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Selection Rules for the Charge Transfer Transitions in the Symmetrical Tetracyano-*p*-quinodimethane–Anthracene Molecular Complex

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Abstract: The specular reflection spectra and their Kramers–Kronig transforms for the crystalline TCNQ–anthracene molecular complex have been obtained from 5 to 46 kK for light polarized along the *a*, *b*, and *c* crystallographic axes as well as one other principal direction. The assignment of the charge transfer transitions observed is made according to the group theoretical selection rules for the approximate C_{2v} symmetry of the complex as well as the exact C_s symmetry. The first two charge transfer transitions are taken to originate from the penultimately occupied molecular orbital of anthracene to the lowest two unoccupied orbitals of TCNQ. Comparison is also made to current exciton theories for crystals of molecular complexes.

There have been many studies of the charge transfer (CT) transitions of electron–donator–acceptor (EDA) complexes in all phases. Of special interest have been studies of crystalline complexes of organic molecules. In these systems it has been possible to observe multiple charge transfer transitions which cannot be observed in vapor phase or solu-

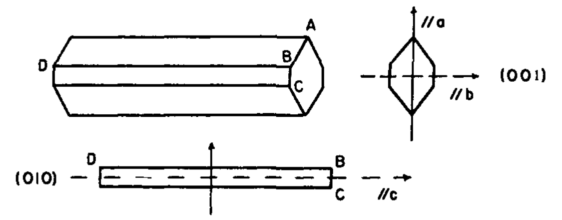

Figure 1, Crystal morphology and principal directions.

tion spectra because of interference and masking by the molecular transitions of the moieties of the complex.

The EDA systems studied often show two CT transitions of low energy. Their origin is attributed to transitions from the ultimately and penultimately filled molecular orbitals of the donor to the first unfilled orbital of the acceptor. The polarization of the lowest energy CT transition is typically along the line of centers joining the donor and acceptor molecules but the polarization of the second CT transition has been observed to be either parallel or perpendicular to the first depending on the complex.

Little in the way of systematization and explanation of these observations had been attempted until the discussion of Anderson.[2a] In this paper the selection rules for the CT transitions in EDA complexes were developed by symmetry arguments based on a previous approach of McGlynn and Boggus.[2b] It was found that the spectra of the EDA complexes follow the selection rules dictated by the group theory for the point group of the specific complexes. The treatment rationalized the polarization behavior of the CT transitions which had been studied experimentally at that time. In particular, predictions were made of the polarizations of the two CT transitions[3] in the tetracyano-*p*-quinodimethane-anthracene (TCNQ-A) EDA complex.

Further theoretical development has been made by I'Haya and Suzuki[4] who were specifically concerned with the solid state interactions which may be displayed by the spectra of crystalline EDA complexes. In this approach, the EDA complexes are treated as interacting "triads". This is suggested by the observation that the typical EDA complex crystal consists of stacks of alternating donor and acceptor molecules wherein any given donor molecule may have a CT transition to either or both of the two acceptor molecules which "sandwich" it. Calculations are made and spectra are predicted for the crystalline TCNQ-A crystal according to the proposed theory.

The TCNQ-A system is of interest because it is one of the few crystalline EDA complexes of known structure which is found to have rigorous symmetry.[5] This symmetry for the complex is C_s although to a good approximation the point group symmetry (PGS) may be taken as C_{2v}. Additionally, since there is evidence for multiple CT transitions in the crystalline complexes of anthracene,[6] its EDA complex with the strong acceptor TCNQ may then be expected to show at least two CT transitions in the crystal. Also, the fact that there exist relatively detailed experimental and theoretical treatments of the electronic structure of the TCNQ[7,8] and anthracene[9,10] molecules enhances interest in the study of the complex.

We report the spectra of the crystalline TCNQ-A EDA complex obtained from polarized near-normal incidence specular reflection spectroscopy. The observed spectra are found to be in varying degrees of disagreement with each of the two sets of predictions.

I. Experimental Section

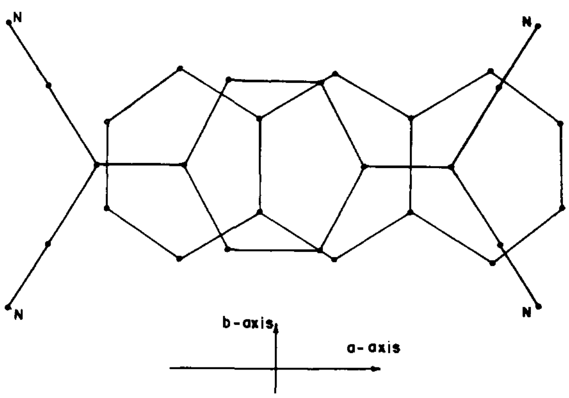

Figure 2, Projection of the TCNQ-A complex onto (001).

