nism is of general significance and deserves further experimental work which we hope to undertake.

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On the Electronic States of Crystalline Naphthalene

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In this paper, we attempt to correlate the observed electronic spectrum of crystalline naphthalene with the observed spectrum of the free molecule. The normal Frenkel exciton theory is extended to include ion-pair states and the effect of these on the spectrum is taken into account. It is found that the observed spectrum can be accounted for in the present analysis, if the ion-pair state is energetically close to the first excited singlet state of naphthalene.

I. INTRODUCTION

ONE of the objectives of ths study of the spectra of molecular crystals is to provide a correlation between the stationary states of the free molecule and those of the crystal. With this objective in mind, the study of the naphthalene crystal becomes of particular interest. For, it is observed that the lowest electronic transition (α) in the naphthalene crystal shows a Davydov splitting of about 150 cm^{-1} in the 0–0 vibrational component,[1] while the parent free molecule transition is so weak that the observed splitting cannot be accounted for in terms of transition dipole interactions.[2] This failure of the usual formulation of exciton theory led Craig and co-workers to consider higher transition multipole interactions as the source of the splitting.[2] Indeed, the transition octopole moments required to fit the observed spectrum are not large, and it is conceivable that they are good approximations to the true moments. On the other hand, the octopole moments estimated using either Hückel or Pariser wavefunctions[3] vanish in the approximation of zero differential overlap.[4] Wheland orbitals (including nearest-neighbor overlap) lead to transition octopole moments in fair agreement with those suggested by Craig. However, it must be remembered that the use of Wheland orbitals leads to a transition dipole moment a factor of 10–15 larger than is observed,[5] and therefore the estimated octopole moment may be seriously in error. In view of this uncertainty in the magnitude of the transition moments, in this paper we present an alternative explanation of the observed splitting. The interpretation we suggest differs not in quantitative detail, but rather by making a qualitative modification of the explanation of the origin of the Davydov splitting for the case of very weak transitions.

In recent papers[6] we have discussed the role of ion-pair exciton states in the spectrum of molecular crystals, and have shown that mixing of these states into neutral exciton states by the crystal field may influence the Davydov splitting of the neutral states. In this paper we apply that analysis to the study of the states of the naphthalene crystal. It is shown that the magnitude of the splitting and the polarization ratios can be accounted for if we conjecture that the ion-pair states lie very close to the α state in energy.

Calculations are also presented for the p and β bands of naphthalene, but since the parent free molecule transitions are relatively strong, these cases are not of as much interest as is the study of the α band.

II. GENERAL REMARKS

Although the theory of molecular excitons has been reviewed in several recent articles,[7] we find it convenient

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[1] D. P. Craig, L. E. Lyons, and J. R. Walsh, Mol. Phys. **4**, 97 (1961).

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

[3] R. Pariser, J. Chem. Phys. **24**, 250 (1956).

[4] This is a consequence of the pairing of molecular orbitals in these approximate theories and would be true for any molecular wavefunction preserving the pairing of orbitals in the α band. See Appendix I.

[5] E. Konijnenberg, thesis, University of Amsterdam, 1963.

[6] (a) S. Choi, J. Jortner, S. A. Rice, and R. Silbey, J. Chem. Phys. **41**, 3294 (1964); (b) R. Silbey, J. Jortner, and S. A. Rice, *ibid.* **42**, 1515 (1965).

[7] D. S. McClure Solid State Phys. **8**, 1 (1959); O. Schnepp, Ann. Rev. Phys. Chem. **14**, 35 (1963); D. P. Craig 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); A. S. Davydov, *Theory of Molecular Excitons* (McGraw-Hill Book Company, Inc., New York, 1962); R. Knox; Solid State Phys. Suppl. **5**, (1964).

to display in this section the fundamental formulas required for our analysis.

In general, the excited states of a molecular crystal may be represented in terms of the excitation waves

$$E(\mathbf{K},\boldsymbol{\beta})=(N)^{-\frac{1}{2}}\sum_{m=1}^{N}\exp(i\mathbf{K}\cdot\mathbf{R}_m)\,|\,\mathbf{m}+\tfrac{1}{2}\boldsymbol{\beta},\mathbf{m}-\tfrac{1}{2}\boldsymbol{\beta}\rangle,\tag{1}$$

where the state vector $|\,\mathbf{m}+\tfrac{1}{2}\boldsymbol{\beta},\mathbf{m}-\tfrac{1}{2}\boldsymbol{\beta}\rangle$ represents a hole and an electron in the crystal separated by the vector distance $\boldsymbol{\beta}$ and having no relative motion. This excitation (electron–hole pair) moves in the crystal with momentum $\hbar\mathbf{K}$. The limiting case of the Frenkel exciton corresponds to $\boldsymbol{\beta}=0$, and the general excited state can be represented as a linear combination of excitation waves for all values of $\boldsymbol{\beta}$.[8] In our previous study[6] of the interaction between ion-pair exciton states and neutral exciton states, terms in (1) were kept corresponding to the hole and electron being localized on near-neighbor molecules.

For the case of small overlap, such as characterizes crystals of aromatic molecules (for both ground and excited states), it is usually assumed that the ground-state wavefunction is a product of free molecule wavefunctions. Correspondingly, the Hamiltonian operator is represented as a sum of free molecule Hamiltonians and an interaction operator, with the interaction assumed to be sufficiently small that the excited states of the crystal resemble those of the free molecule. Given these conditions, the determination of the eigenstates of the crystal reduces to the diagonalization of the Hamiltonian matrix in the basis of the excited states of the free molecule.

Crystalline naphthalene has a monoclinic unit cell with space group $C_{2h}{}^5$ (two molecules per unit cell).[9] For the fth excitation wave (with $\boldsymbol{\beta}=0$) it is readily found that, for $\mathbf{K}$ parallel to or perpendicular to the monoclinic axis,

$$\chi_{\pm}{}^{f}(\mathbf{K})=(1/\sqrt{2})\{\Psi_1{}^{f}(\mathbf{K})\pm\Psi_2{}^{f}(\mathbf{K})\exp(i\mathbf{K}\cdot\boldsymbol{\tau})\},\tag{2}$$

where

$$\Psi_{1(2)}{}^{f}(\mathbf{K})=(N)^{-\frac{1}{2}}\sum_{j=1}^{N}\exp(i\mathbf{K}\cdot\mathbf{R}_j)\,\Phi_{1(2)}{}^{f}(\mathbf{R}_j),\tag{3}$$

$$\Phi_{1(2)}(\mathbf{R}_j)=\mathcal{A}\phi_{j1(2)}{}^{f}\prod_{n\alpha\neq j1(2)}{}'\,\phi_{n\alpha}{}^{0},\tag{4}$$

$$\boldsymbol{\tau}=\tfrac{1}{2}(\mathbf{a}+\mathbf{b}),\tag{5}$$

where N is the number of unit cells, ϕ_n is the free molecule wavefunction for Molecule n, $\mathcal{A}$ is the antisymmetrizer which exchanges electrons between molecules, the subscripts 1(2) refer to the two distinguishable molecules in the unit cell, and $\mathbf{R}_j$ is the vector to the jth unit cell. The elements of the energy matrix $(\mathcal{H}-\mathcal{H}_{00}\,\mathbf{l}=H)$ in the basis set χ are given by (energy measured relative to the ground state)

$$H_{\pm}{}^{fg}=(\Delta w^{f}+D)\,\delta_{fg}$$
$$+\sum_{m=1}^{N}\{[\cos\mathbf{K}\cdot(\mathbf{R}_{n1}-\mathbf{R}_{m1})](J_{n1,m1}{}^{fg}\pm J_{n1,m2}{}^{fg})$$
$$+(K_{n1,m2}{}^{fg}+K_{n1,m1}{}^{fg})(1-\delta_{fg})\},\tag{6}$$

where Δw^{f} is the excitation energy to the fth excited state and D is the environmental shift

$$D=\sum_{m,\alpha}\{\langle\mathcal{A}\phi_{n1}{}^{f}\phi_{m\alpha}{}^{0}\,|\,V_{n1,m\alpha}\,|\,\phi_{n1}{}^{f}\phi_{m\alpha}{}^{0}\rangle$$
$$-\langle\mathcal{A}\phi_{n1}{}^{0}\phi_{m\alpha}{}^{0}\,|\,V_{n1,m\alpha}\,|\,\phi_{n1}{}^{0}\phi_{m\alpha}{}^{0}\rangle\}.\tag{7}$$

In Eq. (7) $V_{n1,m\alpha}$ is the interaction between Molecules $n1$ and $m\alpha$, and in Eqs. (6) and (7) the summation on m is over all unit cells and that on α over all molecules in a unit cell. The integrals $J_{n1,m\alpha}{}^{fg}$ are defined by

$$J_{n1,m\alpha}{}^{fg}=\tfrac{1}{2}\{\langle\mathcal{A}\phi_{n1}{}^{f}\phi_{m\alpha}{}^{0}\,|\,V_{n1,m\alpha}\,|\,\phi_{n1}{}^{0}\phi_{m\alpha}{}^{g}\rangle$$
$$+\langle\mathcal{A}\phi_{n1}{}^{g}\phi_{m\alpha}{}^{0}\,|\,V_{n1,m\alpha}\,|\,\phi_{n1}{}^{0}\phi_{m\alpha}{}^{f}\rangle\},\tag{8}$$

while

$$K_{n1,m\alpha}{}^{fg}=\langle\mathcal{A}\phi_{n1}{}^{f}\phi_{m\alpha}{}^{0}\,|\,V_{n1,m\alpha}\,|\,\phi_{n1}{}^{g}\phi_{m\alpha}{}^{0}\rangle.\tag{9}$$

In the usual treatment[2,7] the matrix elements of V_{nm} are expanded into a multipole series, where the n-poles are the *transition* n-poles.

