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The phosphorescence blue shift of anthracene in a charge transfer configuration: A consequence of the donor acceptor overlap in anthracene-PMDA crystals

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A 500 cm^{-1} blue shift of the phosphorescence origin of anthracene in anthracene-PMDA single crystals has been measured. Calculations based on a perturbation theory approach show that the symmetry of the highest occupied and lowest unoccupied orbitals of the anthracene and PMDA molecule, together with the specific geometry of a charge transfer complex, are responsible for the observed shift. The simple model yields the surprising result that the energy of the excited triplet state is less affected by the interaction with a charge transfer state than the energy of the ground state.

I. INTRODUCTION

The anthracene molecule has a low ionization potential of about 7.5 eV. It forms charge transfer (CT) complexes with most common acceptor molecules like TNB (trinitrobenzene),¹ TCNB (tetracyanobenzene),² PMDA (pyromellitic-acid-dianhydride),³ and others. The lowest singlet state of the complexes can be described with Mulliken's valence-bond theory.⁴ The wavefunction is, according to Mulliken, given by

$$\psi_{\text{CT}} = c_1 \psi_{AD} + c_2 \psi_{A^+D^-} \quad (1.1)$$

The above description assumes an idealized "no bond" wavefunction ψ_{AD} and a totally ionic "dative" wavefunction $\psi_{A^+D^-}$. The wavefunctions are not orthogonal and have a finite overlap integral S_0 .

For typical singlet CT states like those mentioned above, there is plenty of evidence that the excited state is mostly ionic, i. e., $c_2 \geq c_1$. In the case of the lowest triplet level of a CT complex, the situation is more complicated. One has to distinguish between two classes of complexes. In the first class the lowest triplet state has an appreciable degree of ionicity (or charge transfer). This class is characterized by broad and structureless CT-phosphorescence spectra.⁵ Generally, c_1 and c_2 range in the same order of magnitude.⁶ In the second class, the lowest triplet state is a "localized" triplet state of the donor (or acceptor) molecule. In this case the optical and EPR spectra are characteristic for the donor (or acceptor) molecule and therefore the coefficient c_2 is very small such that c_2^2 is on the order of 10% or less. It has been shown recently that a variation of the donor molecules from anthracene to pyrene and phenanthrene with a given acceptor, namely, TCNB, leads from the situation of a localized triplet state to the situation of a CT triplet state.^{7,8}

Anthracene belongs to the second class of triplet states in all CT combinations which have been published so far. Its lowest triplet state is only slightly perturbed by a CT interaction. There is, however, one strange aspect of this CT interaction which does not offer a straightforward explanation. It is a blue shift of the electronic origin of the phosphorescence. This blue shift has been observed in the systems anthracene-TNB,² anthracene-PMDA,³ and anthracene-TCNB.⁷ Simple arguments, based on perturbation theory, would

predict a red shift of the phosphorescence, as has been pointed out by McGlynn and co-workers. The objective of this paper is to show that it is the specific geometry of a CT complex which gives rise to the observed blue shift. A calculation of the molecular overlap between anthracene and PMDA in the geometry of the CT crystal is consistent with the measured blue shift of the phosphorescence origin.

Figure 1 shows the lowest levels of a CT system in the singlet and triplet manifold. It contains the unperturbed ground state E_{AD} , the unperturbed "ionic" states $E_{3A^+D^-}$ and $E_{1A^+D^-}$ and the unperturbed localized triplet state E_{3L} . If one allows a mixing of the wavefunctions which belong to the different levels, the $AD-{}^1A^+D^-$ splitting will increase by the amount $\approx 2\Delta_S$ (neglecting the effect of higher singlet states), and the ${}^3L-{}^3A^+D^-$ splitting will increase by the amount $\approx 2\Delta_T$. If Δ_S is larger than Δ_T , one expects a blue shift of the phosphorescence; if Δ_S is smaller than Δ_T , one expects a red shift. Since the singlet-singlet energy denominator is much larger than the triplet-triplet energy gap, one would generally expect a red shift of the phosphorescence. The calculation in Sec. III will show that the difference between the

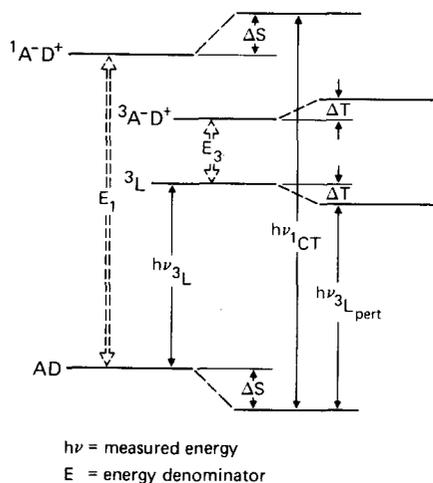


FIG. 1. Diagram of the unperturbed and perturbed singlet and triplet energy levels of a CT complex. The dotted arrows indicate the energy splittings between the unperturbed states; the full arrows indicate transition energies which can be observed by optical spectroscopy.