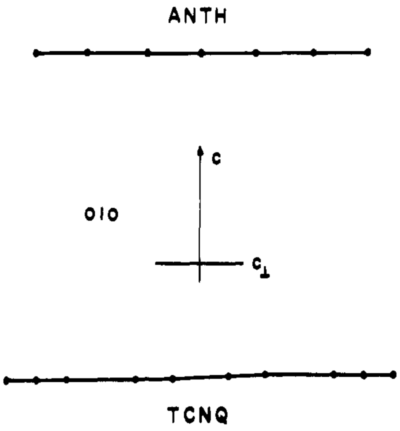

Figure 3, Projection of the TCNQ-A complex onto (010).

A. Materials. The TCNQ obtained from Eastman Organics was purified by repeated vacuum sublimation. The blue-violet fluorescence grade anthracene obtained from the same supplier was used without further purification. Equimolar amounts of the two compounds were used to prepare two separate solutions in warm tetrahydrofuran. The complex formed immediately upon mixing of these two solutions. The resulting solution was filtered and allowed to stand until crystals formed. The black shiny acicular crystals were subsequently harvested and mounted for study.

The needle axis is the *c*-crystallographic axis. Optical goniometry and x-ray photographs were used to determine the crystal faces. Zonal to the *c*-axis were (010) and the form {110}. The (001) face was also observed. Note that this set of naturally occurring faces provides spectra polarized along all three crystallographic axes. The crystal morphology is shown in Figure 1.

B. Crystal Data and Projections. The room-temperature crystal structure[5] indicates a crystal of space group $C_{2/m}$ (C_{2h}^3) with a = 11.48 Å, b = 12.95 Å, and c = 7.00 Å and β = 105.4°. There are two complexes in the unit cell. There is also evidence for disorder in the positions of the anthracene molecules.[11]

C. Projections. Measurement of the polarized spectra for the two faces, (001) and (010), permits assignment of the two CT transitions. The projections of the complex onto these faces are shown in Figures 2 and 3. The projections are shown for only one complex in the unit cell since the other gives an equivalent projection.

The (001) projection shows that the *b* axis is parallel to the short (y) axes of the molecules. The constituent molecules appear displaced because the *a* axis is at an angle of 15.4° to the long (x) axes of the molecules. Projection of the TCNQ onto the anthracene least-squares plane would show the ring of the TCNQ exactly superimposed upon the central ring of the anthracene. These two projections make clear the rigorous C_s PGS of the complex and how closely it may be approximated by the C_{2v} group.

The projection onto (010) is shown in Figure 3. The *c* axis is also a principal direction in this face and it connects the line of centers of the complex. The *c* axis shall be identified with the *z* axis of the complex since the long axes of the TCNQ and anthracene molecules are collinear with the principal direction ($c_\perp$) which is per-

Table I

	TCNQ		Anthracene
	Molecular Axes[a]		
	(0.9683, 0.0, 0.2498)	x	(0.9653, 0.0, 0.2613)
	(0.0, 1.0, 0.0)	y	(0.0, 1.0, 0.0)
	(−0.2498, 0.0, 0.9683)	z	(−0.2613, 0.0, 0.9653)
		Principal Directions[a]	
a	(1.0, 0.0, 0.0)	c	(−0.2656, 0.0, 0.9641)
b	(0.0, 1.0, 0.0)	$c_\perp$	(.9641, 0.0, .2656)

[a] Vectors are referred to the a, b, and c^* Cartesian system.

Table II

ν_{max}, kK	Method	ϵ_{max} l./(mol cm)	K_{eq}, l./mol
12.58	Benesi-Hildebrand	843 ± 140	5.2 ± 0.8
(CT-I)	Scott	940 ± 135	4.6 ± 0.6
	F-H-W	933 ± 40	4.7 ± 0.1
22.47	Benesi-Hildebrand	7540 ± 1420	4.5 ± 0.7
(CT-II)	Scott	9400 ± 1700	3.6 ± 0.6
	F-H-W	9320 ± 600	3.6 ± 0.2

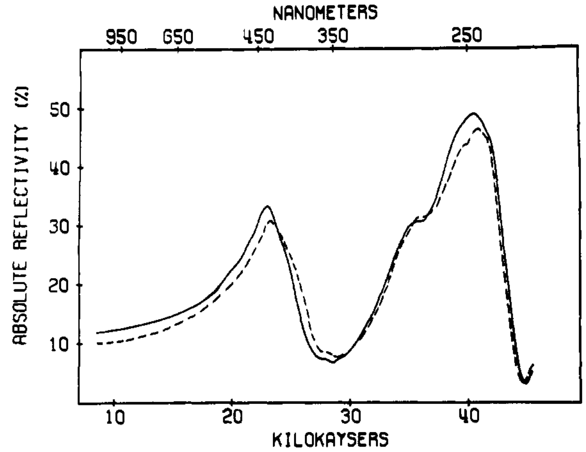

Figure 4. Reflection spectra obtained with light polarized along the a axis (dashed line) and the $c_\perp$ axis (solid line) on (010).

pendicular to the c axis in this face. Thus the spectra for this face will give the x and z polarized transitions. Vectors for the molecular axes and the principal directions for (010) and (001) are given in Table I.

