

## Reexamination of the Theoretical Interpretations of the Spectra of Crystalline Benzene and Naphthalene

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In the Column 3 of Table VI are given the TPRC recommended values.<sup>16</sup> These are always smaller than the currently measured values by amounts varying between 1.0 and 5.6%. As the trend and magnitude would appear alarming a brief discussion will be presented. These values are generated<sup>16</sup> by fitting a cubic polynomial function of temperature to the data of Kannuliuk and Carman,<sup>17</sup> which was used to produce values up to 500°K. Values between 500° and 1000°K were obtained from a smooth curve drawn to pass through the data of Collins and Menard<sup>18</sup> at 1000°K and again above 1000°K values were obtained from an equation given by these workers<sup>18</sup> as a fit of their data on shock tube. It is thus to be noted that the recommendations are essentially based on the two sets of data<sup>17,18</sup> and the latter<sup>18</sup> are likely to be uncertain by even more than 10%. In view of these facts one cannot attach much importance to the disagreement seen between our measured values and TPRC recommended set.

The complete absence of experimental  $\lambda$  data for

temperatures above 800°K by an established technique is to be noticed with concern. The shock-tube measurements, though valuable, are usually contaminated by large uncertainties. The fact that one has to assume *a priori* the form for the temperature dependence of thermal conductivity to interpret the shock-tube data has been puzzling. At least for this reason it will be preferable to develop a reliable method to measure  $\lambda$  up to 3000°K or so. This will provide enough of the overlap for temperature to enable an assessment of the shock-tube technique. In our opinion, the column method has this potentiality because it can operate for temperatures between 300° and 3000°K. This will also permit to check even the column method against measurements from established techniques. Our experiments extend only up to 1500°K because of the use of the platinum wire. Nevertheless the effort brings to light the prospect of the technique and the urgent need for its careful further development at higher temperatures. Indeed the Russians<sup>2</sup> have extended their measurements up to 2400°K.

<sup>16</sup> Purdue University Thermophysical Properties Research Center Data Book, Y. S. Touloukian, Ed., December 1966, Vol. 2, Chap. 1.

<sup>17</sup> W. G. Kannuliuk and E. H. Carman, Proc. Phys. Soc. (London) **65B**, 701 (1952).

<sup>18</sup> D. J. Collins and W. A. Menard, J. Heat Transfer **88C**, 52 (1966).

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## Re-examination of the Theoretical Interpretations of the Spectra of Crystalline Benzene and Naphthalene

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In order to explain the crystal spectra of naphthalene and benzene, a theory is presented in which the combined effects of charge delocalization and interactions via transition octupole moment coupling are important. Charge delocalization, achieved by means of configuration interaction of the lowest crystal charge-transfer states with the lowest singlet neutral exciton state, is predicted to explain most of the environmental shift and to contribute approximately one-third of the Davydov splitting. The transition-octupole-transition-octupole interactions, on the other hand, are predicted to induce the remaining two-thirds of the splitting and to determine the polarization ratios for the different Davydov components. Either of the two interactions alone shows drawbacks if it is used to explain the spectra, but when combined, the two interactions lead to a theory in good agreement with experiment.

### I. INTRODUCTION

In molecular crystals of organic compounds the intermolecular interactions are very much smaller than the intramolecular interactions. When this observation is incorporated into the description of the excited states

of the crystal, there results a strong correlation between the states of the crystal and those of the free molecule. In the Frenkel limit the nature of this correlation may be succinctly summarized by the statement that the crystal states have unique parentage in free-molecule states. Furthermore, because the transition dipole moments corresponding to excitation of the lowest singlet

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states of benzene and naphthalene are very small, a description of the observed Davydov splittings and polarization ratios requires that the interaction between molecules in the excited crystal arise from transition-multipole-transition-multipole coupling, of which the octupole-octupole terms are presumed to be dominant. However, the transition octupole moments required to fit the experimental data for naphthalene and for benzene are much larger than those predicted by molecular orbital theory. Because the molecular wavefunctions presently available for conjugated aromatic molecules are only approximate, the cited disagreement between calculated and fitted transition octupole moments may not really signal a serious discrepancy between theory and experiment. Nevertheless, the disagreement does suggest that extension of the tight-binding Frenkel model to include charge delocalization into the excited states of the crystal<sup>1</sup> might lead to an interpretation in agreement with experimental data and to a reduction in the size of the required transition octupole moments. A further reason for examining charge delocalization arises from the observation that passage from the Frenkel to the Wannier limits must occur eventually as higher excited states are considered and overlap increases. Previous papers from this laboratory<sup>1</sup> have considered the configuration interaction between neutral (i.e., Frenkel) exciton states and ion-pair (charge-transfer, CT) exciton states at  $\mathbf{k}=0$ . It has been shown that the spectra of naphthalene and benzene can be fitted if the charge-transfer level is close to the neutral exciton level. Recent experiments have located the charge-transfer levels of anthracene and naphthalene<sup>2</sup>; they are close to the positions predicted from a classical analysis. Using these data it now appears that the charge-transfer and neutral exciton levels are sufficiently separated that configuration interaction between these levels can account for only a portion of the total Davydov splitting and polarization ratios (the reader is referred to Secs. III and IV for details). Indeed, with the new data the interaction resulting from mixing of CT and neutral states is predicted to contribute approximately one-third of the Davydov splitting, most of the environmental shift, and to have a negligible effect on the polarization ratios. By difference we infer that the octupole-octupole coupling determines the polarization ratio and leads to about two-thirds of the Davydov splitting. The octupole moments required are, of course, smaller than those deduced by Craig and Walmsley.<sup>3</sup>

In order to make a complete comparison between the octupole-octupole coupling and the ion-pair-neutral-state configuration-interaction descriptions, in this paper we examine the effect of ion-pair crystal states

on the neutral exciton states in the  $\mathbf{k}\neq 0$  portion of the Brillouin zone. Our analysis is used to describe the exciton band structure of the lowest excited singlet states of crystalline benzene and naphthalene. In the Frenkel limit these states have parentage in the  ${}^1B_{2u}$  state of free benzene<sup>4</sup> and in the  ${}^1B_{3u}$  state of free naphthalene,<sup>5</sup> respectively.

## II. REVIEW OF EXPERIMENTAL DATA

The following facts must be considered in any interpretation of the crystal spectra of naphthalene and benzene.

### A. Singlet Electronic States of the Free Molecules

The lowest electronic state ( $\alpha$ ) in naphthalene is of  ${}^1B_{3u}$  symmetry, and the pure electronic transition (polarized along the long molecular axis) is formally allowed but very weak ( $f_{el}\sim 10^{-4}$ ). The symmetric progression of  $722\text{ cm}^{-1}$  built upon the pure electronic transition is characterized by Franck-Condon vibrational overlap integrals of 0.8 for the 0-0 transition and 0.2 for the 0-1 transition.<sup>6</sup> The major source of intensity ( $f\sim 10^{-3}$ ) in this spectral region originates from a short-axis-polarized vibronically induced transition superimposed on false origins corresponding to the nontotally symmetrical vibrations of  $433$  and  $905\text{ cm}^{-1}$ .<sup>5,6</sup>

The pure electronic transition to the lowest singlet  ${}^1B_{2u}$  in the isolated benzene molecule is symmetry forbidden; the observed intensity arises from vibronic coupling by an  $e_{2g}$  vibration ( $520\text{ cm}^{-1}$ ) and a progression of totally symmetric vibrations of  $923\text{ cm}^{-1}$  superimposed on the false origin. The true (forbidden) electronic origin is located at  $38\,089\text{ cm}^{-1}$ , as inferred from the fluorescence spectrum.<sup>5</sup> The Franck-Condon vibrational overlap integrals, obtained from the vapor spectrum, are 0.19 for the 0-0 transition, 0.28 for the 0-1, 0.25 for the 0-2, 0.17 for the 0-3, and 0.09 for the 0-4 transitions.<sup>7</sup>

### B. Crystal Energy Levels

The pure electronic transition in crystalline naphthalene consists of two Davydov components, with a total splitting of  $186\text{ cm}^{-1}$ .<sup>1,8</sup> The splitting in the 0-0 vibronic band is  $150\text{ cm}^{-1}$ ,<sup>8</sup> this result being consistent with the predictions of weak-coupling theory. The  $a$ -polarized component is located at lower energy, the polarization ratio being  $P(a/b)\sim 1/100$ .<sup>5</sup> The center of gravity of the two Davydov components in the 0-0 band is red shifted by  $-470\text{ cm}^{-1}$  relative to the

<sup>4</sup> V. L. Broude, Sov. Phys.—Usp. **4**, 584 (1962) [Usp. Fiz. Nauk **74**, 577 (1961)].

<sup>5</sup> V. L. Broude, Opt. Spectry. Suppl. **2**, 25 (1967).

<sup>6</sup> D. P. Craig, Phys. Chem. Org. Solid State **1**, 585 (1963).

<sup>7</sup> T. Thirunamachandran, thesis, University College, London, 1961.

<sup>8</sup> D. P. Craig, L. E. Lyons, and J. R. Walsh, Mol. Phys. **4**, 97 (1961).

<sup>1</sup> R. Silbey, J. Jortner, M. T. Vala, Jr., and S. A. Rice, J. Chem. Phys. **42**, 2948 (1965); R. Silbey, S. A. Rice, and J. Jortner, J. Chem. Phys. **43**, 3336 (1965).

<sup>2</sup> N. Geacintov and M. Pope, J. Chem. Phys. **45**, 3884 (1966).

<sup>3</sup> D. P. Craig and S. H. Walmsley, Mol. Phys. **4**, 113 (1961).

TABLE I. Naphthalene ( $\mathbf{k}=0$ ) (energies in  $\text{cm}^{-1}$ ).

Crystal <sup>a</sup> spectrum with polariza- tion in parentheses	Average over Davydov manifold	Assignment <sup>b</sup>	Vapor <sup>a</sup> analog	Vapor-to- crystal shift	$D$	$I_{00}^{\text{c}}$
31 475(a)		0-0				
31 626(b)	31 550	( $A_g \rightarrow B_{3u}$ )	32 020	-470	-478	8
31 960(b)		0+438				
31 961(a)	31 960	( $A_g \rightarrow B_{3u} \cdot b_{1g}$ )	32 458	-498	-498	0
32 231(a)		0+702				
32 259(b)	32 245	( $A_g \rightarrow B_{3u} \cdot a_g$ )	32 722	-477	-478	1
32 411(a)		0+911				
32 414(b)	32 412	( $A_g \rightarrow B_{3u} \cdot b_{1g}$ )	32 931	-519	-519	0
32 675(a)		0+438+702				
32 678(b)	32 676	( $A_g \rightarrow B_{3u} \cdot b_{1g} \cdot a_g$ )	33 159	-483	-483	0
32 948(a)		0+438+987				
32 952(b)	32 950	( $A_g \rightarrow B_{3u} \cdot b_{1g} \cdot a_g$ )	33 445	-495	-495	0
32 956(a)		0+1435				
32 952(b)	32 954	( $A_g \rightarrow B_{3u} \cdot a_g$ )	33 455	-501	...	...

