i=1}^{N/2}\langle u_n{}^{N/2}|K_n{}^i|u_m{}^{N/2}\rangle\\
&-\langle u_n{}^{N/2}u_m{}^{N/2}|u_m{}^{(N/2)+1}u_m{}^{(N/2)+1}\rangle+\langle u_n{}^{N/2}|u_m{}^{N/2}\rangle\langle u_n{}^{N/2}|V_m{}^{\mathrm{GMS}}|u_m{}^{N/2}\rangle\\
&+2\langle u_m{}^{N/2}|K_m{}^{(N/2)+1}|u_n{}^{N/2}\rangle+2\langle u_n{}^{N/2}|u_m{}^{(N/2)+1}\rangle\langle u_m{}^{(N/2)+1}|V_n{}^{\mathrm{GMS}}-J_n{}^{N/2}|u_m{}^{N/2}\rangle\\
&+\sum_{i=1}^{(N/2)-1}\{\langle u_m{}^{N/2}|u_n{}^i\rangle\langle u_n{}^{N/2}|V_m{}^{\mathrm{GMS}}|u_n{}^i\rangle-\langle u_m{}^{N/2}|u_n{}^{N/2}\rangle\langle u_m{}^{N/2}|K_n{}^i|u_n{}^{N/2}\rangle\}\\
&+\sum_{i=1}^{(N/2)-1}\langle u_n{}^{N/2}|u_m{}^i\rangle\langle u_m{}^i|K_m{}^{(N/2)+1}|u_m{}^{N/2}\rangle.\end{aligned}\tag{44b}$$

The Coulomb interaction has been described in terms of the Goeppert-Mayer–Sklar potential

$$V_A{}^{\mathrm{GMS}}=V_A{}^{Nuc}+\sum_{s=1}^{N/2}2J_A{}^S,\tag{44c}$$

which involves the screening of the nuclear charge by the Hartree field. The Coulomb exchange integrals were calculated by Katz *et al.* The new feature of these results is the exchange interaction expressed in terms of hybrid integrals, $\langle u_m|K_n|u_n\rangle$. Details of the computation of these integrals are given in Appendix I. The configuration-interaction matrix elements $B$ and $C$ are presented in Table IV.

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[28] R. Daudel, R. Lefevre, and C. Moser, *Quantum Chemistry* (Interscience Publishers, Inc., New York, 1959).

TABLE IV. Configuration-interaction matrix elements for triplet states with charge-transfer states.

| | $\bar{B}(0,\tau)$ ($10^{-2}$ eV) | $\bar{B}(0,c+\tau)$ ($10^{-2}$ eV) | $\bar{C}(0,\tau)$ ($10^{-2}$ eV) | $\bar{C}(0,c+\tau)$ ($10^{-2}$ eV) |
|---|---|---|---|---|
| Anthracene | +4.70 | −0.343 | +0.706 | +2.54 |
| Naphthalene | +2.68 | +1.29 | +1.05 | −0.559 |

## VIII. RESULTS AND DISCUSSION

Our calculations lead to the following contribution by the ion-pair states to the Davydov splittings of the first triplet state:

$$\text{naphthalene} = 26/\Delta E(\text{eV})\ \text{cm}^{-1},$$

$$\text{anthracene} = 31/\Delta E(\text{eV})\ \text{cm}^{-1}.$$

Setting $E=-1.7$ eV for naphthalene and $E=-1.5$ eV for anthracene, the contributions of the ion-pair states to the first triplet exciton state are finally obtained. The results displayed in Table V indicate the relative importance of the ion-pair states, which increase the triplet band splitting due to exchange interactions by about 50%. It should also be noted that both the (neutral exciton) exchange (interaction) and the charge-transfer contributions to the triplet band Davydov splitting are found to be of the same sign, and arkward cancellations do not occur in the cases investigated by us.

