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# Charge-transfer Exciton State and Ionic Energy Levels in Anthracene Crystal

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**Abstract**—By means of external electron emission produced by double-exciton annihilation inside anthracene crystal, evidence is produced for the existence of a charge-transfer (CT) exciton in anthracene at 3.45 eV, with a lifetime conjectured to be $2 \times 10^{-7}$ sec. The efficiency of generating the CT exciton increases markedly at an incident light energy greater than 4 eV. This value is associated with that of an upper conductivity band. The lowest conductivity level in anthracene must be larger than 3.45 eV, and is estimated to lie at 3.7 eV. Delayed fluorescence produced by α-particle bombardment of anthracene is discussed in terms of CT excitons.

In a previous paper[1] experimental evidence was given for the existence of a mobile charge-transfer (CT) exciton state in tetracene at 2.9 eV. The lowest energy CT exciton consists of a nearest neighbor hole-electron pair. In addition, it was stated that there was a CT state in anthracene at 3.45 eV. In this paper we present the evidence for the existence of a mobile CT exciton in anthracene at 3.45 ± 0.05 eV, and assign values to some ionic energy levels in anthracene. We also make some conjectures about the origin of the delayed components in the fluorescence of anthracene induced by ionizing radiation.

The technique used for these measurements has already been described,[1, 2] and should be referred to for a proper understanding of the present paper. With this technique, we have measured the ionization energy of anthracene (5.65 eV),[5] tetracene (5.25 eV),[1] metal-free phthalocyanine (5.20 eV),[31] Cu phthalocyanine (5.0 eV),[31] Mg phthalocyanine (4.85 eV),[2] and perylene (5.36 eV).[5]

These values are within 0.1 eV of the average of the best measurements made on the same compounds by different investigators, using traditional techniques.[15]

Briefly, it has been found that external photoelectric emission can be produced in anthracene, tetracene, perylene, and most recently, chlorophyll *a*, by means of a double-quantum process. In the case of anthracene, two excited singlet excitons annihilate to deliver the required energy, and in the case of tetracene and perylene, the two excitons are postulated to be CT excitons. The identification of the energy states involved in the double-quantum photo-emission process depends on the measurement of the maximum kinetic energy of the ejected electrons. Knowing this energy and the ionization energy of the crystal, one can calculate the energy delivered to the electron inside the crystal by using the Einstein photoelectric equation.

$$E = I_c + \text{K.E.} \tag{1}$$

where $E$ is the energy absorbed by the electron inside the crystal, $I_c$ is the ionization energy of the crystal, and K.E. is the maximum kinetic energy of the emitted electrons. In the usual application of (1), $E$ is the energy of the incident quanta of light. In the case of double-quantum effects, $E$ is the net energy delivered to the electron by the double-quantum process, and is not simply related to the energy of the incident photons because there is a strong likelihood that the energy of the incident photon will be degraded somewhat before it becomes involved with another energy state. However, since K.E. and $I_c$ in (1) can be measured, it is possible to calculate $E_e$, which is defined as the energy of a single absorbed quantum that will eject an electron from the crystal with the same kinetic energy as that produced by the utilization of two interacting energy states in the crystal. The reason $E_e$ is defined in this way is that in our experiment, $E_e$ is in effect determined by finding the energy of a single quantum that will eject an electron from the crystal with the same energy as that produced by the double-quantum process. After finding $E_e$, then one has the problem of showing that the two states involved have equal energy, namely

$1/2\ E_e$. This energy, $1/2\ E_e$ is then the energy of the interacting states, and one can proceed to further identify this state. It should be emphasized that the value obtained for $E_e$ is independent of any band distortion at the surface of the crystal, and is independent of whether the value chosen for $I_c$ in (1) is correct. This is because the technique used to determine $E_e$ is a substitution method.

In the earlier paper dealing with tetracene,[1] we showed that there was a double-quantum external photoelectric effect. Singlet exciton–exciton interactions were ruled out on energetic grounds. The exciton that was involved had a fixed energy $E$(CT), independent of the energy of the exciting light, and was generated efficiently only if the exciting light energy was greater than $E$(CT). The efficiency of generating the exciton had the same energy dependence as the bulk photo ionization efficiency as determined by photoconductivity (to be published.[30]) In other words, as electrons and holes were generated efficiently in the bulk, precisely so was the $E$(CT) state generated efficiently. On this basis, the exciton state responsible for the electron emission in tetracene was identified as a CT exciton, and the process that generated this state efficiently was judged to be the recombination of holes and electrons. As will be shown later the same parallelism exists between the efficiency of bulk photogeneration of holes and electrons in anthracene[8] and the efficiency of forming the CT exciton.

