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# A Theory of Excitons in Strained Molecular Crystals

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# A Theory of Excitons in Strained Molecular Crystals

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This paper examines theoretically the effects of strain on the exciton properties of some molecular crystals. It is found that the parameters of exciton theory are relatively sensitive to changes in lattice parameters of the crystal, and thus strain can result in significant changes in the crystal spectrum. The method proceeds through strain derivatives of the exciton parameters, which are evaluated for the unstressed crystal geometries. In this way, the influence of pressure and temperature on the spectrum is examined. The strain derivatives are evaluated for anthracene and naphthalene for light incident on the *ab*-face, and the theory used to re-examine some of the features of the first singlet of anthracene. Good agreement with experiment is obtained.

## INTRODUCTION

The exciton energies of a molecular crystal are functions of the interactions between the molecules constituting the crystal, and thus of lattice geometry. When the crystal is subjected to stress (pressure) or temperature changes, the geometry undergoes changes resulting in a shift of the exciton energies. Experimentally this is manifest in the sensitivity of spectral measurements to the conditions under which the spectra are taken. For example, the glues sometimes used for mounting thin crystals shrink significantly on drying; this shrinkage can set up large stresses in the crystal, resulting in appreciable crystal deformation and changes in the subsequently-measured spectrum. Strain effects are also important when very thin crystals are used. Such crystals may be strongly attracted to quartz plates so that they may be under considerable strain when the spectrum is measured.[1] The dependence of the factor group splitting for anthracene

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on crystal thickness is a good example of such a case.[2]

Systematic experimental studies of the effect of pressure and temperature on spectra have been reported for a number of both pure and mixed crystals.[3-6] Such studies provide quantitative relationships between spectral shifts and strain, provided the elastic constants and the temperature-dependence of the lattice parameters are known. Theoretical work on such effects has been restricted mainly to the effect of pressure on mixed-crystal spectra, for which the host induces a 'solvent shift' in the guest spectrum.[4] Such models are inappropriate for the pure crystal, for which exciton transfer terms cannot be neglected.

In this paper, the crystal energies are determined by the use of finite-basis methods in the usual way.[7,8] Matrix elements for the stressed crystal are expanded in terms of those for the unstressed crystal using a Taylor expansion in terms of suitably defined crystal strains. This yields the shifts in energy levels on stressing (or cooling) the crystal as functions of strain derivatives of site shift and exciton transfer terms, which are evaluated for the unstressed (room temperature) geometry. Use of simple elasticity theory finally yields the energies of the crystal as functions of temperature and pressure.

The derivatives are determined for the dispersion site shift and exciton transfer terms for both anthracene and naphthalene. The results for anthracene are used to discuss the pressure and temperature dependence of the first singlet system of anthracene.

## BASIC EXCITON THEORY

The electronic properties of molecular crystals may be calculated in terms of suitable combinations of free-molecule functions[7,8] The wave equation for an isolated oriented molecule at site m may be written

$$H_m \; \varphi \; {}^{s}_{m} = E^s \; \varphi \; {}^{s}_{m}$$

where $H_m$ is the molecular Hamiltonian, and $\varphi_m^s$ the $s$th excited state wave function with eigenvalue $E^s$. The ground state is given by $s = 0$. The Hamiltonian for an aggregate of such molecules may be written

$$H = \sum_{m} H_m \; + \; \tfrac{1}{2} \sum_{m,n} V_{mn}$$

where $V_{mn}$ is the interaction operator between molecules on sites $m$ and $n$. The eigenfunctions for the crystal may be set up from the following localised excitation functions:

$$\Psi_G = \prod_{m} \varphi_m^0, \; \phi^s_m \; = \varphi^s_m \; \Psi_G \; (\varphi^0_m)^{-1}. \qquad (1)$$

Doubly and higher excited states are neglected. The states of the aggregate are then assumed to be linear combinations of the above localised excitation functions

$$\bar{\Psi} = \sum_m \sum_s b_m^s \, \phi_m^s.$$

The ground state is assumed not to mix with higher states, so that the ground state energy of the crystal becomes

$$E_G = < \bar{\Psi}_G \mid H \mid \bar{\Psi}_G >.$$

For the excited states, the coefficients $b_m^s$ are determined from variation theory by the secular equations

$$\sum_{n,t} [ < \phi_m^s \mid H \mid \phi_n^t > - (E + E_G) \, \delta_{st} \, \delta_{mn} ] \, a_n^t = 0$$

and the energy $E$ relative to the perturbed crystal ground state from the solutions of

$$\det | < \phi_m^s \mid H \mid \phi_n^t > - (E + E_G) \, \delta_{st} \, \delta_{mn} | = 0$$

For crystals with more than one molecule in the unit cell, the double index $m = ip$ may be used, where $i$ indexes the $h$ sites in the unit cell and $p$ the unit cells. The translational symmetry of the crystal requires that the coefficients have the form

$$a_{ip}^s = N^{-\frac{1}{2}} \exp [\mathbf{ik}.\mathbf{r}_{ip}] \; A_i^s (\mathbf{k})$$

where $\mathbf{k}$ are the exciton wave vectors defined in the usual way, and $\mathbf{r}_{ip}$ is the position vector of the molecule at $ip$. Cyclic boundary conditions have been assumed, with $N$ unit cells per periodic volume. The secular equations are diagonal in $\mathbf{k}$, so that there will be a secular equation for each $\mathbf{k}$ value of the form

$$\sum_j [ < \phi_i^s (\mathbf{k}) \mid H \mid \phi_j^t (\mathbf{k}) > - (E + E_G) \, \delta_{st} \, \delta_{mn} ] \, A_j^t = 0$$

where

$$\phi_i^s (\mathbf{k}) = N^{-\frac{1}{2}} \sum_p \exp [\mathbf{ik}.\mathbf{r}_{ip}] \; \phi_{ip}^s.$$

The secular equations contain the general matrix element

$$< \phi_i^s (\mathbf{k}) \mid H \mid \phi_j^t (\mathbf{k}) > = [E_G + E^s - E^0] \, \delta_{st} \, \delta_{ij} + D^{st} \, \delta_{ij} \, \Sigma \, I_{ij}^{st} (\mathbf{k}) \qquad (2)$$

where

$$D^{st} = \sum_n{}' [ (\varphi_m^s \, \varphi_n^0 \mid V_{mn} \mid \varphi_m^t \, \varphi_n^0) - \delta_{st} (\varphi_m^0 \, \varphi_n^0 \mid V_{mn} \mid \varphi_m^0 \, \varphi_n^0)] = \sum_n{}' D_{mn}.$$

and

$$I_{ij}^{st} (\mathbf{k}) = \sum_q{}' \exp [\mathbf{ik}. (\mathbf{r}_{ip} - \mathbf{r}_{jq})] \, I_{ip,\,jq}^{st} \qquad (4)$$

$$I_{ip,\,jq}^{st} = \tfrac{1}{2} [ (\varphi_{ip}^s \, \varphi_{jq}^0 \mid V_{ip,\,jq} \mid \varphi_{ip}^0 \, \varphi_{jq}^t ) + (\varphi_{ip}^t \, \varphi_{jq}^0 \mid V_{ip,\,jq} \mid \varphi_{ip}^0 \, \varphi^s{}_{jq})].$$

$D^{st}$ is the gas to crystal site shift matrix, and $I_{ij}^{st}$ (k) the exciton transfer or resonance interaction matrix.