D. Solution Spectra. The spectrum of the first CT band (CT-I) in tetrahydrofuran is a broad Gaussian peaked at 12.6 kK. The equilibrium constant and molar absorptivity were determined according to the Benesi-Hildebrand,[12] Scott,[13] and Foster-Hammick-Wardley[14] methods. The entire absorption band was weighted into the calculation using the method of Liptay.[15] Similar data were obtained for a second CT transition (CT-II) observed in tetrahydrofuran solution. This band was masked by the TCNQ molecular transition which has a peak extinction at 24.9 kK. The data for the second CT band were obtained by differential spectrophotometry wherein the reference and sample cells were maintained at identical TCNQ concentrations. The amounts of anthracene added to the sample were the only quantities varied. Results of these analyses for both CT bands are given in Table II.

The equilibrium constants obtained by the various methods are within error of each other for the measurement for each CT transition. The agreement of the equilibrium constants obtained from the analysis of the two bands is remarkably good considering the error inherent in the differential measurement and the Benesi-Hildebrand type procedure. The best value of K_{eq} is taken as 4.4 l./mol.

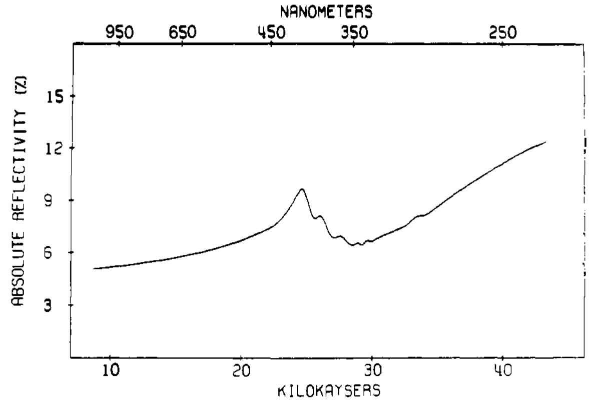

Figure 5. Reflection spectrum obtained with light polarized along the b axis.

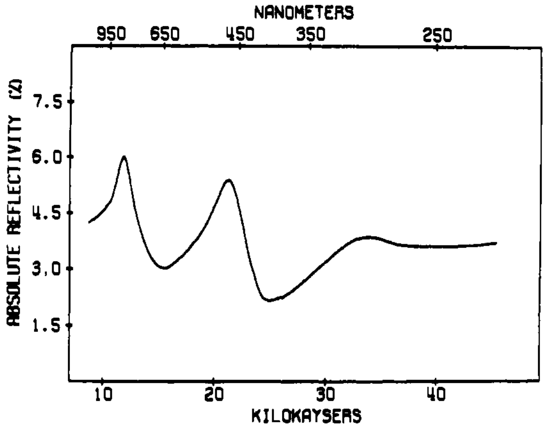

Figure 6. Reflection spectrum obtained with light polarized along the c axis.

The peak molar absorptivities are also in good agreement for each method of analysis for each CT band. The first CT band peak absorptivity for TCNQ-A is approximately an order of magnitude less than that of the second CT band. The nature of the differential experiment reduces the accuracy of the assignment of the peak frequency of 22.5 kK for CT-II.

E. Apparatus. Reflection spectra were obtained using methods and apparatus which have been previously described.[16,17] The angle of incidence was 8° from normal with a band-pass of 1 nm and a 2% error in the measured reflectivities. Spectra for the (010) and (001) faces were taken from 5.0 to 43.5 kK.

II. Results

The reflection spectra for light polarized along the a and $c_\perp$, b, and c crystallographic axes are shown in Figures 4, 5, and 6. These spectra were taken from the (010) and (001) faces. The spectra taken normal to the c-axis perpendicular direction on (010) are quite similar to the spectra polarized along the a axis.

The c-axis reflection spectrum shows three separate bands each of which becomes broader with increasing frequency. The first band peak occurs at 11.8 kK with a reflectivity of 6.0% and the second peak occurs at 21.2 kK with 5.4% reflectivity. The high-energy band has the lowest reflectivity of only 3.9%, and a broad maximum centered at 33.7 kK. Because of their z components of polarization these bands may be expected to be charge transfer in character.

