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Davydov Splitting and Band Structure for Triplet Excitons in Pyrene[†] *

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The first peak (0–0 transition) of the singlet-triplet delayed fluorescence excitation spectrum in pyrene has been investigated in polarized light. The *b*-polarized transition is found to be at higher energy than the *a*-polarized transition by a Davydov splitting of 2.4 ± 0.6 cm^{-1}. An expression for the energy bands $\epsilon(\vec{k})$ is derived and related to the Davydov splitting. Transport properties of the triplet excitons have been evaluated and indicate that the diffusion of triplet excitons in pyrene is due more to a hopping process than to coherent band motion.

INTRODUCTION

The dynamical properties of triplet excitons in aromatic hydrocarbons are of interest because of their importance in the transfer of energy between molecules. The relatively long lifetime of the triplet excitons compared to singlet excitons and their diffusion length before decay of the order of microns permits efficient energy transfer over distances of this magnitude.

There are several ways of studying triplet-exciton diffusion in organic crystals. Most involve a determination of the diffusion length.[1] Such measurements have helped to show the importance of triplet excitons in energy transfer. The results, however, may be sensitive to trapping by impurities or lattice defects. Recently, Avakian *et al.*[2] have shown that information about triplet-exciton diffusion can be obtained from spectroscopic measurements of the ground-state to triplet-state transition. The absorption of the exciting light is detected indirectly by monitoring the intensity of the delayed fluorescence produced when two triplet excitons annihilate.

Davydov[3] has shown that in crystals with two or more molecules per unit cell, the excited states will be split by the intermolecular interactions. Jortner *et al.*[4] calculated that in anthracene with two molecules per unit cell the splitting of the triplet-exciton levels at $\vec{k}=0$ is principally due to the exchange interaction between nearest neighbors. These calculations were quantitatively confirmed by measurements of the triplet-exciton Davydov splitting in the anthracene absorption spectrum at low temperatures by Clark and Hochstrasser[5] and in the triplet-exciton excitation spectrum by Avakian *et al.*[2] This latter group showed that the triplet diffusion constant could be estimated from the Davydov splitting and the linewidth of the transition. A diffusion constant obtained in this way should not be sensitive to the purity of the crystal as long as the delayed fluorescence is detectable.

Measurements of the Davydov splitting are useful in another way. Since the exchange integrals are quite sensitive to the form of the wave functions at large distances from the molecule, and since the nearest-neighbor exchange integral is often directly related to the Davydov splitting,[4] a measurement of this splitting can provide an important test of the accuracy of the molecular wave functions chosen.

In the present investigation, we have studied the room-temperature Davydov splitting and linewidth of the triplet-exciton excitation spectrum in pyrene, which has four molecules per unit cell. Because of the crystal symmetry, only two of the four levels at $\vec{k}=0$ can be excited optically.[6] A band calculation which includes interactions with up to fourth nearest neighbors has been made. This calculation shows that if the nearest-neighbor interaction is large compared to the others, the data for pyrene may be interpreted in the same manner as for anthracene. The results indicate that the diffusion of triplet excitons in pyrene is due more to a hopping process than to coherent band motion.

SAMPLES AND PROCEDURE

Pyrene purchased from the Eastman Kodak Company was further purified by chromatography, vacuum sublimation, and zone refining. The residual impurity concentration was too small to be detected by gas chromatography (less than 1 ppm). Single crystals were grown by the Bridgman method, and sections were cleaved with a razor along the *ab* plane. Both sides of the crystal were then polished to an optical finish with a xylene-soaked tissue. The typical sample was 1 cm^2 in the *ab* plane and approximately 1 mm thick in the c' direction.

As indicated in the Appendix, the excited states of pyrene are split into four components. Only two of these components can be optically excited and these transitions are polarized parallel and perpendicular to the *b* direction. In order to align the samples for excitation, the samples were oriented by birefringence. Since the *bc* plane is the mirror plane in pyrene, the maximum birefringence occurs in the *a* direction. The orientation was checked by looking at samples between crossed polarizers. This method is applicable because the *b* direction is a principal direction in pyrene.[7]