III. COMPUTATIONAL DETAILS

For the present analysis we take the molecular wavefunctions to be linear combinations of antisymmetrized products of molecular orbitals. In particular, we have used Hückel orbitals and Pariser[3] semiempirical configuration-interaction molecular wavefunctions to represent all the states. The molecular wavefunctions are listed in Table I.

Hückel molecular orbitals for an alternant hydrocarbon are paired in the sense that there are two distinct sets of atoms (starred and unstarred) and each orbital has a twin which differs from the other only in that the Hückel coefficients of the starred atoms have changed sign. If one of the pair of orbitals has energy ϵ with respect to the energetic center of gravity of all the orbitals, then the other orbital has energy $-\epsilon$.

There are three important singlet bands in the ultraviolet spectrum of naphthalene: They are listed in Table II along with the experimental oscillator strengths and symmetries in the group D_{2h}. The lowest singlet

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[8] G. Wannier, Phys. Rev. **52**, 191 (1937).

[9] A. Kitaigorodskii, *Organic Crystallography* (Consultants Bureau Enterprises, Inc., New York, 1961).

TABLE I. Molecular wavefunctions.[a]

Symmetry	Energy (eV)	f_{calc}	Wavefunctions
$^1B_{3u}(\alpha)$	3.99	0.000	$(0.97472/\sqrt{2})(\phi^{4-6}-\phi^{5-7})+(0.11987/\sqrt{2})(\phi^{5-10}-\phi^{1-6})$ $-(0.18853/\sqrt{2})(\phi^{3-9}-\phi^{2-8})$
$^1B_{2u}(p)$	4.47	0.256	$0.96682\phi^{5-6}+0.23643\phi^{4-7}-0.07683\phi^{3-8}-(0.04265/\sqrt{2})(\phi^{4-10}+\phi^{1-7})$ $+0.02432\phi^{2-9}-0.03226\phi^{1-10}$
$^1B_{3u}(\beta)$	5.91	2.115	$(0.95369/\sqrt{2})(\phi^{4-6}+\phi^{5-7})-(0.20707/\sqrt{2})(\phi^{5-10}+\phi^{1-6})$ $+(0.21818/\sqrt{2})(\phi^{3-9}+\phi^{2-8})$
$^1B_{2u}$	6.28	0.699	$-0.23156\phi^{5-6}+0.95596\phi^{4-7}+0.11478\phi^{3-8}-(0.10230/\sqrt{2})(\phi^{4-10}+\phi^{1-7})$ $+0.09427\phi^{2-9}+0.00020\phi^{1-10}$
$^1B_{3u}$	7.93	0.043	$(0.29286/\sqrt{2})(\phi^{4-6}+\phi^{5-7})+(0.80625/\sqrt{2})(\phi^{5-10}+\phi^{1-6})$ $-(0.51410/\sqrt{2})(\phi^{3-9}+\phi^{2-8})$
$^1B_{2u}$	8.16	0.851	$0.09883\phi^{5-6}-0.08973\phi^{4-7}+0.97270\phi^{3-8}-(0.11131/\sqrt{2})(\phi^{4-10}+\phi^{1-7})$ $-0.15247\phi^{2-9}+0.01980\phi^{1-10}$

[a] Reference 3.

state is, $^1B_{3u}$ (α in Clar's notation, ^1L_b in Platt's notation) and is the weakest allowed band in the spectrum. Craig *et al.*[10] have shown that this transition is approximately 90% vibrationally induced.

In order to evaluate the necessary matrix elements, we assume that the intermolecular pair potential has the form

$$V_{kl}=\sum_{I,J}\frac{Z_IZ_Je^2}{R_{IJ}}-\sum_{I,j}\frac{Z_Ie^2}{R_{Ij}}-\sum_{J,i}\frac{Z_Je^2}{R_{Ji}}+\sum_{i>j}\frac{e^2}{r_{ij}}, \quad (10)$$

where I and J refer to nuclei on Molecules k and l, respectively, and i and j to electrons on Molecules k and l.

In previous applications of exciton theory to aromatic crystals[2,6] the following procedure has usually been followed:

(a) As already mentioned, a multipole expansion for the matrix elements of V_{kl} is introduced and truncated after only a few terms.

(b) The dipole terms in the above expansion are evaluated using the experimental oscillator strengths (obtained from solution spectra).

(c) For allowed transitions the higher multipoles are not calculated. (In one case[2] the octopole moment has been used as an adjustable parameter to obtain agreement with experiment.) Moreover, the dipole–dipole sums are usually computed only in the limit $\mathbf{K}=0$ and neglecting the retardation of the interaction.

In the present analysis a different procedure is employed. For molecules within a distance of 50 A from the molecule at the origin, the integrals are calculated using the above-mentioned π-electron molecular wavefunctions; for molecules farther apart than 50 Å, the multipole expansion is used and truncated after dipole terms. Although higher-order multipoles are of importance for the case of nearby molecules, these terms tend to zero quickly with increasing distance. It should be noticed that the dipole–dipole sum for $\mathbf{K}\equiv0$ does not converge uniformly for an infinite volume and depends on the shape of the region. For this reason, it is necessary to compute the long-range interactions taking into account both the modulation introduced by the requirement of conservation of momentum, $\mathbf{K}=\mathbf{q}$ (with $\mathbf{q}$ the wave vector of the photon) and the retardation of the interaction due to the finite velocity of light.[6b]

The terms $J_{nm}{}^{ff}$ required for the computation of the first-order Davydov splitting may be represented in terms of the molecular wavefunctions

$$J_{nl,mi}{}^{pp}=2\langle u_{mi}{}^5(1)u_{mi}{}^6(1)\,|\,r_{12}{}^{-1}\,|\,u_{nl}{}^5(2)u_{nl}{}^6(2)\rangle \quad (11)$$

for the p state ($^1B_{2u}$), and

$$J_{nl,mi}{}^{\beta\beta}=\langle\{u_{nl}{}^4(1)u_{nl}{}^6(1)+u_{nl}{}^5(1)u_{nl}{}^7(1)\}\,|\,r_{12}{}^{-1}\,|\,\{u_{mi}{}^4(2)u_{mi}{}^6(2)+u_{mi}{}^5(2)u_{mi}{}^7(2)\}\rangle \quad (12)$$

for the β state ($^1B_{3u}$). Expressions (11) and (12) are written in terms of Hückel wavefunctions. When Pariser CI wavefunctions are used, a more complicated expression (with the form of a sum of integrals of the above type) is obtained. The molecular orbitals u^n are represented in terms of a linear combination of $2pz$ carbon-atom functions, w^i:

$$u^n=\sum_i w^ic^{ni}, \quad (13)$$

and the c^{ni} are Hückel coefficients without overlap. The integrals over molecular orbitals may now be

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[10] D. P. Craig, M. Hollas, M. F. Kedies, and S. C. Wait, Phil. Trans. Roy. Soc. (London) **A253**, 543 (1961).

broken up into a sum of integrals over atomic orbitals, e.g.,

$$\langle u_{n1}{}^{5}(1)u_{n1}{}^{6}(1) \mid r_{12}{}^{-1} \mid u_{mi}{}^{5}(2)u_{mi}{}^{6}(2) \rangle$$
$$= \sum_{i,j,k,l} c^{5i}c^{6j}c^{5k}c^{6l} \langle w^{i}(1)w^{j}(1) \mid r_{12}{}^{-1} \mid w^{k}(2)w^{l}(2) \rangle. \quad (14)$$