The possible effect of charge-transfer states on the triplet exciton states of the benzene crystal is of considerable interest. Nieman and Robinson have recently studied the phosphorescence of isotopically mixed benzene crystals,[29] deriving a value of 12 $\text{cm}^{-1}$ for the nearest-neighbor pair-interaction matrix element. Hence the total electronic matrix element for this interaction is estimated to be of the order of 50 $\text{cm}^{-1}$.[30] Theoretical estimates, taking into account exchange interactions in a rigid lattice, lead to a value of ~5 $\text{cm}^{-1}$ for this interaction matrix element.[31] It is plausible that, since the experimental value was determined from emission spectra, intra- and intermolecular relaxation processes may be important. Intramolecular distortions of the benzene ring in the first triplet state, as estimated from ESR data,[32] seem to have only a small effect on the calculated exchange interaction. Tilting the benzene ring in the crystal showed that in certain configurations the matrix element can increase from 5 to 10 $\text{cm}^{-1}$, which is still smaller than the experimental result. Charge-transfer interactions might be of considerable importance in determining the intermolecular triplet excitation-transfer interactions in this system.

The contribution of the ion-pair states to the Davydov splitting might be of considerable importance for those singlet exciton states where the energy denominator $\Delta E$ is small. In these cases, contributions to $\Delta\epsilon$ of the order of 100–200 $\text{cm}^{-1}$ are quite plausible. This is, indeed, the case for the first absorption band of naphthalene which has recently been studied by us.

There is an obvious relationship between our treatment of charge-transfer exciton states and the Mulliken theory of charge-transfer molecular complexes,[33] suitably extended to account for the symmetry properties of the crystal. Although the existence of charge-transfer states in aromatic crystals has not yet been experimentally established, we feel that many puzzling observations can be reconciled by the conjecture that these states are located in the vicinity of the first observed neutral exciton states in these systems.

The formulation we have presented in this paper is not complete. However, for the study of configuration interaction with neutral exciton states, higher charge-transfer states are of no importance.

We note that a complete treatment of the problem studied herein would involve the construction of Wannier-type exciton states of the form

$$\sum_{\beta} C_{\beta}\,|\,\mathbf{R},\,\mathbf{R}+\beta\rangle.$$

For simple crystals characterized by a high dielectric constant $C_\beta$ can be represented by a hydrogenic envelope function. However, for an anisotropic aromatic crystal, a proper treatment of the problem would be much more complicated. Further work concerning both the experimental observation and the theoretical description of these intermediate exciton states in aromatic crystals will be of considerable interest.

TABLE V. The contribution of electron-exchange and charge-transfer interactions to the Davydov splitting of the first triplet state.

| Crystal | Electron-exchange[a,b] contribution ($\text{cm}^{-1}$) | Charge-transfer[b] contribution ($\text{cm}^{-1}$) |
|---|---|---|
| Naphthalene | −36 | −15 |
| Anthracene | −35 | −20 |

[a] J. Jortner, S. A. Rice, J. L. Katz, and S. I. Choi, J. Chem. Phys. **39**, 1897 (1963).

[b] The negative sign of the Davydov splitting implies that the $B_u$ component ($\perp\mathbf{b}$) is located at lower energy than the $A_u$ component ($\parallel\mathbf{b}$).

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[29] G. C. Niemann and G. W. Robinson, J. Chem. Phys. **38**, 1298 (1963).

[30] H. Sternlicht, G. C. Niemann, and G. W. Robinson, J. Chem. Phys. **38**, 1326 (1963).

[31] R. Silbey, J. Jortner, and S. A. Rice (to be published).

[32] M. de Groot and J. H. van der Waals, Mol. Phys. **6**, 545 (1963).

[33] R. S. Mulliken, J. Am. Chem. Soc. **64**, 811 (1952).

## ACKNOWLEDGMENTS

We wish to thank the National Science Foundation, the U. S. Public Health Service, and the U. S. Air Force Office of Scientific Research for financial support. We have also benefited from the use of general facilities provided by the Advanced Research Projects Agency for material research at The University of Chicago, and The University of North Carolina.

## APPENDIX: CALCULATION OF INTEGRALS

The calculation of the intermolecular integrals describing the interaction between charge-transfer and neutral exciton states involves a number of exchange integrals which are of interest for the quantitative treatment of several problems involving excited states and band structure of molecular crystals. For this reason their evaluation will be described in some detail.