The excitation was provided by dispersing the light from a 1000-W xenon lamp (Hanovia model 976 C-1) with a quarter-meter monochromator (Jarrell-Ash model 82-410) fitted with 1-mm slits (33-Å/mm linear dispersion). Second harmonics from the monochromator were eliminated with a long-wavelength pass filter (Corning CS 3-69). The beam was then polarized by a Glan-Thompson prism and directed normal to the *ab* crystal plane. The crystal was rotated so that *a*- and *b*-polarized spectra could be obtained with light of the same intensity. The monochromator drive was modified to scan cyclically over the (0, 0) triplet line in pyrene. This line has been reported by Avakian and Abramson[8] to be at 5935 Å in unpolarized light. The eximer fluorescence of pyrene[6] which results from triplet-triplet annihilation was isolated with two Corning glass filters (CS 4-72 and CS 5-58) and viewed by a photomultiplier (EMI 9558) which was cooled to − 20 °C. The fluorescence was found to be proportional to the square of the incident intensity; this ensures that the fluorescence arises from triplet-triplet annihilation.[9] The photomultiplier output was fed to an ammeter with a time constant of 20 msec and the output from the ammeter was recorded by a computer of average transients (Northern Scientific model NS-550). This computer was programmed to scan over 254 channels at 80 msec per channel after being triggered by a microswitch which was coupled to the monochromator drive shaft. The channel separation was found to be 0.34 Å per channel, by using neon lines in the region of the triplet absorption peak of pyrene. For proper enhancement of the signal-to-noise ratio, 50 scans were averaged for each run. The point at which the maximum occurred in the signal-averaged data was found by fitting the data with an eighth-order polynomial and finding the point at which the polynomial had its maximum in the region of the fit.

RESULTS

In unpolarized light, the excitation spectrum of the delayed fluorescence from 6000 to 5200 Å was similar to that observed by Avakian and Abramson.[8] The maximum of the (0, 0) triplet transition was found to be at 5928 ± 16 Å, in good agreement with the value 5935 Å reported in Ref. 8. In polarized light, the peak of the (0, 0) triplet transition was at higher energy for *b*-polarized light than for light polarized in the *a* direction. The polarization was alternated until five runs (each run represents 50 signal-averaged scans) at each polarization were made on each sample. The Davydov splitting was found by calculating the difference between the *a*- and *b*-polarized fluorescence maxima, and also by finding the shift in the centroids of the fluorescence lines for the two polarizations. Both of these methods gave the same results. The three samples used in the experiment were found to have Davydov splittings of 0.95 ± 0.24, 0.78 ± 0.14, and 0.82 ± 0.21 Å. (The variation in the mean deviations of these numbers is due to differences in the thicknesses of the three samples.) The average value of the Davydov splittings for the three crystals is 0.85 ± 0.21 Å. Using the value of 5928 Å for the position of the unpolarized singlet-triplet absorption peak, the average splitting in energy units is found to be 2.4 ± 0.6 cm^{-1}. This splitting is a factor of 7 smaller than that reported for anthracene by Avakian *et al.*[2] However, as will be shown below, the splitting for pyrene is the difference between two matrix elements which could be of the same order of magnitude, while in anthracene only one matrix element is involved. A comparison cannot be made until at least the signs of the two matrix elements for pyrene are known.

Both the *a*- and *b*-polarized delayed-fluorescence peaks were found to have the same shape; however, the delayed fluorescence at the maximum of the *b*-polarized transition peak was found to be 40% greater than the delayed fluorescence at the maximum of the *a*-polarized transition peak. Since the delayed fluorescence is proportional to the square of the absorption coefficient, the ratio of the *a* absorption maximum to the *b* absorption maximum is 1 : 1.2. The intensity ratios were reproducible to within 10% for the three crystals measured. Therefore, uncertainties arising because the incident light passed through different regions of the crystal for the two polarizations are not greater than this value. The corresponding oriented gas ratios from the crystallographic data[10] for long, short, and perpendicular molecular axis transitions are 5.1 : 1, 1 : 1, and 1 : 1.5, respectively. A comparison of these oriented gas ratios with the experimental ratio indicates that the (0, 0) triplet-transition moment has little or no component in the long-axis direction. Hochstrasser and Lower[11] found from measurements of phosphorescence of pyrene in benzophenone that the transition was polarized largely perpendicular to the plane of the molecule. Singlet-triplet transitions polarized out of plane are found in many aromatic hydrocarbons[11] so that the present result is reasonable.