The b-axis spectrum shows no clear structure in the region of the first two c-axis bands. The structure has a 1.4 kK progression where the first peak in the reflection spectrum occurs at 24.7 kK. Since the polarization is also along

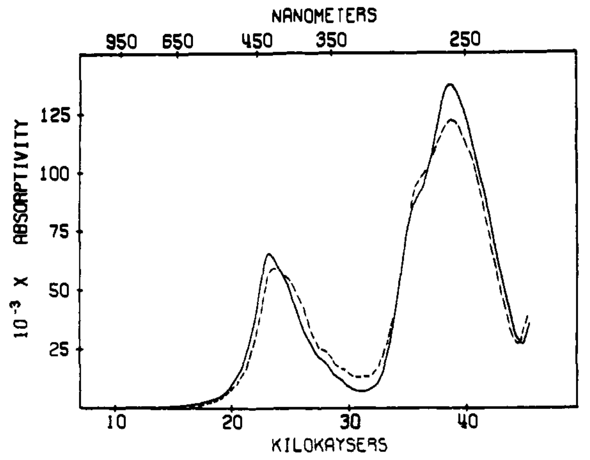

Figure 7. Kramers-Kronig transform of the *a* axis (dashed line) and $c_\perp$ axis (solid line) reflection spectra.

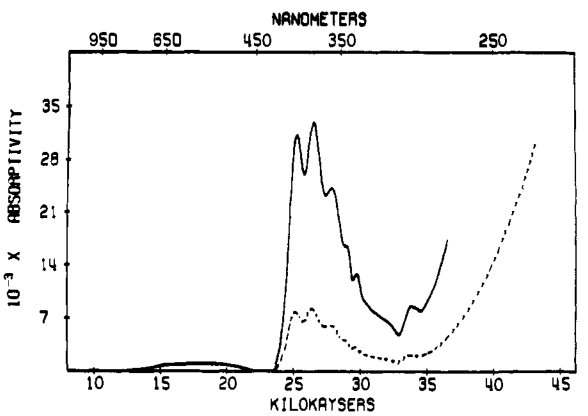

Figure 8. Kramers-Kronig transform of the *b* axis reflection spectrum (dashed line). The solid line plot is scaled to five times the true absorptivities.

Table III

Polarization	Transition Energy (kK)	Dipole strength, Å^{2a}
Crystal		
c	12.6	0.435
	22.6	0.645
	~36	
b	25.3	0.575
	~48	
a	23.5	5.78
	38.9	10.6
Solution		
Anthracene-I	26.3	0.372
Anthracene-II	39.0	3.51
TCNQ-I	24.9	3.36
CT-I	12.5	0.12
CT-II	22.5	0.71

[a] Crystal dipole strength is the full intensity observed along the principal direction. There are no geometrical corrections.

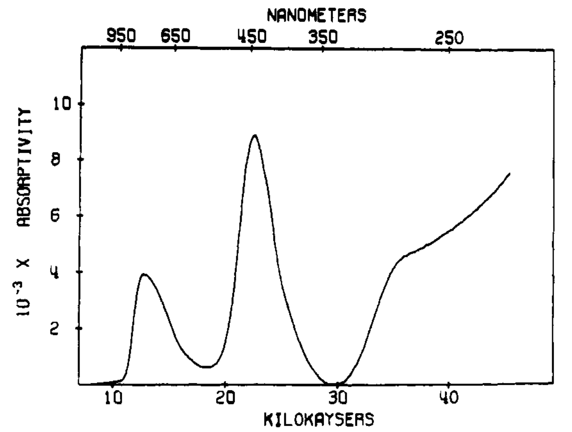

Figure 9. Kramers-Kronig transform of the *c*-axis reflection spectrum.

the *y* axis of the anthracene molecule, the structure may be attributed to the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of anthracene.

The $c_\perp$-axis polarization for (010) yields an intense band in the frequency region of CT-II. However, this peak comes at 21.0 kK and it is thus 0.6 kK blue shifted from the *c*-axis spectrum of CT-II. Here the light is polarized along the long axis of the molecule and, judging from its substantial reflectivity, it may be regarded as mainly due to the $^1B_{2u} \leftarrow {}^1A_g$ transition of TCNQ.[16,17] Anthracene has no absorption in this frequency region. However, anthracene does have a most intense absorption observed at 39.0 kK in solution which is polarized along the long axis of the molecule. Further, since the *a*-axis spectrum has a structure which parallels that of the $c_\perp$ spectrum for (010), the structure may be attributed to the same molecular transitions as for $c_\perp$. Thus, the data would indicate that CT-I is *z* polarized, but that the other two bands with *c*-axis polarization may be polarized in the *yz* plane. Since arguments from reflection spectra alone may be dangerous, especially with reference to intensity effects, the absorption spectra were obtained from Kramers-Kronig transforms of the three reflection spectra.[17] These are shown in Figures 7, 8, and 9.