### Application to anthracene and naphthalene

For certain crystals, an explicit expression may be obtained for the exciton energies by making approximations in the secular determinant. Firstly, it may be assumed that the free-molecule excited states do not mix, so that the secular equations reduce further into a seperate set for each $s$ with elements $<\phi_j^s(\mathbf{k})|H|\phi_j^s(\mathbf{k})>$. For anthracene and napthalene, with two molecules per unit cell, there equations for each value of $\mathbf{k}$. The further assumption that $I_{11}^{ss}(\mathbf{k}) = I_{22}^{ss}(\mathbf{k})$ in these crystals for $\mathbf{k}$ in the region of $\mathbf{k} = 0$ leads to the two energy solutions[9]

$$E_{\pm}^{s}(\mathbf{k}) = [(E^s - E^0) + D^{ss} + I_{11}^{ss}(\mathbf{k})] \pm [I_{12}^{ss}(\mathbf{k})]. \tag{5}$$

The special shift term $D^{ss}$ is strictly the difference in the Coulomb interactions in the excited ($s$) and ground states of a given molecule with all other molecules in the crystal. This vanishes in the dipole approximation for molecules without a permanent dipole moment. The corresponding difference in the dispersion energy, which is thought to provide the main contribution to the experimentally-observed shift arises from second-order terms involving multiple excitations. This dispersion term is conventionally included in $D^{ss}$ (the theoretical justification is discussed in the appendix) and we shall thus refer to $D^{ss}$ as the van der Waals shift term.

With the energy in the form (5) the mixing with higher states may now be included as a correction using second-order perturbation theory. This correction has the form[7]

$$\delta E_{\pm}^{s}(\mathbf{k}) = \sum_{t(\neq s)} \frac{[D^{st} + I_{11}^{st}(\mathbf{k}) \pm I_{12}^{st}(\mathbf{k})]^2}{[E_{\pm}^{s}(\mathbf{k}) - E_{\pm}^{t}(\mathbf{k})]}. \tag{6}$$

### Effects of stress

When the crystal is put under stress, the resultant deformation will change the intermolecular interaction operator, and thus change the values of the matrix elements defined above from their values for the unstressed case. This in turn will shift the crystal energies. In order to express these shifts in the crystal energies in terms of the crystal deformation, some approximentations must be made about the nature of the deformation.

Throughout this work the deformation is assumed sufficiently small so that the overall symmetry of the crystal is not reduced. Any stress applied to the crystal is thus assumed to be uniformly distributed through the entire crystal. The importance of this assumption arises as follows. Suppose the wave vector $\mathbf{k}$ in the unstressed crystal becomes $\mathbf{k}'$ in the stressed crystal, and the vector $\mathbf{T}_{mn}$ linking molecules $m,n$ in the crystal becomes $\mathbf{T}'_{mn}$. Then under the conditions imposed above, it follows from the definition of $\mathbf{k}$ that

$$\mathbf{k}.\mathbf{T}_{mn} = \mathbf{k}'.\mathbf{T}'_{mn} \quad \textit{if} \quad \mathbf{T}_{mn} = \mathbf{T}^{\circ}_{mn} = \mathbf{t}^{ij}$$

where $\mathbf{T}^0_{mn}$ is a translation by an integral number of lattice vectors, and $\mathbf{t}^{ij}$ is a translation by *symmetry-determined* fractions of the lattice vectors. We shall for convenience deal only with crystals for which this is so.

For anthracene and naphthalene, the shift in the energy on stressing the crystal is directly related to the shifts in the matrix elements from Eq. (11) by

$$\Delta E^s_{\pm}(\mathrm{k}) = [\Delta D^{ss} + \Delta I^{ss}_{11}(\mathrm{k})] \pm \Delta I^{ss}_{12}(\mathrm{k}). \tag{7}$$

In order to relate this energy shift directly to the deformation of the crystal, the matrix elements must be expanded in terms of the deformation set up by a given stress or temperature change. This requires the explicit expression of the deformation in terms of suitable crystal strain coordinates.

## THE STRAIN DERIVATIVES

### Crystal strains

The deformation of a molecular crystal may be expressed in terms of two types of crystal strain: external and internal. The external strains describe the changes in the shape and size of the unit cell whereas the internal strains describe consequent changes within the new unit cell.

The *external strains* resulting from the application of small macroscopic stresses are most easily defined in the following way. For a general deformation, a point with initial position vector $\mathbf{r}$ is shifted to $\mathbf{r}'$ where

$$\mathbf{r}' = \mathbf{r} + \mathbf{d}$$

and $\mathbf{r} = (xyz)$, $\mathbf{d} = (uvw)$ in an $(xyz)$-coordinate system. The external strains are then defined as

$$\epsilon_1 = \frac{\partial u}{\partial x}\ \epsilon_2 = \frac{\partial v}{\partial y}\ \epsilon_3 = \frac{\partial w}{\partial z}\ \epsilon_4 = [\frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}]\ \epsilon_5 = [\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}]\ \epsilon_6 = [\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}].$$

$\epsilon_1$ to $\epsilon_3$ are the normal strains, and describe linear changes; $\epsilon_4$ to $\epsilon_6$ are shear strains, and describe angular changes of the medium. As we have assumed that there is no loss of symmetry on deformations it is possible to transform to a new set of strain coordinates: $a$, $b$, $c$ (unit cell lengths) and $\alpha$, $\beta$, $\gamma$ (unit cell angles). Denoting these six coordinates respectively by $u_i$ (i = 1, ... ,6), it is possible to write

$$\epsilon_i' = \frac{\delta u_i}{u_i} = \sum_j \mathrm{T}_{ij}\ \epsilon_j. \tag{8}$$

The estimation of the strain transformation matrix T for any particular lattice is a purely geometrical problem. The external strains may be determined from the

applied stresses (assumed sufficiently small) if the elastic constants are known. In matrix form, the relationship may be written

$$\tau = C\,\epsilon \tag{9}$$

where $\epsilon$ is a column matrix with elements $\epsilon_i$, C the matrix of elastic constants $C_{ij}$ and t the column matrix of stress components $t_i$ defined in the usual way.