The Coulomb-type interactions were approximated by the Goeppert-Mayer–Sklar potential of the neutral carbon atoms, so that

$$V_m^{\mathrm{GMS}}=\sum_i v_m^i. \tag{A1}$$

By classical electrostatic arguments within the framework of the Hartree scheme, this potential is derived by averaging over the charge distribution of the four $2s$, $2p_x$, $2p_y$, and $2p_z$ carbon atom electrons, so that

$$v^i=\frac{-e^2}{r_i}\sum_{k,l}\left(\frac{a_la_k\alpha_l^{\frac{5}{2}}\alpha_k^{\frac{5}{2}}}{\beta_{kl}^5}\right)^{\frac{1}{2}}\sum_{k,l}\exp(-2\beta_{k,l}r_i)\frac{a_ka_l\alpha_k^{\frac{5}{2}}\alpha_l^{\frac{5}{2}}}{\beta_{kl}^5}$$
$$\times[\tfrac{4}{3}(\beta_{kl}r_i)^3+4(\beta_{kl}r_i)^2+6(\beta_{kl}r_i)+4], \tag{A2}$$

where $\beta_{kl}=\frac{1}{2}(\alpha_k+\alpha_l)$. The integrals of interest were expanded in terms of atomic orbitals:

$$\langle u_n^{(N/2)+1}\mid V_m^{\mathrm{GMS}}\mid u_m^{(N/2)+1}\rangle$$
$$=\sum_{i,j,k}C_{i,(N/2)+1}C_{j,(N/2)+1}\int\omega_i^n v_k^m\omega_j^m d\tau. \tag{A3}$$

The numerical computation of these integrals using carbon atom SCF wavefunctions has previously been described in detail. Only the two-center integrals were calculated, as previous experience[27] has shown that the contribution of three center terms is only about 25%. It should be noted that the representation of the electrostatic interactions in terms of the Goeppert-Mayer–Sklar potential involves screening of the nuclear framework by both $\pi$- and $\sigma$-type electrons, so that the complete penetration term is considered. When the other exchange interactions are considered, only the effect of the $\pi$-electrons will be taken into account.

The hybrid (ionic) integrals of the form

$$I=\langle u_n^i\mid K_m^s\mid u_m^j\rangle\equiv\langle u_n^iu_m^s\mid u_m^su_m^j\rangle$$
$$\equiv\int u_n^i(1)^*u_m^s(1)(r_{12})^{-1}u_m^s(2)u_m^j(2)^*d\tau_1d\tau_2 \tag{A4}$$

were computed by a technique similar to that previously employed for the computation of exchange integrals. The general expression for $I$ is

$$I=\sum_{\alpha,\beta,\gamma,\delta}C_{\alpha i}C_{\beta s}C_{\gamma s}C_{\delta j}\langle\omega_\alpha^n\omega_\beta^m\mid\omega_\gamma^m\omega_\delta^m\rangle. \tag{A5}$$

Three- and four-center intermolecular integrals were neglected. Considering then only two-center hybrid integrals, Eq. (A5) is reduced to

$$I=\sum_{\alpha,\beta}C_{\alpha i}C_{\beta s}^2C_{\beta j}\langle\omega_\alpha^n\omega_\beta^m\mid\omega_\beta^m\omega_\beta^m\rangle. \tag{A6}$$

The SCF carbon-atom wavefunctions used in the computation of the hybrid integrals are characterized by the parameters[34]

$$a_1=0.00842,\quad a_2=0.17442,\quad a_3=0.45191,\quad a_4=0.43645;$$
$$\alpha_1=6.827,\quad \alpha_2=2.779,\quad \alpha_3=1.625,\quad \alpha_4=1.054.$$

The carbon-atom wavefunctions were expressed in terms of the product of a radial function and a spherical harmonic function $R(r)Y_{lm}(\theta,\varphi)$, and the three $2p$ wavefunctions $p_{+1}(m=1)$, $p_{-1}(m=-1)$, and $p_z(m=0)$ were used.