<sup>a</sup> Reference 8.<sup>b</sup> Based on vibration frequencies of the  $B_{3u}$  excited free-molecule states.

transition in the gas phase. This shift corresponds to the sum of an environmental interaction and a resonance interaction between translationally equivalent molecules. The splitting of the vibronically induced bands is negligibly small. In the benzene crystal the pure electronic transition is observed because of the reduction from  $D_{6h}$  symmetry in the free molecule to the site symmetry  $C_2$ . The order of the Davydov components in the crystal is uncertain, being either  $a < c < b$  or  $c < a < b$ , although most workers favor the first possibility. Transitions to only three of the four predicted Davydov components are symmetry allowed. Two absorption bands corresponding to the 0-0 transition have definitely been observed at 37 803 and 37 843  $\text{cm}^{-1}$ .<sup>4</sup> Furthermore, Broude<sup>4</sup> reports that under high resolution the band at 37 843 is seen to consist of two components with energies 37 839 and 37 846  $\text{cm}^{-1}$ . Unfortunately, the polarizations of these transitions are still uncertain. The doublet at 37 843  $\text{cm}^{-1}$  is approximately 3/2 as intense as the component at 37 803  $\text{cm}^{-1}$ , while the two members of the doublet exhibit approximately equal intensity. The red shift of the center of gravity of the four Davydov components cannot be determined from experimental data in the present case, because the exact location of the fourth  $A_u$  component is unknown. However, we have approximated the po-

sition of the  $A_u$  component from a theoretical estimate<sup>9</sup> of the energy extension of the crystal density of states as outlined in Appendix D. A short summary of the available experimental data is given in Table I (naphthalene) and in Table II (benzene).

### C. Exciton Bandwidths

The locations of the Davydov components provide very little information about the exciton band structure since only the  $\mathbf{k}=0$  states are amenable to optical excitation at low temperatures. From a study of the hot-band spectrum (i.e., excitation from ground electronic vibrational exciton states to the electronic exciton state) a rough estimate of the exciton density of states for all  $\mathbf{k}$  may be obtained. The exciton bandwidth in crystalline naphthalene estimated by this method is  $\sim 200 \text{ cm}^{-1}$ ,<sup>10</sup> which is nearly the same as the Davydov splitting at  $\mathbf{k}=0$ .

### D. Location of the Exciton Band Minimum

Low-temperature emission spectra of crystalline naphthalene and benzene provide evidence that the

<sup>9</sup> B. Sommer and J. Jortner, "Electronic States of Mixed Molecular Crystals" (unpublished).

<sup>10</sup> A. S. Davydov, Sov. Phys.—Usp. **7**, 145 (1964) [Usp. Fiz. Nauk **82**, 393 (1964)].

TABLE II. Benzene ( $\mathbf{k}=0$ ) (energies in  $\text{cm}^{-1}$ ).

Crystal <sup>a</sup> spectrum with polariza- tion in parentheses	Average over <sup>b</sup> Davydov manifold	Assignment <sup>c</sup>	Theoret or exptl vapor analog <sup>a</sup>	Vapor-to- crystal shift	$D$	$I_{\text{ex}}^f$	Crystal Franck- Condon factor <sup>d</sup>
37 803(c) 37 839(a) 37 846(b)	37 844	0-0 ( $A_{1g} \rightarrow B_{2u}$ )	38 089	-245	-254	7	0.28
38 724(c) 38 764(a) 38 772(b)	38 769	0+923 ( $A_{1g} \rightarrow B_{2u} \cdot a_{1g}$ )	39 012	-243	-254	9	0.31
39 665(c) 39 687(a) 39 696(b)	39 694	0+2×923 ( $A_{1g} \rightarrow B_{2u} \cdot a_{1g} \cdot a_{1g}$ )	39 935	-241	-248	7	0.21
38 351 38 360	38 356	0+523 ( $A_{1g} \rightarrow B_{2u} \cdot e_{2g}$ )	38 617	-252	-252	0	...
38 980	38 980	0+523+923 ( $A_{1g} \rightarrow B_{2u} \cdot e_{2g} \cdot a_{1g}$ )	39 534	-254	-254	0	...
40 204	40 204	0+523+2×923 ( $A_{1g} \rightarrow B_{2u} \cdot e_{2g} \cdot a_{1g}^2$ )	40 456	-252	-254	0	...
41 130	41 130	0+523+3×923 ( $A_{1g} \rightarrow B_{2u} \cdot e_{2g} \cdot a_{1g}^3$ )	41 378	-248	-248	0	...
40 317	40 317	( $A_{1g} \rightarrow B_{2u} \cdot e_{2g} \cdot e_{2g} \cdot a_{2g} \cdot a_{1g}$ )	40 559	-242	-242	0	...
39 205 39 216	39 210	0+1375(?)	39 464	-254	-254	0	...

<sup>a</sup> Reference 4.

<sup>b</sup> The forbidden  $A_u$  fourth Davydov component for the 0-0 band and for all totally symmetric progressions built upon it is estimated in Appendix D.

<sup>c</sup> Based on vibration frequencies of the excited  $B_{2u}$  excited free molecule states.

<sup>d</sup> Estimated from crystal data in Appendix D.

lowest  $\mathbf{k}=0$  Davydov component (the  $a$ -polarized state for naphthalene, and the  $c$ - or  $a$ -polarized state for benzene) is located at the bottom of the exciton band.<sup>11</sup>

### E. Effect of Isotopic Substitution

The Davydov splittings in crystalline naphthalene,  $\text{C}_8\text{H}_{10}$ , and perdeuteronaphthalene,  $\text{C}_8\text{D}_{10}$ ,<sup>12</sup> are the same within  $2 \text{ cm}^{-1}$ . The center of gravity of the Davydov components in  $\text{C}_8\text{H}_{10}$  is red shifted by  $118 \pm 4 \text{ cm}^{-1}$  relative to the center of gravity in  $\text{C}_8\text{D}_{10}$ . This shift corresponds to the difference ( $115 \text{ cm}^{-1}$ ) in the excitation energies of the two molecules.

## III. THEORETICAL POSITION

Before discussing the predictions of the octupole-octupole interaction description or of the description based on configuration mixing of neutral with charge-transfer states, we present a brief summary of the necessary formalism.

<sup>11</sup> V. L. Broude, E. F. Sheka, and M. T. Shpak, Opt. Spectry, Suppl. 1, 53 (1966).

<sup>12</sup> P. Sarti Fantoni, Mol. Cryst. 1, 457 (1966).

For the molecular crystals under consideration, each consisting of  $N$  unit cells with  $\sigma$  molecules per cell, the Hamiltonian may be approximated by

$$\mathcal{H} = \sum_{n\alpha} H_{n\alpha} + \frac{1}{2} \sum_{n\alpha \neq m\beta} \sum_{m\beta} V_{n\alpha, m\beta}, \quad (1)$$

where  $H_{n\alpha}$  is the free-molecule Hamiltonian for the  $\alpha$ th molecule in the  $n$ th unit cell, and  $V_{n\alpha, m\beta}$  represents the potential of interaction between the molecules at sites  $n\alpha$  and  $m\beta$ . Let  $\phi_{n\alpha}^f$  represent the electronic wavefunction of the  $f$ th excited state of the molecule at site  $n\alpha$ . Then an excitation localized at  $n\alpha$  is represented by

$$|X_{n\alpha}^f\rangle = \mathcal{A}(\phi_{n\alpha}^f \prod_{m\beta} \phi_{m\beta}^0) \quad (2)$$

in the limit of zero intermolecular interaction. The molecular wavefunctions  $\phi_{n\alpha}^f$  are assumed to be properly antisymmetrized so that  $\mathcal{A}$  permutes electrons between molecules. As a result of intermolecular electron antisymmetrization there arise exchange interactions between molecules of the crystal, but these are quite small compared to other interactions in the singlet state. We shall, consequently, neglect exchange

interactions in all that follows. As explained in Appendix C, the crystal wavefunctions based on  $|\mathbf{X}_{n\alpha}^f\rangle$  are represented by

$$\Psi_{\nu}^f(\mathbf{k}) = \sum_{\alpha=1}^{\sigma} a_{\nu\alpha}(\mathbf{k}) \Phi_{\alpha}^f(\mathbf{k}), \quad \nu=1, 2, \dots, \sigma, \quad (3)$$

where

$$\Phi_{\alpha}^f(\mathbf{k}) = N^{-1/2} \sum_n \exp(i\mathbf{k} \cdot \mathbf{X}_{n\alpha}) |\mathbf{X}_{n\alpha}^f\rangle, \quad \alpha=1, 2, \dots, \sigma, \quad (4)$$

and the  $a_{\nu\alpha}(\mathbf{k})$  are elements of a unitary matrix that depends, in general, on  $\mathbf{k}$ . For  $\mathbf{k}$  along particular symmetry directions, the expansion coefficients take the simple form  $a_{\nu\alpha} = \pm 1/\sigma^{1/2}$  in naphthalene and benzene crystals.

In particular, for the monoclinic naphthalene crystal, when  $\mathbf{k}$  is perpendicular to or parallel to  $\mathbf{b}$ ,

$$\Psi_{\pm}^f(\mathbf{k}) = 2^{-1/2} [\Phi_1^f(\mathbf{k}) \pm \Phi_2^f(\mathbf{k})]. \quad (5)$$

Similarly, for the benzene crystal when  $\mathbf{k}$  is parallel to any of the three crystal axes,

$$\begin{aligned} \Psi_{\alpha}(\mathbf{k}) &= 4^{-1/2} [\Phi_1(\mathbf{k}) + \Phi_2(\mathbf{k}) + \Phi_3(\mathbf{k}) + \Phi_4(\mathbf{k})], \\ \Psi_{\beta}(\mathbf{k}) &= 4^{-1/2} [\Phi_1(\mathbf{k}) + \Phi_2(\mathbf{k}) - \Phi_3(\mathbf{k}) - \Phi_4(\mathbf{k})], \\ \Psi_{\gamma}(\mathbf{k}) &= 4^{-1/2} [\Phi_1(\mathbf{k}) - \Phi_2(\mathbf{k}) + \Phi_3(\mathbf{k}) - \Phi_4(\mathbf{k})], \\ \Psi_{\delta}(\mathbf{k}) &= 4^{-1/2} [\Phi_1(\mathbf{k}) - \Phi_2(\mathbf{k}) - \Phi_3(\mathbf{k}) + \Phi_4(\mathbf{k})]. \end{aligned} \quad (6)$$

For these particular symmetry directions the energy levels in the weak-coupling limit are given in the form

$$E_{\nu}^f(\mathbf{k}) = \Delta\epsilon^f + D + \sum_{\alpha,\beta=1, \alpha \neq \beta}^{\sigma} a_{\nu\alpha}^* a_{\nu\beta} I_{\alpha\beta}^f(\mathbf{k}) + I_{\alpha\alpha}^f(\mathbf{k}), \quad (7)$$

where

$$D = D^f + W^f. \quad (8)$$

In Eqs. (7) and (8)  $\Delta\epsilon^f$  is the excitation energy of the free molecule to the vibronic excited state  $fi$ , where  $f$  corresponds to the electronic state and  $i$  to its vibrational component. The environmental shift  $D$  consists of two terms: the first-order term  $D^f$  represents the change in the static interactions in the two states. The second contribution to the environmental shift arises from a second-order dispersion term  $W^f$  which is due to two electron excitations. In the following formalism the  $D$  term is assumed to be independent of  $i$  for weak transitions, although it is known to exhibit some dependence on  $i$  as shown in Tables I and II. The resonance terms  $I_{\alpha\beta}^f(\mathbf{k})$  arise from excitation exchange and can be displayed in the form

$$I_{\alpha\beta}^f(\mathbf{k}) = \sum_n M_{m\beta, n\alpha}^f \exp[i\mathbf{k} \cdot (\mathbf{X}_{m\beta} - \mathbf{X}_{n\alpha})], \quad (9)$$

where the excitation exchange matrix elements are, in

the weak-coupling approximation,

$$M_{m\beta, n\alpha}^f = \langle \phi_{m\beta}^f \phi_{n\alpha}^0 | V_{n\alpha, m\beta} | \phi_{m\beta}^0 \phi_{n\alpha}^f \rangle |\langle \chi^{f(i)} | \chi^{0(0)} \rangle|^2, \quad (10)$$

and where  $\chi^{f(i)}$  is the  $i$ th molecular vibrational wavefunction in the electronic state  $f$ . The Franck-Condon vibrational overlap integrals  $|\langle \chi^{f(i)} | \chi^{0(0)} \rangle|^2$  can be obtained from the intensities of the vibronic components in the crystal spectrum. (The Franck-Condon vibrational overlap integrals may differ in the vapor and in the crystal spectrum because of crystal-field mixing.) For the special directions of  $\mathbf{k}$  for which  $a_{\nu\beta} = \pm 1/\sigma^{1/2}$  we can rewrite Eq. (7) in the form

$$E_{\nu}^f(\mathbf{k}) = \Delta\epsilon^f + D + I_{\text{eq}}^f(\mathbf{k}) + [I_{\text{ineq}}^f(\mathbf{k})]_{\nu}. \quad (11)$$