Owing to the quadratic nature of the fluorescence, the half-width of the absorption line at half-maximum Γ corresponds to the half-width of the delayed-fluorescence line at quarter maximum, after correcting for the finite slit width of the monochromator. Measurements of the unpolarized excitation spectrum with 2-, 1-, and 0.5-mm slits (33-Å/mm dispersion) gave values for the half-width of 152, 112, and 98 cm^{-1}. The true half-width was estimated by convoluting a curve of Lorentzian shape and variable width with the appropriate slit function for the monochromator and comparing the resulting linewidth with the experimental values. Measurements of neon lines showed that the slit function could be approximated by an isosceles triangle with a base of twice the slit width. In this way, values for Γ of 89, 92, and 92 cm^{-1} were found for the three slits, respectively. Furthermore, a value of $\Gamma \approx 95\ \text{cm}^{-1}$ can be estimated from the spectrum measured at higher resolution by Avakian and Abramson.[8]

DISCUSSION

For anthracene, with two molecules per unit cell, the Davydov splitting of the triplet-exciton excitation spectrum yields important information about the triplet-exciton band structure. Jortner *et al.*[4] have shown that the triplet-exciton band structure for anthracene is determined primarily by two exchange integrals involving nearest and next nearest neighbors and that the Davydov splitting is almost entirely due to the nearest-neighbor interaction. Furthermore, Avakian *et al.*[2] have evaluated the triplet-exciton velocity in the *a* direction in terms of the Davydov splitting and have estimated the scattering length and diffusion coefficient from this velocity and the linewidth of the triplet absorption spectrum. Although pyrene has four molecules per unit cell,[10] we show in the following analysis that the splitting and linewidth of the pyrene triplet level yield similar information about the triplet-exciton band structure in this material.

As shown in the Appendix, the $\vec{k}$-dependent part of the exciton energy, $\epsilon^f(\vec{k})$, can be obtained from a solution of a secular determinant

$$\left|\sum_q e^{i\vec{k}\cdot(\vec{r}_q-\vec{r}_p)} M_{p\delta,q\rho} + (\xi^f - \epsilon^f)\,\delta_{\delta\rho}\right| = 0\ , \tag{1}$$

where q and p index the primitive cells and δ and ρ index the molecules within a cell. In the present perturbation treatment $M_{p\delta,q\rho}$ is the interaction between molecules $p\delta$ and $q\rho$, primarily due to electron exchange,[4] ξ^f is a constant which includes the transition energy for an isolated molecule and the difference in binding energy of an excited and unexcited molecule.

Because the electric dipole transitions are spin forbidden and the exchange interactions are very short ranged,[4] only a small number of neighbors must be considered in constructing the secular determinant.

A projection of the pyrene molecules on the *ab* plane is shown in Fig. 1. In this investigation only interactions between the first four neighbors were considered. These interactions are labeled A_2, A_3, A_4, and A_5 in Fig. 1 with center-to-center molecular distances of 6.03, 7.18, 3.93, and 7.62 Å, respectively.[10] The interactions in the *c* direction were ignored because the closest intermolecular distance in this direction is 8.37 Å.

The analysis at the band structure is simplified by the assumption that the closest interaction A_4 is large compared to the others. Since the second-nearest-neighbor distance is more than 50% longer than that for A_4, and since the exchange interaction is expected to fall off exponentially with distance,[4] this assumption seems quite reasonable. It is shown in the Appendix that with this assumption the secular determinant can be solved approximately to give the following four solutions for ϵ^f_μ:

$$\begin{aligned}
\mu = 1 \quad \epsilon^f_1 &= \xi^f - A_4 - A_5 \cos\vec{k}\cdot\vec{b} \\
&\quad + 2\,(A_2 - A_3)\cos\tfrac{1}{2}\vec{k}\cdot\vec{a}\cos\tfrac{1}{2}\vec{k}\cdot\vec{b}\ , \\
\mu = 2 \quad \epsilon^f_2 &= \xi^f - A_4 - A_5 \cos\vec{k}\cdot\vec{b} \\
&\quad - 2\,(A_2 - A_3)\cos\tfrac{1}{2}\vec{k}\cdot\vec{a}\cos\tfrac{1}{2}\vec{k}\cdot\vec{b}\ , \\
\mu = 3 \quad \epsilon^f_3 &= \xi^f + A_4 + A_5 \cos\vec{k}\cdot\vec{b} \qquad\qquad \text{(A13)} \\
&\quad + 2\,(A_2 + A_3)\cos\tfrac{1}{2}\vec{k}\cdot\vec{a}\cos\tfrac{1}{2}\vec{k}\cdot\vec{b}\ , \\
\mu = 4 \quad \epsilon^f_4 &= \xi^f + A_4 + A_5 \cos\vec{k}\cdot\vec{b} \\
&\quad - 2\,(A_2 + A_3)\cos\tfrac{1}{2}\vec{k}\cdot\vec{a}\cos\tfrac{1}{2}\vec{k}\cdot\vec{b}\ .
\end{aligned}$$