The hybrid integrals in Eq. (A6) involve interactions between $2p$ orbitals at various relative orientations determined by the crystal structure. The intermolecular hybrid integrals were computed for all the pairs of atoms $\alpha$ and $\beta$ located on adjacent molecules using the known crystal structure of the aromatic compounds. The coordinate system used is the same as that employed by Kotani *et al.*[35] The atoms $\alpha$ and $\beta$ were located on the $Z$ axis; then, by defining $X_\alpha$, $Y_\alpha$, $Z_\alpha$ and $Z_\beta$, $X_\beta$, $Y_\beta$ as the coordinate system located on the centers $\alpha$ and $\beta$, the hybrid integrals can be expressed in terms of the direction cosines of the unit vectors $\mathbf{n}$ and $\mathbf{m}$ defining the spatial direction of the $2p$ orbitals located on the centers $\alpha$ and $\beta$, respectively:

$$A=\mathbf{n}\cdot\mathbf{x}_\alpha;\qquad B=\mathbf{n}\cdot\mathbf{y}_\alpha=0;\qquad C=\mathbf{n}\cdot\mathbf{z}_\alpha;$$
$$D=\mathbf{m}\cdot\mathbf{x}_\beta;\qquad E=\mathbf{m}\cdot\mathbf{y}_\beta;\qquad F=\mathbf{m}\cdot\mathbf{z}_\beta. \tag{A7}$$

The hybrid integrals are then expressed in the form

$$\langle\omega_\alpha^n\omega_\beta^m\mid\omega_\beta^m\omega_\beta^m\rangle=A^3D\langle p_+p_-\mid p_+p_-\rangle$$
$$+\tfrac{1}{2}A^3D\langle p_+p_+\mid p_+p_+\rangle+2A^2CF\langle p_zp_+\mid p_-p_z\rangle$$
$$+2AC^2D\langle p_zp_+\mid p_zp_+\rangle+AC^2D\langle p_zp_z\mid p_+p_+\rangle$$
$$+A^2CF\langle p_+p_+\mid p_zp_z\rangle+C^3F\langle p_zp_z\mid p_zp_z\rangle. \tag{A8}$$

These hybrid integrals were computed on an IBM 7094 computer using an integral program written by A. C. Wahl and P. E. Cade at the Laboratory of Molecular Structure and Spectra, The University of Chicago. The basic integrals used are presented in Table VI. Using

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[34] P. S. Bagus, T. L. Gilbert, C. C. J. Roothaan, and H. Cohen (to be published).

[35] M. Kotani, E. Ishiguro, and K. Hijikata, J. Phys. Soc. Japan **9**, 553 (1954).

Table VI. Molecular integrals for the calculation of the configuration mixing of the triplet state with charge-transfer states (units—$10^{-2}$ eV). Single primes refer to Orbital $N/2$ and the double primes to orbital $N/2+1$.

| | Anthracene | | | | Naphthalene | | | |
|---|---|---|---|---|---|---|---|---|
| | $m\ n$<br>$0\text{–}\tau$ | $n\ m$<br>$\tau\text{–}0$ | $m\ n$<br>$0\text{–}(c+\tau)$ | $n\ m$<br>$(c+\tau)\text{–}0$ | $m\ n$<br>$0\text{–}\tau$ | $n\ m$<br>$\tau\text{–}0$ | $m\ n$<br>$0\text{–}(c+\tau)$ | $n\ m$<br>$(c+\tau)\text{–}0$ |
| 1. $(u_m'' \mid V_n^{\mathrm{GMS}} \mid u_n'')$ | −0.447 | −0.447 | −0.416 | −0.416 | −0.540 | −0.540 | −0.034 | −0.034 |
| 2. $(u_m'' \mid \sum_i^{N/2} K_n^i \mid u_n'')$ | −2.55 | −2.55 | −0.074 | −0.074 | −1.24 | −1.24 | 00.170 | 0.170 |
| 3. $(u_n''u_n' \mid u_m'u_m')$ | 8.03 | 30.43 | 1.01 | 8.22 | −8.02 | −29.4 | −0.530 | −13.3 |
| 4. $(u_m'' \mid K_m' \mid u_n'')$ | −0.626 | −1.02 | −0.051 | −0.017 | −0.320 | −0.608 | 0.203 | 0.049 |
| 5. $(u_m'' \mid J_m' \mid u_m'')$ | 521.8 | 521.8 | 521.8 | 521.8 | 607.1 | 607.1 | 607.1 | 607.1 |
| 6. $(u_m'' \mid u_n'')$ | 0.0044 | 0.0044 | −0.0001 | −0.0001 | 0.0019 | 0.0019 | 0.0021 | 0.0021 |
| 7. $(u_m'' \mid u_n')$ | −0.0043 | −0.0030 | −0.0005 | −0.0005 | −0.0018 | −0.0004 | 0.0003 | 0.0008 |
| 8. $(u_m''u_m' \mid u_n''u_n')$ | 0.670 | 0.670 | 0.700 | 0.700 | 0.220 | 0.220 | 0.930 | 0.930 |
| 9. $(u_m' \mid u_n')$ | 0.0034 | 0.0034 | −0.0018 | −0.0018 | −0.0024 | −0.0024 | 0.0002 | 0.0002 |
| 10. $(u_n' \mid V_n^{\mathrm{GMS}} \mid u_m')$ | −1.96 | −1.96 | −1.65 | −1.65 | 0.293 | 0.293 | −0.335 | −0.335 |
| 11. $(u_n' \mid \sum_i^{N/2} K_n^i \mid u_m')$ | −1.26 | −1.26 | 0.848 | 0.848 | 1.34 | 1.34 | −0.894 | −0.894 |
| 12. Remaining terms in Eqs. (44a) and (44b). | −0.717 | −0.367 | −0.025 | −0.025 | −0.173 | 0.183 | 0.202 | 0.200 |