It is important to notice that the total medium shift consists of the sum  $D + I_{\text{eq}}^f$ . In Eq. (11)  $I_{\text{eq}}^f$  is the resonance interaction term representing excitation transfer between translationally equivalent molecules in the vibronic crystal state  $fi$

$$I_{\text{eq}}^f(\mathbf{k}) = \sum_n M_{m\alpha, n\alpha}^f \exp[i\mathbf{k} \cdot (\mathbf{X}_{m\alpha} - \mathbf{X}_{n\alpha})], \quad (12)$$

while  $I_{\text{ineq}}^f$  represents transfer of excitation energy between translationally inequivalent molecules:

$$[I_{\text{ineq}}^f(\mathbf{k})]_{\nu} = \sum_{\beta=1}^{\sigma} a_{\nu\beta} \sum_{n\alpha, \alpha \neq \beta} a_{\nu\alpha}^* M_{m\beta, n\alpha}^f \times \exp[i\mathbf{k} \cdot (\mathbf{X}_{m\beta} - \mathbf{X}_{n\alpha})]. \quad (13)$$

The vibrational sum rule,

$$\sum_i |\langle \chi^{f(i)} | \chi^{0(0)} \rangle|^2 = 1, \quad (14)$$

leads to the total electronic contribution in terms of sums of interactions over translationally equivalent and translationally inequivalent molecules:

$$I_{\text{eq}}^f(\mathbf{k}) = \sum_i I_{\text{eq}}^f(\mathbf{k}), \quad (15)$$

$$[I_{\text{ineq}}^f(\mathbf{k})]_{\nu} = \sum_i [I_{\text{ineq}}^f(\mathbf{k})]_{\nu}. \quad (16)$$

These terms can be calculated theoretically or deduced from a comparison of the crystal- and vapor-phase spectra.

The formalism cited above neglects mixing of molecular electronic states. Calculations indicate that crystal-induced state mixing leads to small changes, of the order of  $5 \text{ cm}^{-1}$ , in the energies of the states of a molecular crystal when the intermolecular interactions are short ranged.<sup>13</sup>

The one-configuration formalism used herein makes it possible to evaluate the contribution of the term

<sup>13</sup> Estimated from data of Refs. 2 and 3.

$I_{\text{eq}}^{fi}$  for  $\mathbf{k}=\mathbf{0}$  from the crystal spectrum.<sup>14,15</sup> Application of the diagonal sum rule,

$$\sum_{\nu=1}^{\sigma} [I_{\text{ineq}}^{fi}(\mathbf{0})]_{\nu} = 0, \quad (17)$$

for each  $i$  leads to the result

$$\sigma^{-1} \sum_{\nu=1}^{\sigma} \{E_{\nu}^{fi}(\mathbf{0}) - \Delta\epsilon^{fi}\} = D + I_{\text{eq}}^{fi}(\mathbf{0}), \quad (18)$$

where  $\sigma$  is the number of molecules per unit cell.

Thus, the observed shifts of the crystal vibronic states depend on the intensity of the band as inferred from Eqs. (9), (10), and (12). Accordingly, from a knowledge of the Franck-Condon vibrational overlap integrals one can calculate the values of  $I_{\text{eq}}^{fi}$  and hence obtain  $I_{\text{eq}}^{fi}$ . This procedure is discussed in Appendix D.

To summarize, the experimental spectroscopic data provide the following information concerning the  $\mathbf{k}=\mathbf{0}$  crystal energy levels:

(a) Knowledge of the Davydov splittings of the vibronic components enables us to deduce the interaction  $I_{\text{ineq}}^{fi}$  between translationally inequivalent molecules.

(b) Knowledge of the order of the energy levels enables us to deduce the relative sign of the interaction terms between inequivalent molecules.

(c) Knowledge of the shift of the center of gravity of the Davydov manifold enables us to deduce the sum  $D + I_{\text{eq}}^{fi}$ . In the weak-coupling limit, which is valid for the crystals under consideration in this paper, it is possible to extract the value of  $I_{\text{eq}}^{fi}$  by comparison of the crystal and vapor spectra.

Previous studies of the electronic states of organic crystals have mainly emphasized the calculation of the absolute magnitudes of the Davydov splitting and the polarization ratios. A knowledge of the magnitude of the terms  $I_{\text{eq}}^{fi}$  and  $D$  from the experimental data provides an independent test of the applicability of various models of the intermolecular interactions which are purported to lead to the Davydov splitting in crystalline benzene and naphthalene.

#### IV. A COMPARISON OF THE TRANSITION OCTUPOLE-OCTUPOLE INTERACTION THEORY AND THE CHARGE-TRANSFER CONFIGURATION MIXING THEORY

The exciton band shapes along and perpendicular to the crystal symmetry axes, obtained from the description of crystal states including configuration mixing

between charge-transfer and neutral exciton states of crystalline naphthalene and benzene, are displayed in Figs. 1 and 2. Two features of these results for naphthalene should be stressed: the minimum of the exciton band is located at the  $\mathbf{k}=\mathbf{0}$  state, and the total bandwidth is of the order of the Davydov splitting. Both results are consistent with the experimental data.

Now, a completely satisfactory theoretical description of the naphthalene and benzene crystal spectra should predict the quantities  $I_{\text{eq}}^{fi}$ ,  $I_{\text{ineq}}^{fi}$ ,  $D$  and the polarization ratios for the Davydov components. Considering the transition octupole coupling model alone for the moment, we note that Craig and Walmsley<sup>3</sup> obtain good agreement between calculated and observed  $I_{\text{ineq}}^{fi}$  and  $P(a/b)$  for the crystal spectrum of naphthalene. Nonetheless, the transition octupole moments required are rather large, and use of their data reveals  $I_{\text{eq}}^{fi} = -29 \text{ cm}^{-1}$  instead of the experimentally observed  $+10 \text{ cm}^{-1}$ . Their work does not include a calculation of  $D$ , nor do we know of any other attempts to calculate this term.

The predicted values of  $D$  and of the Davydov splittings based on the charge-transfer-neutral-exciton mixing theory for naphthalene and benzene are listed in Tables III and IV as a function of energy of the lowest charge-transfer states. If we place the charge-transfer states at classically approximated energies<sup>1</sup> (4.4 eV in naphthalene and 5.9 eV in benzene), we find for naphthalene a configuration-interaction contribution of  $79 \text{ cm}^{-1}$  to the Davydov splitting and of  $-471 \text{ cm}^{-1}$  to the observed  $D$  value, while the experimental result is  $D = -498 \text{ cm}^{-1}$ . There is no contribution of the charge-transfer states to the polarization ratios, nor is there any effect on  $I_{\text{eq}}^{fi}$  from charge-transfer interaction with the neutral state. Thus the transition octupole coupling model need only explain two-thirds of the splitting and almost the entire polarization ratio, for which, of course, smaller transition octupole moments are required. The necessary octupole moments are  $-6.8$  and  $9.1 \text{ \AA}^3$  in the new model instead of  $-9$  and  $12 \text{ \AA}^3$  required if the octupole moment interactions are used to explain the entire Davydov splitting.

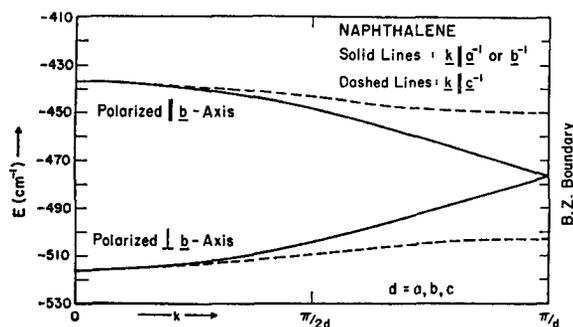


FIG. 1. Lowest singlet exciton band with splitting and shift induced by configuration mixing with charge transfer states in crystalline naphthalene. Lowest charge-transfer state at 4.4 eV.

<sup>14</sup> S. A. Rice and J. Jortner, *Physics of Solids at High Pressure*, C. T. Tomizuka and R. M. Emrick, Eds. (Academic Press Inc., New York, 1965), p. 63.

<sup>15</sup> J. Jortner, S. A. Rice, J. L. Katz, and S. I. Choi, *J. Chem. Phys.* **42**, 309 (1965).

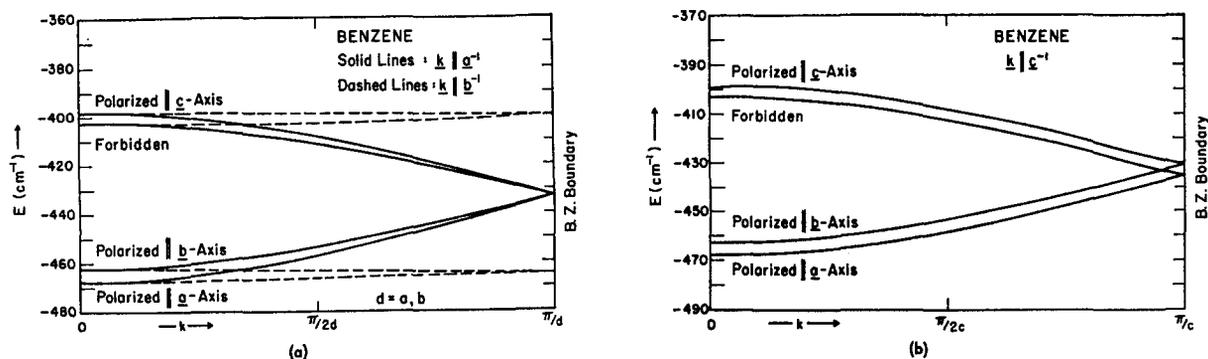


FIG. 2. Lowest singlet exciton band with splitting and shift induced by configuration mixing with charge-transfer states in crystalline benzene. Lowest charge-transfer state at 5.9 eV.

A comparison of the charge-transfer and transition octupole contributions to the Davydov splitting in crystalline benzene is quite similar in all respects to the aforementioned naphthalene case. Thirunamachandran<sup>7</sup> estimates that a transition octupole of magnitude  $61 \text{ \AA}^3$  is required to fit the observed splitting of  $140 \text{ cm}^{-1}$  between the *a*- and *c*-polarized components (the quoted splitting is the sum of splittings over all totally symmetric vibrations built onto the 0-0 band). This value is undoubtedly too large for a free-molecule transition octupole moment, since an LCAO scheme which is known to overestimate transition dipole moments predicts only  $\sim 24 \text{ \AA}^3$ .<sup>7</sup> Moreover, the  $A_u$  state at  $\mathbf{k}=0$  is predicted to be below the *b*-polarized state for any value of the transition octupole moment in disagreement with the present experimental interpretations. In the octupole-octupole coupling calculations of Thirunamachandran the sum of excitation transfer integrals over translationally equivalent molecules again leads to the prediction of a slight red shift of  $-0.0013 \times Q^2 \text{ cm}^{-1}$ , where  $Q$  is the transition octupole moment (only one nonvanishing component exists for the  $B_{2u}$  state of benzene).