The external strains describe only the changes in the shape and size unit cell. Within the new unit cell defined by the external strains, however, the molecules may change their positions and orientations. They will do so in such a way as to minimize the increase in potential energy associated with the change in unit cell shape. The parameters decribing these changes are called *internal strains*. These strains are functions of both the force constants of the crystal and the external strains. Their derivation is fully discussed elsewhere.[10] The translational shift of the molecule m will be denoted by the cartesian components $\delta X_i^m$ $(i = 1,2,3)$ relative to the lattice point. Orientational shifts will be denoted by the three infinitesimal rotation coordinates $\delta\theta_j^m$ $(j = 1,2,3)$ about suitably chosen molecular axes. We shall refer to them collectively as $\delta w_i^m$.

In general then there will be six external strain components describing the change in unit cell shape, and six internal strain components for each molecule in the unit cell. The symmetry of the lattice may reduce the number of non-zero strain components in any particular lattice.

### Expansion of a general matrix element

The interaction operator $V_{mn}$ between the two molecules $m$ and $n$ in the stressed crystal may be expanded in a Taylor series in the crystal strain about the value for the unstressed crystal $V_{mn}^0$. This will lead in turn to an expansion for the matrix elements. Consider the general matrix element $M_{mn}^0$ connecting the wave functions of molecules $m$ and $n$ in the unstressed crystal. Let $(x_i)$ represent the $i$th coordinate of a cartesian system fixed in the crystal, so that $x_i^m$ is the $i$th coordinate of molecule $m$. Defining $x_i^{mn} = (x_i^m - x_i^n)$, the matrix element for the stressed crystal expanded in terms of the displacements $\delta x_i^{mn}$, $\delta\theta_i^m$, $\delta\theta_i^n$ about the value for the unstressed crystal has the form

$$M_{mn} = M_{mn}^0 + \sum_{i=1}^{3}\left\{\left(\frac{\partial M_{mn}}{\partial x_i^{mn}}\right)_0 \delta x_i^{mn} + \left(\frac{\partial M_{mn}}{\partial \theta_i^m}\right)_0 \delta\theta_i^m + \left(\frac{\partial M_{mn}}{\partial \theta_i^{mn}}\right)_0 \delta\theta_i^n\right\}$$

The displacements describe shifts from the unstressed crystal values of the respective coordinates, and are assumed sufficiently small to allow truncation at linear terms. The derivatives are evaluated for the unstressed crystal geometry. The displacements $\delta x_i^{mn}$ contain both internal and external strain components, which may be separated by putting

$$\delta x_i^m = \delta\varrho_i^m + \delta X_i^m$$

where $\delta\varrho_i^m$ is the shift of molecule $m$ due to the overall change in the unit cell geometry, and $\delta X_i^m$ any internal shift within the unit cell. It is thus possible to rewrite the above expansion in the following way:

$$\Delta M_{mn} = \sum_j M'_{mn}(u_j)\,\delta u_j + \sum_k M'_{mn}(w_k)\,\delta w_k$$

where $j$ runs over the 6 external strains and $k$ over the 9 internal strains affecting the interaction term. $\Delta M_{mn}$ is the shift in the matrix element from its unstressed crystal value. The $M'_{mn}(u_j)$ will be referred to as the external strain derivatives of $m$, and defined as

$$M'_{mn}(u_j) = \sum_i \left(\frac{\partial M_{mn}}{\partial x_i^{mn}}\right)_0 \left(\frac{\partial x_i^{mn}}{\partial u_j}\right)_0 = \left(\frac{\partial M_{mn}}{\partial u_j}\right)_0.$$

The internal derivatives are analogously defined as

$$M'_{mn}(X_i^{mn}) = \left(\frac{\partial M_{mn}}{\partial x_i^{mn}}\right)_0, \quad \underset{o}{M'_{mn}}(\theta_i^m) = \left(\frac{\partial M_{mn}}{\partial \theta_i^m}\right)_0$$

Note that all the derivatives are evaluated at the unstressed crystal geometry, so that only a single set of derivatives requires evaluation. This expansion can now be applied directly to the matrix elements appearing in the expression for the crystal energies.

## THE ENERGY SHIFTS

When a crystal is deformed, there is a change in the matrix elements $M_{mn}$ connecting molecules $m$ and $n$ because of the changes in both their separation and their relative orientations. In the previous section, this change is expressed in terms of external and internal strain derivatives. It now remains to find suitable expressions for the matrix elements so that these derivatives may be easily evaluated.

By expanding $V_{mn}$ in terms of multipole interactions, the general matrix element $M_{mn}$ may be written symbolically in the form

$$M_{mn} = \frac{Q_m\,Q_n}{R_{mn}^{\mu}}\,F_{mn} \tag{12}$$

where $Q_m$, $Q_n$ are terms involving products of molecular multipole moments (referred to intramolecular axes), $R_{mn}$ is the separation of molecules $m$ and $n$, and $F_{mn}$ contains all factors pertaining to the relative orientation of $m$ and $n$. $F_{mn}$ may be expressed in terms of crystal-fixed or intermolecular axes. The effect of strain on $M_{mn}$ will thus be restricted to changes in $R_{mn}$, $F_{mn}$ only.

The external strain derivatives have the form

$$M'_{mn}(u_i) = \frac{Q_m Q_n}{R^{\mu}_{mn}} \left\{ \left( \frac{\partial F_{mn}}{\partial u_i} \right)_0 - \frac{\mu F_{mn}}{R_{mn}} \left( \frac{\partial R_{mn}}{\partial u_i} \right)_0 \right\}. \quad (13)$$

Note that $(\partial F_{mn}/\partial u_i)_0$ is not zero as the relative orientation is a function of the vector $R_{mn}$, which changes with strain. The internal strain derivatives have the same form, except that for the orientational derivatives, $(\partial R_{mn}/\partial \theta_i^m) = 0$.

### The site shift terms

It has already been noted that for molecules without a permanent dipole moment the first contribution to $D^{ss}_{mn}$ is a quadrupole-quadrupole term, for which $\mu = 5$. It has been suggested [11, 12] that the major contributions from the $D$ terms arise from dispersion terms for which $\mu = 6$. As dispersion terms for molecular crystals have been found to be relatively insensitive to angular shifts of the molecules, [13] the orientation factor $F_{mn}$ for this case may then be put equal to a constant. The dispersion contribution may then be written in the simplified form

$$D^{ss}_{mn} = \frac{A^s}{R^6_{mn}}$$

where $A^s$ is assumed to be constant for a given $s$.

The shift in the dispersion term $\Delta D^{ss}$ for the stressed crystal then follows directly from Eq. (11), (13). All orientational internal strain derivatives will be zero. Then

$$D^{ss} = \sum_{n(\neq m)} \Delta D_{mn} = \sum_{n(\neq m)} \left\{ \sum_i D'_{mn}(u_i)\delta u_i + \sum_j D'_{mn}(X_j^{mn})\delta X_j^{mn} \right\} \quad (14)$$

and the derivatives have the form

$$D'_{mn}(u_i) = -\frac{6A^s}{R^7_{mn}} \left( \frac{\partial R_{mn}}{\partial u_i} \right)_0.$$

The parameter $A^s$ may be determined empirically from the unstressed crystal spectrum.

