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Anisotropic Effects in Optical Excitation of Excitons in Molecular Crystals*

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The expression for the energy of an exciton state contains certain dipole lattice sums. These sums are strongly dependent on the direction of the propagation vector of the exciton, even when the magnitude of this vector is very small. As a result, the energy of an optically-excited exciton may depend strongly on the direction of propagation of the absorbed radiation, if the excitation takes place coherently over a region whose linear dimensions are comparable with or much larger than a wavelength. The behavior of the lattice sums may also introduce a dependence of the exciton polarization and of the absorption coefficient on the direction of propagation. The magnitudes of these effects were calculated for the cases of the first and second transitions of naphthalene and of anthracene. Experimental observations of the extent to which these effects occur could provide information on the dimensions of the region of excitation of the exciton.

I. INTRODUCTION

OPTICAL transitions from the ground state of a crystal to an exciton level are forbidden unless the propagation vector $\mathbf{k}$ of the exciton equals $\mathbf{k}_0$, that of the absorbed radiation.[1] The number of exciton states corresponding to a given excited molecular energy level, and having a given $\mathbf{k}$, equals the number of molecules per unit cell times the degeneracy of the molecular level.[2,3] There may, therefore, be more than one allowed transition from the crystal ground state to each exciton band, even when the corresponding molecular level is nondegenerate. These allowed transitions generally differ from one another in energy and polarization. Splitting of nondegenerate molecular levels (Davydov splitting[2]) has been observed by Craig and Hobbins[4] and by Sidman[5] in anthracene, by McClure and Schnepp[6] in naphthalene, and by Broude, Medvedev, and Prikhot'ko[7] in benzene.

The ratio of $\mathbf{k}_0$ to the magnitude of a primitive translation vector of the reciprocal lattice is small (10^{-2} to 10^{-3}). For this reason, it was assumed by Davydov that in calculating the magnitude of the splitting and predicting the polarizations, one may take $\mathbf{k}=0$ as an approximation. If the intermolecular interaction energy which causes this splitting can be expanded as a series of multipole interactions in which all the terms are of higher order than dipole-dipole,[8] this approximation is valid. However, if the expansion does contain dipole-dipole terms, the convergence problems of dipole lattice sums must be considered;[9–11] if an exciton packet is excited with coherent phase over a region whose linear dimensions are greater than a wavelength of the absorbed radiation, the sums are strongly dependent on the direction of $\mathbf{k}$, even for small k. As a result of this direction dependence, the frequencies and polarizations of the absorbed radiation vary with $\mathbf{k}$-direction, if the exciton-packet dimensions are sufficiently large at the time of excitation (Secs. III and IV).

In addition to a discussion of these variations we present the results of calculations of the magnitudes of the various effects in the cases of the first and second electronic transitions in naphthalene and anthracene. For two reasons, these numerical values should not be taken as predictions of the results of future experiments, but rather as a guide to the interpretation of these experiments. First, the calculations are based on the assumption that each photon is absorbed over a region of dimensions large compared with a wavelength; if this is not so (i.e., if a small exciton packet is excited) the variations will be reduced, and possibly not observable. Second, in at least one case (the second transition in anthracene), there is some question as to the rapidity of convergence of the perturbation calculation which was used, so that even with assumption of coherent absorption over a large region, the results are good only in order of magnitude.

The Davydov splitting itself indicates some degree of nonlocalization of the excitation at the time of absorption. In each of the experiments performed to date, the

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observations were made with only one direction of $\mathbf{k}_0$. A study of the dependence of transition energies and polarizations on direction of $\mathbf{k}_0$ can yield further information as to the extent of coherent excitation.

II. EXCITON ENERGIES AND DAVYDOV SPLITTING

The material of this section has been described in detail elsewhere.[1–4,12,13] We shall discuss, without proof, certain results which will be required.

The crystal Hamiltonian may be written as $H=H_0+V$, where H_0 is the sum of molecular Hamiltonians, and V is the sum of interactions between molecules. In treating the lowest states of molecular crystals, the term V may be taken as a perturbation.

The ground state of the crystal, in lowest order, is the product of ground state functions of all the molecules. In a crystal with one molecule per unit cell, the exciton functions[1]

$$\varphi_{\mathbf{k}}{}^{\alpha}=\sum\nolimits_J e^{i\mathbf{k}\cdot\mathbf{r}_J}\Psi_J{}^{\alpha} \tag{1}$$

may be constructed from crystal states $\Psi_J{}^{\alpha}$ in which the Jth molecule is excited to the αth (nondegenerate) state, and all other molecules are in their ground states; $\mathbf{r}_J$ is the position of the center of the Jth molecule with respect to some arbitrary origin. The functions $\Psi_J{}^{\alpha}$ are antisymmetric with respect to electron exchange. For a given α, they are degenerate eigenfunctions of H_0. The functions (1) (with $\mathbf{k}$ taking on the usual allowed values in the first zone of $\mathbf{k}$-space) are, therefore, also eigenfunctions of H_0, but they diagonalize the submatrix of V which corresponds to a fixed α (the α submatrix), and V splits the degeneracy.