If the lowest charge-transfer state in crystalline benzene is at 5.9 eV, as is estimated classically, the charge-

transfer induced environmental shift is  $-430 \text{ cm}^{-1}$  which is to be compared with the experimental environmental shift of  $-250 \text{ cm}^{-1}$ . The reported charge-transfer induced shift, however, is an upper bound to the true effect, since the off-diagonal matrix elements between charge-transfer and neutral exciton states in the Born-Oppenheimer approximation contain overlap integrals between the ground, excited electronic, and ionic vibrational states. Thus an effective Franck-Condon factor of  $\sim 0.6$  is quite reasonable and gives an environmental shift of  $-250 \text{ cm}^{-1}$ . We also note that the lowest charge-transfer state at 5.9 eV with a scaling factor of 0.6 is equivalent to the lowest charge-transfer state at 6.6 eV with no scaling. The Davydov splittings between the four components in the combined charge-transfer-transition-octupole interaction model are listed in Table V as a function of the octupole moment. The octupole-octupole interactions were obtained from the calculations of Thirunamachandran.<sup>7</sup> The agreement between the theoretical and experimental results is not perfect, but the discrepancy in the splittings is not as great when the unscaled charge-transfer interaction is used as when the Franck-Condon scaled charge-transfer interaction is used. Unfortunately the unscaled charge transfer contribution predicts an environmental shift larger than that observed.

TABLE III. Effect of charge-transfer configuration interaction on crystalline naphthalene lowest singlet ( $\alpha$  state) for  $\mathbf{k}=0$ .

Charge-transfer energy <sup>a</sup>	Davydov splitting of $\alpha$ state	Energy of $\alpha$ state relative to free-molecule energy <sup>b</sup>
(200)	123	-1353
(1 000)	119	-1036
(2 000)	106	-765
4.4 eV (4 000)	79	-471
(6 000)	61	-338
4.9 eV (9 000)	44	-233
(12 000)	35	-178
(15 000)	29	-143

<sup>a</sup> Numbers in parentheses denote the energy of the charge-transfer state above the free-molecule excited-state energy (3.9 eV) in  $\text{cm}^{-1}$ .

<sup>b</sup> Measured with respect to the energetic center of gravity of the two Davydov components.

TABLE IV. Effect of charge-transfer configuration interaction on crystalline benzene  $\alpha$  state for  $\mathbf{k}=0$ .

Charge-transfer energy <sup>a</sup>	Davydov splitting of $\alpha$ state <sup>b</sup>	Energy of $\alpha$ state relative to free-molecule energy <sup>c</sup>
(1 700)	157	-1276
(2 700)	140	-1020
5.4 eV (5 000)	105	-705
6.0 eV (10 000)	63	-394
6.6 eV (15 000)	44	-270
(20 000)	34	-205

<sup>a</sup> Numbers in parentheses represent the relative energy of the charge-transfer state and the free-molecule  $\alpha$  state (4.7 eV) in  $\text{cm}^{-1}$  units.

<sup>b</sup> Measured between the *c*- and *a*-polarized components.

<sup>c</sup> Measured with respect to the energetic center of gravity of the four Davydov components.

TABLE V. Comparison of experimental observations and theoretical predictions in the combined charge-transfer-transition-octupole interaction model for crystalline benzene (energy in  $\text{cm}^{-1}$ ;  $\mathbf{k}=0$ ).

Spectral shift -250	Experimental observations <sup>a</sup>			
	$A_u$ - $b$ splitting 47	$b$ - $c$ splitting 18	$c$ - $a$ splitting 140	
Theoretical predictions with lowest charge-transfer state at 5.9 eV				
Transition octupole moment ( $\text{\AA}^3$ )	Spectral shift	$A_u$ - $b$ splitting	$b$ - $c$ splitting	$c$ - $a$ splitting
30	-430	28	-4	102
35	-430	17	18	114
40	-430	4	43	128
45	-430	-10	71	143
50	-430	-27	102	161
Theoretical predictions with effect of charge-transfer mixing scaled to give correct spectral shift				
30	-250	6	19	77
35	-250	-4	41	89
40	-250	-18	66	103
45	-250	-32	94	118
50	-250	-49	126	136

<sup>a</sup> S. D. Colson, thesis, California Institute of Technology, 1967, and Ref. 4.

Nearly perfect agreement between the observed and calculated Davydov splittings could be obtained if one were to allow the lowest charge-transfer state to lie lower than 5.9 eV, but the predicted spectral shift is then even larger, as can be seen from Table IV.

We should note that the energy of the  $A_u$  state at  $\mathbf{k}=0$  which has a vanishing transition moment with the crystal ground state, is uncertain. The estimated energy is obtained from density of states measurements extracted from hot band absorption spectra. Nevertheless, even if the  $\mathbf{k}=0$   $A_u$  component were to lie below the  $b$  component, we still could not fit all of the Davydov splittings and the spectral shift adequately in the case

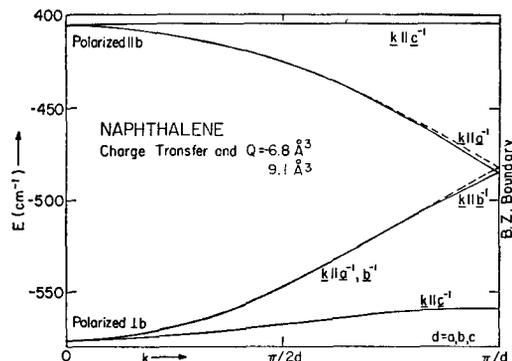


FIG. 3. The energy bands for the lowest singlet state in crystalline naphthalene in the combined charge-transfer-transition-octupole interaction model. The transition octupole moments required are  $-6.8$  and  $9.1 \text{ \AA}^3$ , and the lowest charge-transfer state is at  $4.4$  eV above the crystal ground state.

of crystalline benzene. Broude<sup>4</sup> reports that it is the higher of the two components which are split by about  $140 \text{ cm}^{-1}$  that is  $a$  polarized, and that the lower component is  $c$  polarized. However, Zmerli, Poulet, and Pestel,<sup>16</sup> Claxton,<sup>17</sup> and Wolf<sup>18</sup> all agree that the  $a$ -polarized component lies below the  $c$ -polarized one. This is also in agreement with Broude's earlier assignment and with the predictions of both the transition octupole interaction model and the charge-transfer configuration interaction model. Although we cite the

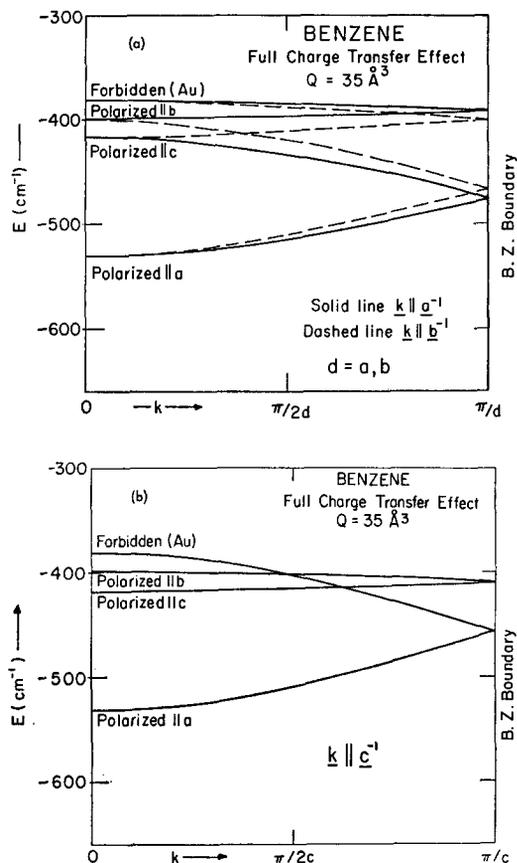


FIG. 4. The energy bands for the lowest singlet state in crystalline benzene in the combined charge-transfer-transition-octupole interaction model. The octupole moment is  $35 \text{ \AA}^3$ , and the lowest charge-transfer state is at  $5.9$  eV.

experimental measurements of Broude in Table II for benzene, we believe that his assignments of the  $a$  and  $c$  polarization should be reversed, and we have assumed just that in comparing the theories with the experimental data.

The best over-all transition octupole moment is  $Q=35 \text{ \AA}^3$  when the charge-transfer state at  $5.9$  eV exerts an unscaled influence upon the neutral states,

<sup>16</sup> Zmerli, Poulet, and Pestel, Colloque de Bellevue, July 1957 (unpublished), referred to in Ref. 7.

<sup>17</sup> T. A. Claxton, doctoral thesis, University of London, 1961.

<sup>18</sup> H. C. Wolf, Solid State Phys. **9**, 1 (1959).

and  $Q=30 \text{ \AA}^3$  in the model with the scaled charge-transfer effect. Although perfect agreement in all spectral characteristics cannot be obtained in the combined charge-transfer-transition-octupole model, the combined theory is superior to either theory considered separately.

The exciton energy bands for both crystalline naphthalene and benzene in the combined charge-transfer-transition-octupole-moment interaction model are displayed in Figs. 3-5.

## V. DISCUSSION

The previously proposed theory<sup>2,19</sup> interpreting the crystal spectra of benzene and naphthalene solely in terms of charge-transfer configuration mixing, with the charge-transfer states located  $\sim 1000 \text{ cm}^{-1}$  above the 0-0 neutral exciton state, must be modified for the following reasons:

(a) The experimental studies of Geacintov and Pope<sup>2</sup> located the charge-transfer states in molecular organic

crystals close to the positions predicted from a classical analysis. Thus for crystalline anthracene the classical estimate of 3.5 eV is in good agreement with the experimental value of 3.45 eV. For crystalline naphthalene the classical estimate gives 4.4 eV while the preliminary experimental value is  $4.4 \pm 0.2 \text{ eV}$ . The contribution of the charge-transfer states to the Davydov splitting is still significant. However, the charge-transfer and neutral exciton states are sufficiently separated that the former do not influence the polarization ratio.

(b) If the charge-transfer states were located only  $1000 \text{ cm}^{-1}$  above the neutral exciton states the configuration interaction between states would lead to an appreciable negative value for  $D$ , thereby resulting in a large red shift of the exciton states relative to the free molecule states. Such a situation is indeed encountered in the emission spectra of excimers and the absorption spectra of the paracyclophanes, where charge-transfer interactions are dominant.<sup>20</sup> Our analysis of the crystal spectra of naphthalene and benzene shows that the major contribution to the observed spectral red shift,  $D+I_{eq}^f$ , arises from the  $D$  term, while  $I_{eq}^f$  is small and positive. Thus the charge-transfer states in these crystals must be located at the classically estimated energies. The theoretical position at present may be summarized in the following way: in crystals composed of aromatic compounds there are important contributions to the interactions from both charge delocalization and higher-order multipole moments. An upper limit on the contribution of charge delocalization to the Davydov splitting is about one-third of the total effect, whereas the transition octupole interaction accounts for about two-thirds of the splitting. The polarization ratios of the transitions are determined solely by the transition moment interactions. A combination of the charge-transfer mixing and transition-moment coupling theories accounts for what is known about the width of the exciton band, for the location of the lowest Davydov component at the bottom of the band, for the effects of isotopic substitution, for the environmental shift, and for the relative ordering of Davydov components.