The peak frequencies as well as integrated intensities obtained from the transforms are listed in Table III together with similar information from solution measurements.

It is clear that CT-I is completely *z*-axis polarized since no absorption is observed for other directions in its frequency region. The case is not substantially clarified for CT-II or CT-III. The possibility exists that intensity for these transitions may project on either the *b* or *c* axes or both. However, in the case of CT-II there is no indication of any intensity projecting in the *b* direction and thus only polarization in the *xz* plane is experimentally indicated.

As a working hypothesis, it is assumed that CT-I and CT-II are polarized completely in the *z* direction. Justification of this comes from the large difference between the energies of CT-II and TCNQ-I (22.6 vs. 23.5 kK) which would rule out any likely Davydov splitting given by the two peaks due to the low dipole strength of the CT transition. Further, the fact that the PGS of the complex is nearly C_{2v} argues that the polarizations of the transitions should lie within a few degrees of the molecular axes. Because of its diffuseness, the assignment of CT-III is difficult to make. It is even less certain that it is charge transfer in origin since there is some structure in the *a*-axis and *b*-axis spectra near 34 kK which may be related.

The rest of the paper will only treat CT-I and CT-II in detail. While the intramolecular transitions are of interest, they will be treated elsewhere since the nature and origin of their interactions are substantially different from those observed for the CT transitions.

III. Discussion

A. Assignment of CT Transitions. Only a brief resume of EDA complex theory will be given here. Extensive reviews on the general theoretical and experimental aspects are available.[18]

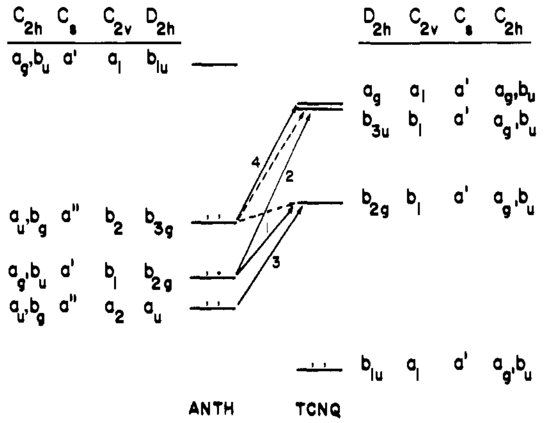

Figure 10. π orbital energy level diagrams of TCNQ and anthracene. The orbital symmetries are shown for the various PGS applicable to the complex in the crystal. Dashed lines are forbidden transitions.

In an EDA complex, the orbitals on adjacent donor (D) and acceptor (A) molecules interact to form a complex stabilized by a resonance interaction of a no-bond configuration $|D,A\rangle$ with polar excited configurations (e.g., $|D^+,A^-\rangle$):

$$\begin{aligned}|N\rangle &= a|D,A\rangle + b|D^+,A^-\rangle + c|D^-A^+\rangle + \ldots\\ &= |0\rangle + \alpha|1\rangle + \gamma|2\rangle + \ldots \end{aligned} \qquad (1)$$

where for most complexes $\gamma \ll \alpha < 1$.

The charge transfer transition is made to an excited state which is essentially ionic because of the nearly complete transfer of an electron from D to A. This state is represented as:

$$|E\rangle = |1\rangle + \beta|0\rangle + \delta|2\rangle + \ldots \qquad (2)$$

where usually $\delta \ll \beta < 1$. The lowest energy CT transition $E \leftarrow N$ has a polarization given by

$$\mathbf{q}_{EN} = \langle E|\mathbf{r}|N\rangle \qquad (3)$$

which after expansion of the wave functions, consideration of orthogonality, and application of approximations suggested by Mulliken[19] leads to:

$$\mathbf{q}_{EN} \approx \alpha(\bar{\mathbf{r}}_A - \bar{\mathbf{r}}_A) + S_{01}(\bar{\mathbf{r}}_D - \bar{\mathbf{r}}_{AD}) \qquad (4)$$

where the $\bar{\mathbf{r}}$ designate average positions of the subscripted components and $S_{01} = \langle 0|1\rangle$. Equation 4 indicates that the polarization of the first transition should lie along the line of centers of the molecules comprising the complex.

The rigorous definition of the polarization for any transition is given by eq 3. It is this equation which shall be pertinent to the discussion of the CT-I and CT-II polarizations.

Anderson has discussed the polarizations of the first two transitions for TCNQ-A using purely group theoretical arguments. These are based on the approximate C_{2v} symmetry for the complex as well as its rigorous C_s symmetry.