### The resonance (exciton transfer) terms

The general resonance term defined in Eq. (4) may be put in the form (12) by expanding $V_{mn}$ in terms of multipole interactions. In practice, it is often possible to consider only the dipole–dipole term, so that

$$I^{st}_{mn} = \frac{d^s d^t}{R^3_{mn}} F^{[kk']}_{mn}$$

$d^s$, $d^t$ are the dipole lengths for the three-molecule transitions $s$ and $t$ respectively. The orientation factor may be written in the form

$$F_{mn}^{[kk']} = \tfrac{1}{2}\left[\beta_{1k}^m \beta_{1k'}^n + \beta_{1k'}^m \beta_{1k}^n + \beta_{2k}^m \beta_{2k'}^n + \beta_{2k'}^m \beta_{2k}^n - 2\beta_{3k}^m \beta_{3k'}^n - 2\beta_{3k'}^m \beta_{3k}^n\right]$$

$\beta_{ij}$ are the direction cosines, with the indices $k$, $k'$ referring to the polarizations of the transitions $s$ and $t$ respectively. $\beta_{ij}$ is the cosine between axis $i$ of an intermolecular $(xyz)$ system and axis $j$ of an intramolecular $(lmn)$ system. The $(lmn)$ system is molecule-fixed, and the $(xyz)$ system is chosen so that the $z$-axis joins the molecules $m$ and $n$, with $x,y$ orthogonal to $z$. In practice, the direction cosines are usually defined in terms of the $(lmn)$ and an orthogonal $(abc)$ system which is crystal-fixed. If $\hat{\beta}_{ii'}$ is the matrix of direction cosines connecting the $(ijk)$ and $(i'j'k')$ systems, the required $\hat{\beta}_{xl}$ is given by

$$\hat{\beta}_{xl} = \hat{\beta}_{xa}\ \hat{\beta}_{al}.$$

The shifts in the resonance terms on stressing the crystal may be found using Eq. (11), (13). Defining

$$G_{mn}^{[kk']} = \frac{F_{mn}^{[kk']}}{R_{mn}^3}$$

for convenience, it follows that the shif in $I_{mn}^{st}$ is given by

$$\Delta I_{mn}^{st} = d^r\, d^s\, \Delta G_{mn}^{[kk']} \tag{15}$$

where

$$\Delta G_{mn}^{[kk']} = \sum_i G_{mn}^{'\,[kk']}(u_i)\ \delta u_i + \sum_k G_{mn}^{'\,[kk']}(w_k)\ \delta w_k. \tag{16}$$

The external strain derivatives have the form (13)

$$G_{mn}^{'\,[kk']}(u_i) = R_{mn}^{-3}\left\{\left(\frac{\partial F_{mn}^{[kk']}}{\partial u_i}\right)_0 - \frac{3F_{mn}^{[kk']}}{R_{mn}}\left(\frac{\partial R_{mn}}{\partial u_i}\right)_0\right\}$$

Both terms have an effective $R_{mn}^{-3}$ dependence. The derivatives $(\partial F_{mn}^{[kk']}/\partial u_i)_0$ contain terms of the form $\beta_{jk}^m\,(\partial\beta_{jk}^n/\partial u_i)_0$, so that the evaluation of the $F_{mn}^{[kk']}$ derivatives require, in effect, the evaluation of the derivative matrices

$$\frac{\partial}{\partial u_i}(\hat{\beta}_{xa}^m),\quad \frac{\partial}{\partial u_i}(\hat{\beta}_{xa}^n).$$

The cartesian internal strain derivatives are analogously defined.

The orientational changes associated with the internal relaxation yield relatively straightforward derivatives. Use of the theory of infinitesimal rotations and noting that, to first order, [14]

$$\frac{\partial \beta^m_{j'j}}{\partial \theta^m_k} = \sum_i \beta_{j'i} \epsilon_{ijk}$$

the orientational internal strain derivatives have the form

$$G'_{mn}(\theta^n_i) = \tfrac{1}{2}(\epsilon_{ij'k}[\beta^m_{1k}\beta^n_{1j} + \beta^m_{2k}\beta^n_{2j} - 2\beta^m_{3k}\beta^n_{3j}] + \epsilon_{ijk}[\beta^m_{1k}\beta^n_{1j} + \beta^m_{2k}\beta^n_{2j} - 2\beta^m_{3k}\beta^n_{3k}])R^{-3}_{mn}.$$

$\epsilon_{ijk}$ is the antisymmetric third-order tensor, which vanishes if any two of the subscripts are equal, is equal to +1 if the subscripts are in increasing cyclic order (e.g. 123, 231), and −1 if they are in decreasing cyclic order (e.g. 321, 213).

### Lattice sums

It follows from Eq. (4) that changes in the matrix elements determining the energy shift due to crystal strain involve sums of the form

$$\sum_n \exp[i\mathbf{k}.(\mathbf{r}_m - \mathbf{r}_n)]\, G'^{[kk']}_{mn}.$$

In the dipole–dipole approximation, these are conditionally convergent in the same way as are the normal dipole sums. This problem is extensively discussed elsewhere[15, 16]. There are a number of summation techniques: direct summation, Ewald-Kornfeld method, and planewise summation. Of these, the latter as developed by Philpott is most suitable for this work.[17] Planewise summation provides a rapidly converging result, and avoids the necessity of including a macroscopic polarization term which would have to be treated separately for strain effects.

Summation for the dispersion problems is absolutely convergent, and thus no such problems arise.

### Pressure and temperature effects

Once all the strain derivatives of the matrix elements have been determined for the unstressed crystal, the energies are given directly as a function of the strain. Consider in particular the especially simple case for anthracene and naphthalene in which the energy shift is given by Eq. (7) directly as a function of the strain derivatives and the crystal strains (see Eqs. 14, 16). This shift is then expressed as a function of pressure and temperature in the following way.

Consider an applied pressure $P$ assumed to act hydrostatically on the crystal. By resolving the pressure into normal stresses $\tau_1, \tau_2, \tau_3$ each equal to $(-P)$, the cartesian strains $\epsilon_j$ are found using the elastic constants of the crystal from Eq. (9). These are then transformed to the external unit cell strains by Eq. (8). If the internal strains are neglected, the strains are linear in $P$, so that the energy shift is

directly determined as a linear function of $P$. Similar calculations may be done for any homogeneous stress vector $\tau$. Inclusion of the internal strains requires knowledge of the force constants of the crystal and the external strains. We shall not discuss these in detail here.

