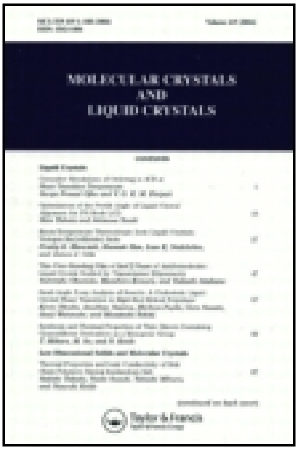

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Charge-transfer exciton state, ionic energy levels, and delayed fluorescence in anthracene

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Charge-transfer exciton state, ionic energy levels, and delayed fluorescence in anthracene

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Abstract—Our work on the delayed electroluminescence of anthracene crystal has shown that the recombination of holes and electrons produces the normal fluorescence of anthracene, and that the time dependence of the fluorescence can be modified by an external electric field. We have also shown that the recombination of holes and electrons produces what appears to be an ion-pair or charge-transfer (CT) exciton, that this CT exciton diffuses through the anthracene crystal, and can form a dimer with another CT-exciton; the decay of the dimer produces one photon, at most. The normal decay of the nearest neighbor CT exciton, and the CT-exciton dimer produces a tail that extends into the microsecond region. Some estimates are given for the lifetime of the CT exciton; ionic energy levels for anthracene crystal are also given.

We have recently been able to outline most of the energy levels in anthracene and tetracene crystal that are relevant to the discussion of electrical conductivity in these materials. These compounds have been models for the interpretation of electrical conductivity in other organic materials, and the implications of the energy level structure are rather far-reaching; we shall therefore describe how the energy levels were determined.

The fixing of the energy levels depends in large part on the location of the CT exciton relative to the ground state of the crystal. The CT exciton is defined as a crystal state in which a hole and electron on different molecules are bound together by their Coulomb force, and diffuse as a pair. We shall be concerned with the nearest neighbor CT exciton, in which the hole and electron are on adjacent sites in the crystal. This state has not been definitely observed in optical absorption spectra[1a], but has nevertheless been proposed as a state that can interact significantly with the triplet manifold of polyacene crystals[1b].

The importance of this state for electrical conductivity lies in the fact that the energy required to produce the CT exciton, E(CT) must be lese than that required to ionize a molecule completely, E_c. In the paper by Choi et al,[1] estimates are given for E(CT) for anthracene and naphthalene, but the uncertainty in the calculation makes it impossible to decide whether E(CT) is greater than or less than E_s, the energy of the first excited singlet state. Subsequent papers by Kearns[2] and Berry et al[3] suggested that $E(\mathrm{CT}) > E_s$.

In the course of our studies of external photoelectric emission in organic crystals,[4] we found that in anthracene, singlet exciton-exciton annihilation could produce electron emission if the reaction took place near the surface of the crystal. In other words, although the ionization energy of anthracene is 5.65 eV, it is possible to produce electron emission with light of much lower energy. This conclusion was based on the following evidence:

(a) The photoemission current varied as the square of the light intensity. (b) The maximum kinetic energy of the emitted electrons was constant and independent of the incident photon energy in the range $3.2 < h\nu < 4$ eV. This indicated that the interacting states were mobile, and of a fixed energy. Direct photon involvement was also ruled out by this experiment. (c) The efficiency of producing the interacting states was independent of photon energy in the above range. This means that the interacting states were produced with the same efficiency, regardless of the vibrational level to which the molecule was excited. This would be the case, for instance, if the interacting state were the lowest energy singlet excitons. (d) The maximum kinetic energy of the emitted electrons in the double-quantum process was the same as the maximum kinetic energy of electrons that were emitted when light of energy 6.3 eV was incident on the anthracene crystal. This means that the double-quantum process was delivering 6.3 eV to a single molecule in the crystal and this energy is twice that of the first excited singlet exciton, 3.15 eV. Other processes were ruled out.

The same experiment was repeated with tetracene, which has a singlet exciton at 2.4 eV and a crystal ionization energy (I_c) of 5.25 eV. Again, a double-quantum photoemission process was observed, despite the fact that the mutual annihilation of two singlet excitons could not provide enough energy to exceed I_c. The following results were observed:

(a) The photoemission varied as the square of the light intensity.

(b) The maximum kinetic energy of the emitted electrons was constant and independent of the incident photon energy in the range $3.4 < h\nu < 5$ eV. This indicated, as in the case of anthracene, that the interacting states were mobile and of fixed energy.

(c) The maximum kinetic energy of the emitted electrons in the double-quantum process indicated that 5.8 eV was being delivered to the ionizing molecule. It was shown that the two interacting states were identical. This meant that each interacting state had an energy of 2.9 eV. There is no absorption peak in tetracene at this energy.