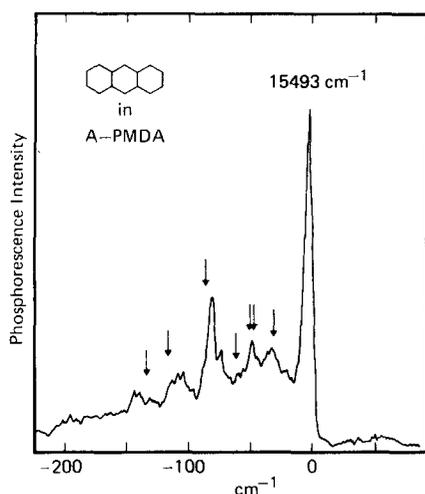


FIG. 2. Origin of the anthracene phosphorescence in an anthracene-PMDA single crystal at 2°K. The arrows correspond to the measured Raman frequencies (see text).

matrix elements in the singlet and in the triplet manifold is rather large. This difference will more than offset the difference in energy denominators and thus predict a blue shift of the phosphorescence. It is interesting to note that the difference of the calculated matrix elements is due to the geometry of the CT complex and to the symmetry of the excited state wavefunctions. The overlap calculations are not only in agreement with the phosphorescence data, they also agree very well with recent EPR data on the "ionicity" of the triplet wavefunction.

II. EXPERIMENTAL

The anthracene and the PMDA material have been zone refined as described earlier³; the crystals have been grown from multiple distilled MEK.⁹

All phosphorescence experiments have been performed at 2°K. The triplet states were excited by direct excitation using the 6328 Å line of a He-Ne laser at a power level of about 50 mW. In order to suppress Raman lines which would overlap the wavelength region of the phosphorescence, a "crossed chopper" phosphoroscope was used. The phosphoroscope operated at a frequency of 90 Hz.

Figure 2 shows the origin of the anthracene phosphorescence emission of a 1:1 CT crystal of anthracene-PMDA at 2°K. The singlet-triplet transition energy is $15493 \pm 5 \text{ cm}^{-1}$. If one compares this transition energy with the energies measured for anthracene in a matrix isolated situation, one gets the following comparison. Anthracene in *n*-pentane, *n*-hexane, and *n*-heptane phosphoresces as 15051 ± 2 , 15004 ± 2 , and $14860 \pm 2 \text{ cm}^{-1}$.¹⁰ The difference between the "CT-perturbed" phosphorescence and the "matrix-isolated" phosphorescence is 440 cm^{-1} to 630 cm^{-1} . This blue shift is rather large; it is too large to be explained as "matrix shift" and will be discussed below.

The measured vibrational progression of the phosphorescence spectrum is given in Table I; it is compared with progressions which had been measured by

other authors in phosphorescence and fluorescence experiments.

The arrows on the low energy side of the phosphorescence spectrum in Fig. 2 correspond to the strongest lattice modes of the Raman spectrum of anthracene-PMDA crystals.¹² The frequencies (with the exception of one) are in rather good agreement. Therefore, one can safely assume that the measured structure on the low energy side of the 0-0 phosphorescence transition is due to phonon sidebands. (Note that phonon dispersion can be responsible for small differences between the Raman modes and the phonon sidebands.)

III. THEORETICAL

In this section, the energy lowering Δ_T and Δ_S (see Fig. 1) will be estimated in order to determine whether the observed blue shift in the phosphorescence is consistent with the other observations on this system.

To begin with, the unperturbed energies of the states in the system must be estimated. Taking the unperturbed ground state energy E_{AD} to be zero, the triplet state energy ($h\nu_{3L}$) will be approximately 15000 cm^{-1} above this. The charge transfer energies are difficult to estimate; however, as a first approximation, the singlet charge transfer state (${}^1A^*D^*$) will be approximately 18000 cm^{-1} above ground and the triplet CT state will be close to this, say at 17500 cm^{-1} (putting it below the singlet makes the triplet CT- 3L interaction larger than it would be if the order were reversed). If the matrix element of the Hamiltonian between these two states is labeled V_3 and that between the singlet CT state and the ground state is labeled V_1 , then the energy lowerings, Δ_T and Δ_S , can be found by perturbation theory:

$$\Delta_T = \frac{V_3^2}{E({}^3A^*D^*) - E({}^3L)} \cong \frac{V_3^2}{2500} \text{ cm}^{-1}, \quad (2.1)$$

$$\Delta_S = \frac{V_1^2}{E({}^1A^*D^*) - E(AD)} \cong \frac{V_1^2}{18000} \text{ cm}^{-1}. \quad (2.2)$$

Thus, in order for a blue shift to be observed in the phosphorescence, $(V_1)^2/(V_3)^2$ must be larger than 7, or $(V_1/V_3) > 2.5$.

This ratio may be estimated from the EPR data¹³; it is found that the triplet state has approximately 5% charge transfer character. From perturbation theory,

$$C_{CT} = \frac{V_3}{2500} \cong 0.2-0.3, \quad (2.3)$$

TABLE I. Measured vibrational progression of the phosphorescence spectrum.

(cm^{-1}) ^a	(cm^{-1}) ^b	(cm^{-1}) ^c
396	396	394
1168	1166	1161
1261	1269	1262
1402	1410	1405
1557	1567	1558

^aOwn data.