On the other hand the term  $I_{eq}^f$  is predicted to be small and negative, but is known experimentally to be small and positive<sup>21,22</sup> ( $I_{eq} \sim 10 \text{ cm}^{-1}$  in crystalline naphthalene and  $I_{eq} \sim 35 \text{ cm}^{-1}$  in crystalline benzene). Since the over-all discrepancy is only of the order of  $30 \text{ cm}^{-1}$ , perhaps the difference is not serious. In fact a careful examination of short-range repulsive contributions might entirely erase the disagreement. Even in the combined theory the required transition octupole moments are larger than one would expect on the basis

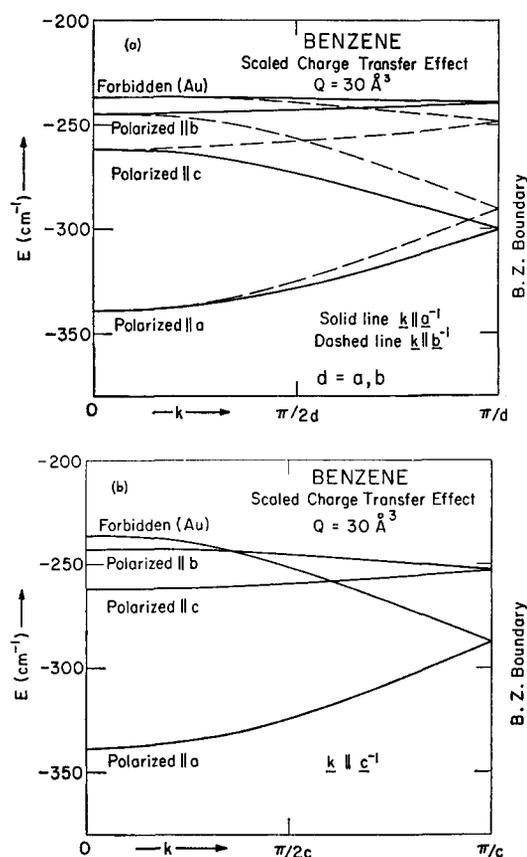


FIG. 5. The energy bands for the lowest singlet state in crystalline benzene in the combined charge-transfer-transition-octupole interaction model. The octupole moment is  $30 \text{ \AA}^3$  and the charge-transfer state is at 5.9 eV with scaling to reproduce the observed environmental shift (or at 6.6 eV with no scaling).

<sup>19</sup> S. I. Choi, J. Jortner, S. A. Rice, and R. Silbey, *J. Chem. Phys.* **41**, 3294 (1964).

<sup>20</sup> M. T. Vala, Jr., I. H. Hillier, S. A. Rice, and J. Jortner, *J. Chem. Phys.* **44**, 23 (1966).

<sup>21</sup> D. P. Craig, R. Mason, P. Pauling, and D. P. Santry, *Proc. Roy. Soc. (London)* **A286**, 98 (1965).

<sup>22</sup> D. Fox and O. Schnepp, *J. Chem. Phys.* **23**, 767 (1955).

of LCAO calculations in free molecules, but they have been reduced to somewhat more acceptable values than they would have been if transition octupole interactions alone accounted for the entire Davydov splitting.

We note again that the cited charge-transfer interaction effects are an upper limit to what they would be if the charge-transfer energies were more precisely known, and if better vibrational wavefunctions were used in the ground, ionic, and excited electronic states.

### ACKNOWLEDGMENTS

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### APPENDIX A: CRYSTAL STRUCTURES

Naphthalene crystallizes in the monoclinic system with space group  $C_{2h}^5(P_{2_1}/a)$  with two molecules per unit cell. One molecule is located at the origin and the other at the center of the  $ab$  face.<sup>23-25</sup> The crystal symmetry is conveniently described as follows. The nonsymmorphic space group of the crystal,  $\mathcal{G}$ , possesses the invariant translational subgroup  $\mathfrak{T}$  (which is composed of pure translation operations  $\{E | \mathbf{t}\}$ ) and cosets of  $\mathfrak{T}$  with rotation-translation operations. For naphthalene these are

$$\{C_2^b | \boldsymbol{\tau}\}, \{\sigma^{ac} | \boldsymbol{\tau}\},$$

and

$$\{i | \mathbf{0}\}. \quad (\text{A1})$$

In (A1)  $C_2^b$  is a twofold rotation about the  $b$  axis,  $\sigma^{ac}$  represents a reflection in the  $ac$  plane,  $i$  is the inversion operation,  $\mathbf{t}$  a direct lattice vector, and  $\boldsymbol{\tau} = \frac{1}{2}(\mathbf{a} + \mathbf{b})$ . As usual, the space group operations define coordinate transformations of the form

$$\{A | \mathbf{1}\}\mathbf{X} = \mathbf{A}\mathbf{X} + \mathbf{1}. \quad (\text{A2})$$

The benzene crystal belongs to the orthorhombic system with space group  $D_{2h}^{16}(P_{bca})$  and has four translationally inequivalent molecules in a unit cell. If one molecule is located at the cell origin, the other three are located at the centers of the  $ab$ , the  $bc$ , and the  $ac$  faces.<sup>26</sup> In this case the crystal space group contains

cosets of  $\mathfrak{T}$  with the following operations:

$$\begin{aligned} \{E | \mathbf{0}\}, \quad \{i | \mathbf{0}\}, \quad \{C_2^a | \boldsymbol{\tau}_2\}, \quad \{C_2^b | \boldsymbol{\tau}_3\}, \\ \{C_2^c | \boldsymbol{\tau}_4\}, \quad \{\sigma^{bc} | \boldsymbol{\tau}_2\}, \quad \{\sigma^{ac} | \boldsymbol{\tau}_3\}, \quad \{\sigma^{ab} | \boldsymbol{\tau}_4\}, \end{aligned} \quad (\text{A3})$$

where

$$\begin{aligned} \boldsymbol{\tau}_2 &= \frac{1}{2}(\mathbf{a} + \mathbf{b}), \\ \boldsymbol{\tau}_3 &= \frac{1}{2}(\mathbf{b} + \mathbf{c}), \\ \boldsymbol{\tau}_4 &= \frac{1}{2}(\mathbf{a} + \mathbf{c}). \end{aligned} \quad (\text{A4})$$

### APPENDIX B: GROUP-THEORETICAL DETERMINATION OF CRYSTAL WAVEFUNCTIONS FOR $\mathbf{k} \neq \mathbf{0}$

We note that each  $\Phi_{\alpha'}(\mathbf{k})$  in Eq. (4) transforms according to the  $\mathbf{k}$ th irreducible representation of the invariant translational subgroup  $\mathfrak{T}$  of the crystal space group  $\mathcal{G}$  (The ground state belongs to the  $\mathbf{k} = \mathbf{0}$  irreducible representation only.) Charge-transfer states which satisfy Bloch's theorem may also be constructed in the following manner:

If the localized charge-transfer wavefunctions are denoted by

$$|\mathbf{X}_{n\alpha^+}, \mathbf{X}_{m\beta^-}\rangle = \epsilon \mathcal{A}(\phi_{n\alpha^+} \phi_{m\beta^-} \prod_{\gamma\gamma'} \phi_{\gamma\gamma'}), \quad (\text{B1})$$

one obtains ion-pair wavefunctions symmetrized with respect to the translation group which have the form

$$N^{-1/2} \sum_n \exp[i\mathbf{k} \cdot \frac{1}{2}(\mathbf{X}_{n\alpha^+} + \mathbf{X}_{m\beta^-})] |\mathbf{X}_{n\alpha^+}, \mathbf{X}_{m\beta^-}\rangle. \quad (\text{B2})$$

Using these functions we may obtain proper stationary state functions in the fixed-lattice weak-interaction scheme by appealing to the general theorem which states that all eigenfunctions of the Hamiltonian  $\mathcal{H}$  are basis functions for the irreducible representations of that group of operations which leave  $\mathcal{H}$  invariant, i.e., the space group  $\mathcal{G}$ . Since we are interested in crystal eigenfunctions for particular  $\mathbf{k}$ , we focus our attention on the group of  $\mathbf{k}$ , denoted by  $\mathcal{K}$ . Our criterion for the choice of suitable wavefunctions for a particular  $\mathbf{k}$  is that they transform according to the rows of the irreducible representations of  $\mathcal{K}$ .  $\mathcal{K}$  possesses all the operations from  $\mathcal{G}$  of the form  $\{A | \boldsymbol{\tau}\}$  such that  $A\mathbf{k} = \mathbf{k} + \mathbf{G}$  where  $\mathbf{G}$  is zero or one of the vectors of the reciprocal lattice, and  $A$  is a proper or improper rotation. The set of such rotational operations alone constitutes a point group  $\mathcal{R}_{\mathbf{k}}$ . The factor group of  $\mathcal{K}$  with respect to the translational subgroup  $\mathfrak{T}$  is isomorphic to  $\mathcal{R}_{\mathbf{k}}$ , and the

<sup>23</sup> G. Castro and R. M. Hochstrasser, J. Chem. Phys. **46**, 3617 (1967).

<sup>24</sup> G. Castro and R. M. Hochstrasser, J. Chem. Phys. **44**, 412 (1966).

<sup>25</sup> J. M. Robertson, Rev. Mod. Phys. **30**, 155 (1958).

<sup>26</sup> E. G. Cox, Rev. Mod. Phys. **30**, 159 (1958).

irreducible representations of  $\mathcal{K}$  are simply related to those of  $\mathcal{R}_k$  in the following manner<sup>27</sup>:

$$\Gamma_{(A|\tau)}^{(j)} = \exp(i\mathbf{k}\cdot\tau) \Gamma_A^{(j)}, \quad (\text{B3})$$

where  $\Gamma_{(A|\tau)}^{(j)}$  is the matrix representation of  $\{A|\tau\}$  corresponding to the  $j$ th irreducible representation of  $\mathcal{K}$ , and  $\Gamma_A^{(j)}$  is the matrix representative of the rotation  $A$  corresponding to the  $j$ th irreducible representation of  $\mathcal{R}_k$ . In general this expression (B3) is valid for  $\mathbf{k}$  not on a Brillouin-zone boundary, but in practice one may extend the expression arbitrarily close to the boundary.

The Wigner projection operator for the  $j$ th representation of  $\mathcal{K}$  is given by<sup>28</sup>

$$\mathcal{P}^{(j)} = (l_j/h) \sum_{(B|\tau)} \chi_{(B|\tau)}^j \hat{P}(\{B|\tau\}), \quad (\text{B4})$$

where  $l_j$  is the order of the  $j$ th irreducible representation,  $h$  is the order of  $\mathcal{K}$ ,  $\chi_{(B|\tau)}^j$  is the character of  $\{B|\tau\}$  in the  $j$ th irreducible representation, and  $\hat{P}(\{B|\tau\})$  is a function operator analogous to the coordinate operator  $\{B|\tau\}$  and is defined by

$$\begin{aligned} \hat{P}(\{B|\tau\})f(\mathbf{X}_1, \dots, \mathbf{X}_n) \\ = f[B^{-1}(\mathbf{X}_1 - \tau), \dots, B^{-1}(\mathbf{X}_n - \tau)] \end{aligned} \quad (\text{B5})$$

for  $f$  an arbitrary function of  $n$  vectors. Operation with  $\mathcal{P}^{(j)}$  on the translation symmetrized neutral and charge transfer exciton functions will project out those functions which transform according to the  $j$ th irreducible representation of  $\mathcal{K}$ . This has been carried through for  $\mathbf{k}=\mathbf{0}$  for which  $\mathcal{K}=\mathcal{G}$ , and the factor group  $\mathcal{K}/\mathcal{G}=\mathcal{G}/\mathcal{G}$  is isomorphous to the crystal point group ( $D_{2h}$  for benzene and  $C_{2h}$  for naphthalene crystals). Application of  $\mathcal{P}$  to  $\Phi_{\alpha}^f(\mathbf{k})$  for  $\mathbf{k}$  parallel and perpendicular to  $\mathbf{b}$  in the naphthalene crystal, and for  $\mathbf{k}$  along  $\mathbf{a}$ ,  $\mathbf{b}$ , or  $\mathbf{c}$  in the benzene crystal yields, after normalization, the following neutral exciton wavefunctions:

#### Naphthalene:

$$\begin{aligned} |0, 0^f, \pm\rangle &= (2N)^{-1/2} \sum_n \exp(i\mathbf{k}\cdot\mathbf{X}_n) \\ &\quad \times \{|\mathbf{X}_n^f\rangle \pm \exp(i\mathbf{k}\cdot\tau) |\mathbf{X}_n^f + \tau\rangle\} \\ &= 2^{-1/2} [\Phi_1^f(\mathbf{k}) \pm \Phi_2^f(\mathbf{k})]. \end{aligned} \quad (\text{B6})$$

<sup>27</sup> G. F. Koster, Solid State Phys. 5, 173 (1957).