If the structure of the crystal is known for two temperatures $T$, $T^\circ$, it is possible to define linear expansion coefficients $\alpha(u_i)$ for this temperature range from the expression

$$\delta u_i = \alpha(u_i)\, \delta T \tag{17}$$

where $\delta u_i = (u_i - u_i^0)$, $\delta T = (T - T^0)$. $u_i^0$ is the lattice parameter at room temperature $T^0$, at which we shall refer to the crystal as unstrained. Note that the strain derivatives are defined for the unstressed geometry at temperature $T^0$. $u_i$ is the lattice parameter at another temperature $T$. The expansion coefficients for the internal strains are analogously defined. The energy shifts are then given as linear functions of the temperature change. In a later section, we shall apply these ideas to the first singlet of anthracene.

## CALCULATIONS FOR ANTHRACENE AND NAPHTHALENE

Antracene and naphthalene have monoclinic lattice structures characterised by unit cell sides $a, b, c$ and the monoclinic angle $\beta$ [18, 19]. For small stresses, the assumption that the overall symmetry is not reduced leads to changes in these four quantities alone. Estimation of the transformation matrix T (see Eq. 9) is effected by choosing the $x$, $y$ axes to correspond with the crystal $a$, $b$ axes, and subtracting the coordinates of the strained and unstrained unit cells. The matrix T is found to have the following non-vanishing elements:

$$T_{11} = 1 \quad T_{22} = 1 \quad T_{33} = \sin^2\beta \quad T_{55} = -\frac{\sin^2\beta}{\beta} \quad T_{31} = \cos^2\beta$$

$$T_{35} = \frac{\sin 2\beta}{2} \quad T_{51} = -\frac{\sin 2\beta}{2\beta} \quad T_{35} = \frac{\sin 2\beta}{2\beta}.$$

Thus there will be four non-zero unit cell strains. These may be determined for an arbitrary stress from Eq. (9) using the elastic constants as determined by experiment. [20, 21]

Both anthracene and naphthalene have two molecules per unit cell related through a glide plane, and also there is an inversion centre at each lattice point. Retention of the glide plane on deformation ensures that the orientations of the two molecules in a unit cell do not become independent, so that only the internal strains for one molecule need be considered. Thus there will be three orientational strain coordinates $\delta\theta_j$. Retention of the inversion centre restrains the molecules to their lattice points, so that all the $\delta X_j$ vanish.

Having determined which strains we need to consider, we now turn to a

consideration of which matrix elements will be important in these crystals. We shall be interested in the absorption states of the crystal for light normally incident on the *ab*-face of the crystal. If **k** is the exciton wave vector, and **q** that of the incident light, the selection rules for absorption may be written [16]

$$|\mathbf{k}| = 0, \qquad \hat{\mathbf{k}} = \hat{\mathbf{q}}$$

where ^ indicates a unit vector. The first part of the selection rule is the result of the wavelength of light being large compared with the lattice parameters, whereas the second part preserves the propagation direction of the absorbed photon. It follows that **k** will be perpendicular to the ab-crystal planes. The approximate energies for the weak transitions of these crystals for this case may be written from (5) as

$$E_{\pm}(0) = [(E^s - E^0) + D^{ss} + I_{11}^{ss}(0)] \pm I_{12}^{ss}(0)$$

where the resonance terms are obtained by planewise summation over the *ab*-planes. It follows from the above that there are two absorption components, split by an energy

$$E_D = 2 I_{12}^{ss}(0)$$

which is referred to as the Davydov or factor group splitting. Note that to first order it is a function only of the resonance terms. The mean shift of the absorption from that of the free molecule is defined as

$$E_S = \tfrac{1}{2} [D^{ss} + I_{11}^{ss}(0)]$$

and is a function of both resonance and dispersion terms. If mixing with higher states is included (Eq. 6), it is necessary to consider also the terms $I_{11}^{st}(0)$, $I_{12}^{st}(0)$ for strong transitions $t$ close to $s$. The $D^{st}$ terms for $t \neq s$ will be neglected here. The results of calculations of the sums mentioned above for anthracene and naphthalene are given below.

TABLE 1

The dispersion derivatives for anthracene and naphthalene[a]

| | Anthracene | Naphthalene |
|---|---|---|
| $D'(a)$ | −98.8 | −122.1 |
| $D'(b)$ | −112.9 | −135.3 |
| $D'(c)$ | −6.0 | −20.6 |
| $D'(\beta)$ | 45.0 | 115.3 |
| $D^{ss}$ [b] | 265.7 | 332.6 |

[a] All values must be multiplied by the factor $10^{-6} A^S$. $D'(u_i)$ then has units $cm^{-1} A^{-1}$ or $cm^{-1}$ $rad^{-1}$.

[b] This is the dispersion shift for the unstressed crystal.

### The dispersion derivatives

The dispersion derivatives for these crystals are found directly from Eq. (14). They converge rapidly, and are given in Table 1 in terms of the empirical parameter $A^S$ which must be determined from the unstressed crystal spectrum. (This is illustrated in the next section for the weak system of anthracene).

### The resonance derivatives

The resonance derivatives were calculated by planewise summation, and the results are given in Tables 2 and 3. Convergence within 2% was achieved for summation radii of 300 Å, † and the contributions of planes beyond the nearest neighbour planes were found to be negligible. Note that the $c$- and $\beta$-derivatives are zero for the in-plane sums, so that the total contribution to these derivatives come from neighbouring planes.

TABLE 2

Resonance derivatives for anthracene

| $kk' =$ | $LL$ | $MM$ | $NN$ | $LM$ | $LN$ | $MN$ |
|---|---|---|---|---|---|---|
| $G'_{11}$ $(a)$ | −147 | −25 | 161 | −167 | −277 | 39 |
| $G'_{11}$ $(b)$ | −728 | 827 | −135 | −351 | −90 | −693 |
| $G'_{11}$ $(c)$ | −32 | 4 | 28 | −6 | −2 | 16 |
| $G'_{11}$ $(\beta)$ | 44 | −46 | −16 | −179 | −357 | −87 |
| $G'_{11}$ $(\theta_L)$ | 0 | −1223 | 1223 | −490 | 602 | −658 |
| $G'_{11}$ $(\theta_M)$ | 981 | 0 | −981 | 611 | −1141 | −602 |
| $G'_{11}$ $(\theta_N)$ | −1205 | 1205 | 0 | 1798 | −611 | 490 |
| $G'_{12}$ $(a)$ | −671 | −554 | 11 | −311 | −535 | −650 |
| $G'_{12}$ $(b)$ | −365 | 286 | 742 | −537 | −823 | 61 |
| $G'_{12}$ $(c)$ | 30 | −9 | −29 | 7 | 2 | −13 |
| $G'_{12}$ $(\beta)$ | −40 | 83 | 16 | 168 | 348 | 60 |
| $G'_{12}$ $(\theta)$ | 0 | 650 | −650 | −1588 | 971 | 1228 |
| $G'_{12}$ $(\theta_M)$ | 3177 | 0 | −3177 | −325 | −1979 | −971 |
| $G'_{12}$ $(\theta_N)$ | −1944 | 1944 | 0 | 750 | 325 | 1588 |
| $G_{11}{}^b$ | 1987 | −1610 | −294 | 1205 | 981 | 1223 |
| $G_{12}{}^b$ | 2538 | 1038 | −1419 | 1944 | 3177 | −650 |

[a] Units $cm^{-1}$ $Å^{-1}$ or $cm^{-1}$ $rad^{-1}$

[b] Unstressed crystal dipole sums

† summation to larger radii to obtain the extra few % was not pursued for all sums as (1) the theory does not warrant such accuracy (2) computation time required is relatively long for derivative sums.