^bAnthracene in *n*-heptane.¹⁰

^cAnthracene crystal fluorescence at 4.2°K.¹¹

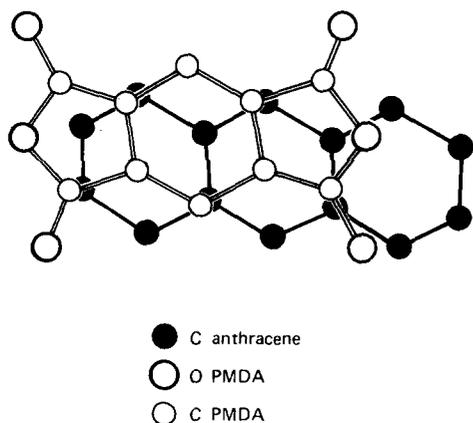


FIG. 3. Projection of the PMDA molecule onto the molecular plane of anthracene according to Ref. 14.

or

$$V_3 \approx 500-700 \text{ cm}^{-1}. \quad (2.4)$$

Combining Eq. (2.4) with the estimate of V_1/V_3 given above, it is found that V_1 must be larger than $\sim 1500 \text{ cm}^{-1}$; therefore, the coefficient of the CT state in the true ground state will be larger than 0.1. This is certainly consistent with the observed ground state properties which indicate a charge transfer character of about 5% in the ground state as well.

Thus, these *qualitative* estimates show that the EPR data, the phosphorescence data, and the ground state properties are all consistent with a rather small matrix element between the localized triplet state and the triplet charge transfer state. The question then arises as to the reason why this matrix element is small. We propose that this is due to the extremely weak overlap between these two states in the crystal; we will show that the ratio of overlap between the ground state and the singlet CT state, S_1 , to the overlap between the triplet state and the triplet CT, S_3 , is about 12.

The crystal structure is known approximately from the work of Herbstein.¹⁴ A more accurate structure has been determined recently.¹⁵ A glance at Fig. 3 shows that the long axis of the anthracene molecule and the long axis of the PMDA molecule are almost parallel and that the plane containing both is almost perpendicular to the planes of both molecules. This means that the symmetry plane containing the long axes of the molecules and which is perpendicular to the molecular planes is almost preserved in going from the free molecules to the crystal. If it were exactly preserved, then the overlap between the anthracene triplet and the charge transfer triplet would be zero because the lowest unoccupied orbital (LUMO) of anthracene and the LUMO of PMDA have opposite symmetries with respect to reflection in that plane. In addition, the highest occupied orbital (HOMO) of anthracene has the same symmetry properties under reflection as the LUMO of PMDA, thus the ground state singlet CT state overlap is nonzero. In this simple argument, it has been assumed that the charge transfer state is formed simply by removing an electron from the HOMO of anthracene and placing it in the LUMO of PMDA, while the triplet state of anthracene

is formed by taking the electron out of the HOMO of anthracene and placing it in the LUMO of anthracene. This is, of course, a gross simplification⁴; however, we believe that this is warranted for the simple qualitative explanation we are offering. A more complete theory would require substantially more effort and, we believe, would be no more conclusive.

In order to see whether the above argument has merit, the overlaps discussed above have been computed using the structural data,¹⁵ the molecular orbital coefficients of Ref. 16 for PMDA, Hückel coefficients for anthracene, and assuming that only the $2p_x$ orbitals are important in forming the molecular orbitals. Double zeta atomic functions were used¹⁷ for both carbon and oxygen. We find

$$\frac{\langle \text{anthracene(HOMO)} | \text{PMDA(LUMO)} \rangle}{\langle \text{anthracene(LUMO)} | \text{PMDA(LUMO)} \rangle} \approx 12,$$

showing that the symmetry plane, while not preserved exactly, is preserved enough to give merit to the above argument.

If it is now assumed that V_1/V_3 is proportional to the ratio of the overlaps, as is usually done in discussing charge transfer interactions, then all the experimental and theoretical data are in agreement. We emphasize that we are *not* interested in an exact quantitative fit between theory and experiment (although this is possible within this model),¹⁸ but merely a qualitative fit. A more realistic model would include the effect of higher charge transfer states on both the singlet and triplet manifolds.¹⁹ The effect of these would be to depress the energies of both the lowest triplet and the ground state.

IV. CONCLUSIONS

The observed blue shift of the phosphorescence of anthracene in the anthracene-PMDA crystal can be qualitatively understood on the basis of a small interaction between the triplet and a low lying triplet CT state. We have proposed that the weakness of this interaction is due to the small overlap of these states and that this is due to the presence of an approximate symmetry in the crystal structure which is reflection in a plane perpendicular to the molecular planes and along the long axis of the molecules.

Another approach to the calculation of blue (and red) shifts of spectral lines is to compute the intermolecular interaction energies of the ground and excited states²⁰; the calculation outlined here is, in fact, in the same spirit. The terms we are calculating are presumably the dominant terms in the intermolecular forces in these CT crystals for both the ground and excited triplet states.

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