Anthracene and TCNQ span the operations of the D_{2h} point group. Thus the representations of the molecular orbitals under this group must be correlated to the irreducible representations of the point group of the complex. The ordering of the pertinent anthracene and TCNQ orbital energy levels is shown in Figure 10 together with their symmetries. The anthracene orbital symmetries are taken from the Pariser-Parr-Pople-LCAO-SCF-CI calculations of Peacock[9] and Fraga[20] and an ab initio pseudopotential SCF calculation by Gallup.[21] The symmetry of the lowest energy vacant orbital is also the same in the three calculations. However, the paper of Anderson makes a completely different assignment of the ultimately and penultimately filled orbitals of anthracene although the work of Peacock is cited for the assignments. Since the same axial systems are used in all the calculations, the discrepancy cannot be attributed to this cause. Because of this difference, the predictions of the polarizations of the CT transitions for TCNQ-A will differ from those given by Anderson. The symmetries for the TCNQ orbitals are in accord with a PPP-LCAO-SCF-CI calculation of Lowitz,[7] an ab initio calculation,[22] and an Xα-scattering calculation.[8] The energy level spacings are determined from the photoionization[23,24] and optical spectra[16,17,25] for anthracene and TCNQ. Correlations of the D_{2h} symmetries to representations under the C_{2v}, C_s, and C_{2h} groups are also diagrammed in Figure 10.

The photoionization spectra show that the top two filled anthracene orbitals differ by 9.0 kK. The difference between the two lowest unfilled orbitals is calculated to be 11.2 kK.

Anderson's orbital assignments under the approximate C_{2v} symmetry give a z polarization for the lowest energy CT transition. This is attributed to a transition from the top filled orbital of anthracene (Ab_{2g}) to the lowest unoccupied TCNQ orbital (Tb_{2g}). (A and T are used to identify the orbitals with their molecules. In this paragraph, the orbital symmetries are those of Anderson.) The second CT transition thought to arise from a transition from the Ab_{3g} orbital to the Tb_{2g} orbital was shown to be forbidden under C_{2v} but weakly allowed with a y polarization under the rigorous C_s symmetry of the complex. This prediction is not in agreement with the experiment. There are two major reasons for this. The origin of the transitions is mistaken and the symmetry assignment of the anthracene orbitals is not in agreement with calculations.

According to the symmetries given in Figure 10, the transition from the highest occupied anthracene orbital (Ab_{3g}) to the lowest unoccupied TCNQ orbital (Tb_{2g}) is forbidden for both the approximate and rigorous symmetries of the complex. The CT transition is also forbidden from the Ab_{3g} orbital to the second unoccupied orbital of TCNQ, Tb_{3u}. However, this orbital is nearly degenerate with the Ta_g orbital which would give a y-polarized CT transition originating from Ab_{3g}. Since this is not observed, the CT transitions must originate from other anthracene orbitals.

From the diagram, it is seen that the transition from Ab_{2g} to Tb_{2g} will be z polarized as will be the transition from this same anthracene orbital to the vacant Tb_{3u}. The energy scale is set such that the $Tb_{2g} \leftarrow Ab_{2g}$ (transition 1) is at 12.6 kK. From the other data, this predicts the energy of the $Tb_{3u} \leftarrow Ab_{2g}$ (transition 2) to be 28 kK. This is in reasonable agreement with the experimental value of 22.6 kK. From Figure 10 it is clear that the unoccupied Ab_{1u}, Ta_g, and Tb_{3u} orbitals have the same symmetry under the C_s PG of the complex. Thus, interaction among these states may be expected and the energy of either one of the TCNQ orbitals involved (most likely Tb_{3u}) would be lowered. Thus the predicted CT-II transition energy is probably less than the estimate given here and thereby closer to the experimentally observed value. Both the transitions designated 3 and 4 are allowed and they should be y polarized with approximate energies of 17 and 20 kK. Very weak structure is observed in this frequency region in the b-axis spectrum shown in Figure 8. However, there is some uncertainty whether this structure is real or due to the Kramers-Kronig transform.

It should be understood that the arguments made thus far for the crystal polarizations are not complete. Because the arguments seek to relate to spectra obtained from crystals, the molecular or complex point groups should be correlated through their site groups to the factor group (FG) of the unit cell. This has potential importance in this system since the C_2 axis of the FG which is coincident with the crystal b axis is perpendicular to the C_2 axis of the approximate C_{2v} PG of the complex. The site group of the complex is C_s which is, of course, the same as for the rigorous symmetry of the complex. The correlations with the C_{2h} FG are given in Figure 10. When they are considered, no change occurs in the above predictions of polarizations. Therefore, questions regarding the CT transitions' polarizations need not consider the FG interactions explicitly.