Three- and four-center integrals were neglected. On the basis of past experience,[11] we feel that the multicenter terms will be relatively small. The carbon-atom wavefunction chosen was the best available SCF $2p\pi$ function for the ^3P state of carbon.[12,13] The integrals were carried out on an IBM 7094 and were calculated for all molecules within a sphere of approximately 60-Å radius. The results of the calculation for equivalent and inequivalent molecules (for the p band) are displayed in Table III. The columns represent the results using Hückel functions, Pariser functions, and the dipole–dipole approximation. Since the Hückel functions overestimate the transition dipole in the p state by a factor of $5^{\frac{1}{2}}$ and the Pariser functions overestimate it by a factor of $(2.5)^{\frac{1}{2}}$, we estimate the higher multipole contribution to the interaction energy by subtracting from the total integral calculation the interaction energy of the dipoles multiplied by the factor by which the wavefunctions used overestimate the dipole term (5 and 2.5, respectively). As is shown in Table III the differences (Δ_{PA}, Δ_{HU}) for the inequivalent molecules also scale by the same factors as do the dipole–dipole terms. Although the differences for the equivalent molecules do not scale in this manner, the Davydov splitting to first order does not depend on these sums. We, therefore, scale the entire integral result by this factor. For the β state, the results were reasonably independent of the wavefunction and so no scaling was performed [see Table III(b)]. This behavior of the β state is in agreement with previous work on anthracene.[6] The crystal-field mixing terms (i.e., J^{fg}) were found in the same way for the 50-Å sphere, again using the scaling procedure [see Table III(c)]. The K^{fg} are zero in the Hückel approximation and in the dipole approximation. A detailed description has already been given of the method of evaluation of long-range dipole–dipole interactions; here we only state the assumptions used and the results of the calculation. We assume that the dipoles 50 Å and farther away may be replaced by a density of dipoles, whereupon the summation is converted to an integration. Previous work[6b] has shown that the use of a continuum density and the neglect of higher multipole interactions are good approximations. The results obtained are displayed in Table IV.

TABLE II. Naphthalene singlet states vapor-phase experimental data.

Band	Symmetry	f	$E(\text{cm}^{-1})$
α	$^1B_{3u}$	0.001–0.002	32 000
p	$^1B_{2u}$	0.11	35 500
β	$^1B_{3u}$	1.70	45 500

Crystal-field mixing (the off-diagonal matrix elements) is extremely important, as was first pointed out by Fox and Yatsiv[14] and by Craig.[15] We have calculated the off-diagonal matrix elements using the same procedure as for the diagonal matrix elements. The results are given in Tables III and IV.

IV. RESULTS OF THE FIRST-ORDER COMPUTATION FOR THE α BAND

The α band remains unsplit in the approximation described in Sec. III. Therefore, the three-center integral contribution to the matrix elements for the α band was estimated. It is shown in Appendix I that, even if all three-center integrals are included, the diagonal element vanishes due to the pairing property of the molecular orbitals. For the off-diagonal elements, i.e., the mixing between α and other states, the pairing property shows that one-half of the terms will be zero (those in which the molecule with one center has the α excitation on it). The other half of these terms and all the four-center terms were estimated using the Mulliken approximation

$$u^{i}(1)u^{j}(1) = (S_{ij}/2)\{u^{i}(1)u^{i}(1) + u^{j}(1)u^{j}(1)\}. \quad (15)$$

These matrix elements are small (of order 10 cm^{-1}) and certainly cannot account for the splitting, but might conceivably account for the observed polarization ratio. It may be argued that including atomic overlap in the Hückel functions will destroy the pairing property and give some splitting in the α band. Such wavefunctions were calculated by Konijnenberg.[4] The calculated oscillator strength of the α band using a Hückel-type function with overlap is 25 times larger than the experimental value (vapor). But it has been shown that the intensity of this band is largely due to the vibronic mixing of p state into the α state by a b_{1g} vibration. (The α state is b_{3u}; $b_{3u} \times b_{1g} = b_{2u}$ which is the same symmetry as the p state.) In fact, Craig *et al.*[10] report that the "true" electronic oscillator strength for the α state is 10% to 20% of the entire oscillator strength. Therefore, the oscillator strength calculated using the Konijnenberg wavefunction is of the order of 125 to 250 times too large, and the use of Wheland orbitals is inadequate. Using this as a scale factor in the same spirit as before, we find that the splitting of the α band (including crystal-field mixing) is of the order of a few ($\sim$5) cm^{-1}. Even if the scale factor is much smaller ($\sim$10–25), the splitting, although larger, is of the wrong sign. Clearly then, the analysis thus

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

[12] P. Bagus, T. Gilbert, C. Roothaan, and H. Cohen "Analytic SCF Functions for the First Row Atoms" (to be published).

[13] R. Silbey, N. Kestner, J. Jortner, and S. Rice (to be published).

[14] D. Fox and S. Yatsiv, Phys. Rev. **108**, 938 (1957).

[15] D. P. Craig, J. Chem. Soc. **1955**, 2302.

TABLE III. Convergence of dipole sums and integral sums (cm^{-1}).[a]

	Inequivalent molecules					Equivalent molecules				
R	I_{dd}	HU	Δ_{HU}	PA	Δ_{PA}	I_{dd}	HU	Δ_{HU}	PA	Δ_{PA}
					(a) p band					
					Spherical convergence					
20	24	−324	444	−156	216	−232	−1057	−103	−787	207
25	29	−302	447	−145	218	−204	−922	−98	−707	196
30	54	−177	447	−73	208	−220	−999	−101	−755	205
35	77	−66	451	−9	202	−260	−1197	−103	−867	215
40	98	39	451	52	193	−290	−1343	−107	−948	210
45	123	160	455	124	185	−309	−1437	−108	−1000	225
50	142	254	456	176	179	−324	−1508	−122	−1050	240
55	145	279	446	190	173	−328	−1527	−113	−1060	240
60	145	281	445	190	173	−328	−1528	−113	−1060	240
					Slab convergence					
No. of cells										
2	−125	−1072	447	−592	280	−167	−733	−100	−594	176
3	−26	−898		−490		−240	−841	−359	−660	60
4	−23	−553	438	−290	228	−235	−1084	−91	−801	211
5	31	−287	442	−135	208	−228	−1260	−120	−903	333
6	76	−68	448	−9	199	−308	−1410	−130	−989	219
7	117	127	458	113	180	−307	−1526		−1060	
8	148	279	445	190	180	−328	−1526	−114	−1060	240

	Inequivalent molecules			Equivalent molecules		
R	I_{dd}	HU	PA	I_{dd}	HU	PA
			(b) β band			
			Spherical convergence			
20	4560	5389	5433	1782	1848	1886
25	4210	4919	4960	1801	1883	1929
30	4845	5974	5819	1957	2098	2138
35	5514	6682	6735	2595	2967	3040
40	6080	7444	7501	3153	3723	3773
45	6500	8012	8074	3582	4303	4359
50	6940	8602	8662	3852	4668	4730
55	7142	8879	8940	4018	4892	4948
60	7240	9010	9075	4070	4962	5022
65	7281	9066	9136	4095	4999	5060
			Slab convergence			
No. of cells						
2	3159	3490	3540	1573	1614	1650
3	4745	4575	4615	2795	2149	2171
4	5175	6167	6217	2905	3447	3482
5	6045	7350	7408	3224	4312	4367
6	6669	8150	8243	3900	4751	4809
7	7090	8703	8769	3925	5005	5065
8	7281	9000	9136	4108	5005	5065

TABLE III (*Continued*)

	Inequivalent molecules			Equivalent molecules		
R	I_{dd}	HU	PA	I_{dd}	HU	PA
			(c) p–β mixing			
			Spherical convergence			
20	−343	−458	−447	−1076	−1782	−1584
25	−284	−312	−333	−1052	−1719	−1535
30	−327	−420	−417	−1047	−1708	−1528
35	−402	−608	−560	−1051	−1718	−1535
40	−469	−778	−695	−1071	−1774	−1580
45	−525	−921	−805	−1079	−1796	−1592
50	−559	−1006	−870	−1100	−1851	−1650
55	−576	−1051	−905	−1112	−1881	−1664
60	−584	−1071	−922	−1112	−1907	−1680
65	−584	−1083	−932	−1130	−1925	−1700
			Slab convergence			
No. of cells						
2	−630	−1201	−1020	−1144	−1947	−1712
3	−639	−875	−770	−1201	−1758	−1568
4	−521	−915	−812	−1100	−1834	−1629
5	−533	−990	−860	−1125	−1904	−1684
6	−563	−1040	−900	−1136	−1939	−1713
7	−572	−1086	−936	−1136	−1939	−1713
8	−591	−1086	−936	−1136	−1939	−1713

[a] I_{dd} is the dipole–dipole interaction sum. HU is the Huckel wavefunction interaction sum. PA is the Pariser wavefunction interaction sum. $\Delta_{\mathrm{HU}}=5\ I_{dd}-\mathrm{HU}$. $\Delta_{\mathrm{PA}}=2.5\ I_{dd}-\mathrm{PA}$.

far used is inadequate to explain the splitting in the α band of naphthalene.