TABLE 3
Resonance derivatives for naphthalene[a]

| $kk' =$ | $LL$ | $MM$ | $NN$ | $LM$ | $LN$ | $MN$ |
|---|---|---|---|---|---|---|
| $G'_{11}$ $(a)$ | −209 | −18 | 227 | −143 | −194 | 82 |
| $G'_{11}$ $(b)$ | −741 | 808 | −68 | −495 | −18 | −687 |
| $G'_{11}$ $(c)$ | −51 | −19 | 70 | −55 | −93 | 22 |
| $G'_{11}$ $(\beta)$ | 898 | −195 | −703 | −125 | −615 | −568 |
| $G'_{11}$ $(\theta_L)$ | 0 | −1086 | 1086 | −418 | 771 | −409 |
| $G'_{11}$ $(\theta_M)$ | 836 | 0 | −836 | 542 | −1447 | −771 |
| $G'_{11}$ $(\theta_N)$ | −1543 | 1543 | 0 | 1858 | −542 | 418 |
| $G'_{12}$ $(a)$ | −819 | −658 | 64 | −325 | −586 | 250 |
| $G'_{12}$ $(b)$ | −599 | 317 | 951 | −588 | −751 | 97 |
| $G'_{12}$ $(c)$ | 31 | −24 | −79 | 56 | 79 | −3 |
| $G'_{12}$ $(\beta)$ | −768 | 410 | 703 | 95 | 634 | 422 |
| $G'_{12}$ $(\theta_L)$ | 0 | 871 | −871 | −1444 | 953 | 1554 |
| $G'_{12}$ $(\theta_M)$ | 2887 | 0 | −2887 | −435 | −2462 | −953 |
| $G'_{12}$ $(\theta_N)$ | −1908 | 1908 | 0 | 908 | 435 | 1444 |
| $G_{11}$[a] | 2204 | −1511 | −691 | 1543 | 836 | 1086 |
| $G_{12}$[b] | 3073 | 1248 | −1851 | 1908 | 2887 | −871 |

[a] Units $cm^{-1}$ $Å^{-1}$ or $cm^{-1}$ $rad^{-1}$
[b] Unstressed crystal dipole sums

## THE FIRST SINGLET SYSTEM OF ANTHRACENE

The transition energies of the excited states of anthracene in the vapour phase and in solution are summarized in Table 4. The polarization of the first and second singlets is relatively well established but the assignment of higher states is speculative. The solution spectrum of the first singlet exhibits a clear vibrational progression based on a 1400 $cm^{-1}$ vibration. In the crystal spectrum, each of these vibrational levels is split into two levels, with energies summarized in Table 5. The splitting measurements are very sensitive to strain effects resulting from the mounting of the very thin crystals, so that a range of measurements have been reported in the literature.

### Calculations for the unstrained crystal

A treatment of the stressed crystal requires a knowledge of the unstressed crystal energies and the determination of the parameter $A^s$ for the dispersion term. The theory previously described (Eqs. 5, 6) may be modified for the first anthracene singlet to include the vibrational structure. For the electronic weak coupling limit[7] (splitting $\ll 1400$ $cm^{-1}$), the $k = 0$ energy of the $\alpha$th vibrational level (frequency $\nu$) of the first singlet $s$ is written

$$E_{\pm}^{s\alpha} = E_{\pm}^{1s\alpha} + E_{\pm}^{2s\alpha}$$

where

$$E_{\pm}^{1s\alpha} = [E^s + \alpha h\nu - E_0] + D^{ss} + \xi^2(\alpha)[I_{11}^{ss} \pm I_{12}^{ss}]$$

and

$$E_{\pm}^{2s\alpha} = \sum_{r(\neq s)} \frac{\xi^2(\alpha)[I_{11}^{sr} \pm I_{12}^{sr}]^2}{[E_{\pm}^{1s\alpha} - E_{\pm}^{1r}]}.$$

$\xi(\alpha)$ is the Franck-Condon factor for the $\alpha$-quantum vibrational function in the in the first excited state and the zeroth level in the ground state. For the first singlet,

$$\xi^2(0) = 0.324 \quad \xi^2(1) = 0.316 \quad \xi^2(2) = 0.218 \quad \xi^2(3) = 0.093 \quad \xi^2(4) = 0.050.$$

The vibrational structure of the excited states $r$ ($\neq s$) is neglected in the calculations.

The unstressed crystal energies were calculated for the first singlet using the above equations, incorporating mixing only with the strong second singlet, and putting the free-molecule energies equal to the vapour phase values of Table 4. Although inclusion of higher states $t'$, $t''$ has been shown to give an increase in calculated splittings, [22] their effect is relatively less than that of the t state, and will be

TABLE 4

Anthracene vapour and solution data[7, 22]

| System [r] | Transition energy ($cm^{-1}$) Vapour | Solution | Dipole length (Å) | Polarization |
|---|---|---|---|---|
| $[s\alpha]$ | 27700 [a] | 26000+ 1400$\alpha$ | 0.61 | $M$ |
| $[t]$ | 42270 | 39000 | 1.87 | $L$ |
| $[t']$ | | 45200 | 0.64 | $M$ [b] |
| $[t'']$ | | 54000 | 0.83 | $M$ [b] |

[a] Band origin[23]
[b] Assignment uncertain

TABLE 5

Crystal energies of first singlet system of anthracene [a]

| $\alpha$ | Observed energies[7] | | Splitting [b] |
|---|---|---|---|
| 0 | 25500 | 25310 | 190 |
| 1 | 26930 | 26820 | 110 |
| 2 | 28360 | 28300 | 60 |

[a] for [001] face
[b] all energies in $cm^{-1}$

neglected here. The $D^{rr}$ terms in the denominator are also neglected. The transition energies relative to the dispersion shift $D^{ss}$ [viz. $E_{\pm}^{s\alpha} - D^{ss}$] are summarized in Table 6. In order to find a value of $A^s$, the dispersion shift $D^{ss}$ is determined empirically by subtracting the calculated values for $(E_{\pm}^{s\alpha} - D^{ss})$ from the experimentally determined values of $E_{\pm}^{s\alpha}$ of Table 5. The mean of the six values thus found yields $D^{ss} = -1980\ \text{cm}^{-1}$, and thus from the results of Table 1 it follows that $A^s = -7.4 \times 10^6\ \text{cm}^{-1}\text{Å}^6$. This value of $A^s$ can now be used to determine the dispersion derivatives for the s transition.