If there are q molecules per unit cell, and the αth molecular level is again nondegenerate, we may take the "one-site excitons"

$$\varphi_{j\mathbf{k}}{}^{\alpha}=\sum\nolimits_J e^{i\mathbf{k}\cdot\mathbf{r}_{jJ}}\Psi_{jJ}{}^{\alpha} \tag{2}$$

as basis functions.[2,3] The antisymmetrized function $\Psi_{jJ}{}^{\alpha}$ represents a crystal state in which the molecule at the jth molecular site of the Jth cell, at position $\mathbf{r}_{jJ}$, is excited to the αth state, and all the other molecules are in the ground state. The function (2) represents a sharing of the excitation among jth-site molecules only. Matrix elements of V between states with different $\mathbf{k}$ will vanish, but the α submatrix will contain nonvanishing off-diagonal elements between states with the same $\mathbf{k}$ but different j. The correct zero-order wave functions, obtained by diagonalization of the α submatrix, will be the q linear combinations

$$\Phi_{\sigma\mathbf{k}}{}^{\alpha}=\sum\nolimits_j C_{\sigma}{}^{j}\varphi_{j\mathbf{k}}{}^{\alpha} \tag{3}$$

of the one-site excitons. The set of coefficients $C_{\sigma}{}^{j}$ depends on both $\mathbf{k}$ and α.

An optical transition from the crystal ground state to one of the exciton states (3) is allowed only if $\mathbf{k}$ is equal to $\mathbf{k}_0$, the propagation vector of the incident radiation.[1] For each direction of $\mathbf{k}_0$, this selection rule permits one transition for each value of σ. Some of these transitions may be prohibited by further selection rules arising from the symmetry restrictions imposed by that subgroup of the factor group which leaves $\mathbf{k}$ invariant.[3]

The polarization vector of an exciton state may be defined as

$$\mathbf{P}_{\sigma}=\sum\nolimits_j C_{\sigma}{}^{j}\mathbf{p}_j{}^{\alpha}, \tag{4}$$

where $\mathbf{p}_j{}^{\alpha}$ is the molecular transition dipole moment taken between the αth excited state and the ground state of a molecule with jth-site orientation. The vector $\mathbf{P}_{\sigma}$ is dependent on $\mathbf{k}$ and α. The integrated absorption coefficient of the transition from the crystal ground state is, in lowest order,

$$(4\pi^2\epsilon_{\alpha}/n\hbar cv)\mathbf{P}_{\sigma}{}^2\cos^2\gamma, \tag{5}$$

where n is the real part of the index of refraction of the crystal, v is the volume of a unit cell, and γ is the angle between $\mathbf{P}_{\sigma}$ and the polarization vector of the absorbed radiation. The maximum possible value of $\cos\gamma$ will be one only if the optically active exciton is transversely polarized. In designating the polarization of an absorption, we shall refer to the polarization of the exciton, rather than to that of the radiation.

With the set of functions (2) as a basis, the elements of the α submatrix of V contain the following types of terms[1,2,4,13]: (a) Coulomb terms, representing interactions between pairs of ground-state molecules, or between ground-state and excited molecules; (b) excitation-exchange terms, which are matrix elements of the interaction between two molecules, taken between one state in which only the first molecule is excited and another in which the excitation has been transferred to the second molecule; (c) electron-exchange terms (arising in the usual way from the antisymmetrization of the wave functions), in which a pair of electrons is exchanged between the two interacting molecules; (d) electron- and excitation-exchange terms, in which both a pair of electrons and the excitation are exchanged.

In crystals of aromatic molecules, terms of type (d) are negligible.[4,8] The terms (c) are either negligible or else cancel in the difference between crystal ground state and exciton state energies, so that they do not affect the transition frequencies. The terms (a) usually cannot be neglected; however, they appear only in the diagonal matrix elements of V, and are independent of $\mathbf{k}$ and j. They will, therefore, not enter into the variation of energy or of polarization with $\mathbf{k}_0$, with which we shall be primarily concerned. Their contributions will be discussed briefly in Sec. III.

The terms (b) are modulated sums of the form

$$\sum_J e^{i\mathbf{k}\cdot\mathbf{r}_{jJ}}\int(\psi_0{}'\psi_{jJ})^*V_0{}^{jJ}\psi_0\psi_{jJ}{}'d\tau_0 d\tau_{jJ}, \tag{6}$$

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[12] D. L. Dexter, Phys. Rev. **101**, 48 (1956).

[13] W. R. Heller and A. Marcus, Phys. Rev. **84**, 809 (1951).

where ψ_0 and ψ_{jJ} are the ground state wave functions of molecules at the origin and at the jth site of the Jth cell respectively, while the primed functions designate the corresponding excited states; V_0^{jJ} is the interaction between the zeroth and the jJth molecule. In the diagonal elements of the α submatrix, the two interacting molecules occupy the same site in their respective cells, while in the off-diagonal elements, they occupy different sites.

If the interaction V_0^{jJ} is expanded as a series of multipole-multipole terms, each matrix element contained in the sum (6) will be expanded into a series of interactions between transition multipoles. If the molecular optical transition is dipole-allowed, the lowest order terms in the expansion will be dipole-dipole.

The preceding discussion may be generalized to the case in which the αth molecular level is m-fold degenerate.[3] The basis functions (2) are then replaced by a set of mq functions in each of which the index α is supplemented by another index, $n=1, 2, \cdots, m$, which designates the particular molecular state of the degenerate level which is excited. The degenerate case is discussed briefly in Sec. VI.

III. FIRST-ORDER PERTURBATION CALCULATIONS

In this section, we shall consider a crystal with two molecules per unit cell; the excited molecular state from which the exciton functions are constructed is nondegenerate. The mixing of states of different exciton bands (in higher order of perturbation theory) will be ignored, and it will be assumed that at the time of absorption, the excitation is coherent over a large enough region that calculations for exciton functions of infinite extent apply.