Thus, the data appear to be consistent only for the CT-I and CT-II transitions arising from the penultimately filled b_{2g} orbital of anthracene to the vacant b_{2g} and b_{3u} orbitals of TCNQ. Further support of this assignment is given by the work of Prout and Kamenar.[26] Molecular orbital coefficients and energies were calculated by these workers for donor and acceptor molecules by the PPP method. CT interactions were determined for possible D–A orientations and the most stable configuration was determined. The ground-state wave function for the TCNQ–A complex was found to be:

$$|\mathrm{N}\rangle = 0.95|0\rangle - 0.27|8 \leftarrow 6\rangle + 0.1|10 \leftarrow 7\rangle + 0.14|9 \leftarrow 4\rangle \quad (5)$$

where the filled π orbitals of the anthracene are numbered 1 through 7 and the vacant TCNQ orbitals are numbered from 8 upwards. Thus, the interaction between the penultimately filled anthracene orbital and the lowest vacant TCNQ orbital is quite important. The excited state may then be approximated by

$$|\mathrm{E}\rangle = 0.97|8 \leftarrow 6\rangle - 0.24|0\rangle \quad (6)$$

A frequent correlation of the energy of a CT transition to the ionization potential of the donor I, the electron affinity of the acceptor A, and the coulombic interaction between the two moieties is made:[18]

$$h\nu_{\mathrm{CT}} = I - A + C \quad (7)$$

In the case of TCNQ–A, the I must be that for the Ab_{2g} orbital. From photoionization studies[23] this is found to be 8.52 eV. The electron affinity of TCNQ is 2.8 eV as determined by collisional ionization and magnetron methods.[27] For the coulombic term, the approximation is made that the donor and acceptor molecules are spherical with a distance between centers which is equal to the interplanar distance of 3.5 Å found in the crystal. The CT excited state is taken as being totally ionic although this is not totally justified by other experiments on EDA complexes.[28] This gives a CT transition energy of 12.9 kK which is in good agreement with the frequency of the first transition. While the crudity of such an approach can prove nothing, it does make the argument for the proposed assignments plausible from an energetic viewpoint.

One last point to be considered is the ordering of the second and third highest filled orbitals of the anthracene. Calculations[9,10] indicate that these two orbitals are nearly degenerate and therefore sensitive to configuration interaction. Thus, there is some question regarding the symmetry of the penultimately filled anthracene orbital. The assignment of the CT transitions made above requires that orbital to be of b_{2g} symmetry for an a_{1u} assignment would not give any agreement with the experimental data. The calculated sequence of these two nearly degenerate filled orbitals of anthracene is supported by these experiments.

B. CT Exciton Interactions. The above assignments raise a question regarding the interaction of the CT transition of the CT transition dipoles in the crystal. A naive application of simple zero-order exciton concepts would indicate that transition dipoles which are aligned head to tail should give rise to a crystal shifted band. Because only transitions to the in-phase combination of dipoles would be permitted, a red shift of the transition from the free molecule value would be observed, i.e., the transition to the bottom of the band is allowed. In the TCNQ–A crystal the CT bands polarized in the ac plane would be allowed but those polarized along the b axis would be forbidden. This bathochromic shift is actually observed in the pyromellitic dianhydride–anthracene EDA crystal[29] where the CT transition dipoles are head to tail. This would be expected for the CT transitions in TCNQ–A.

A zero-order calculation using spherical sums and taking two transition dipoles polarized z in the unit cell gives a crystal shift of 88 cm^{-1} for CT-I and 505 cm^{-1} for CT-II. Considering the width of the bands at 298°K, the shift in CT-I is not detectable. Evidently the small transition dipole of 0.35 Å is too small to afford any large interaction. However, the larger transition dipole of 0.84 Å of CT-II yields a shift of 505 cm^{-1} from the free molecule value of approximately 23.1 kK. (Uncertainly is large in both the energy and intensity of CT-II in the free complex because of the band overlap with the intense TCNQ molecular transition.) Since the band is observed at 22.5 kK in the crystal, there is evidently some validity to the exciton argument. The spectra have been taken to 5 kK with no evidence of a lower energy band.

The question of exciton interactions in CT crystals has been addressed by Suzuki and I'Haya. These workers note, as have others,[30] that the calculated excitation energy to a CT state for a crystal diverges due to the overlap between the ground and excited states in these systems. This problem is met by the construction of so-called intermolecular orbitals (IMO). Since a CT transition may arise from a transition from a donor to either adjacent acceptor molecule in the stack, Suzuki and I'Haya have constructed molecular orbitals over this "triad" or the equivalent triad (D–A–D).