V. ROLE OF CHARGE-TRANSFER STATES

Ion-pair states may be constructed by removing an electron from one molecule and placing it on another. In previous work we have studied the mixing of these states into the triplet states of naphthalene and anthracene[6a] and the mixing into the neutral singlet states of anthracene.[6b] Since the basic theory has been outlined in the above references, we merely point out the feature peculiar to the α band.

As before, the matrix elements between the various charge-transfer states $|\,i,j;\mp\,\rangle$ (where i is the position of the positive ion, j the position of the negative ion, and $\mp$ refer to the symmetry properties of the wavefunction) are expressed as sums of the following types of integrals:

$$B(i,j)=\langle\mathbf{R}_i\,|\,H\,|\,\mathbf{R}_i,\mathbf{R}_j\rangle-\langle\mathbf{R}_i\,|\,\mathbf{R}_i\mathbf{R}_j\rangle\langle\mathbf{R}_i\,|\,H\,|\,\mathbf{R}_j\rangle, \tag{16}$$

$$C(i,j)=\langle\mathbf{R}_i\,|\,H\,|\,\mathbf{R}_j\mathbf{R}_i\rangle-\langle\mathbf{R}_i\,|\,\mathbf{R}_j\mathbf{R}_i\rangle\langle\mathbf{R}_i\,|\,H\,|\,\mathbf{R}_i\rangle, \tag{17}$$

in which $|\,\mathbf{R}_i\rangle$ is a neutral excitation on Molecule i and $|\,\mathbf{R}_i,\mathbf{R}_j\rangle$ is an ion-pair state with positive ion at i and negative ion at j. Now, only near-neighbor interaction is important because of the extremely small overlap between molecular orbitals on different molecules and, moreover, only certain of the $|\,i,j;\mp\,\rangle$ have different mixing coefficients for the − and + states. The states of importance are then $|\,\mathbf{0},\boldsymbol{\tau};\mp\rangle$, $|\,\mathbf{0},\mathbf{c}+\boldsymbol{\tau};\mp\rangle$, $|\,\boldsymbol{\tau},\mathbf{0};\mp\rangle$, $|\,\mathbf{c}+\boldsymbol{\tau},\mathbf{0};\mp\rangle$, where $\boldsymbol{\tau}$ is the vector from a Type 1 molecule to a Type 2 molecule and $\mathbf{c}$ is the vector between Type 1 molecules along

TABLE IV. Long-range dipole–dipole interactions (cm⁻¹).

Long-range sums dipole–dipole	Equivalent molecules	Inequivalent molecules
p–p	−216	+344
β–β	+5760	+6110
p–β	−1253	−763

the **c** axis of the crystal. One may write

$$K_1^{\mp}=\langle \mathbf{0},\boldsymbol{\tau};\mp\,|\,\mathcal{H}\,|\,\alpha;\mp\rangle-\langle \mathbf{0},\boldsymbol{\tau};\mp\,|\,\alpha;\mp\rangle\langle\alpha\,|\,\mathcal{H}\,|\,\alpha\rangle, \tag{18}$$

$$K_2^{\mp}=\langle \boldsymbol{\tau},\mathbf{0};\mp\,|\,\mathcal{H}\,|\,\alpha;\mp\rangle-\langle \boldsymbol{\tau},\mathbf{0};\mp\,|\,\alpha;\mp\rangle\langle\alpha\,|\,\mathcal{H}\,|\,\alpha\rangle, \tag{19}$$

$$K_3^{\mp}=\langle \mathbf{0},\mathbf{c}+\boldsymbol{\tau};\mp\,|\,\mathcal{H}\,|\,\alpha;\mp\rangle-\langle \mathbf{0},\mathbf{c}+\boldsymbol{\tau};\mp\,|\,\alpha;\mp\rangle\langle\alpha\,|\,\mathcal{H}\,|\,\alpha\rangle, \tag{20}$$

$$K_4^{\mp}=\langle \mathbf{c}+\boldsymbol{\tau},\mathbf{0};\mp\,|\,\mathcal{H}\,|\,\alpha;\mp\rangle-\langle \mathbf{c}+\boldsymbol{\tau},\mathbf{0};\mp\,|\,\alpha;\mp\rangle\langle\alpha\,|\,\mathcal{H}\,|\,\alpha\rangle, \tag{21}$$

and we find, as before,

$$K_1^{\mp}=(1/\sqrt{2})\{B(\mathbf{0},\boldsymbol{\tau})+B(\boldsymbol{\tau},\mathbf{0})\mp C(\mathbf{0},\boldsymbol{\tau})\mp C(\boldsymbol{\tau},\mathbf{0})\}, \tag{22}$$

$$K_2^{\mp}=(1/\sqrt{2})\{C(\mathbf{0},\boldsymbol{\tau})+C(\boldsymbol{\tau},\mathbf{0})\mp B(\mathbf{0},\boldsymbol{\tau})\mp B(\boldsymbol{\tau},\mathbf{0})\}, \tag{23}$$

$$K_3^{\mp}=(1/\sqrt{2})\{B(\mathbf{0},\mathbf{c}+\boldsymbol{\tau})+B(\mathbf{c}+\boldsymbol{\tau},\mathbf{0})\mp C(\mathbf{0},\mathbf{c}+\boldsymbol{\tau})\mp C(\mathbf{c}+\boldsymbol{\tau},\mathbf{0})\}, \tag{24}$$

$$K_4^{\mp}=(1/\sqrt{2})\{C(\mathbf{0},\mathbf{c}+\boldsymbol{\tau})+C(\mathbf{c}+\boldsymbol{\tau},\mathbf{0})\mp B(\mathbf{0},\mathbf{c}+\boldsymbol{\tau})\mp B(\mathbf{c}+\boldsymbol{\tau},\mathbf{0})\}. \tag{25}$$

The first singlet state of naphthalene may be represented in the form

$$|\,\mathbf{R}_m^{\alpha}\rangle\equiv(1/\sqrt{2})\,|\,(\phi_m^{4-6}-\phi_m^{5-7})\phi_n^{0}\rangle, \tag{26}$$

and, therefore,

$$\langle\mathbf{R}_m^{\alpha}\,|\,\mathcal{H}\,|\,\mathbf{R}_m^{+}\mathbf{R}_n^{-}\rangle=(1/\sqrt{2})\{\langle\phi_m^{4-6}\phi_n^{0}\,|\,\mathcal{H}\,|\,\mathbf{R}_m^{+}\mathbf{R}_n^{-}\rangle-\langle\phi_m^{5-7}\phi_n^{0}\,|\,\mathcal{H}\,|\,\mathbf{R}_m^{+}\mathbf{R}_n^{-}\rangle\}, \tag{27}$$

$$\langle\mathbf{R}_m^{\alpha}\,|\,\mathbf{R}_m^{+}\mathbf{R}_n^{-}\rangle=(1/\sqrt{2})\{\langle\phi_m^{4-6}\phi_n^{0}\,|\,\mathbf{R}_m^{+}\mathbf{R}_n^{-}\rangle-\langle\phi_m^{5-7}\phi_n^{0}\,|\,\mathbf{R}_m^{+}\mathbf{R}_n^{-}\rangle\}. \tag{28}$$

Similar equations are found for the state represented by $|\,\mathbf{R}_m^{-}\mathbf{R}_n^{+}\rangle$. The $B(i,j)$ and $C(i,j)$ are then found to have the form

$$\begin{aligned}B^{\alpha}(m,n)\equiv{}&\langle\mathbf{R}_m^{\alpha}\,|\,\mathcal{H}\,|\,\mathbf{R}_m^{+}\mathbf{R}_n^{-}\rangle-\langle\mathbf{R}_m^{+}\mathbf{R}_n^{-}\,|\,\mathbf{R}_m^{\alpha}\rangle\langle\mathbf{R}_m^{\alpha}\,|\,\mathcal{H}\,|\,\mathbf{R}_m^{\alpha}\rangle\\ ={}&(1/\sqrt{2})\{\langle\phi_m^{4-6}\phi_n^{0}\,|\,\mathcal{H}\,|\,\mathbf{R}_m^{+}\mathbf{R}_n^{-}\rangle-[\langle\phi_m^{5-7}\phi_n^{0}\,|\,\mathcal{H}\,|\,\mathbf{R}_m^{+}\mathbf{R}_n^{-}\rangle-\langle\phi_m^{5-7}\phi_n^{0}\,|\,\mathbf{R}_m^{+}\mathbf{R}_n^{-}\rangle\\ &\times\langle\phi_m^{5-7}\phi_n^{0}\,|\,\mathcal{H}\,|\,\phi_m^{5-7}\phi_n^{0}\rangle]+\langle\phi_m^{5-7}\phi_n^{0}\,|\,\mathbf{R}_m^{+}\mathbf{R}_n^{-}\rangle\\ &\times[\tfrac{1}{2}\langle\phi_m^{4-6}\phi_n^{0}\,|\,\mathcal{H}\,|\,\phi_m^{4-6}\phi_n^{0}\rangle-\tfrac{1}{2}\langle\phi_m^{5-7}\phi_n^{0}\,|\,\mathcal{H}\,|\,\phi_m^{5-7}\phi_n^{0}\rangle-\langle\phi_m^{4-6}\phi_n^{0}\,|\,\mathcal{H}\,|\,\phi_m^{5-7}\phi_n^{0}\rangle]\}\end{aligned} \tag{29}$$