(d) The 2.9 eV state could not be excited by using incident light of energy 2.9 eV. It was necessary to use light of energy greater than 3.4 eV, and the efficiency of producing this state increased with increasing light energy, peaking at 3.7 eV.

(e) The photoconductivity of tetracene crystal showed bulk-generation of carriers[6] starting at 3 eV and peaking at 3.7 eV. The efficiency of producing the 2.9 eV state in tetracene was parallel to the efficiency of bulk-generation of carriers.

(f) An approximate calculation can be made for the energy of the CT exciton in tetracene, using the expression

$$E(\mathrm{CT}) = I_g - A_g - C - P(\mathrm{CT}) \qquad (1)$$

where I_g, A_g, C and $P(\mathrm{CT})$ are respectively the ionization energy and electron affinity of the gas, C is the Coulomb energy of the ion-pair and $P(\mathrm{CT})$ is the polarization energy of the ion-pair in the crystal. Using the known and calculated values for the parameters in (1), one gets[5] $E(\mathrm{CT}) = 2.9$ eV.

For the above reasons, we conclude that the mobile state in tetracene, lying at 2.9 eV, is a CT exciton state and most efficiently generated as a result of the recombination of free holes and electrons. At 3.6 eV, one would expect a free-electron, broad-band conductivity level (E_c) to set in, using the expression given by Lyons[7]

$$E_c = 2I_c - I_g \qquad (2)$$

where $I_c = 5.25$ eV and $I_g = 6.9$ eV. We therefore attribute the increase in the efficiency of generating the CT state in tetracene beyond 3.4 eV to the increased efficiency of exciting free-electron states in the solid.

The peak at 3.7 eV, both in the photoconductivity efficiency and CT exciton generating efficiency, is not due to the excitation of any new and distinct ionic state. It marks the beginning of an energy region in which the efficiency of charge generation changes either because the $'B_b$ state is excited in this region or, as suggested by Silver,[8] the extinction coefficient for tetracene starts rising in this region after having been relatively low at longer wavelengths. According to Silver, there is a competition between excitation to a free-electron state, and to a neutral exciton state; therefore, as the extinction coefficient increases, the efficiency of the band-to-band transition should decrease.

Having found what appears to be a CT exciton state in tetracene, we returned to anthracene and found that by using an incident light of energy $4 < 4h\nu < 5$ eV, we observed the following:[9]

(a) The external photoelectric emission varied as the square of the incident light intensity.

(b) The maximum kinetic energy of the emitted electrons was constant and independent of the incident light energy in the range $4 < h\nu < 5$ eV.

(c) The maximum kinetic energy of the emitted electrons in the double-quantum process was the same as if the energy delivered to the molecule was 6.9 eV. Assuming two interacting states of equal energy, each mobile state would have an energy of 3.45 eV.

(d) Although the use of equation (1) is subject to uncertainty in the choice of the correct absolute values for A_g, C, and P, there is far less uncertainty in the quantity $[E(\mathrm{CT})\,(A) - E(\mathrm{CT})\,(T)]$, where the letters (A) and (T) stand for anthracene and tetracene respectively; thus, by using the data in references 1 and 3, we get

$$A_g(A) - A_g(T) \sim 0.3 \text{ eV}, \qquad C(T) - C(T) \sim 0.1 \text{ eV},$$
$$P(\mathrm{CT})\,(A) - P(\mathrm{CT})\,(T) \sim 0.1 \text{ eV},$$

and $I_g(A) - I_g(T) = 0.5$ eV. This yields for $\Delta E(\mathrm{CT})$ the quantity 0.6 eV. Since $E(\mathrm{CT})\,(T) = 2.9$ eV, $E(\mathrm{CT})\,(A) \sim 3.5$ eV. This is very close to our measured value of 3.45 eV, and also quite close to the mean value calculated by Choi *et al.*[1]

(e) The 3.45 eV state in anthracene is not characterized in any unique fashion in the optical absorption spectrum, is above that of the second triplet state ($\sim$3.25 eV), and cannot be generated efficiently by using exciting light of energy 3.45 eV. The efficiency of generating this state increases with light energy beyond 4 eV, and peaks at 4.4 eV. As in the case with tetracene, the use of equation (2) yields the value for E_c, which is about 4 eV. We therefore attribute the increase in the efficiency of generating the 3.45 eV state to the onset of free electron production.

(f) The efficiency of bulk-generation of carriers in anthracene has been measured by photoconductive techniques,[10] and the bulk-generation starts at about 4 eV and peaks at 4.4 eV; the efficiency of generating the 3.45 eV state parallels the efficiency of bulk-carrier generation.

For the above reasons we assign the value $E(\text{CT}) = 3.45$ eV for anthracene. The peak described in (f) above does not, in our opinion, mark the onset of any special ionic state, for the same reasons given previously.