The two molecular sites in the various unit cells will be designated by $j=A$ and $j=B$. For simplicity, A and B will also be used to designate the one-site excitons $\varphi_{A\mathbf{k}}{}^{\alpha}$ and $\varphi_{B\mathbf{k}}{}^{\alpha}$, respectively. The matrix elements of V, corresponding to a given $\mathbf{k}$, are V_{AA}, V_{AB}, V_{BA}, and V_{BB}, with the index $\mathbf{k}$ implicit.

In the dipole-dipole (d-d) approximation, the matrix elements (6) may be written[2,4,13]

$$\begin{aligned} V_{ij}=\textstyle\sum_J e^{i\mathbf{k}\cdot\mathbf{r}_{jJ}}[(\mathbf{p}_i\cdot\mathbf{p}_j)\,|r_{jJ}|^{-3} \\ -3(\mathbf{p}_i\cdot\mathbf{r}_{jJ})(\mathbf{p}_j\cdot\mathbf{r}_{jJ})\,|r_{jJ}|^{-5}]; \quad i,j=A,B; \end{aligned} \tag{7}$$

where $\mathbf{p}_A\equiv\mathbf{p}_A{}^{\alpha}$, $\mathbf{p}_B\equiv\mathbf{p}_B{}^{\alpha}$; with Eq. (7) in this form, the origin must be located at an ith-site molecule.

The summation in (7) may be carried out by Ewald's method.[14] If the exciton is excited optically, $\mathbf{k}$ equals $\mathbf{k}_0$, so that ka is of the order of 10^{-2} (where a is the average lattice constant). The result of the summation, except for terms of order k^2a^2, may be written as

$$\begin{aligned} V_{jj}&=4\pi v^{-1}p^2[(\boldsymbol{\eta}\cdot\boldsymbol{\zeta}_j)^2+T_1], \\ V_{AB}=V_{BA}&=4\pi v^{-1}p^2[(\boldsymbol{\eta}\cdot\boldsymbol{\zeta}_A)(\boldsymbol{\eta}\cdot\boldsymbol{\zeta}_B)+T_2], \\ T_1=-\boldsymbol{\zeta}_A\cdot(d_1)\cdot\boldsymbol{\zeta}_A&; \quad T_2=-\boldsymbol{\zeta}_A\cdot(d_2)\cdot\boldsymbol{\zeta}_B, \end{aligned} \tag{8}$$

where v is the volume of the unit cell; $p=|\mathbf{p}_A|=|\mathbf{p}_B|$; $\boldsymbol{\eta}$, $\boldsymbol{\zeta}_A$, and $\boldsymbol{\zeta}_B$ are unit vectors in the directions of $\mathbf{k}$, $\mathbf{p}_A$, and $\mathbf{p}_B$, respectively; (d_1) and (d_2) are tensors (dependent on the lattice structure, but not on $\mathbf{k}$) which may be evaluated by methods described in references 9 and 10.

Lattice sums of higher order in the multipole expansion converge sufficiently rapidly with distance that they are independent of $\mathbf{k}$ for small ka. These contributions, therefore, change only the constant terms, T_1 and T_2, in Eqs. (8). In a molecule which, like naphthalene or anthracene, has a center of symmetry, transition moments will be either all even or all odd, so that if the transition is allowed, the next higher interaction terms will be dipole-octupole (d-o), followed by octupole-octupole (o-o).

Another constant correction, but only to T_1, arises from the Coulomb terms [terms (a) of Sec. II]. In molecules having no permanent dipole moment, these terms are quadrupole-quadrupole and higher, where the Coulombic quadrupole moment of the entire molecule, either in ground or excited state, is involved.

Calculated values of the transition octupole moment or of the Coulombic quadrupole moment are generally inaccurate in these molecules. Furthermore, some of the contributions to T_1 and T_2 from second-order perturbation theory depend on certain unknown parameters (Sec. IV). Since we are primarily concerned here with the variation of frequencies and polarizations with direction of $\mathbf{k}$, the total corrections to the constant terms may be determined empirically by comparing calculated and observed frequencies for the $\mathbf{k}$-direction used in the experiments.

With a large octupole transition moment, the o-o terms of (6) will be of the order of 100 cm^{-1} in crystals like naphthalene and anthracene; with the largest reasonable moment and extremely favorable molecular orientation, one may get about ten times this value.[8] The d-o contributions will be of the order of the geometric mean between the d-d and o-o terms. Usually, the Coulomb terms will be[5] of the order of 1000 cm^{-1}. (All energies are given in wave numbers to facilitate comparison with experimental results.)

Since the A-molecules have the same geometric relationship to one another as do the B-molecules, the $\mathbf{k}$-independent term T_1 in (7) is the same in V_{AA} and V_{BB}. The $\mathbf{k}$-vector, however, spoils this symmetry, and the first term is different in the two matrix elements, unless $\boldsymbol{\eta}\cdot\boldsymbol{\zeta}_A=\pm\boldsymbol{\eta}\cdot\boldsymbol{\zeta}_B$. In the latter case, $V_{AA}=V_{BB}$, and the diagonalization of the matrix is simple. The first-order energy corrections are then $V_{AA}\pm V_{BB}$, corresponding to the eigenfunctions $\Phi_{\pm}=2^{-\frac{1}{2}}\times(A\pm B)$ and the polarization vectors $\mathbf{P}_{\pm}=2^{-\frac{1}{2}}\times(\mathbf{p}_A\pm\mathbf{p}_B)$.[15]

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[14] P. P. Ewald, Ann. Physik **64**, 253 (1921).