and

$$\begin{aligned}C^{\alpha}(m,n)\equiv{}&\langle\mathbf{R}_m^{\alpha}\,|\,\mathcal{H}\,|\,\mathbf{R}_m^{-}\mathbf{R}_n^{+}\rangle-\langle\mathbf{R}_m^{-}\mathbf{R}_n^{+}\,|\,\mathbf{R}_m^{\alpha}\rangle\langle\mathbf{R}_m^{\alpha}\,|\,\mathcal{H}\,|\,\mathbf{R}_m^{\alpha}\rangle\\ ={}&(1/\sqrt{2})\{\langle\phi_m^{4-6}\phi_n^{0}\,|\,\mathcal{H}\,|\,\mathbf{R}_m^{-}\mathbf{R}_n^{+}\rangle-\langle\mathbf{R}_m^{-}\mathbf{R}_n^{+}\,|\,\phi_m^{4-6}\phi_n^{0}\rangle\langle\phi_m^{4-6}\phi_n^{0}\,|\,\mathcal{H}\,|\,\phi_m^{4-6}\phi_n^{0}\rangle-\langle\phi_m^{5-7}\phi_n^{0}\,|\,\mathcal{H}\,|\,\mathbf{R}_m^{-}\mathbf{R}_n^{+}\rangle\\ &-\langle\mathbf{R}_m^{-}\mathbf{R}_n^{+}\,|\,\phi_m^{4-6}\phi_n^{0}\rangle[\tfrac{1}{2}\langle\phi_m^{5-7}\phi_n^{0}\,|\,\mathcal{H}\,|\,\phi_m^{5-7}\phi_n^{0}\rangle-\tfrac{1}{2}\langle\phi_m^{4-6}\phi_n^{0}\,|\,\mathcal{H}\,|\,\phi_m^{4-6}\phi_n^{0}\rangle-\langle\phi_m^{5-7}\phi_n^{0}\,|\,\mathcal{H}\,|\,\phi_n^{0}\phi_m^{4-6}\rangle]\}.\end{aligned} \tag{30}$$

Further breakdown of these terms into matrix elements involving molecular orbitals leads to the following relations (to order S^0):

$$\begin{aligned}&\langle\phi_m^{5-7}\phi_n^{0}\,|\,\mathcal{H}\,|\,\phi_n^{0}\phi_m^{5-7}\rangle-\langle\phi_m^{4-6}\phi_n^{0}\,|\,\mathcal{H}\,|\,\phi_m^{4-6}\phi_n^{0}\rangle\\ &\qquad=2[\langle u_m^{5}\,|\,V_n^{\mathrm{GMS}}\,|\,u_m^{5}\rangle-\langle u_m^{4}\,|\,V_n^{\mathrm{GMS}}\,|\,u_m^{4}\rangle+2\sum_{i=1}^{5}\langle u_n^{i}\,|\,J_m^{5}-J_m^{4}\,|\,u_n^{i}\rangle],\end{aligned} \tag{31}$$

$$\langle\phi_m^{4-6}\phi_n^{0}\,|\,\mathcal{H}\,|\,\phi_m^{5-7}\phi_n^{0}\rangle=2\langle u_m^{4}u_m^{6}\,|\,u_m^{5}u_m^{7}\rangle-\langle u_m^{5}u_m^{4}\,|\,u_m^{6}u_m^{7}\rangle, \tag{32}$$

and (to order S^1):

$$\begin{aligned}&\langle\phi_m^{5-7}\phi_n^{0}\,|\,\mathcal{H}\,|\,\mathbf{R}_m^{+}\mathbf{R}_n^{-}\rangle-\langle\phi_m^{5-7}\phi_n^{0}\,|\,\mathbf{R}_m^{+}\mathbf{R}_n^{-}\rangle\langle\phi_m^{5-7}\phi_n^{0}\,|\,\mathcal{H}\,|\,\phi_m^{5-7}\phi_n^{0}\rangle=\langle u_n^{6}\,|\,V_n^{\mathrm{GMS}}-\sum_{i=1}^{5}K_n^{i}+2K_m^{5}-J_m^{5}\,|\,u_m^{7}\rangle\\ &\quad-\langle u_n^{6}\,|\,u_m^{7}\rangle\langle u_m^{7}\,|\,2K_m^{5}-J_m^{5}\,|\,u_m^{7}\rangle-\sum_{i=1}^{5}\langle u_n^{6}\,|\,u_m^{i}\rangle\langle u_m^{i}\,|\,2K_m^{5}-J_m^{5}\,|\,u_m^{5}\rangle+\sum_{i=1}^{5}\langle u_n^{i}\,|\,u_m^{5}\rangle\langle u_n^{i}\,|\,J_m^{5}\,|\,u_n^{6}\rangle\\ &\qquad+\sum_{i=1}^{5}\sum_{j=1}^{4}\langle u_m^{j}\,|\,u_n^{i}\rangle\langle u_m^{j}u_m^{7}\,|\,u_n^{6}u_n^{i}\rangle-\sum_{i=1}^{5}\langle u_m^{5}\,|\,u_n^{i}\rangle\langle u_m^{5}u_m^{7}\,|\,u_n^{6}u_n^{1}\rangle,\end{aligned} \tag{33}$$

$$\begin{aligned}&\langle\phi_m^{4-6}\phi_n^{0}\,|\,\mathcal{H}\,|\,\mathbf{R}_m^{+}\mathbf{R}_n^{-}\rangle=2\langle u_m^{4}u_m^{6}\,|\,u_m^{5}u_n^{6}\rangle-\langle u_m^{5}u_m^{4}\,|\,u_m^{6}u_n^{6}\rangle+\sum_{i=1}^{5}\{\langle u_m^{6}\,|\,u_n^{i}\rangle\langle u_m^{4}u_m^{5}\,|\,u_n^{6}u_n^{i}\rangle\\ &\quad+\langle u_n^{6}\,|\,u_m^{i}\rangle\langle u_m^{4}u_m^{5}\,|\,u_m^{6}u_m^{i}\rangle-2\langle u_n^{6}\,|\,u_m^{i}\rangle\langle u_m^{6}u_m^{4}\,|\,u_m^{5}u_m^{i}\rangle+2\langle u_m^{5}\,|\,u_n^{i}\rangle\langle u_m^{6}u_m^{4}\,|\,u_n^{6}u_n^{i}\rangle\},\end{aligned} \tag{34}$$

$$\langle\phi_m{}^{4-6}\phi_n{}^0\,|\,\mathcal{H}\,|\,\mathbf{R}_m{}^-\mathbf{R}_n{}^+\rangle-\langle\phi_m{}^{4-6}\phi_n{}^0\,|\,\mathbf{R}_m{}^-\mathbf{R}_n{}^+\rangle\langle\phi_m{}^{4-6}\phi_n{}^0\,|\,\mathcal{H}\,|\,\phi_m{}^{4-6}\phi_n{}^0\rangle$$

$$=-\langle u_m{}^4\,|\,V_m{}^{\mathrm{GMS}}-\sum_{i=1}^{5}K_n{}^i-2K_m{}^6+J_m{}^6\,|\,u_n{}^5\rangle+\sum_{i=1}^{5}\{\langle u_n{}^i\,|\,u_m{}^4\rangle\langle u_n{}^5\,|\,J_m{}^6-J_m{}^4\,|\,u_n{}^i\rangle-\langle u_n{}^i\,|\,u_m{}^6\rangle\langle u_m{}^4u_m{}^6\,|\,u_n{}^5u_n{}^i\rangle\}$$

$$+\sum_{i=1,2,3,5}\langle u_n{}^5\,|\,u_m{}^i\rangle\langle u_m{}^4\,|\,J_m{}^6-K_m{}^6\,|\,u_m{}^i\rangle-\sum_{i=1,2,3,5,6}\langle u_n{}^5\,|\,u_m{}^i\rangle\langle u_m{}^4\,|\,J_n{}^5\,|\,u_m{}^i\rangle, \qquad (35)$$

$$\langle\phi_m{}^{5-7}\phi_n{}^0\,|\,\mathcal{H}\,|\,\mathbf{R}_m{}^-\mathbf{R}_m{}^+\rangle=2\langle u_m{}^5u_m{}^7\,|\,u_m{}^6u_n{}^5\rangle-\langle u_m{}^7u_m{}^6\,|\,u_m{}^5u_n{}^5\rangle-2\langle u_m{}^5\,|\,u_n{}^5\rangle\langle u_m{}^6\,|\,K_m{}^5\,|\,u_m{}^7\rangle$$

$$-\sum_{i=1}^{5}\{2\langle u_m{}^i\,|\,u_n{}^5\rangle\langle u_m{}^6u_m{}^i\,|\,u_m{}^5u_m{}^7\rangle-\langle u_n{}^5\,|\,u_m{}^i\rangle\langle u_m{}^5u_m{}^i\,|\,u_m{}^6u_m{}^7\rangle$$

$$+2\langle u_m{}^6\,|\,u_n{}^i\rangle\langle u_m{}^5u_m{}^7\,|\,u_n{}^5u_n{}^i\rangle-\langle u_m{}^5\,|\,u_n{}^i\rangle\langle u_m{}^6u_m{}^7\,|\,u_n{}^5u_n{}^i\rangle\}. \qquad (36)$$

These integrals were evaluated numerically, and are displayed in Tables V and VI.