In the case of tetracene, the bulk conductivity starts at 3 eV, which is 0.1 eV beyond $E(\text{CT})$ (T). One would expect a small energy of activation to dissociate the CT exciton, and the energy of activation of bulk photoconductivity is about 0.1 eV.[10] We therefore assign the value 3 eV to E_c, the least energy required to produce free carriers inside tetracene; this is therefore the band gap for conductivity in tetracene. In the case of anthracene, the addition of the energy of activation of photoconductivity to $E(\text{CT})$ yields about 3.6 eV for E_c. However, the mutual annihilation of two triplet excitons which yields 3.6 eV in anthracene does not produce any significant bulk-carrier generation.[11] Although it is to be expected that excitation to the lowest conduction band would be an inefficient way to generate free carriers, because of the short mean-free-path[12] and high electron-hole capture cross-section,[13] we place E_c at 3.7 eV.

This completes the assignment of the ionic energy levels which are summarized[5,9] in Table 1. The band gaps in these compounds are so wide that intrinsic carrier generation in the dark at room temperature could never supply sufficient carriers to produce the observed dark

TABLE 1 Energy Levels in Anthracene and Tetracene

	Anthracene	*Tetracene*
Ionization energy of molecule (I_g)	7.4 eV	6.9 eV
Ionization energy of crystal (I_c)	5.65	5.25
Broad-band upper conductivity level (E_c)	4	3.5
Narrow band lower conductivity level ($E_{c'}$)	(3.7)*	3.0
Charge transfer exciton $E(\text{CT})$	3.45	2.9
Ist excited singlet state E_s	3.15	2.4
Ist excited triplet state E_t	1.8	1.4

* estimated

currents. Thus, the dark conductivity in these compounds is produced by thermionic emission from the electrodes (injection of carriers) as was proposed years ago[14] and verified more recently.[15]

As has been shown, the CT exciton is generated most efficiently by the recombination of free holes and electrons. Thus, there should be a considerable CT exciton density in the track of an α-particle passing through anthracene. In our original paper,[9] we interpreted the results of Schmillen[16] and Gibbons et al[17] on the analysis of the delayed fluorescence of anthracene produced by α-particle bombardment as providing evidence that the lifetime of the CT exciton was about 10^{-7} sec. In addition, our work on delayed electroluminescence (*EL*)[18] showed that the recombination of holes and electrons produced the normal fluorescent light. (This was the first piece of conclusive evidence that $E_c > E_s$.) Since the recombination of holes and electrons produces CT excitons, it should be possible to get an estimate of the CT exciton lifetime by examining the decay time of the *field-dependent* delayed *EL*. This was less than 10^{-6} sec, so the estimate of a CT lifetime of 10^{-7} sec is not too far off. We do not have any estimate as yet of the diffusion length of the CT exciton.

We also proposed that delayed scintillation fluorescence could be caused by CT exciton-exciton annihilation. More recent work by King and Voltz[18], however, shows that the delayed fluorescence can be quite convincingly explained by triplet-triplet annihilation. However, in view of the short lifetime of the CT exciton relative to the triplet exciton, the CT exciton is probably a kinetic intermediate to the triplet state and, in fact, King and Voltz proposed that the triplets were formed by the recombination of holes and electrons. It is, however, probable that the CT exciton makes a small contribution to the delayed fluorescence. It is interesting to note that not all delayed fluorescence in anthracene can be explained by triplet-triplet annihilation. Moore and Munroe[20] show that some of the delayed fluorescence seems to come from a singlet trapping state. They suggest that perhaps the decay of an excimer state can be the case for the observed phenomena. The CT exciton can also be a kinetic intermediate to the excimer state.

CT exciton-exciton annihilation is quite efficient, as is shown by our photoemission experiments[9] and the bi-molecular recombination coefficient is at least 10^{-10} cm^3/sec. This annihilation process provides a convenient explanation for the ionization-quenching of the fluorescence in scintillators. Thus, as a result of the annihilation process, one CT exciton disappears, its energy going into the ionization of the other CT exciton, which re-forms. In addition, the CT exciton can also decay via the triplet state, which is radiationless. Furthermore, it is also possible to form a multiple CT exciton complex in the dense ionization channel in which more than one CT exciton can dissipate its energy.

Summarizing it has been shown that there is experimental evidence for the existence of mobile, long-lived CT exciton states. These states have been found in anthracene, tetracene, perylene,[5] and chlorophyll *a*,[5] and can undoubtedly be found in a large number of compounds. The study of the efficiency of forming these CT states yields information about the energy levels that are important for understanding electrical conductivity in these materials. The CT exciton state, in itself, is an important mode of energy transfer and can explain some of the phenomena observed in scintillators. Further work is being carried out to determine the lifetime, diffusion length, velocity and dissociation energy of the CT exciton.

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