### Calculations for the strained crystal

A shift in the energy $E_{\pm}^{s\alpha}$ may be written in terms of the shifts in resonance and dispersion terms as

$$\Delta E_{\pm}^{s\alpha} = \Delta D^{ss} + \xi^2(\alpha)[\Delta I_{11}^{ss} \pm \Delta I_{12}^{ss}] + \frac{2\xi^2(\alpha)[\Delta I_{11}^{st} \pm \Delta I_{12}^{st}][I_{11}^{st} \pm I_{12}^{st}]}{[E_{\pm}^{1s\alpha} - E_{\pm}^{1t}]^0} \cdot$$

$$- \frac{\xi^2(\alpha)[(\Delta I_{11}^{ss} \pm \Delta I_{12}^{ss}) - (\Delta I_{11}^{tt} \pm \Delta I_{12}^{tt})][I_{11}^{st} \pm I_{12}^{st}]^2}{[E_{\pm}^{1s\alpha} - E_{\pm}^{1t}]^2} \cdot$$

The energy shift may be written in the form

$$\Delta E_{\pm}^{s\alpha} = E_{\pm}'(s\alpha, u_i)\,\delta u_i$$

where $E_{\pm}'(s\alpha, u_i)$ is the strain derivative of the energy $\left(\frac{\partial E_{\pm}^{s\alpha}}{\partial u_i}\right)_0$. It follows that the strain derivatives of the energy may be directly evaluated from those of the dispersion and resonance terms. Defining the Davydov splitting $E_D^{s\alpha}$ and the mean shift $E_S^{s\alpha}$ as

$$E_D^{s\alpha} = [E_+^{s\alpha} - E_-^{s\alpha}]\ ,\quad E_S^{s\alpha} = \tfrac{1}{2}[E_+^{s\alpha} + E_-^{s\alpha}],$$

it is also possible to find directly the values of their corresponding derivatives $E_D'(s\alpha, u_i)$, $E_S'(s\alpha, u_i)$. The results of the calculations for the *a*- and *b*-strains are presented in Table 7.

TABLE 6
Calculated first singlet energies for anthracene [a]

| α | $[E_+^{s\alpha} - D_o^{ss}]$ (cm$^{-1}$) | $[E_-^{s\alpha} - D^{ss}]$ (cm$^{-1}$) | Splitting (cm$^{-1}$) |
|---|---|---|---|
| 0 | 27494 | 27362 | 132 |
| 1 | 28893 | 28770 | 123 |
| 2 | 30352 | 30270 | 82 |
| 3 | 31832 | 31800 | 32 |
| 4 | 33263 | 33248 | 15 |

[a] Relative to $D^{ss}$

TABLE 7

Calculated energy derivatives for the first singlet system of anthracene [a]

| $\alpha$ | $u_i$ | $E'_+(s\alpha, u_i)$ | $E'_-(s\alpha, u_i)$ | Resonance contribution | | Dispersion contribution | $E'_S(s\alpha, u_i)$ | $E'_D(s\alpha, u_i)$ |
|---|---|---|---|---|---|---|---|---|
| | | | | (+) | (−) | | | |
| 0 | *a* | 691 | 807 | −40 | 76 | 731 | 749 | −116 |
| 1 | *a* | 693 | 807 | −38 | 76 | 731 | 750 | −114 |
| 2 | *a* | 705 | 784 | −26 | 53 | 731 | 744 | −79 |
| 3 | *a* | 720 | 754 | −11 | 23 | 731 | 737 | −34 |
| 4 | *a* | 725 | 744 | −6 | 13 | 731 | 734 | −19 |
| 0 | *b* | 1027 | 907 | 192 | 72 | 835 | 967 | 120 |
| 1 | *b* | 1025 | 907 | 190 | 72 | 835 | 966 | 118 |
| 2 | *b* | 966 | 885 | 131 | 50 | 835 | 925 | 81 |
| 3 | *b* | 892 | 857 | 57 | 22 | 835 | 874 | 35 |
| 4 | *b* | 867 | 846 | 32 | 11 | 835 | 856 | 21 |

[a] Unit $cm^{-1}$ $Å^{-1}$

[b] $A^S = -7.4 \times 10^6$ $cm^{-1}$ $Å^6$

The results for other strains may be readily estimated from data of Tables 1 and 2.

Some general points may be noted here. The dispersion terms dominate the mean shift derivatives, but contributions from the resonance terms are not negligible. Note that the dispersion contribution is independent of $\alpha$, but the resonance contributions vary for the different vibrational components. The Davydov splitting derivatives are functions only of the resonance terms. The splitting increases with compressions of *a*, and with rarefactions of *b*. Thus the overall shift for a general stress is direction dependent. We return to this anon.

### Pressure effects

The effect on pressure on the first four vibrational components of the first singlet have been studied.[6] The conditions of the experiment did not allow measurements of the Davydov splitting, but the means shifts of the four levels varied linearly with pressure up to about 40,000 atm according to the relationship

$$\Delta E_S^{s\alpha} = -k_S^{\alpha} P \text{ cm}^{-1} \quad (P \text{ in atm})$$

where $k_S^{\alpha}$ has the values

$$-0.051, -0.045, -0.040, -0.039 \ (\text{cm}^{-1} \text{ atm}^{-1})$$

as $\alpha$ ranges from 0 to 3.

Calculations of the shift changes with pressure follow directly from a knowledge of the strains resulting from a hydrostatic pressure for anthracene. Using the procedure discussed in Sect. 4, the strains from a pressure of $P$ atm for anthracene are found to be

$$\delta a = -0.67 \times 10^{-4} P \quad \delta b = -0.31 \times 10^{-4} P \quad \delta c = -010 \times 10^{-4} P \quad \delta\beta = 0.08 \times 10^{-4}$$

in units Å, rad. Neglecting the relatively small $c$- and $\beta$-strains, as well as the effects of internal strains, the use of the derivatives of Table 7 give

$$\Delta E_S^{s\alpha} = E_S'(s\alpha, a)\,\delta a + E_S'(s\alpha, b)\,\delta b = k_S^{\alpha} P$$

where

$$k_S^{\alpha} = -0.080, -0.080, -0.078, -0.076 \text{ for } \alpha = 0, \ldots, 3.$$

Noting that the shift due to the dispersion term is independent of $\alpha$ and contributes $-0.074$ to $k_S^{\alpha}$, the *change* in the constant through the progression is due to the resonance contributions. The dominant contribution is from the dispersion terms, although comparison with experiment suggests that $A^s$ is too high by about 30%. The slow decrease in the magnitude of $\Delta E_S^{s\alpha}$ predicted by the calculations is found in the experimental results discussed above.