Thus, the triplet-exciton levels fall into two double bands with widths at $\vec{k}=0$ of $4(A_2 \pm A_3)$ and separated in energy by $2(A_4 + A_5)$. It is also shown in the Appendix that optical transitions at $\vec{k}=0$ are permitted only to levels 1 and 2 in Eq. (A13), the first with light polarized parallel to the *b* axis, the second with light perpendicular to *b*. The dispersion relation for the band containing the allowed levels is

$$\begin{aligned}
\epsilon^f(\vec{k}) &= -\,(A_4 + A_5\cos\vec{k}\cdot\vec{b}) \\
&\quad \pm 2(A_2 - A_3)\cos\tfrac{1}{2}\vec{k}\cdot\vec{a}\cos\tfrac{1}{2}\vec{k}\cdot\vec{b}\ .
\end{aligned} \tag{2}$$

The Davydov splitting for this band will be

$$\Delta = 4\,|A_2 - A_3|\ . \tag{3}$$

Since the a component of the velocity

$$V_a(\vec{k}) = \frac{1}{\hbar}\frac{\partial \epsilon^f(\vec{k})}{\partial \vec{k}_a} \tag{4}$$

depends only on $(A_2 - A_3)$, we can write the rms velocity in the a direction,

$$\langle V_a^2 \rangle^{1/2} = a\Delta/8\hbar \quad . \tag{5}$$

It is of interest to note that the above expression is the same in the case of anthracene.[2] Following Avakian *et al.*,[2] for an isotropic scattering time τ_s, we can write the aa component of the diffusion tensor,

$$D_{aa} = \tau_s \langle V_a^2 \rangle = \tau_s a^2 \Delta^2 / 64\hbar^2 \quad . \tag{6}$$

The quantity V_a^2 is averaged over the ab plane of the Brillouin zone with the Boltzmann factor assumed constant owing to the small bandwidth. With $\Delta = 2.4 \pm 0.6$ cm^{-1}, $\tau_s = 3\times 10^{-14}$ sec from the measured linewidth and the uncertainty principle, and $a = 13.6$ Å [10] we find $\langle V_a^2\rangle^{1/2} = (8 \pm 2)\times 10^3$ cm/sec and $D_{aa} = (2 \pm 1)\times 10^{-6}$ cm^{2}sec^{-1}. It should be noted that the diffusion coefficient calculated in this manner for anthracene[2] differed by about a factor of 4 from the reported experimental value. The value calculated in the present investigation must therefore be considered only an estimate until the theory relating the linewidth to the relaxation time is refined.

The above numbers give a scattering length $V\tau_s$ of about 0.02 Å, which is much smaller than a lattice constant. This renders the assumption of a band model questionable. Recent calculations by Munn and Siebrand[12] have shown that a simple band picture for triplet-exciton motion in aromatic hydrocarbons may not be completely accurate. Rather, the exciton-phonon interaction should be included and the combination of excitons and phonons treated as a polaron as described by Holstein.[13] In this theory the phonon interaction produces a widening of the linewidth and reduction of the bandwidth with increasing temperature. Although there is not enough experimental information for pyrene for a quantitative test of this theory, the wide linewidth of 184 cm^{-1} compared to the Davydov splitting of 2.4 cm^{-1} suggests that the mechanism for triplet-exciton transport in pyrene is probably closer to hopping (zero bandwidth) than the pure band motion (linewidth small compared to bandwidth), particularly in view of the small scattering length. The results of their measurements led Avakian *et al.* to similar conclusions regarding triplet-exciton diffusion in anthracene.[2]