[15] This is an application, in non-group-theoretical language, of the discussion of reference 3. The condition $\boldsymbol{\eta}\cdot\boldsymbol{\zeta}_A=\pm\boldsymbol{\eta}\cdot\boldsymbol{\zeta}_B$ is equivalent to the statement that $\mathbf{k}$ is invariant to the operations of the symmetry group of the dipole lattice (which may be a larger

In other directions of $\boldsymbol{\eta}$ the difference between V_{AA} and V_{BB} will generally be of the order of the d-d approximation of either matrix element, and the energies, wave functions, and polarizations may be quite different from those given above. The first term of each matrix element of Eqs. (8), which gives rise to these variations, depends on $\boldsymbol{\eta}$, but not on k; it therefore cannot be neglected, even for small ka. (When $k=0$, this term is indeterminate; however, this indeterminacy has no physical meaning, since it would appear only if the exciton were truly infinite in extent.[11])

Details of the calculations of energies and polarizations as functions of $\boldsymbol{\eta}$ are given in Appendix I. We shall discuss here the results as applied to the electronic transitions between the ground state and the two lower excited states of naphthalene and anthracene, limiting ourselves to the case of $\boldsymbol{\eta}$ lying in the *ac* plane, where the condition $\boldsymbol{\eta}\cdot\boldsymbol{\zeta}_A=\boldsymbol{\eta}\cdot\boldsymbol{\zeta}_B$ is satisfied.

In each of these substances, transitions between the ground and the lower excited states of the free molecule are polarized in the molecular plane, along either the short or the long molecular axis. Both crystal lattices[16] are monoclinic, belonging to space group C_{2h}^5. The direction of $\mathbf{p}_B$ may be obtained from that of $\mathbf{p}_A$ by reflection in the *ac* plane; the difference of the dipole vectors is therefore in the direction of the monoclinic *b* axis, while the sum is in the *ac* plane, along what will be called the *u* direction. The orientarion of the *u* axis within the *ac* plane depends on which of the four cases is being considered. The crystals grow with developed *ab* faces. The observations of references 4–6 were carried out with $\boldsymbol{\eta}$ along the normal to the *ab* plane (called the c' direction).

With $\boldsymbol{\eta}$ in the *ac* plane, V_{AA} equals V_{BB}, and the two allowed crystal transitions are *b*- and *u*-polarized. The first-order energy correction for the *b*-polarized exciton, $\epsilon_b^{(1)}$, is independent of θ (the angle between $\boldsymbol{\eta}$ and the c' axis) while that of the *u*-polarized exciton is

$$\epsilon_u^{(1)}=C_1+C_2\cos 2(\theta-\beta)\,, \tag{9}$$

where β is the angle between the *u* and c' directions. Expressions for the constants $\epsilon_b^{(1)}$, C_1, and C_2 are given in Appendix I and values in Table I.

The maximum Davydov splitting occurs when $\boldsymbol{\eta}$ is either in the *b* direction or in the *u* direction, depending on crystal and molecular parameters. In either case, one of the components is longitudinally polarized and so cannot be observed in absorption experiments. The largest observable splitting would then be in the neighborhood of one of these directions.

IV. SECOND-ORDER PERTURBATION CORRECTIONS

Corrections to the transition frequencies arising from second-order perturbation calculations may be important. In determining these corrections, one must take as perturbing states not only "single" excitons (similar to the state of Eq. (3), but with different α), but also, as Dexter and Heller have shown, "multiple" excitons, in each of which more than one molecule is in an excited state.[17]

The mixing of the exciton (3) with other single excitons has been discussed by Craig,[4] who, however, treated only the case in which long-range effects may be neglected. If the exciton is excited coherently over a large volume, the mixing will be $\mathbf{k}$-dependent. In the *ac* plane, where the first-order perturbation energy of the *u*-polarized component is given by (9), the second-order energy is of the form

$$\epsilon_u^{(2)}=C_3+C_4\cos 2(\theta-\beta_1)+C_5\cos 4(\theta-\beta_1), \tag{10}$$

while the corresponding term for the *b* component, $\epsilon_b^{(2)}$, is independent of $\boldsymbol{\eta}$. The sum of Eqs. (9) and (10) is

$$\epsilon_u=\epsilon_u^{(1)}+\epsilon_u^{(2)}=C_6+C_7\cos 2(\theta-\beta_2)+C_5\cos 4(\theta-\beta_1). \tag{10a}$$

Contributions to the second-order energy arising from the mixing with multiple excitons depend in part on transition moments between pairs of excited states of the molecule, which are generally not known. Fortunately, the sum of those terms which cannot be calculated is independent of $\mathbf{k}$ (see Appendix II); furthermore, it is the same for both Davydov components and so contributes nothing to the splitting. The remaining terms give results which are similar to those arising from perturbation by single excitons; in particular, Eqs. (10) and (10a) remain correct, except for a change of the numerical values of the constants, when the multiple-exciton contributions are added, and $\epsilon_b^{(2)}$ is still independent of θ when $\boldsymbol{\eta}$ is in the *ac* plane.

Values of the constants in Eq. (10a), including multiple-exciton contributions, are given in the table. The third term on the right produces an additional "ripple," which, where detectable, can give a measure of the mixing of higher states.