The energies of the charge-transfer states in naphthalene were approximated using classical considerations and have been reported elsewhere.[5a] The states $|\,\mathbf{0},\boldsymbol{\tau};\pm\rangle$ and $|\,\boldsymbol{\tau},\mathbf{0};\pm\rangle$ are estimated to be at 4.4±0.5 eV from the ground state, while the states $|\,\mathbf{0},\mathbf{c}+\boldsymbol{\tau};\pm\rangle$ and $|\,\mathbf{c}+\boldsymbol{\tau},\mathbf{0};\pm\rangle$ are estimated to be 5.2±0.5 eV from the ground state. These estimates place the charge-transfer states close to the α band (4.0 eV). Therefore, instead of using perturbation theory, we have diagonalized the 7×7 energy matrices for the A_u and B_u symmetries. In this calculation the energy of the charge-transfer state was used as a variable, always keeping the second pair of states 0.8 eV above the first pair of states.

VI. ION-PAIR–NEUTRAL EXCITON MIXING RESULTS

The results of the calculation of the matrix elements for mixing of charge-transfer states into the α and p exciton states are given in Tables V and VI, while the results of the diagonalization of the energy matrix and the percentages of α and p character in the relevant states are given in Fig. 1 and Table VII. The numerical results for the α, p, and β bands, assuming the lowest charge-transfer states to be 500 cm^{-1} above the α band, are given in Table VIII. The experimental results are also given in Table VIII.

We now calculate the polarization ratio of the α band from our results. The oscillator strength of the α band in the free molecule is approximately 0.001, but about 90% is vibronically induced, so that the true oscillator strength is approximately 0.0001. Using the values listed in Table I and the transition dipole calculated from them, the polarization ratio is easily obtained from

$$P^f(\mathbf{b}/\mathbf{a})$$
$$=\{[\sum_i c_{fi}{}^-(\mathbf{p}_1{}^f-\mathbf{p}_2{}^f)\cdot\mathbf{b}]/[\sum_i c_{fi}{}^+(\mathbf{p}_1{}^f+\mathbf{p}_2{}^f)\cdot\mathbf{a}]\}^2, \qquad (37)$$

where the $c_{fi}{}^\pm$ are the coefficients of the ith state in the wavefunction of the fth state, and $\mathbf{p}_1{}^f$ is the transition moment of the ith state on one set of molecules. The results of this calculation are given in Table IX. The polarization ratio is extremely sensitive to the actual transition moment of the α band and, in fact,

TABLE V. Charge-transfer state matrix elements for the naphthalene p band (in electron volts).

$B(\mathbf{0},\boldsymbol{\tau})=1.09\times10^{-2}$
$B(\boldsymbol{\tau},\mathbf{0})=1.16\times10^{-2}$
$B(\mathbf{0},\mathbf{c}+\boldsymbol{\tau})=1.20\times10^{-2}$
$B(\mathbf{c}+\boldsymbol{\tau},\mathbf{0})=1.04\times10^{-2}$
$C(\mathbf{0},\boldsymbol{\tau})=1.29\times10^{-2}$
$C(\boldsymbol{\tau},\mathbf{0})=1.43\times10^{-2}$
$C(\mathbf{0},\mathbf{c}+\boldsymbol{\tau})=-0.756\times10^{-2}$
$C(\mathbf{c}+\boldsymbol{\tau},\mathbf{0})=-0.738\times10^{-2}$

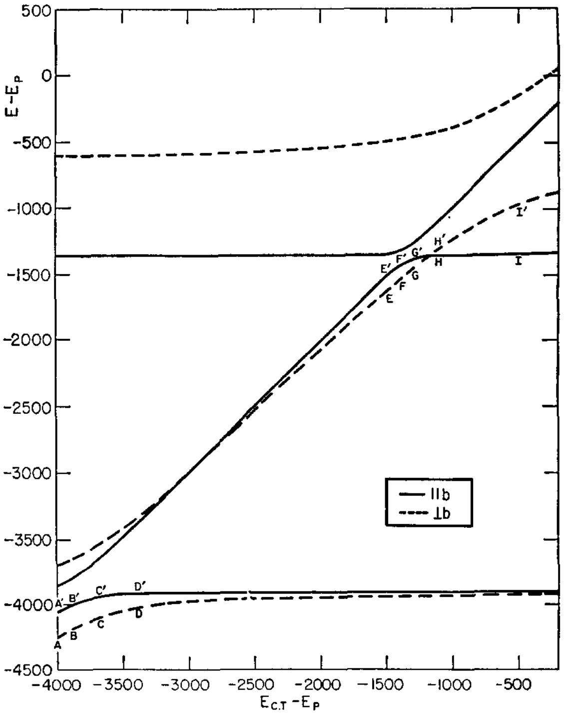

FIG. 1. Energy of crystal states relative to the p state vs energy of the charge-transfer state relative to the p state in naphthalene. The percentages of α character and of p character in the states are given in Table VII (negative sign when coefficient is negative).

TABLE VI. Matrix elements for charge-transfer state—α band in naphthalene (units in 10^{-2} eV).

	$(\mathbf{0}, \boldsymbol{\tau})$	$(\mathbf{0}, \mathbf{c}+\boldsymbol{\tau})$	$(\boldsymbol{\tau}, \mathbf{0})$	$(\mathbf{c}+\boldsymbol{\tau}, \mathbf{0})$
1. $\langle\phi_m^{5-7}\phi_n^0 \mid \mathcal{H} \mid \mathbf{R}_m^+\mathbf{R}_n^-\rangle - \langle\phi_m^{5-7}\phi_n^0 \mid \mathbf{R}_m^+\mathbf{R}_n^-\rangle\langle\phi_m^{5-7}\phi_n^0 \mid \mathcal{H} \mid \phi_m^{5-7}\phi_n^0\rangle$	−1.19	1.379	3.01	−0.78
2. $\langle\phi_m^{4-6}\phi_n^0 \mid \mathcal{H} \mid \mathbf{R}_m^+\mathbf{R}_n^-\rangle$	−0.081	−0.252	−0.446	0.134
3. $\langle\phi_m^{4-6}\phi_n^0 \mid \mathcal{H} \mid \mathbf{R}_m^-\mathbf{R}_n^+\rangle - \langle\phi_m^{4-6}\phi_n^0 \mid \mathbf{R}_m^-\mathbf{R}_n^+\rangle\langle\phi_m^{4-6}\phi_n^0 \mid \mathcal{H} \mid \phi_m^{4-6}\phi_n^0\rangle$	2.06	0.332	−3.05	1.55
4. $\langle\phi_m^{5-7}\phi_n^0 \mid \mathcal{H} \mid \mathbf{R}_m^-\mathbf{R}_n^+\rangle$	−1.26	−0.555	1.63	0.640
5. $2\sum_{i=1}^{5}\langle u_n^i \mid J_m^5 - J_m^4 \mid u_n^i\rangle$	2(28.2)	2(0.5)	2(−4.6)	2(−21.8)
6. $2\langle u_m^4u_m^6 \mid u_m^5u_m^7\rangle - \langle u_m^5u_m^4 \mid u_m^6u_m^7\rangle$	138.7	138.7	138.7	138.7
7. $\langle\mathbf{R}_m^-\mathbf{R}_n^+ \mid \phi_m^{4-6}\phi_n^0\rangle$	−0.0064	−0.0022	0.0102	0.0013
8. $\langle\mathbf{R}_m^+\mathbf{R}_n^- \mid \phi_m^{5-7}\phi_n^0\rangle$	−0.0019	0.0007	0.0034	−0.0002

$B(\mathbf{0}, \boldsymbol{\tau}) = 1.265/\sqrt{2}$ $\quad B(\boldsymbol{\tau}, \mathbf{0}) = -3.96/\sqrt{2}$

$B(\mathbf{0}, \mathbf{c}+\boldsymbol{\tau}) = -1.73/\sqrt{2}$ $\quad B(\mathbf{c}+\boldsymbol{\tau}, \mathbf{0}) = 0.960/\sqrt{2}$

$C(\mathbf{0}, \boldsymbol{\tau}) = 2.07/\sqrt{2}$ $\quad C(\boldsymbol{\tau}, \mathbf{0}) = -3.55/\sqrt{2}$

$C(\mathbf{0}, \mathbf{c}+\boldsymbol{\tau}) = 1.20/\sqrt{2}$ $\quad C(\mathbf{c}+\boldsymbol{\tau}, \mathbf{0}) = 1.03/\sqrt{2}$

agreement between theory and experiment can be obtained by assuming that the oscillator strength represents 80% vibronically induced character and 20% "true" electronic character. As before,[6b] we have also carried through the analysis including the higher π-electron states listed in Table I. The results are not much different from those obtained with these states omitted (see Table IX).