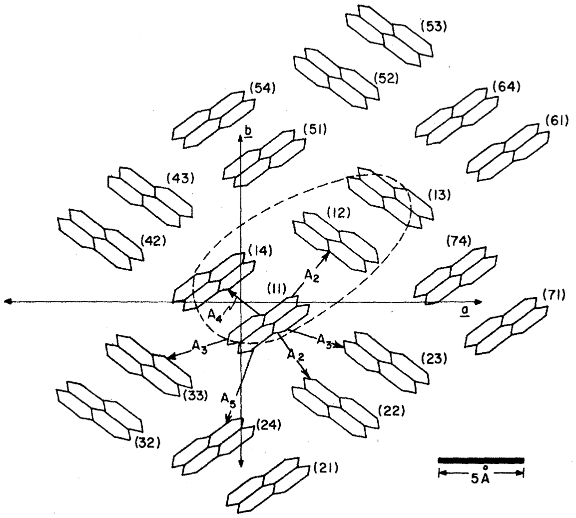

FIG. 1. Projection of 19 pyrene molecules on the ab crystal plane. Each molecule is distinguished by a pair of numbers. The number on the left-hand side designates the unit cell, and the number on the right-hand side indicates the position of the molecule in the unit cell.

APPENDIX

There are several review articles and books[3,14–16] which describe the methods of calculation of exciton band structures. Calculations for singlet excitons in pyrene have been made by Ferguson[6] and Tanaka.[17] For triplet excitons, the intermolecular interactions are dominated by the short-range exchange interaction[4] so that only a few neighbors need be considered. The present treatment is similar in form to most of the work mentioned and the notation is mainly that of Davydov.[3]

The Hamiltonian for the crystal is assumed to be the sum of the free-molecule Hamiltonian plus a perturbation containing the intermolecular interaction,

$$H = \sum H^0_{m\alpha} + {\sum}' V_{m\alpha, n\beta} \quad , \tag{A1}$$

where $H^0_{m\alpha}$ is the Hamiltonian for the αth molecule in the mth unit cell with no intermolecular interactions, and $V_{m\alpha,n\beta}$ is the interaction between molecules $m\alpha$ and $n\beta$. (The prime in the second summation indicates that each pair of interactions is to be counted once, and all self-interactions are to be excluded.) The crystal wave functions are created from the free-molecule wave functions for a first approximation. The ground-state wave function is written

$$\Psi^0 = a\left(\prod_{m\alpha} \phi^0_{m\alpha}\right) \quad , \tag{A2}$$

where $\phi^0_{m\alpha}$ is the ground-state wave function for the isolated molecule $m\alpha$ and a is the antisymmetrization operator. The wave function for the fth excited state is written

$$\Psi^f = (\sigma N)^{-1/2} \sum_{m,\alpha} B_\alpha e^{i\vec{k}\cdot\vec{r}_m} \Phi^f_{m\alpha} \quad , \tag{A3}$$

where

$$\Phi^f_{m\alpha} = a\left(\phi^f_{m\alpha} \prod_{n\beta \neq m\alpha} \phi^0_{n\beta}\right) \tag{A4}$$

is the localized wave function for a state in which one molecule is excited, N is the number of unit cells, and σ the number of molecules per cell. The secular equations for the energy of the excited state are obtained from

$$\int \Phi^{f*}_{m\alpha} H \Psi^f d\tau = E^f \int \Phi^{f*}_{m\alpha} \Psi^f d\tau \quad . \tag{A5}$$

If the interaction between two molecules is independent of the electrons from the remaining molecules in the crystal, the secular equations for the energy relative to the ground state are given by

$$\textstyle\sum_\rho [\sum_q e^{i\vec{k}\cdot(\vec{r}_q - \vec{r}_p)} M_{p\delta, q\rho} + (E^f_{p\delta} + D^f_{p\delta} - \epsilon^f)\,\delta_{\delta\rho}] B_\rho = 0 \ , \tag{A6}$$

where $E^f_{p\delta}$ is the transition energy for an isolated molecule and $D^f_{p\delta}$ is the difference in binding energy of an excited and unexcited molecule:

$$\begin{aligned} D^f_{p\delta} &= \sum_{q\rho}{}' \int \phi^{f*}_{p\delta}\, \phi^{0*}_{q\rho}\, V_{p\delta, q\rho}\, \phi^f_{p\delta}\, \phi^0_{q\rho}\, d\tau \\ &\quad - \sum_{q\rho}{}' \int \phi^{0*}_{p\delta}\, \phi^{0*}_{q\rho}\, V_{p\delta, q\rho}\, \phi^0_{p\delta}\, \phi^0_{q\rho}\, d\tau \ , \end{aligned} \tag{A7}$$