<sup>28</sup> This is the projection operator for the  $j$ th irreducible representation independent of the dimensionality of the representation. If the representation is one dimensional, as it is always in our cases, the projected functions are basis functions for the representation; if the representation is greater than one dimensional the projected wavefunction is a linear combination of functions which transform according to each of the rows of the representation, and must be broken down accordingly to give proper eigenfunctions.

#### Benzene:

$$\begin{aligned} \left| \begin{array}{c} + + + \\ 0, 0^f, \begin{array}{c} + - - \\ - + - \\ - - + \end{array} \end{array} \right\rangle \\ = (4N)^{-1/2} \sum_n \exp(i\mathbf{k}\cdot\mathbf{X}_n) \left[ \begin{array}{c} + \\ |\mathbf{X}_n^f\rangle_+ \exp(i\mathbf{k}\cdot\tau_2) |\mathbf{X}_n^f + \tau_2\rangle \\ - \\ + \\ \exp(i\mathbf{k}\cdot\tau_3) |\mathbf{X}_n^f + \tau_3\rangle_+ \exp(i\mathbf{k}\cdot\tau_4) |\mathbf{X}_n^f + \tau_4\rangle \\ - \\ + \end{array} \right] \\ = (4)^{-1/2} \left( \begin{array}{ccc} + & + & + \\ \Phi_1^f(\mathbf{k})_+ \Phi_2^f(\mathbf{k})_+ \Phi_3^f(\mathbf{k})_+ \Phi_4^f(\mathbf{k}) \\ - & - & + \end{array} \right). \end{aligned} \quad (\text{B7})$$

These are, in fact, the same linear combinations of sublattice wavefunctions  $\Phi_{\alpha}^f(\mathbf{k})$  as were obtained at  $\mathbf{k}=\mathbf{0}$ . The phase convention is the same as that used earlier. Thus for crystalline naphthalene

$$\hat{P}(\{\sigma^{ac}|\tau\})\phi_{01}^f = \phi_{02}^f, \quad (\text{B8})$$

while for crystalline benzene

$$\begin{aligned} \hat{P}(\{C_2^a|\tau_2\})\phi_{01}^f &= \phi_{02}^f, \\ \hat{P}(\{C_2^b|\tau_3\})\phi_{01}^f &= \phi_{03}^f, \\ \hat{P}(\{C_2^c|\tau_4\})\phi_{01}^f &= \phi_{04}^f. \end{aligned} \quad (\text{B9})$$

For general  $\mathbf{k}$ , the crystal eigensolutions are related to the translationally symmetrized sublattice wavefunctions by a unitary transformation which depends on  $\mathbf{k}$ . Only when the group of  $\mathbf{k}$  is sufficiently large (i.e., when  $\mathbf{k}$  lies along special symmetry directions) can we determine the coefficients of the transformation by group theory; otherwise one must diagonalize the matrix based on the sublattice functions. The results of applying the projection operator to the localized ion-pair wavefunctions to generate crystal symmetrized wavefunctions for  $\mathbf{k}$  along the directions specified comprise a very lengthy list, so only the necessary formulas are quoted herein. Interactions involving ion-pairs of translationally inequivalent molecules are found to contribute to the Davydov splitting, whereas interactions involving ion-pairs of translationally equivalent molecules in principle effect the band shape only. Moreover, estimates of the effect of interactions between translationally equivalent ion-pairs show this contribution to be negligibly small. Thus we consider only the

following localized functions in the generation of crystal eigenfunctions:

$$\begin{aligned}
 \text{Naphthalene:} \quad & | \mathbf{X}_n, \mathbf{X}_n + \boldsymbol{\tau} \rangle & | \mathbf{X}_n, \mathbf{X}_n + \boldsymbol{\tau} + \mathbf{c} \rangle \\
 & | \mathbf{X}_n, \mathbf{X}_n - \boldsymbol{\tau} \rangle & | \mathbf{X}_n, \mathbf{X}_n + \boldsymbol{\tau} + \mathbf{c} - \mathbf{b} \rangle \\
 & | \mathbf{X}_n, \mathbf{X}_n + \boldsymbol{\tau} - \mathbf{a} \rangle & | \mathbf{X}_n, \mathbf{X}_n - \boldsymbol{\tau} - \mathbf{c} + \mathbf{b} \rangle \\
 & | \mathbf{X}_n, \mathbf{X}_n + \boldsymbol{\tau} - \mathbf{b} \rangle & | \mathbf{X}_n, \mathbf{X}_n - \boldsymbol{\tau} - \mathbf{c} \rangle,
 \end{aligned} \tag{B10}$$

$$\begin{aligned}
 \text{Benzene:} \quad & | \mathbf{X}_n, \mathbf{X}_n + \boldsymbol{\tau}_2 \rangle & | \mathbf{X}_n, \mathbf{X}_n + \boldsymbol{\tau}_3 \rangle & | \mathbf{X}_n, \mathbf{X}_n + \boldsymbol{\tau}_4 - \mathbf{c} \rangle \\
 & | \mathbf{X}_n, \mathbf{X}_n - \boldsymbol{\tau}_2 \rangle & | \mathbf{X}_n, \mathbf{X}_n - \boldsymbol{\tau}_3 \rangle & | \mathbf{X}_n, \mathbf{X}_n + \boldsymbol{\tau}_4 \rangle \\
 & | \mathbf{X}_n, \mathbf{X}_n + \boldsymbol{\tau}_2 - \mathbf{a} \rangle & | \mathbf{X}_n, \mathbf{X}_n + \boldsymbol{\tau}_3 - \mathbf{b} \rangle & | \mathbf{X}_n, \mathbf{X}_n - \boldsymbol{\tau}_4 \rangle \\
 & | \mathbf{X}_n, \mathbf{X}_n + \boldsymbol{\tau}_2 - \mathbf{b} \rangle & | \mathbf{X}_n, \mathbf{X}_n + \boldsymbol{\tau}_3 - \mathbf{c} \rangle & | \mathbf{X}_n, \mathbf{X}_n + \boldsymbol{\tau}_4 - \mathbf{a} \rangle.
 \end{aligned} \tag{B11}$$

Let

$$\begin{aligned}
 B(m, n) &= \langle m | \mathcal{H} | m, n \rangle - \langle m | \mathcal{H} | m \rangle \langle m | m, n \rangle, \\
 C(m, n) &= \langle m | \mathcal{H} | n, m \rangle - \langle m | \mathcal{H} | m \rangle \langle m | n, m \rangle,
 \end{aligned}$$

where  $\langle m | \mathcal{H} | m, n \rangle$  represents the off-diagonal matrix element between  $| \mathbf{X}_m \rangle$  and  $| \mathbf{X}_m, \mathbf{X}_n \rangle$ .

Then the matrix elements of the Hamiltonian in the basis of both neutral and charge-transfer crystal exciton state functions are

$$\begin{aligned}
 \text{Naphthalene:} \quad & K_1 = \sqrt{2} [B(0, \tau)^2 + C(\tau, 0)^2 \pm 2B(0, \tau)C(\tau, 0) \cos(\mathbf{k} \cdot \boldsymbol{\tau})]^{1/2}, \\
 & K_2 = \sqrt{2} [B(\tau, 0)^2 + C(0, \tau)^2 \pm 2B(\tau, 0)C(0, \tau) \cos(\mathbf{k} \cdot \boldsymbol{\tau})]^{1/2}, \\
 & K_3 = \sqrt{2} [B(0, \tau + c)^2 + C(\tau + c, 0)^2 \pm 2B(0, \tau + c)C(\tau + c, 0) \cos(\mathbf{k} \cdot \boldsymbol{\delta})]^{1/2}, \\
 & K_4 = \sqrt{2} [B(\tau + c, 0)^2 + C(0, \tau + c)^2 \pm 2B(\tau + c, 0)C(0, \tau + c) \cos(\mathbf{k} \cdot \boldsymbol{\delta})]^{1/2},
 \end{aligned} \tag{B12}$$

where

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

and

$$\boldsymbol{\delta} = \boldsymbol{\tau} + \mathbf{c},$$

$$\begin{aligned}
 \text{Benzene:} \quad & K_1 = \sqrt{2} \left[ \begin{array}{c} + \\ B(0, \tau_2)^2 + C(\tau_2, 0)^2 \pm 2B(0, \tau_2)C(\tau_2, 0) \cos(\mathbf{k} \cdot \boldsymbol{\tau}_2) \\ - \end{array} \right]^{1/2}, \\
 & K_2 = \sqrt{2} \left[ \begin{array}{c} + \\ B(\tau_2, 0)^2 + C(0, \tau_2)^2 \pm 2B(\tau_2, 0)C(0, \tau_2) \cos(\mathbf{k} \cdot \boldsymbol{\tau}_2) \\ - \end{array} \right]^{1/2}, \\
 & K_3 = \sqrt{2} \left[ \begin{array}{c} + \\ B(0, \tau_3)^2 + C(\tau_3, 0)^2 \pm 2B(0, \tau_3)C(\tau_3, 0) \cos(\mathbf{k} \cdot \boldsymbol{\tau}_3) \\ - \end{array} \right]^{1/2}, \\
 & K_4 = \sqrt{2} \left[ \begin{array}{c} + \\ B(\tau_3, 0)^2 + C(0, \tau_3)^2 \pm 2B(\tau_3, 0)C(0, \tau_3) \cos(\mathbf{k} \cdot \boldsymbol{\tau}_3) \\ - \end{array} \right]^{1/2}, \\
 & K_5 = \sqrt{2} \left[ \begin{array}{c} + \\ B(0, \tau_4)^2 + C(\tau_4, 0)^2 \pm 2B(0, \tau_4)C(\tau_4, 0) \cos(\mathbf{k} \cdot \boldsymbol{\tau}_4) \\ + \end{array} \right]^{1/2}, \\
 & K_6 = \sqrt{2} \left[ \begin{array}{c} + \\ B(\tau_4, 0)^2 + C(0, \tau_4)^2 \pm 2B(\tau_4, 0)C(0, \tau_4) \cos(\mathbf{k} \cdot \boldsymbol{\tau}_4) \\ + \end{array} \right]^{1/2}.
 \end{aligned} \tag{B13}$$

The matrix elements were derived from the symmetry-adapted functions by a unitary transformation which reduced the complex matrix to real symmetric form, and by Löwdin symmetric orthogonalization as discussed in an earlier publication from this laboratory.<sup>1</sup> All three and four center integrals were neglected in the derivation of (B12) and (B13).

We note that as  $\mathbf{k} \rightarrow 0$  these elements reproduce those obtained previously, except for a minor error in the  $\mathbf{k} = 0$  calculations in which  $\bar{B}$  and  $\bar{C}$  were used instead of  $B$  and  $C$ .  $\bar{B}$  was defined, for example, as  $\bar{B}(0, \tau) = \frac{1}{2}[B(0, \tau) + B(\tau, 0)]$ . The expressions in Eqs. (B12) and (B13) are correct for  $\mathbf{k}$  along the symmetry directions specified and for  $\mathbf{k} = 0$ .