Note added in proof: In the preceding we have described the diagonalization of the Hamiltonian in the strong coupling limit. To demonstrate that the results do not depend on the assumption of strong coupling, we have also carried out a sample diagonalization in the weak coupling limit. The results are as follows. When the ion-pair state is 300 cm⁻¹ above the neutral exciton state, the predicted Davydov splittings are 90 cm⁻¹ in the 0–0 band and 10 cm⁻¹ in the 0–1 band. The corresponding values of $P^f(\mathbf{b}/\mathbf{a})$ are 25 and 1. We therefore conclude that the mixing of ion-pair and neutral exciton states can account for the naphthalene spectrum in either the weak coupling or strong coupling limits.

TABLE VII. The α and p character of the crystal states.

State	α Character (%)	p Character (%)
A	51.8	1.0
B	71.5	0.7
C	93.3	0.2
D	98.5	−0.1
E	−3.6	24.5
F	−3.0	51.1
G	−1.3	89.1
H	−0.0	98.3
I	−0.0	99.2
A'	60.9	−8.5
B'	67.6	−8.0
C'	79.7	−6.7
D'	90.5	−4.7
E'	10.9	37.2
F'	10.4	40.2
G'	9.9	43.4
H'	8.8	51.0
I'	5.6	77.2

In the vapor phase, the first singlet state (α) of naphthalene has an interesting spectrum.[10] There are three vibrational progressions observed: one is entirely an a_g vibration, while the other two are a_g progressions built on a b_{1g} vibration. Since the lowest state of naphthalene is a B_{3u} state, the addition of a b_{1g} vibration transforms the total wavefunction to have symmetry b_{2u}, which symmetry is the same as that of the second excited state, thereby permitting vibronic mixing of the p (B_{2u}) state into the α (B_{3u}) state. We write the ground vibronic function of the α state (to zero order) as

$$\Phi^\alpha = \phi_{\text{elec}}^\alpha \prod_\sigma \chi_\sigma^{(0)}, \tag{38}$$

where the $\chi_\sigma^{(i)}$ are vibrational wavefunctions of the σth symmetry (normal) coordinate with i quanta. Thus the progression built solely on a_g vibrations may be derived from

$$\Phi_{a_g}^\alpha = \phi_{\text{elec}}^\alpha \chi_{a_g}^{(i)} \prod_\sigma{}' \chi_\sigma^{(0)}, \tag{39}$$

where only *one* normal coordinate is assumed to have changed from the ground-state vibronic wavefunction. Actually, of course, almost all the normal coordinates of the excited state are slightly changed from the ground state. This will reduce the calculated splittings, but we assume that only one normal mode changes substantially and that the effect of this will mask the effects of the other vibrations. The progression built

TABLE VIII. Calculated splittings and observed splittings for naphthalene.

Electronic state	Energy of A_u state ($\parallel$ **b**) relative to gas value (cm^{-1})	Energy of B_u state ($\perp$**b**) relative to vapor value (cm^{-1})	Δ[a] (cm^{-1})	Δ_{exptl} (cm^{-1})
	Charge-transfer state 500 cm^{-1} above α band			
α	-20	-130	-110	-186[b]
p	-1470	-630	840	>320[c]
β	-4400	32 000	36 400	···
	Charge-transfer state 1000 cm^{-1} above α band			
α	-12	-75	-63	
p	-1460	-620	840	
β	-4400	32 000	36 400	

[a] $\Delta = E_{B_u} - E_{A_u}$.

[b] D. P. Craig and H. C. Wolf, J. Chem. Phys. **41**, 2057 (1964). This is the total splitting in the entire vibronic band. The splitting in the 0–0 band is 150 cm^{-1} and in the 0–1 band 36 cm^{-1} for the progression that is entirely built on a_g vibrations.

[c] D. S. McClure and O. Schnepp, J. Chem. Phys. **23**, 1575 (1955). The number quoted is the splitting in the 0–0 band.

on a b_{1g} vibration may be obtained from the wavefunction

$$\Phi_{b_{1g}}{}^{\alpha} = \phi_{\text{elec}}{}^{\alpha} \chi_{b_{1g}}{}^{(1)} \chi_{a_g}{}^{(i)} \prod_{\sigma}{}'' \chi_{\sigma}{}^{(0)} + c\phi_{\text{elec}}{}^{p} \chi_{a_g}{}^{(i)} \prod_{\sigma}{}' \chi_{\sigma}{}^{(0)}, \quad (40)$$

where c is the mixing coefficient and may be estimated from the vapor spectrum. The reader should note that the charge-transfer state will mix into both wavefunctions. If we consider the mixing of the charge-transfer states into the $\Phi^{\alpha}{}_{(b_{3g})}$ state, we find for the B and C matrix elements (now including vibrational effects and denoted B_{vibr}, etc.)

$$B_{\text{vibr}} = B_{\text{elec}} \times \langle \chi_{b_{1g}}{}^{(1)} \chi_{a_g}{}^{(i)} \prod{}'' \chi_{\sigma}{}^{(0)} \mid \chi_{\text{total}}{}^{+} \rangle \times \langle \prod \chi_{\sigma}{}^{(0)} \mid \chi_{\text{total}}{}^{-} \rangle, \quad (41)$$

$$C_{\text{vibr}} = C_{\text{elec}} \langle \chi_{b_{1g}}{}^{(1)} \chi_{a_g}{}^{(i)} \prod{}'' \chi_{\sigma}{}^{(0)} \mid \chi_{\text{total}}{}^{-} \rangle \times \langle \prod \chi_{\sigma}{}^{(0)} \mid \chi_{\text{total}}{}^{+} \rangle. \quad (42)$$

Now if the b_{1g} vibration is on the positive ion, then $C_{\text{vibr}} = 0$ (since $\chi_{\text{total}}{}^{\text{ground}}$ is an a_g function), similarly if the b_{1g} vibration is on the negative ion then $B_{\text{vibr}} = 0$. Thus the mixing of the crystal charge-transfer states of A_u and B_u symmetry into the neutral exciton states of corresponding symmetry will be identical (or at most differ in sign), and thus the Davydov splitting in the transitions built on a b_{1g} vibration will *not* be affected by presence of charge-transfer states. The magnitude of the splitting in these bands (built on a false origin) can be estimated in the following manner: The coefficient of vibronic mixing may be estimated from the ratio of oscillator strengths of the α and p bands, i.e., $c \approx (f_{\alpha} \mid f_p)^{\frac{1}{2}}$; since the oscillator strength of the α transition is 80% to 90% vibronically induced, we find $c \approx 1/10$. Therefore, the entire Davydov splitting in the bands built on a b_{1g} vibration will be given by $c^2 \times p$ band splitting, which is 8 cm^{-1}. In the different vibrational components, we should then have a splitting of ~ 2 cm^{-1}.

We conclude that the progression built on the b_{1g} vibrations should have a much smaller Davydov splitting than the progression built on the a_g vibration, in agreement with the experimental data.

The above argument and the agreement it gives with experiment rest on the assumption that the charge-transfer state lies very close to the α state and above it. There is no

TABLE IX. Calculated and observed polarization ratios for naphthalene transitions.

State	Charge transfer 500 cm^{-1} above α[a]			Charge transfer 1000 cm^{-1} above α[a]			Oriented gas	Exptl.
	a	b	c	a	b	c		
α	1.0	40.	25.	2.0	2.4	2.5	0.25	>10[b]
p	4.0	4.0	4.0	4.0	4.0	4.0	7.7	3.0
β	0.6	0.7	0.6	0.6	0.6	0.6	0.25	···

[a] a: α state is 90% vibronically induced, all π states included; b: α state is 80% vibronically induced, all π states included; c: α state is 80% vibronically induced, only p and β included.