and $M_{p\delta, q\rho}$ is given by

$$M_{p\delta, q\rho} = \int_{p\delta \neq q\rho} \phi^{f*}_{p\delta}\, \phi^{0*}_{q\rho} V_{p\delta, q\delta}\, \phi^0_{p\delta}\, \phi^{f*}_{q\rho} d\tau \ , \tag{A8}$$

where the wave-function products are still assumed to be properly antisymmetrized. Since all of the pyrene molecules are equivalent, the subscripts on $E^f_{p\delta}$ and $D^f_{p\delta}$ will be dropped and the two quantities will be considered a constant $\xi^f = E^f + D^f$. For a given origin, say, $p = 0$, $\vec{r}_p = 0$, (A6) is a set of four equations and the determinant of the coefficients of the B_ρ must vanish:

$$\left|\textstyle\sum_q e^{i\vec{k}\cdot\vec{r}_q} M_{p\delta, q\rho} + (\xi^f - \epsilon^f)\,\delta_{\delta\rho}\right| = 0 \ . \tag{A9}$$

The short-range exchange terms will dominate the matrix elements in (A8) so only the few neighbors shown in Fig. 1 have been considered. We have written, for example,

$$M_{11,12} = M_{11,22} = A_2 \ ,$$

$$M_{11,23} = M_{11,33} = A_3 \ .$$

For these four nearest neighbors, the secular determinant is found to be

$$\begin{vmatrix} \xi^f - \epsilon^f & A_2[1 + e^{i\vec{k}\cdot\vec{b}}] & A_3[e^{-i\vec{k}\cdot\vec{b}} + e^{-i\vec{k}\cdot(\vec{a}+\vec{b})}] & A_4 + A_5 e^{-i\vec{k}\cdot\vec{b}} \\ & \xi^f - \epsilon^f & A_4 + A_5 e^{-i\vec{k}\cdot\vec{b}} & A_3[1 + e^{i\vec{k}\cdot\vec{a}}] \\ & & \xi^f - \epsilon^f & A_2[e^{i\vec{k}\cdot(\vec{a}+\vec{b})} + e^{i\vec{k}\cdot\vec{a}}] \\ & & & \xi^f - \epsilon^f \end{vmatrix} \ . \tag{A10}$$

The remainder of the terms are found from the relation, $a_{ji} = a^*_{ij}$. Since A_4 is expected to be large compared to the other A_i, the secular determinant can be rearranged so that the large terms are on the diagonal,

$$\begin{vmatrix} \frac{1}{2}(a_{14} + a^*_{14}) + \xi^f - \epsilon^f & \frac{1}{2}(a^*_{14} - a_{14}) & \frac{1}{2}(a_{12} + a_{13} + a^*_{24} + a^*_{34}) & \frac{1}{2}(a_{12} - a^*_{13} + a^*_{24} - a^*_{34}) \\ & -\frac{1}{2}(a_{14} + a^*_{14}) + \xi^f - \epsilon^f & \frac{1}{2}(a_{12} + a_{13} - a^*_{34} - a^*_{24}) & \frac{1}{2}(a_{12} - a_{13} + a^*_{34} - a^*_{24}) \\ & & \frac{1}{2}(a_{14} + a^*_{14}) + \xi^f - \epsilon^f & \frac{1}{2}(a^*_{14} - a_{14}) \\ & & & \frac{1}{2}(a_{14} + a^*_{14}) + \xi^f - \epsilon^f \end{vmatrix} \ , \tag{A11}$$

and the matrix is again Hermitian. We now let

$$\epsilon^f = \xi^f + \tfrac{1}{2}(a_{14} + a^*_{14}) + \delta \ , \tag{A12}$$

where δ is assumed to be small, and $(a_{14} + a^*_{14})$ large, so that two of the diagonal elements will be large compared to the others.