The mixing of exciton states will also mix transition moments and so will change the intensities of the two components. In this connection, one must take into account both the perturbation of the function (3) by other single excitons and of the ground state by double excitons.[12,17]

McClure and Schnepp reported changes from molecular to crystal frequencies of -545 and -379 cm^{-1} for the *u* and *b* components, respectively, in the first electronic transition in naphthalene at 20°K. The values calculated from Eq. (9), with $\theta=0$, are both less than 10 cm^{-1}, with negligible corrections from (10). Even if

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group than that of the actual crystal; in higher orders of perturbation theory, it is the group of the actual crystal that must be considered).

[16] Abrahams, Robertson, and White, Acta Cryst. **2**, 233, 238 (1949); Sinclair, Robertson, and Matheison, Acta Cryst. **3**, 245, 251 (1950).

[17] D. L. Dexter and W. R. Heller, Phys. Rev. **91**, 273 (1953).

an average value over a packet in **k**-space must be taken (Sec. V), the results cannot be changed by more than a few wave numbers. The contributions from the remaining ($\boldsymbol{\eta}$-independent) corrections could easily account for the observed values, if the unknown parameters are large enough. The corrected values of T_1 and T_2 would then be so large as to overwhelm the $\boldsymbol{\eta}$-dependent terms in Eq. (8). The diagonalization of the matrix V_{ij} would then be as predicted group-theoretically for the case $\mathbf{k}=0$,[2-4] and one polarization vector will be in the b direction, the other in the ac plane for any $\boldsymbol{\eta}$; however, as will be shown later, the magnitude of either polarization vector and the direction of the latter one within the ac plane may vary. The variation of transition frequencies will be very small, and probably not detectable.

In the same transition, McClure and Schnepp observed a ratio of less than 0.005 between the intensities of the u and b components, while the predicted value for unperturbed excitons is 4. They proposed the mixing with single excitons of the next higher band (short-axis transition) as an explanation of this discrepancy. They showed that a mixing coefficient of -0.068[18] for the u component would lead to cancellation of the polarization contributions from the perturbed and perturbing states, so that a coefficient in this neighborhood is required to explain the small intensity ratio. We have calculated an effective coefficient of -0.052 for the u component (the effective coefficient takes into account the perturbation of the ground state) and of $+0.006$ for the b-component, leading to a value of 0.8 for the intensity ratio. This result is still far from the experimental value, but because of the near-cancellation of the polarization contributions, an increase of only 30% in the mixing coefficient for the u component leads to agreement with the observed value. Alternatively, an increase of 30% in the molecular transition moment of the higher excited state would also give the correct value. Part of the required correction may arise from mixing with still higher exciton states, and part from d-o and o-o terms in the calculation of the mixing coefficient.

Although the transition frequencies are independent of $\boldsymbol{\eta}$ in this transition, the ratio of intensities of the two components will vary in a fairly complicated way. With $\boldsymbol{\eta}$ in the ac plane, the b axis is always perpendicular to $\boldsymbol{\eta}$, and the b component mixing turns out to be independent of θ, so that the absorption coefficient of this component will be constant. The absorption coefficient of the u component will vary for two reasons. First, the angle γ between the polarizations of the exciton and of the radiation would vary with θ, even if there were no mixing with the higher state. Second, the mixing coefficient will vary; since the polarizations of the perturbed and perturbing excitons are not parallel in this component, both the magnitude and the direction of the resultant will vary with θ. The first effect alone would give an absorption coefficient proportional to $\sin^2(\theta-\delta)=\frac{1}{2}[1-\cos2(\theta-\delta)]$; to give agreement with the small observed ratio at $\theta=0$, the angle δ would have to be of the order of 1°, so that the absorption would be nearly symmetric about $\theta=0$. With the second (long-range) effect taken into account, the absorption coefficient will contain "ripples" of the form $\cos4(\theta-\delta')$ and $\cos6(\theta-\delta'')$ and the near symmetry about the c' axis will be removed.

In the last three columns of the table are listed the values of the Davydov splitting when **k** is in the c' direction: first the calculated values to first order then the calculated values with second-order corrections included and in the last column the experimental values. It may be seen that the agreement is not good. We have already seen that for the first transition in naphthalene, corrections such as the o-o terms can account for the discrepancy. For the second transition the same may be true if the components of the transition octupole moment are very large and if the molecular orientations are unusually favorable, but it is more likely that part of the discrepancy indicates that the exciton-packet dimensions are not very large compared with a wavelength. A variation of frequency with direction may still show up if these dimensions are somewhat smaller than a wavelength, but it would be smaller than that calculated here.

The smallness of the exciton packet may also account for the discrepancies in the two anthracene transitions, but here there is also a question as to the rapidity of convergence of the perturbation calculation. In the case of the first transition, the second-order correction is larger than the first, while for the second transition, both calculated and experimental corrections are comparable with the spacing between molecular states. The slowness of convergence will probably not change the order of magnitude of the energy variations described here, but it may seriously affect them in detail. It should be noted that perturbation corrections of still higher order can show up as higher-order ripples in the energy variation but again only if there is long-range coherence of the excitation.

V. EXCITON PACKETS[19]

The calculations of the preceding sections were based on the assumption that the dimensions of the region of coherent excitation are large compared to a wavelength. Lattice vibrations and other crystal imperfections may limit this region seriously. Even in a perfect crystal, if the absorption is strong, the exciton at the time of the optical excitation will be a packet whose depth below the surface of the crystal is no greater than the absorption depth of the radiation.

If all the packet dimensions are at least an order of

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[18] McClure and Schnepp's value is $+0.068$, but they apparently have a different convention for the sign of one of the molecular transition moments.