To compute the band structure, we have used values of  $B(m, n)$  and  $C(m, n)$  reported earlier.<sup>1</sup> The molecular wavefunctions were taken to be antisymmetrized products of Hückel molecular orbitals. Charge-transfer states were created by removing an electron from the highest occupied orbital of the neutral molecule at one site and placing it in the lowest unoccupied orbital of a neighboring molecule. The twofold degeneracy of both the highest occupied and lowest unoccupied Hückel orbitals of benzene leads to four times as many matrix elements as implied by expression (B13), thereby leading to a  $25 \times 25$  matrix to be diagonalized. The corresponding naphthalene matrix is  $5 \times 5$ .

Off-diagonal elements between charge-transfer states were set equal to zero to be consistent with the approximation of neglecting three- and four-center integrals.

In crystalline naphthalene the energy of the second charge-transfer state, corresponding to crystal symmetrized functions based on the localized functions  $|\mathbf{X}_n, \mathbf{X}_n + \mathbf{C} + \boldsymbol{\tau}\rangle$  was kept  $6400 \text{ cm}^{-1}$  above the lowest charge-transfer state. The energy of the lowest charge-transfer state was parametrically varied.

In crystalline benzene the energies of the second and third charge-transfer states relative to that of the lowest charge-transfer state were maintained at  $1000$  and  $3000 \text{ cm}^{-1}$ , respectively, during the variation of the energy of the lowest charge-transfer state.

Diagonalization of the secular matrix was facilitated by combining states with the same diagonal elements in the following manner. A matrix similar to the ones with which we are concerned is

$$\begin{bmatrix} 0 & A & B \\ A & E & 0 \\ B & 0 & E \end{bmatrix},$$

$$E^\pm(\mathbf{k}) - E_0 = \Delta\epsilon' + D' + \sum_n \cos(\mathbf{k} \cdot \mathbf{X}_n) \langle \phi_{n1}^0 \phi_{01}^f | V_{n1,01} | \phi_{n1}^f \phi_{01}^0 \rangle$$

which is considered to be a secular matrix in the real basis

$$\mathbf{V} \equiv \begin{bmatrix} \xi_0 \\ \xi_1 \\ \xi_2 \end{bmatrix}.$$

The application of an orthogonal transformation of the form

$$\mathbf{C} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & A(A^2+B^2)^{-1/2} & B(A^2+B^2)^{-1/2} \\ 0 & B(A^2+B^2)^{-1/2} & -A(A^2+B^2)^{-1/2} \end{bmatrix}$$

to  $V$  yields a new basis,

$$\mathbf{V}' = \begin{bmatrix} \xi_0 \\ (A\xi_1 + B\xi_2)(A^2+B^2)^{-1/2} \\ (B\xi_1 - A\xi_2)(A^2+B^2)^{-1/2} \end{bmatrix},$$

in which the matrix has now been partially diagonalized to the block form

$$\begin{bmatrix} 0 & (A^2+B^2)^{1/2} & 0 \\ (A^2+B^2)^{1/2} & E & 0 \\ \hline 0 & 0 & E \end{bmatrix}.$$

If matrices larger than the  $3 \times 3$  example have in their basis vectors  $\mathbf{V}$  several components with the same diagonal elements, successive applications of the above technique will reduce the size of the matrix to be diagonalized. In this manner we reduced the  $25 \times 25$  secular matrix for crystalline benzene to a  $4 \times 4$  matrix, since only four unequal diagonal elements (ion-pair energies) are involved. The matrix for the naphthalene crystal was also reduced from  $5 \times 5$  to  $3 \times 3$  in the same manner.

### APPENDIX C: DAVYDOV COMPONENT ENERGY EXPRESSIONS

The neutral exciton state energies, relative to  $E_0$ , the crystal ground-state energy, are obtained by taking the matrix elements of  $\mathcal{H}$  in the basis of the neutral exciton wavefunctions and diagonalizing the secular matrix. For  $\mathbf{k}$  in the directions specified in crystalline naphthalene we find, using the crystal inversion symmetry,

$$\pm \sum_n \cos[\mathbf{k} \cdot (\mathbf{X}_n + \boldsymbol{\tau})] \langle \phi_{n2}^0 \phi_{01}^f | V_{n2,01} | \phi_{n2}^f \phi_{01}^0 \rangle, \quad (\text{C1})$$

$$\text{where } D' = \sum_{n\alpha} \{ \langle \phi_{m\beta}^f \phi_{n\alpha}^0 | V_{m\beta,n\alpha} | \phi_{m\beta}^f \phi_{n\alpha}^0 \rangle - \langle \phi_{n\alpha}^0 \phi_{m\beta}^0 | V_{n\alpha,m\beta} | \phi_{n\alpha}^0 \phi_{m\beta}^0 \rangle \},$$

and  $\Delta\epsilon' = \epsilon' - \epsilon_0$  is the free-molecule excitation energy.

The Davydov splitting between the + and - states in (C1) vanishes as  $\mathbf{k}$  approaches the Brillouin zone boundary along  $\mathbf{a}^{-1}$  or  $\mathbf{b}^{-1}$ , but not along  $\mathbf{c}^{-1}$ , as is required by group theory.

The energies of the neutral exciton states of benzene are similar in form to (C1):

$$E^f(\mathbf{k}) - E_0 = \left\langle 0, 0^f, \begin{array}{c} +++ \\ +-- \\ -+- \\ ---+ \end{array} \middle| \mathcal{H} - \varepsilon_0 \middle| 0, 0^f, \begin{array}{c} +++ \\ +-- \\ -+- \\ ---+ \end{array} \right\rangle$$

$$= \Delta \varepsilon^f + D^f + \sum_n \cos(\mathbf{k} \cdot \mathbf{X}_n) \langle \phi_{01^f} \phi_{n1^0} | V_{01,n1} | \phi_{01^0} \phi_{n1^f} \rangle + L^f(\mathbf{k}), \quad (\text{C2})$$

where  $L^f(\mathbf{k})$  contains all of the terms defining the state symmetry and is given by

$$L^f(\mathbf{k}) = \frac{1}{2} \sum_n \left[ \begin{array}{c} + \\ + \\ - \\ - \end{array} M_{01,n2} \cos\{\mathbf{k} \cdot [\mathbf{X}_n + \frac{1}{2}(\mathbf{a} + \mathbf{b})]\} \begin{array}{c} + \\ + \\ - \\ - \end{array} M_{03,n4} \cos\{\mathbf{k} \cdot [\mathbf{X}_n + \frac{1}{2}(\mathbf{a} + \mathbf{b})]\} \right.$$

$$\left. \begin{array}{c} + \\ + \\ - \\ - \end{array} M_{01,n3} \cos\{\mathbf{k} \cdot [\mathbf{X}_n + \frac{1}{2}(\mathbf{b} + \mathbf{c})]\} \begin{array}{c} + \\ + \\ - \\ - \end{array} M_{02,n4} \cos\{\mathbf{k} \cdot [\mathbf{X}_n + \frac{1}{2}(\mathbf{b} - \mathbf{c})]\} \right.$$

$$\left. \begin{array}{c} + \\ + \\ - \\ - \end{array} M_{01,n4} \cos\{\mathbf{k} \cdot [\mathbf{X}_n + \frac{1}{2}(\mathbf{a} + \mathbf{c})]\} \begin{array}{c} + \\ + \\ - \\ - \end{array} M_{02,n3} \cos\{\mathbf{k} \cdot [\mathbf{X}_n + \frac{1}{2}(\mathbf{c} - \mathbf{a})]\} \right]. \quad (\text{C3})$$

In (C3),

$$M_{n\alpha, m\beta} = \langle \phi_{n\alpha^f} \phi_{m\beta^0} | V_{n\alpha, m\beta} | \phi_{n\alpha^0} \phi_{m\beta^f} \rangle. \quad (\text{C4})$$

In the case of benzene, as  $\mathbf{k}$  approaches the Brillouin-zone boundary along the three axes of the reciprocal lattice, the four symmetry components become degenerate in pairs:

$$\left. \begin{array}{l} E^{+++}(\mathbf{k}) = E^{-+-}(\mathbf{k}) \\ E^{+--}(\mathbf{k}) = E^{-+}(\mathbf{k}) \end{array} \right\} \text{as } |\mathbf{k}| \rightarrow \pi/a,$$

$$\left. \begin{array}{l} E^{+++}(\mathbf{k}) = E^{-+}(\mathbf{k}) \\ E^{+--}(\mathbf{k}) = E^{-+-}(\mathbf{k}) \end{array} \right\} \text{as } |\mathbf{k}| \rightarrow \pi/b,$$

$$\left. \begin{array}{l} E^{+++}(\mathbf{k}) = E^{+--}(\mathbf{k}) \\ E^{-+-}(\mathbf{k}) = E^{-+}(\mathbf{k}) \end{array} \right\} \text{as } |\mathbf{k}| \rightarrow \pi/c, \quad (\text{C5})$$

Expressions (C1) and (C2) are used when one assumes a particular interaction potential, such as transition octupole coupling chosen by Craig in the study of crystalline naphthalene. Configuration mixing of the neutral exciton states with charge-transfer states has no effect on the general formalism and the predicted degeneracies, but does allow for a smaller interaction potential than would be required without the inclusion of such mixing.

#### APPENDIX D: SEPARATION OF $D$ AND $I_{\text{eq}}^f$ FROM THE TOTAL VAPOR-TO-CRYSTAL SPECTRAL SHIFT

The quantities  $D$  and  $I_{\text{eq}}^f$  which appear in the weak-coupling model energy expression may be calculated from observed spectral data with an accuracy of about  $\pm 10 \text{ cm}^{-1}$  in the following manner.

We start by noting that the shift of each vibronic component is  $D + I_{\text{eq}}^f$ . It is then assumed that the vibrational frequencies in the excited free-molecule state are the same as those in the corresponding state in the crystal. The observed environmental shift of each vibronic component depends on the intensity of this component in the crystal spectrum, since the Franck-Condon factors determine the value of  $I_{\text{eq}}^f$  (vibrational frequencies are known to change by a few  $\text{cm}^{-1}$  in organic crystals in going from the vapor to the crystal phase, but these changes are negligibly small for our purposes). The estimate of  $I_{\text{eq}}^f$  rests upon the general prediction in the weak-coupling limit that  $I_{\text{eq}}^f$  is proportional to the Franck-Condon factor for the  $i$ th vibronic component.

The environmental shift  $D$  is the same as the vapor-to-crystal spectral shift for vibronic states which are constructed from nontotally symmetric vibrational wavefunctions and the pure electronic wavefunctions.

since the vanishing of the Franck-Condon factor makes  $I_{\text{eq}}^{f_i} = I_{\text{ineq}}^{f_i} = 0$ .  $D$  shows some small dependence on the vibronic state to which it refers and varies by about  $30 \text{ cm}^{-1}$  in the different vibronic states listed in Tables I and II. Using the data tabulated in Table I for the naphthalene spectrum at  $\mathbf{k} = \mathbf{0}$ , we find that

$$\begin{aligned} \Delta\epsilon^{f_0} - E_{\pm}^{f_0} &= -470 \text{ cm}^{-1} \pm I_{\text{ineq}}^{f_0}; & 0-0 \\ \Delta\epsilon^{f_1} - E_{\pm}^{f_1} &= -477 \text{ cm}^{-1} \pm I_{\text{ineq}}^{f_1}; & 0-1, \end{aligned} \quad (\text{D1})$$

and that

$$\begin{aligned} I_{\text{ineq}}^{f_0} &= -74 \text{ cm}^{-1} & \text{in the } 0-0 \text{ bands,} \\ I_{\text{ineq}}^{f_1} &= -15 \text{ cm}^{-1} & \text{in the } 0-1 \text{ bands.} \end{aligned} \quad (\text{D2})$$

The result

$$I_{\text{ineq}}^{f_0}/I_{\text{ineq}}^{f_1} = |\langle \chi^{0(0)} | \chi^{f(0)} \rangle|^2 / |\langle \chi^{0(0)} | \chi^{f(1)} \rangle|^2 = 5 \quad (\text{D3})$$

is consistent with the vibrational overlap Franck-Condon factors in the pure electronic spectrum. Assuming that

$$|\langle \chi^{0(0)} | \chi^{f(0)} \rangle|^2 + |\langle \chi^{0(0)} | \chi^{f(1)} \rangle|^2 = 1,$$

and defining

$$\begin{aligned} I_{\text{eq}}^{f_0} &= I_{\text{eq}}^f |\langle \chi^{0(0)} | \chi^{f(0)} \rangle|^2, \\ I_{\text{eq}}^{f_1} &= I_{\text{eq}}^f |\langle \chi^{0(0)} | \chi^{f(1)} \rangle|^2, \end{aligned} \quad (\text{D4})$$

we solve (D1) to obtain

$$D = -478 \text{ cm}^{-1}$$

and

$$I_{\text{eq}}^f = 10 \text{ cm}^{-1}, \quad (\text{D5})$$

so that

$$\begin{aligned} I_{\text{eq}}^{f_0} &= 8 \text{ cm}^{-1}, \\ I_{\text{eq}}^{f_1} &= 1 \text{ cm}^{-1}. \end{aligned} \quad (\text{D6})$$

These values have been introduced into Table I for comparison with the values of  $D$  for other vibronic states. We also note that unless the values of  $D$  for the 0-0 and 0-1 $a_g$  bands were very much smaller than those for the other vibronic states,  $I_{\text{eq}}^f$  is a small number, and is expected to be positive for naphthalene.