[b] In the 0–0 band; in the 0–1 band the polarization ratio is $\backsim$ 4.

evidence supporting this assumption. Crude estimates of the energy of the charge-transfer state put it in the vicinity of the α band in naphthalene, but it is impossible to go further at present.

In the analysis presented above, the energy of the charge-transfer state was assumed to be a constant, independent of the nature of the vibrational state of the ions. We believe that the energy of the charge-transfer state should depend on the vibrational state of the ions. A dependence of this sort could arise as follows:

(a) Although both the ionization potential of the molecule and the electron affinity of the molecule are altered in a parallel fashion when the molecule is in an excited vibrational state, they may be altered by slightly different amounts, leading to a possible change in $I-A$ of up to several hundred cm^{-1} between the nonvibrating and vibrating molecules.

(b) Because all molecular vibrations are somewhat anharmonic, the mean atomic positions in the vibrating molecule differ slightly from those in the nonvibrating molecule. Examination of the various contributions to the energy of the charge-transfer state leads to the calculation that a 1% change in bond lengths (and hence intermolecular distance) could lead to a change in energy of up to several hundred cm^{-1}.

(c) There are other miscellaneous small changes in molecular parameters between the nonvibrating and vibrating molecules which can lead to energy differences of a few hundred cm^{-1} in the positions of the charge-transfer bands of the nonvibrating and vibrating molecules. For example, the intensity of the α band arises largely from the mixing in the p band by a b_{1g} vibration. This suggests that the polarizability of the molecule is slightly dependent on the vibrational state of the molecule.

We conclude from the analysis presented in the paper that a plausible interpretation can be given of the several sdlittings (large and small) and of the polarization ratios observed in the spectrum of crystalline naphthalene. Our treatment has been parametric in the sense that uncertainties in the location of the charge-transfer state and in the exact amount of vibronic character in the lowest free-molecule transition make a complete calculation of the spectrum impossible at the present time. The important question of whether the observed spectrum is better described in terms of octopole–octopole interactions, or through the use of ion-pair exciton state mixing can be definitely settled only by further experimentation.

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APPENDIX I: CONSEQUENCES OF THE PAIRING OF π ORBITALS

In the Hückel and SCF approximations, the α bands of benzene and naphthalene are formed from orbitals that are paired. To the first order in perturbation theory, this pairing leads to a vanishing of the Davydov splitting. To prove this statement, we start with the general matrix element

$$\langle(\phi_m{}^{4-6}-\phi_m{}^{5-7})\phi_n{}^0\mid V_{mn}\mid(\phi_n{}^{4-6}-\phi_n{}^{5-7})\phi_m{}^0\rangle$$

$$=\langle u_m{}^6u_m{}^4\mid V_{nm}\mid u_n{}^6u_n{}^4\rangle+\langle u_m{}^5u_m{}^7\mid V_{nm}\mid u_n{}^5u_n{}^7\rangle$$

$$-\langle u_m{}^6u_m{}^4\mid V_{nm}\mid u_n{}^5u_n{}^7\rangle-\langle u_m{}^5u_m{}^7\mid V_{nm}\mid u_n{}^4u_n{}^6\rangle \quad \text{(A1)}$$

in the standard notation. The matrix element (A1) can be written in the form

$$\sum_{i,j,k,l}\langle\omega_i{}^m(1)\omega_j{}^m(1)\mid r_{12}{}^{-1}\mid\omega_k{}^n(2)\omega_l{}^n(2)\rangle$$

$$\times\{c_{6i}c_{4j}c_{6k}c_{4l}+c_{5i}c_{7j}c_{5k}c_{7l}-c_{6i}c_{4j}c_{5k}c_{7l}-c_{5i}c_{7j}c_{4l}c_{6k}\}. \quad \text{(A2)}$$

For the case of Coulomb interactions, the matrix element of V_{mn} over the orbitals ω_i is $\langle ij\mid kl\rangle$, whereas for the exchange interactions it is $\langle il\mid kj\rangle$, again in the standard notation. For the particular case of three-center terms, $i=j$ or $l=k$. Now, for the paired orbitals under consideration

$$c_{6i}c_{4i}=c_{5i}c_{7i}, \quad \text{(A3)}$$

whereupon all two-center and three-center terms vanish. For crystal-field mixing (off-diagonal terms), all two-center integrals vanish, using the same reasoning as outlined above, and one-half of the three-center integrals also vanish. Thus, as indicated, the effect of crystal-field mixing is small for this state. Our conclusions are not affected by the use of configuration-interaction wavefunctions in place of Hückel functions.

APPENDIX II: GEOMETRY OF THE NAPHTHALENE CRYSTAL

Naphthalene crystallizes in the monoclinic system with space group $C_{2h}{}^5$ $(P2_1/a)$ with two molecules per unit cell.[9] Denoting the long axis by L and the short axis by M and the axis perpendicular to the plane by

N, then the axes of one set of translationally equivalent molecules have the direction cosines in the **a**, **b**, **c** (crystal) system of axes

$$L_1=\begin{pmatrix}-0.435\\-0.223\\+0.875\end{pmatrix},\quad M_1=\begin{pmatrix}-0.322\\-0.870\\-0.371\end{pmatrix},$$

$$N_1=\begin{pmatrix}+0.840\\-0.443\\+0.331\end{pmatrix}.$$

The second set of translationally equivalent molecules may be found by reflection in a plane perpendicular to the b axis of the crystal:

$$L_2=\begin{pmatrix}-0.435\\+0.223\\+0.875\end{pmatrix},\quad M_2=\begin{pmatrix}-0.322\\+0.870\\-0.371\end{pmatrix},$$

$$N_2=\begin{pmatrix}+0.840\\+0.443\\+0.331\end{pmatrix}.$$

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Closed Form of Infinite Series Used in Some Atomic Integrals Containing $\mathbf{r}_{12}$, $\mathbf{r}_{13}$, and $\mathbf{r}_{23}$

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In an excellent scheme recently developed for evaluating the integral

$$\int f_1(r_1)f_2(r_2)f_3(r_3)g_1(r_{12})g_2(r_{23})g_3(r_{13})\,(dv)$$

met in the calculation of correlated atomic wavefunctions, certain functions required in the computational scheme had to be evaluated by an infinite series expansion. As many as 40 terms may be needed in each of the three required infinite summations to get eight significant figures. We give a closed form expression for such functions avoiding all infinite sums. The new result is very compact and avoids the previous difficulty of numerical stability.

INTRODUCTION

An excellent scheme for evaluating certain atomic integrals that have an explicit dependence on three interelectronic coordinates, e.g., r_{12}, r_{13}, and r_{23}, in the integrand has been described by Öhrn and Nordling.[1] This is the most difficult integral in the calculation of correlated atomic wavefunctions for it contains the three interelectronic coordinates in a nonseparable way:

$$\int f_1(\mathbf{r}_1)f_2(\mathbf{r}_2)f_3(\mathbf{r}_3)g_1(r_{12})g_2(r_{23})g_3(r_{13})\,(dv). \qquad (1)$$

This integral is expressed[1] as a rapidly convergent infinite series of other integrals. With the radial parts of the functions $f_i(\mathbf{r}_i)$ restricted to Slater-type orbitals and $g(r_{ij})$ to powers of the interelectronic distance, these latter integrals are expressed in terms of auxiliary functions V and W.[1] For certain arguments of these auxiliary functions their computational scheme includes three infinite sums requiring as many as 40 to 60 terms each to get eight significant figures in the answer. We remove this difficulty by giving a closed-form expression for such terms. This avoids problems of numerical stability. With a very special choice of the arguments of our functions we have found a known expression for a special case of a hypergeometric function that comes up in the study of multiple correlation coefficients in statistics.[2] Our results agree with available tabulations throughout.

THEORY AND RESULTS

To put our results in context we first need some of Öhrn and Nordling's results. The simplest nontrivial type of integral [Eq. (1)] can be written, after decomposition of products of spherical harmonics, as a finite sum of integrals, $I_{hij}{}^{tuv}$

$$I_{hij}{}^{tuv}=(4\pi)^{-\frac{3}{2}}\int f_1(r_1)f_2(r_2)f_3(r_3)\,Y_h{}^t(1)\,Y_j{}^v(2)\,Y_i{}^u(3)$$
$$\times g_1(r_{12})g_2(r_{23})g_3(r_{13})\,(dv). \qquad (2)$$

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[1] Y. Öhrn and J. Nordling, J. Chem. Phys. **39**, 1864 (1963).

[2] Editorial appendix to a paper by J. Wishart, Biometrika **22**, 362 (1930).