[19] We wish to thank Dr. M. Cohen for his criticisms of an earlier version of the material of this section.

magnitude smaller than a wavelength, the change in phase across the packet will be very small and the long-range effects previously discussed will not show up. In such a case the energy will be strongly dependent on the shape and size of the packet. Furthermore, there will be a contribution to the width of the absorption, either because the packet is a mixture of eigenstates, or because $\mathbf{k}$ is no longer a good quantum number (in the case of serious limitation by imperfections), or for both reasons.

The spread of energy over the $\mathbf{k}$-packet (the transform of the exciton packet in $\mathbf{k}$-space) is a lower limit for the width of the absorption, so that the latter sets upper limits for the dimensions of the $\mathbf{k}$-packet. Because the energy [Eq. (8)] depends strongly on the direction of $\mathbf{k}$, this limit is fairly small for the width of the $\mathbf{k}$-packet in directions perpendicular to $\mathbf{k}_0$. On the other hand, in the direction of $\mathbf{k}_0$, the limit is large; in fact, if the expressions for the lattice sums in Eqs. (8) were accurate for all $\mathbf{k}$, there would be no energy spread in this direction. The corrections for larger k become significant when the length of the $\mathbf{k}$-packet in the $\mathbf{k}_0$ direction is about a tenth the magnitude of a primitive reciprocal lattice vector or greater, corresponding to an exciton-packet depth of $10a$ or less.

The absorption coefficient of the b component of the second electronic transition in anthracene was estimated by Craig and Hobbins[4] to be about 4×10^5 cm^{-1}; the width of the absorption at room temperature is an order of magnitude smaller than the $\mathbf{k}$-dependent terms of Eqs. (8). If the exciton packet were limited only by the strength of the absorption, its depth below the surface would be about $30a$, while the dimensions parallel to the surface would be those of the crystal; in that case, only a small part of the absorption width would come from the spread of energy over the $\mathbf{k}$-packet. On the other hand, if all the absorption width were attributed to this spread, the depth of the exciton below the surface would be greater than $10a$, and the average lower limit in other directions would be about ten times as large. The excitation would then be shared coherently by at least 10^5 molecules.

Craig and Hobbins estimated the absorption in the u component to be at least five times stronger than in the b component. The absorption width of the former at room temperature is comparable with the $\mathbf{k}$-dependent terms of (8). In such a strong absorption, the corrections to (8) for large k become important, and the calculations of the preceding sections and of the appendices should be correct only in order of magnitude. At low temperatures and in good crystals, the packet size may be increased considerably in this absorption if the polarizations of the radiation and of the exciton are almost perpendicular to one another; in that case, the variation of the energy should be like that predicted here. Alternatively, one could obtain a continuous variation of transition frequency by rotating the polarization of the radiation while keeping $\mathbf{k}_0$ fixed (preferably not close to the normal to the crystal surface).

VI. GENERAL CASE

Winston[3] has discussed the general case of an exciton formed from an n-fold degenerate excited molecular state in a crystal containing q molecules per unit cell. He assumed that the energies of optically active excitons are very close to the energy for $k=0$. The modifications to take into account the strong dependence of energy on $\boldsymbol{\eta}$ are straightforward. For a given $\mathbf{k}$, a qn-dimensional matrix is to be diagonalized. In the d-d approximation, the off-diagonal matrix elements are now sums of interactions between dipoles which are at different sites, or which are not parallel, or both. Winston discusses the extent to which group-theoretical methods can be used in diagonalizing the energy matrix when k is not close to 0; his discussion must also be applied to optically active excitons.

One new feature is introduced by the large energy variation in the neighborhood of $k=0$. In crystals with more than two molecules per unit cell, some of the transitions allowed by the condition $\mathbf{k}=\mathbf{k}_0$ are forbidden by selection rules arising from factor-group symmetry.[3,20] Winston developed a procedure for finding these selection rules, on the assumption that one may take $k=0$. If this assumption is not correct, the group which leaves $\mathbf{k}$ invariant[3,21] must be used in predicting these rules. For most directions of $\mathbf{k}$, the selection rules break down, and all qn components, except those which are longitudinally polarized, have allowed transitions to the ground state.

There is at least one case in which none of the new features discussed in this paper will appear. This is the cubic atomic crystal, in which the optically active exciton states are constructed from atomic p-states.[13] In this lattice, (d_1) is one-third the unit tensor. If, for each $\mathbf{k}$, the three p states are chosen in such a way that each exciton is polarized either transversely or longitudinally, then for small k, the three-by-three matrix will be diagonal. For any $\boldsymbol{\eta}$, the first-order energy correction of either transversely polarized state will be $-4\pi p^2/3$, and that of the longitudinally polarized state $8\pi p^2/3$. Since the latter state is optically inactive, there is no Davydov splitting. The polarizations and energies are independent of $\boldsymbol{\eta}$. (For large k, the excitons will not be transversely or longitudinally polarized unless $\mathbf{k}$ lies on a symmetry element of the crystal.)

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One of us (DF), who was a guest at the Institute of Optics of the University of Rochester when the work was concluded, wishes to express his appreciation to Professor D. L. Dexter for his hospitality and encouragement during this period.

APPENDIX I

In the first order of perturbation theory, the matrix elements of V are given by Eq. (8). Solution of the secular equation yields as corrections to the molecular transition energies the values $\epsilon_1^{(1)}$ and $\epsilon_2^{(1)}$, corresponding to the wave functions $\varphi_1=(aA+bB)$ and $\varphi_2=(-bA+aB)$, respectively, where $a^2+b^2=1$; the coefficients a and b are real, since the V_{ij} are real. The ratio $R_1=a/b$ (or $R_2=-1/R_1$) determines the functions φ_1 and φ_2, as well as the corresponding polarizations: $\mathbf{P}_1=(a\mathbf{p}_A+b\mathbf{p}_B)$ and $\mathbf{P}_2=(-b\mathbf{p}_A+a\mathbf{p}_B)$.