To analyze the spectrum of crystalline benzene we must make more approximations than in our analysis of the spectrum of naphthalene, but we still are able to obtain a reasonable estimate of  $D$  and  $I_{\text{eq}}^f$ .

Because only three of the four Davydov components possess nonzero transition moment matrix elements with the  $A_g$  crystal ground state, the fourth component (symmetry  $A_u$ ) is unobservable. Hence, the center of gravity of the four Davydov components is not known experimentally. We have made the assumption that the density of states for the 0-0 band extends over  $85 \text{ cm}^{-1}$  based on calculations by Sommer and Jortner,<sup>9</sup> so there should be an  $85\text{-cm}^{-1}$  energy separation between the lowest and highest energy components at  $\mathbf{k} = \mathbf{0}$ . An experimental estimate for this energy separation is  $\sim 60 \text{ cm}^{-1}$  (Table V). Since the splitting between the

TABLE VI. Franck-Condon  $A_g$  vibrational overlaps for the lowest singlet of crystalline and free benzene.

F-C overlap	Crystal	Vapor*
$ \langle \chi^{0(0)}   \chi^{f(0)} \rangle ^2$	0.28	0.19
$ \langle \chi^{0(0)}   \chi^{f(1)} \rangle ^2$	0.31	0.28
$ \langle \chi^{0(0)}   \chi^{f(2)} \rangle ^2$	0.21	0.25
$ \langle \chi^{0(0)}   \chi^{f(0)} \rangle ^2$	0.17	0.17
$ \langle \chi^{0(0)}   \chi^{f(4)} \rangle ^2$	0.08	0.09

\* Reference 7.

highest and lowest energy components of the three observed 0-0 bands is  $43 \text{ cm}^{-1}$ , we have placed the  $A_u$  component at the upper limit, i.e.,  $85 \text{ cm}^{-1}$  above the lowest component at  $37\,803 \text{ cm}^{-1}$ . The position of the  $A_u$  component in the totally symmetric vibrational progression is obtained by scaling the energy extension of the density of states by the ratio of Franck-Condon factors in the 0-0 band and in the band under consideration, since the splittings between components are proportional to Franck-Condon overlaps.

The results obtained using the scheme outlined above are reasonable, for the centers of gravity of the four components are separated by  $925 \text{ cm}^{-1}$  from the center of gravity of the next highest totally symmetric vibrational band, which is very close to the gas-phase separation of  $923 \text{ cm}^{-1}$ .

The Franck-Condon factors were obtained by a procedure analogous to the method used for crystalline naphthalene. The ratio of vibrational overlaps squared is assumed to be equal to the ratio of Davydov splitting for a given pair of components. Using the splitting between the  $a$ - and  $c$ -polarized components in the totally symmetric vibrational progressions built on the 0-0 bands, and applying the vibrational sum rule as in the naphthalene crystal,

$$\sum_i |\langle \chi^{0(0)} | \chi^{f(i)} \rangle|^2 = 1,$$

we have calculated the crystal Franck-Condon factors. They are displayed in Table VI along with gas-phase Franck-Condon factors. The calculated values agree with the absorption intensities for crystalline benzene reported by Wolf.<sup>13</sup>

The values of  $D$  for crystalline benzene quoted in Table II for the 0-0 and for the totally symmetric vibrational progressions built thereupon were taken to be equal to  $-252$  and  $-248 \text{ cm}^{-1}$  by borrowing the value of  $D$  directly from the progressions built upon  $e_{2g}$  vibrations. The bands corresponding to  $A_{1g} \rightarrow B_{2u}a_{1g}a_{1g}$  were given a value of  $D = -248 \text{ cm}^{-1}$  instead of  $-252 \text{ cm}^{-1}$  in order that the ratio of  $I_{\text{eq}}^i$  values would be the same as the crystal Franck-Condon factors.

If we solve two simultaneous equations for the ben-

zene crystal as we did for naphthalene,

$$\begin{aligned} D + I_{\text{eq}}^f |\langle \chi^{0(0)} | \chi^{f(0)} \rangle|^2 &= -245 \text{ cm}^{-1}, \\ D + I_{\text{eq}}^f |\langle \chi^{0(0)} | \chi^{f(1)} \rangle|^2 &= -243 \text{ cm}^{-1}, \end{aligned} \quad (\text{D7})$$

we obtain

$$\begin{aligned} I_{\text{eq}}^{f0} &= 18 \text{ cm}^{-1}, \\ I_{\text{eq}}^{f1} &= 20 \text{ cm}^{-1}, \\ D &= -263 \text{ cm}^{-1}, \end{aligned} \quad (\text{D8})$$

for which the values of  $I_{\text{eq}}^{fi}$  are twice those in Table II, but still small and positive. Use of Franck-Condon factors from Table II and (D8) gives

$$I_{\text{eq}}^{f3} = 13 \text{ cm}^{-1},$$

and by difference,

$$D = -254 \text{ cm}^{-1}. \quad (\text{D9})$$

We conclude that the value of  $I_{\text{eq}}^f = \sum_i I_{\text{eq}}^{fi}$  for crystalline naphthalene is  $\sim 10 \text{ cm}^{-1}$  and for crystalline benzene is  $\sim 35 \text{ cm}^{-1}$ .

#### APPENDIX E: EFFECT OF TIGHT-BINDING AND CHARGE-TRANSFER MIXING ON THE VIBRONIC MANIFOLD OF THE $\alpha$ STATE

One observes in the crystal spectra of naphthalene and benzene both totally symmetric and nontotally symmetric vibrations built upon the purely electronic origin. Neglecting intensity changes due to crystal field mixing, the crystal spectra resemble the vapor phase spectra except for the following features: (1) an over-all red shift of the entire vibronic manifold in the crystal spectra, (2) Davydov splitting of the totally symmetric vibrational progressions built upon the electronic origin, and (3) essentially no splitting of totally symmetric vibrational progressions built upon nontotally symmetric false origins. These three experimental observations are consistent with both the tight-binding (Frenkel) model upon which the transition octupole coupling calculations were based and with charge-transfer configuration mixing with the tight binding model as detailed below.

In the tight-binding case,  $D + I_{\text{eq}}^{fi}$  represents the total vapor-to-crystal spectral shift. The term  $I_{\text{eq}}^{fi}$  vanishes for nontotally symmetric vibrations in the excited electronic state, but even for the cases for which it is formally nonvanishing (i.e., for  $a_g$  vibrational states) we see from Tables I and II that  $I_{\text{eq}}^{fi}$  is only of the order of  $10\text{--}30 \text{ cm}^{-1}$ , so the entire vibronic manifold is essentially depressed uniformly by the term  $D$  which is independent of vibronic states and depends only on the electronic state. Because of vanishing Franck-Condon integrals between the ground state  $a_g$  vibrational state and nontotally symmetric vibrations of the excited electronic state,  $I_{\text{ineq}}^{fi}$ , which defines the Davydov splitting for the  $f$ th vibronic state, is formally zero for nontotally symmetric vibrations and nonzero for  $a_g$  vibrational states.

Charge-transfer configuration interaction with the neutral exciton states gives rise to off-diagonal elements in the Hamiltonian matrix. Focusing our attention on the effect of the entire charge-transfer vibronic manifold on each vibronic state  $fi$  of the neutral state, we observe the following:

The  $B$  and  $C$  values quoted in Appendix B must be

$$\begin{aligned} B' &= B \langle \chi^{f(i)} | \chi^{+(j)} \rangle \langle \chi^{-(i)} | \chi^{0(0)} \rangle, \\ C' &= C \langle \chi^{f(i)} | \chi^{-(i)} \rangle \langle \chi^{+(j)} | \chi^{0(0)} \rangle, \end{aligned} \quad (\text{E1})$$

for the configuration interaction with the vibronic state  $fi$  of the charge transfer state in which the positive ion is in its  $j$ th vibrational state and the negative ion is in its  $i$ th vibrational state. Assuming that the ionic vibrational wavefunctions are the same as those of the excited electronic state  $f$ , we obtain

$$\begin{aligned} \langle \chi^{f(i)} | \chi^{+(j)} \rangle &= \delta_{ij}, \\ \langle \chi^{f(i)} | \chi^{-(i)} \rangle &= \delta_{ii}, \end{aligned} \quad (\text{E2})$$

which has the following significance for totally and nontotally symmetric vibrational states:

(a) If  $\chi^{f(i)}$  transforms as  $a_g$ , both  $C'$  and  $B'$  are nonvanishing for appropriate choices of charge-transfer vibronic states  $\chi^{+(j)}$ ,  $\chi^{-(i)}$ , and the off-diagonal matrix element is, as outlined in Appendix B,

$$[(B')^2 + (C')^2 \pm 2B'C' \cos \mathbf{k} \cdot \boldsymbol{\tau}]^{1/2}. \quad (\text{E3})$$

Since  $\pm B'C'$  determines the Davydov splitting, one observes Davydov splitting in totally symmetric vibrational states.

(b) If  $\chi^{f(i)}$  does not transform according to  $a_g$ , for a given choice of  $\chi^{+(j)}$  and  $\chi^{-(i)}$  for which  $B'$  does not vanish,  $C'$  will be formally zero by symmetry by (E1) and (E2); similarly when  $C'$  is nonzero,  $B'$  is zero by symmetry. However, in our approximation, isoenergetic with the charge transfer state which possesses vibrational states denoted by the functions  $(\chi^{+(j)}, \chi^{-(i)})$  is a charge-transfer state with vibrational functions  $(\chi^{+(i)}, \chi^{-(j)})$ . Thus, if  $B'$  were vanishing for configuration interaction involving the first charge transfer state and  $C'$  were nonzero, then in the case of the second charge-transfer state,  $B'$  is nonzero and  $C'$  is zero. By means of the matrix block diagonalization scheme outlined in Appendix B the effect of these two charge transfer states may be combined to give the matrix element

$$[(B')^2 + (C')^2]^{1/2}. \quad (\text{E4})$$

Thus, nontotally symmetric vibrational states are not split, but are depressed by the same amount as the totally symmetric vibrational states, in accordance with experimental observations. From the form of  $B'$  and  $C'$  in Eq. (E1) one can easily see that the use of  $B$  and  $C$  in the calculations of this paper provides an upper bound to the effect of charge-transfer configuration interaction with the neutral state.