The effect of pressure on the Davydov splitting is readily calculated in the same way to be

$$\Delta E_D^{s\alpha} = k_D^{\alpha} P$$

where $k_D^{\alpha} = 0.004, 0.004, 0.0028, 0.0012, 0.0007$ ($\text{cm}^{-1}$ $\text{atm}^{-1}$) as $\alpha = 0, \ldots, 4$. The splitting is a function only of resonance terms. Strains of $\delta a = -0.67$ Å, $\delta b = -0.31$ Å corresponding to a pressure $10^4$ atm lead to an increase of about 40 $\text{cm}^{-1}$. For more general stresses, it is interesting to note that the splitting derivatives for the $a$ and $b$ parameters are approximately equal in magnitude but opposite in sign so that we can write

$$\Delta E_D^{s0} = E_D'(s0, a)\,[\delta a - \delta b]$$

where $E_D'(s0, a) = -120\ \text{cm}^{-1}\text{Å}^{-1}$. As anthracene is more 'compressible' in the $a$-direction, it may be expected that mounting crystals causes compressive stresses in the crystal for which $-\delta a > -\delta b$ and thus $\Delta E_D^{s\alpha} > 0$. For very thin crystals, such compression could occur through strong attractive forces between the crystal and the plate which increase as the crystal approaches zero thickness. These results thus agree qualitatively with the increases in the splitting found experimentally when the crystal is mounted[1], and the increase in splitting for mounted crystals as the thickness is reduced[2].

### Temperature effects

The effects of temperature on the lattice parameters of anthracene have been studied [24, 25] and the structures determined at 95, 290°K. Linear expansion coefficients may be calculated as previously described for $T^\circ = 290°K$, $T=95°K$. They have the values

$$\alpha(a) = 0.61 = 10^{-3}\ \alpha(b) = 0.18 \times 10^{-3}\ \alpha(c) = 0.31 \times 10^{-3}\ \alpha(\beta) = -0.08 \times 10^{-3}$$

(in units Å $^0K^{-1}$, rad $^0K^{-1}$). Neglecting again all strains except $\delta a$ and $\delta b$, the changes in the Davydov splittings and mean shifts as functions of $\delta T = [T - T^0]$ may be calculated to be

$$\Delta E_D^{s\alpha} = c_D^\alpha\ \delta T \qquad \Delta E_S^{s\alpha} = c_S^\alpha\ \delta T$$

where $c_D^\alpha = -0.049,\ -0.048, -0.034,\ -0.015,\ -0.007$ and $c_S^\alpha = 0.631,\ 0.631,\ 0.620,\ 0.606,\ 0.602$ for $\alpha = 0, \ldots, 4$ (units $cm^{-1}\ ^0K^{-1}$). Again, $c_D^\alpha$ arises purely from resonance terms; $c_S^\alpha$ contains a constant dispersion contribution of 0.596, the remainder being contributions from resonance term $s$. In general, then, this suggests that a decrease in temperature leads to an increase in the splittings and a general shift of the system to lower frequencies. These effects are found experimentally [26].

## SUMMARY

The theory and calculations presented in this paper suggest that strain in anthracene can have significant effects on the mean shift and the Davydov splittings of the first singlet system. Theoretically estimated changes with pressure and temperature are in relatively good agreement with experimental results. The scope of the theory is limited to strains for which the expansion of the interaction operator may be restriced to linear terms. The point where deviations from linearity become important may be found in two ways: by comparison with experiment and by calculation of the dispersion and resonance terms directly for lattices of varying dimensions. Such calculations suggest that deviations from linearity become appreciable only for strains in excess of 10%, so that it would appear that restriction to linear terms is valid over a high range of pressure (up to 40,000 atm in anthracene). Strains due to temperature changes less than 10%.

As a final comment, it is worth noting that such strain derivatives may be defined for any property depending on matrix elements of intermolecular interaction, terms. For example, applications to simple models for conductivity in molecular crystals could be envisaged.

## APPENDIX

The dispersion contributions to the site shift term may be incorporated in the following way. In addition to the localised excitation functions (1) we define the doubly excited states

$$\phi_{mn}^{st} = \varphi_m^s \, \varphi_n^t \, \Psi_G \, (\varphi_m^0 \, \varphi_n^0)^{-1},$$

and for convenience, adopt the convention that

$$\phi_{mn}^{00} = \Psi_G \; ; \; \phi_{mn}^{s0} = \phi_m^s \; .$$

Consider now the localized excitation function $\phi_m^s$. It is possible to incorporate the effect of interactions with all other states $\phi_{mn}^{st}$ *not* degenerate with it by perturbation theory, so that the perturbed localized excitation function $\psi_m^s$ has the form

$$\psi_m^s = \phi_m^s + \sum_{\substack{n \\ (\neq m)}} \frac{<\phi_m^s \mid V \mid \phi_{mn}^{rt}>}{[E^s + E^0 - E^r - E^t]} \phi_{mn}^{rt} \; .$$

The summation is over all states $r, t$, except those for which the energy denominator is zero. The ground state wave function becomes

$$\Psi_G' = \Psi_G + \sum_{m<n} \frac{<\Psi_G \mid V \mid \phi_{mn}^{rt}>}{[2E^0 - E^t - E^r]} \phi_{mn}^{rt} \; .$$

If these perturbed functions $\psi_m^s$ are now used instead of $\phi_m^s$ in the variation treatment leading to (21), it is not difficult to see that the diagonal terms become

$$<\Psi_i^s \, (\mathrm{k}) \mid H \mid \Psi_i^t \, (\mathrm{k})> = <\phi_i^t \, (\mathrm{k}) \mid H \mid \phi_i^t \, (\mathrm{k})> + D^s \, (\mathrm{ind}) + D^s \, (\mathrm{disp})$$

where $D^s$(ind) is the induction shift term, which we need not consider here (since there is no permanent dipole) and $D^s$ (disp) is the dispersion shift term which is given by the expression

$$D^s \, (\mathrm{disp}) = \sum_{n(\neq m)} \frac{V_{m,n}^{sr,\,t} \, V_{m,n}^{rs,\,t}}{[E^s + E^0 \, E^t \, E^r]} - \tfrac{1}{2} \sum_{n,m'} \frac{V_{m',n}^{r,t} \, V_{m',n}^{t,r}}{[2E^0 - E^t - E^r]}$$

where

$$V_{m,n}^{rs,\,t} = (\varphi_m^r \, \varphi_n^0 \mid V_{mn} \mid \varphi_m^s \, \varphi_n^t)$$

$$V_{m,n}^{s,t} = (\varphi_m^0 \, \varphi_n^0 \mid V_{mn} \mid \varphi_m^s \, \varphi_n^t) \text{ and so on.}$$

The first term is the dispersion interaction of the molecule m in its $s$th state with all other molecules in the crystal, whereas the second term is obviously the dispersion energy of the unexcited crystal. The major contribution to $D^s$(disp),

if $s$ is the first excited state, may be expected to come from states $t$ such that

$$| E^s - E^t | \ll | E^s - E^0 | .$$

In this case, the first term gives a large negative contribution which accounts for the negative shifts for the first excited state found in several aromatic molecular crystals.

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