We define new variables

$$\begin{aligned} &x=\zeta_u\eta_u T_2^{-\frac{1}{2}}, \quad y=\zeta_b\eta_b T_2^{-\frac{1}{2}}, \\ &\lambda_m=(-T_1+v\epsilon_m^{(1)}/4\pi p^2)T_2^{-1}; \quad m=1,2, \end{aligned} \tag{11}$$

where η_u and η_b are the components of $\boldsymbol{\eta}=\mathbf{k}/k$ in the u and b directions, respectively; ζ_u and ζ_b are the corresponding components of $\boldsymbol{\zeta}_A=\mathbf{p}_A/p_A$; the components of $\boldsymbol{\zeta}_B$ are ζ_u and $-\zeta_b$; v, T_1 and T_2 are defined in Sec. III. It is assumed here that $T_2>0$; the alternative possibility is discussed below.

In terms of the new variables, equations are obtained which do not depend explicitly on the parameters of the crystal or of the transition,

$$\begin{aligned} &\lambda_m=x^2+y^2\pm Q, \\ &R_m=(-2xy\pm Q)/(x^2-y^2+1), \\ &Q^2=(x^2-y^2+1)^2+4x^2y^2, \end{aligned} \tag{12}$$

with $m=1$ corresponding to the upper, and $m=2$ to the lower, of the signs $\pm$.

If $T_2<0$, the variables x and y are imaginary. We may define the real variables $x'=ix$ and $y'=iy$ and find that

$$\lambda_{1\,(\text{or }2)}(x,y;T_2)=-\lambda_{2\,(\text{or }1)}(y',x';-T_2).$$

A similar relationship holds for R_m. In the following, it will be assumed that $T_2>0$.

While the behavior in the infinite xy plane is the same for all crystals of the type considered here, important differences arise from the fact that the relationship $\eta_u^2+\eta_b^2\leqslant 1$, or

$$x^2/\zeta_u^2+y^2/\zeta_b^2\leqslant T_2^{-1} \tag{13}$$

restricts the variables to the interior of the limiting ellipse whose equation is obtained by taking the equal sign in (13). Because of this restriction, a large value of T_2 (small limiting ellipse) leads to a small variation of λ_m or of R_m with change of $\mathbf{k}$ direction, as would be expected from the form of Eq. (8).

The lines of constant energy are the coordinate curves of a two-dimensional elliptical coordinate system with foci at $x=0$, $y=\pm 1$. Lines of constant R_m are hyperbolas whose axes intersect at the origin and have slopes R_1 and R_2.

When $\boldsymbol{\eta}$ is in the ac plane (the symmetry plane of the crystal), y is zero. The behavior in this plane was described in Sec. III; the constants used there have the values

$$C_1=K(T_1+T_2+\zeta_u^2), \quad C_2=K\zeta_u^2, \quad \epsilon_b^{(1)}=K(T_1-T_2),$$

where $K=4\pi p^2/v$.

A plane through the b axis and perpendicular to the u direction ($x=0$) is another symmetry plane of the dipole lattice, but not of the actual crystal. As a consequence, the behavior in this plane is somewhat similar to that in the ac plane, but only to first order, since a perturbing state may have a different u direction. To this order, the optically active excitons will be b- and u-polarized, but in this case, it is the energy of the u component which is independent of angle, while the variation of energy of the b component is of the form of Eq. (9).

In other directions, the polarizations will not necessarily be in the b and u directions. The nature of the variation of polarization direction with change of $\mathbf{k}$ direction [Eq. (12)] depends on the parameters of the crystal and of the transition. For example, one of the polarizations may always be close to the b direction, the other close to the u direction, for any $\boldsymbol{\eta}$. On the other hand, for different values of the parameters, there may be a continuous change of one of the polarizations from the b to the u direction, and of the other polarization from u to b as $\boldsymbol{\eta}$ is varied.

APPENDIX II

We shall outline the calculations involved in the mixing of single excitons of different bands only for the case in which $\mathbf{k}$ is in the ac plane. Primes will be added to previously defined symbols to designate quantities associated with the molecular excited state α'. For example, diagonalization of the α' matrix leads to the eigenfunctions $\varphi_n'=2^{-\frac{1}{2}}(A'\pm B')$ when $\mathbf{k}$ is in the ac plane; the index $\mathbf{k}$ is omitted again, since only states of the same $\mathbf{k}$ will be mixed by the perturbation. It may be shown by symmetry arguments[4,6] that there will be mixing between φ_m and φ_n' only if $m=n$. The second-order corrections will be

$$\epsilon_m^{(2)}=|V_{AA'}\pm V_{AB'}|^2(E_\alpha-E_{\alpha'})^{-1}, \tag{14}$$

where E_α and E_α' are the energies of the molecular states. In deriving this expression, the relationships $V_{AA'}=V_{BB'}$ and $V_{AB'}=V_{BA'}$ (valid in the ac plane) were used. In the d-d approximation, the matrix elements are

$$\begin{aligned} &V_{AA'}=4\pi pp'v^{-1}[(\boldsymbol{\eta}\cdot\boldsymbol{\zeta}_A)(\boldsymbol{\eta}\cdot\boldsymbol{\zeta}_A')-\boldsymbol{\zeta}_A\cdot(d_1)\cdot\boldsymbol{\zeta}_A'], \\ &V_{AB'}=4\pi pp'v^{-1}[(\boldsymbol{\eta}\cdot\boldsymbol{\zeta}_A)(\boldsymbol{\eta}\cdot\boldsymbol{\zeta}_B')-\boldsymbol{\zeta}_A\cdot(d_2)\cdot\boldsymbol{\zeta}_B'], \end{aligned} \tag{15}$$