If only terms in the expansion which contain the two elements are retained, the four solutions ϵ^f_μ are found to be

$$\begin{aligned} \mu = 1 \quad \epsilon^f_1 &= \xi^f - A_4 - A_5 \cos\vec{k}\cdot\vec{b} \\ &\quad + 2(A_2 - A_3)\cos\tfrac{1}{2}\vec{k}\cdot\vec{a}\cos\tfrac{1}{2}\vec{k}\cdot\vec{b} \ , \\ \mu = 2 \quad \epsilon^f_2 &= \xi^f - A_4 - A_5 \cos\vec{k}\cdot\vec{b} \\ &\quad - 2(A_2 - A_3)\cos\tfrac{1}{2}\vec{k}\cdot\vec{a}\cos\tfrac{1}{2}\vec{k}\cdot\vec{b} \ , \\ \mu = 3 \quad \epsilon^f_3 &= \xi^f + A_4 + A_5 \cos\vec{k}\cdot\vec{b} \\ &\quad + 2(A_2 + A_3)\cos\tfrac{1}{2}\vec{k}\cdot\vec{a}\cos\tfrac{1}{2}\vec{k}\cdot\vec{b} \ , \\ \mu = 4 \quad \epsilon^f_4 &= \xi^f + A_4 + A_5 \cos\vec{k}\cdot\vec{b} \\ &\quad - 2(A_2 + A_3)\cos\tfrac{1}{2}\vec{k}\cdot\vec{a}\cos\tfrac{1}{2}\vec{k}\cdot\vec{b} \ . \end{aligned} \tag{A13}$$

It will now be shown that optical transitions at $\vec{k} = 0$ to only two of the four energy levels are allowed. If the solutions in Eq. (A13), $\vec{k} = 0$, are inserted in the secular equations (A6), the following values for the B_α are obtained:

$\mu = 1 \quad B = (+1,\ +1,\ -1,\ -1)$,

$\mu = 2 \quad B = (+1,\ -1,\ +1,\ -1)$,

$$\mu = 3 \qquad B = (+1,\ +1,\ +1,\ +1) \ ,$$

$$\mu = 4 \qquad B = (+1,\ -1,\ -1,\ +1) \ . \tag{A14}$$

The transition moment $\vec{M}$ for the unit cell can be obtained from the moments of the four molecules:

$$\vec{M} = \int \Psi^{f} \vec{r}\, \Psi^{0} d\tau = \sum_{\alpha} B_{\alpha} \vec{M}_{\alpha} \ , \tag{A15}$$

where

$$\vec{M}_{\alpha} = \int \phi_{\alpha}^{f*}\, \vec{r}_{\alpha}\, \phi_{\alpha}^{0} d\tau$$

is the transition moment for the α molecule.

If the transition moments transform like vectors and one is known, the other three can be generated by the symmetry operations that transform one molecule to another. $\vec{M}_4$ is obtained from $\vec{M}_1$ and $\vec{M}_2$ from $\vec{M}_3$ by inversion; $\vec{M}_3$ is obtained from $\vec{M}_1$ by a reflection in the ac plane.[10] In terms of the three components of $\vec{M}_1$, the total transition moment will have the following components along the a, b, and c' directions for the four levels:

$$\begin{aligned} \mu &= 1 \qquad \vec{M} = (0,\ 2M_b,\ 0) \ , \\ \mu &= 2 \qquad \vec{M} = (2M_a,\ 0,\ 2M_{c'}) \ , \\ \mu &= 3 \qquad \vec{M} = (0,\ 0,\ 0) \ , \\ \mu &= 4 \qquad \vec{M} = (0,\ 0,\ 0) \ . \end{aligned} \tag{A16}$$

Thus, it is seen that only the first two transitions are allowed and that they will absorb light polarized either parallel or perpendicular to the b axis, respectively. The difference in energy between the two levels at $\vec{k} = 0$ is the Davydov splitting.

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Lattice Dynamics of Rutile*

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The phonon dispersion relation for rutile (TiO_2) has been measured by the coherent inelastic scattering of thermal neutrons along principal symmetry directions of the Brillouin zone. Theoretical models based on rigid-ion and shell models, with either axially symmetric or tensor first- and second-neighbor forces, have been fitted to the measured dispersion relation. Only the shell model with tensor forces for all interactions except the second-neighbor oxygen-oxygen interaction was able to give acceptable qualitative agreement with the data, and that agreement is good for only some modes. A frequency distribution and Debye temperature spectrum are presented for that model. The temperature dependence of the frequency of the Γ_1^- (A_{2u}) transverse optic mode is measured from 4 to 300 °K, and the behavior of the square of the frequency is in good agreement with that predicted by the static dielectric constant measurements of Parker.

I. INTRODUCTION

Many of the physical, optical, and chemical properties of a compound are reflected in the lattice dynamics of the crystal. For example, information related to the elastic behavior, specific