Eq. (A6), the intermolecular hybrid integrals were evaluated.

The hybrid sums over all the occupied $\pi$ orbitals can be simplified by using the Coulson–Rushbrooke relation

$$\sum_{s=1}^{N/2} C_{\alpha s}{}^2 = \tfrac{1}{2},$$

so that

$$\sum_{s=1}^{N} \langle u_n{}^{(N/2)+1} \mid K_m{}^s \mid u_m{}^{(N/2)+1} \rangle$$

$$= \sum_{\alpha,\beta} C_{\alpha 1(N/2)+1} C_{\beta 1(N/2)+1} \langle \omega_\alpha{}^n \omega_\beta{}^m \mid \omega_\beta{}^m \omega_\beta{}^m \rangle.$$

For an order-of-magnitude estimate the nonorthogonality corrections are not important, as they do not contribute more than 50% to the final estimate of the configuration-interaction matrix elements. However, in order to get reliable quantitative estimates, these terms have to be included. The evaluation of intermolecular overlap has been described. The nonorthogonality corrections to the Goeppert-Mayer–Sklar potential of the form

$$\langle u_n{}^{(N/2)+1} \mid u_m{}^{(N/2)+1} \rangle \langle u_n{}^{(N/2)+1} \mid V_m{}^{\mathrm{GMS}} \mid u_n{}^{(N/2)+1} \rangle$$

were found to be two orders of magnitude smaller than the term

$$\langle u_n{}^{(N/2)+1} \mid V_m{}^{\mathrm{GMS}} \mid u_m{}^{(N/2)+1} \rangle,$$

so they could be safely neglected. This result can be rationalized in terms of the Mulliken approximation, which, although being by no means adequate for quantitative calculations of intermolecular interactions, is expected to lead to correct order-of-magnitude estimates. Furthermore, in view of the short range of $V^{\mathrm{GMS}}$, this result is reasonable.

Other nonorthogonality corrections involve intramolecular interaction integrals of the form

$$\langle u_n{}^j \mid K_n{}^i \mid u_n{}^k \rangle \quad \text{or} \quad \langle u_n{}^j \mid J_n{}^j \mid u_n{}^k \rangle.$$

For the calculation of these intramolecular integrals (and only these) we have proceeded in the spirit of the conventional $\pi$-electron theory, using atomic orbitals characterized by a single orbital exponent $\xi = 1.625$. The intramolecular integrals were calculated using the well-known expressions for the one- and two-center Coulomb integrals for Atoms $p$ and $q$ located on the same molecule

$$\langle pp \mid pp \rangle = e^2\xi(501/1280),$$

$$\langle pp \mid qq \rangle = e^2\xi F(\xi R),$$

where $R$ is the distance between the centers $p$ and $q$ and the function $F$ is given by

$$F(x) = \left(\frac{1}{x} - \frac{3}{x^3} + \frac{20.25}{x^5}\right) - e^{-2x}\left(\frac{20.25}{x^5} + \frac{40.5}{x^4} + \frac{37.5}{x^3} + \frac{21}{x^3} + \frac{8.5}{x} + 3.0085938 + 1.017188x + 0.28943452x^2 + 0.0559524x^3 + 0.00535714x^4\right).$$

Three- and four-center intramolecular integrals were evaluated by the Mulliken approximation.