TABLE I. Values of constants for naphthalene and anthracene. All quantities, except the angles, are in wave-number units (cm^{-1}). The letters N and A in the first column designate naphthalene and anthracene, respectively; the numbers 1 and 2 refer to the first and second electronic transitions, respectively. The constants in the following ten columns are those used in Eqs. (9) and (10a) and in the adjacent text. The constants of Eq. (10a) are omitted where the second-order corrections are negligible. The last three columns list the Davydov splitting for **k** in the c' direction ($\theta=0$), with a positive sign indicating that the u component has the higher energy; the first of these columns contains the theoretical value to first order of perturbation theory, the next contains the values corrected to second order, while the last contains the experimental values. Two experimental values are listed in the second row because of an uncertainty in the identification of one of the components[6]; the two values in the third row were taken from different authors.[4,5]

											Davydov splitting		
Trans.	C_1	C_2	C_5	C_6	C_7	β	β_1	β_2	$\epsilon_b^{(1)}$	$\epsilon_b^{(2)}$	$\Delta\epsilon^{(1)}$	$\Delta\epsilon^{(2)}$	Exptl.
$N1$	5	6				−26°			−1		10	10	166
$N2$	−165	450				41°			−1300	−30	1200	1200	170 or 320
$A1$	−270	210	−190	−1000	−840	46°	8°	1°	−920	−100	660	−940	0 or 25
$A2$	17 000	16 000	−1800	12 000	9200	−30°	−30°	−28°	−3000	−75	28 000	21 000	∼13 000

where the tensors (d_1) and (d_2) are those which appear in Eq. (8). Equation (10) follows from the fact that in the ac-plane, $\boldsymbol{\eta}\cdot\boldsymbol{\zeta}_A=\zeta_u\cos(\theta-\beta)=\boldsymbol{\eta}\cdot\boldsymbol{\zeta}_B$ and similarly for the primed quantities; the constants of Eq. (10) are

$$C_3=L(T^2+\tfrac{1}{2}\zeta_u{}^2\zeta_u{}'^2),\quad C_4=2LT\zeta_u\zeta_u{}',\quad C_5=\tfrac{1}{2}L\zeta_u{}^2\zeta_u{}'^2,$$
$$L=(4\pi pp'/v)^2(E_\alpha-E_{\alpha'})^{-1},$$
$$T=\zeta_u\zeta_u{}'\cos(\beta-\beta')-\boldsymbol{\zeta}_A\cdot(d_1)\cdot\boldsymbol{\zeta}_A{}'-\boldsymbol{\zeta}_A\cdot(d_2)\cdot\boldsymbol{\zeta}_B{}'.\quad(16)$$

The procedure for the other directions of **k** is the same, except for the fact that the lower symmetry allows mixing of states with $m\neq n$. The algebra is further complicated by the fact that the coefficients a, b, a', and b' appearing in φ_m and $\varphi_n{}'$ are direction-dependent in the general case.

We must consider the perturbation of the state (3) not only by other single excitons, but also by double and triple excitons.[17] In the case of anthracene, the contributions of the latter are significant.

It may be shown that the total energy correction arising from the mixing of an entire band of double excitons with the state (3) is independent of **k** and is therefore not important for the present discussion; furthermore, this correction is the same for both φ_1 and φ_2, so that it contributes only to the average shift, but not to the Davydov splitting. Calculation of these terms is not feasible at present, since it requires the knowledge of transition moments between excited states.

A triple exciton state will not mix with (3) unless one of the three molecular excitations is the same as that involved in (3) (i.e., the αth). We shall designate by $(\alpha,\alpha',\alpha'')$ a triple exciton state in which there is one α, one α', and one α'' excitation; for a complete description, one would also have to specify a propagation vector for each of the excitations.[17]

The total second-order energy contribution arising from the mixing of (3) with all the states of the band of excitons $(\alpha,\alpha',\alpha'')$ will contain **k**-dependent terms and contributions to the splitting if and only if one or both of the molecular states α' and α'' is the same as α. The total of the **k**-dependent terms from the band of states (α,α,α') (where now α and α' may or may not be equal) is

$$|V_{AA'}\pm V_{AB'}|^2(\delta_{\alpha\alpha'}-2)(E_\alpha+E_{\alpha'})^{-1}.\quad(17)$$

This expression has the same **k**-dependence as does the right member of Eq. (14). In the case of anthracene, if one of the states α or α' represents the first excited electronic state and the other represents the second, the energies are such that (17) is about a third of (14); if one is interested primarily in order-of-magnitude results, the contribution of (17) is not important. However, there is a case in which it may be important. The largest values of the numerators in (14) and (17) are found when both α and α' represent the state with the strongest transition from the ground state (in anthracene, the second excited state). However in Eq. (14), α cannot equal α', that is, the exciton (3) is not to be mixed with itself; on the other hand, α may equal α' in (17), and if both represent the second excited state of anthracene, (17) is of the order of 1000 cm^{-1}.

As long as we may neglect electron exchange terms, excitons of higher multiplicity need not be considered in this order of perturbation theory.[17]