These orbitals are obtained by constructing intermolecular density matrices of D, A, and the intermolecular D–A combinations in the triad. These matrices are formed from the set of Pariser–Parr–Pople orbitals for the constituent molecules in the complex. IMO's are obtained by an iterative procedure until two sets of IMO's are obtained for triads A–D–A and D–A–D.

The IMO's are used to construct wave functions which represent exciton configurations. The excitonic wave functions are used with the crystal hamiltonian to obtain the eigenvalue spectrum and interaction energies. Detailed development of these arguments may be found in the original papers.

Calculations for the polarization and energies of the two CT transitions in TCNQ–A are given in these papers. The lowest energy transition is calculated to occur at 11.04 kK with a polarization parallel to the b axis (y molecular axis) but with an oscillator strength of zero. The next higher transition is predicted to occur at 18.11 kK with an oscillator strength of 1.0 and a polarization in the ac plane but lying almost completely along the a axis. These predictions are in complete disagreement with the experimental spectra. The authors cite possible librational interactions which could affect the polarization of the crystal transitions.

Indeed, the concept of interactions of donors with each other through the orbitals of the adjacent acceptors (and vice versa) is valid. However, the formulation of the theory which may account for this does not appear to be successfully based on triads in the stack of EDA complexes in the crystal. It is clear also that the straightforward exciton calculation discussed above does yield reasonable agreement for the CT-I and CT-II transitions found in the crystal.

Further discussion of the exciton interactions between the intramolecular states will be given in another paper.

The TCNQ–A orbital assignments approximate an energetic situation recently discussed by Merrifield.[31] It is argued that in an EDA crystal wherein states of zero and unit charge transfer are close in energy that the degree of charge transfer will be dictated by the energy required for the transfer of the electron between the donor and acceptor and the ensuing change in lattice energy. Were such a CT transition thermally allowed, the crystal would be expected to go from a state of low conductivity to one of higher conductivity.

Although the $Tb_{2g} \leftarrow Ab_{3g}$ transition in TCNQ–A is optically forbidden, it is thermally allowed. However, the gap of approximately 0.4 eV does allow some thermal population of Tb_{2g} ($n_T/n_A \sim 2 \times 10^{-7}$). However, at 250 °C, near the melting point of the complex, the population ratio is 1×10^{-4}. At such a population level optical transitions from the Tb_{2g} to higher unoccupied orbitals of the complex should be observable. However, the conductivity of the crystal should also be observed to significantly increase according to the Merrifield model. Thermomodulation experiments may be expected to be useful in establishing this effect. Thus, the possibly unique electronic structure of the TCNQ–A crystal may afford a model system useful to the understanding of the metal–insulator transitions in organic EDA solids.

C. **Effects of Disorder.** It has already been noted that the crystal is considered to be disordered.[11] If extreme, this could have significant effect upon the spectroscopic assignments. The most likely disorder, namely that of the anthracene or TCNQ molecules being somewhat rotated about the stacking axis, would not destroy the C_s symmetry. Thus, the assignments made above would still be valid. In fact, the spectra do indicate this disorder for the anthracene molecules since the *b*-axis spectra clearly show a slight amount of the structure characteristic of the anthracene first singlet transition. However, some discrepancies exist in optical crystallographic studies of these crystals as well as in the correlation of the intensities of some of the molecular transitions. This could indicate that the unit cell parameters and possibly the space group may be incorrect. Of course, it is also possible that the complex may crystallize with different crystal morphologies but we have not found such exceptions.

IV. Conclusion

The TCNQ–A crystalline EDA complex affords a system which allows an examination of the correlation of orbital symmetries of the constituent molecules to the symmetry of the complex and finally to the factor group of the crystal. Comparison is made to earlier predictions for this complex and for polarizations of CT transitions observed in the TNB–anthracene crystalline EDA complex. In opposition to these, the polarization of the second CT transition in TCNQ–A is found to originate from the penultimately filled MO of anthracene to the lowest unfilled MO of the TCNQ.

In contrast to the crystal spectra of other crystalline EDA complexes wherein the CT transition dipoles are also aligned in a head-to-tail arrangement, the CT transition in TCNQ–A shows no strong bathochromic shift over the value observed in solution. This is attributed to the very weak interaction which would arise from the small CT transition dipole found for the complex in solution. The assignments made are consistent with the orbital symmetries determined by calculation for the two lowest unoccupied orbitals of TCNQ and the two highest filled orbitals of anthracene.

Further comparison of the experimental data with exciton theory for CT crystals is made. There is no agreement of the observations with the specific predictions made for the TCNQ–A. However, the spectra related to the molecular transitions do show some influence of the crystal. The detailed analysis of the molecular transitions will be treated elsewhere. Further work at 4 K is also underway.

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