## Experimental Technique

Zone-refined anthracene was powdered in the dark under argon for use in the Millikan apparatus, and the electron emission measurements were made in an argon atmosphere at a pressure of 1 atmosphere. The experiment was carried out in two successive steps on the *same* crystal, both steps being identical to that used to determine $E_e$ for the double-quantum process in the case of tetracene.[1] In the case of anthracene, two distinct values were found for $E_e$, depending on the energy of the incident light (called double-quantum light). Using monochromatic light of energy $3.1 < h\nu < 4$ eV, $E_e = 6.3$ eV regardless of the photon energy. This energy is produced by the mutual annihilation of two singlet excitons, each of energy 3.15 eV.[3] $E_e$ is constant because the photon energy is quickly degraded to that of the lowest excited singlet state. Since the ionization energy of the crystal is 5.65 eV[4, 5] this singlet exciton-exciton annihilation process causes external electron emission. Using polychromatic light of energy $4 < h\nu < 5$ eV on the *same* crystal that had been exposed to the lower energy light, additional electron emission was observed; this emission varied as the square of the light intensity and was caused by the interaction of two states yielding a total energy $E_e' = 6.95 \pm 0.05$ eV. This result was also obtained on three different crystals. Using monochromatic light, it was shown that $E_e'$ was independent of photon energy in the range $4 < h\nu < 5$ eV. These states are observed efficiently only if the energy of the incident light is greater than 4 eV. As was shown in the case of tetracene,[1] only exciton–exciton interactions can explain the square dependence on light intensity of the photoemission, and the constancy of $E_e'$ with changing wavelength. Having established the fact that a double-exciton interaction is involved in the generation of $E_e'$, one is faced with several possible exciton–exciton mechanisms. Thus, it is possible to have CT–CT, or CT-neutral exciton annihilation, the neutral exciton including the singlet, or higher triplet states. The higher triplet state is ruled out for two reasons: the efficiency of generating a triplet state is poor and the lifetime of an upper electronic state is generally short, of the order of $10^{-10}$ sec or less. There is, however, a possibility that the CT–CT impact produces a transitory complex that, without exception, decays to a lower energy state before the annihilation occurs. Thus, the CT–CT complex could decay to a CT–S complex, where S is the neutral exciton; this implies that the energy liberated by the decay is not sufficient to dissociate the CT exciton, because the dissociated CT exciton would be incapable of receiving the energy liberated by the subsequent decay of the S exciton, and hence, no external electon emission would be observed. In the case of tetracene,[30] bulk generation of holes and electrons commences at 3 eV, indicating that $E$(CT) is less than 3 eV. This agrees with the value of

2.9 eV given in our previous paper,[1] and substantiates our conclusion that a CT–CT annihilation can take place in tetracene.

The singlet exciton–CT annihilation cannot be ruled out, but we would not see this process unless the CT–CT annihilation is impossible. This is because our technique measures the process that yields the *greatest* energy. Since the CT–CT interaction occurs in tetracene and perylene (where singlet exciton involvement has been ruled out) we postulate that the CT–CT annihilation is quite general, and that it occurs in anthracene. We thus conclude that $E_e'$ represents the mutual annihilation of two energy states, of energy 3.45 ± 0.05 eV.

The CT exciton is formed by the pairing of a free hole and electron generated in the bulk by light of energy $>4$ eV and represents the energy of the nearest neighbor ion-pair. We shall show later that the recombination coefficient for two CT excitons should be larger than that for two neutral excitons. An approximate value for $E$(CT) was calculated by Choi *et al.*,[6] who obtained 3.4 ± 0.5 eV.

### *Interpretation of Photoemission Peak near* 4.4 *eV*

We have determined an energy region in which the efficiency of CT exciton generation is a maximum. This is shown in Table 1 and in Fig. 1, where the photoemission current density is normalized with respect to $(I\epsilon)^2$. $I$ is the light intensity at a given wavelength and $\epsilon$ is the extinction coefficient at that wavelength. The curve in Fig. 1 was obtained on the same particle, by measuring the emission current $J$ as a function of the incident light energy $E$, going from the low energy region, to the high energy region, back down in reverse to the low energy region, up again, and down again. An arithmetic average was taken of the $J$ values at each $E$, the deviation being less than 30 %. The determination of $J$ is subject to error because of particle drift. (Particle drift has practically no effect on the determination of $E_e$, which is not a kinetic property.) The same process was repeated for three other crystals, with the exception that the run was made in one direction only. The general shape of the curves was the same, peaking in the region between

4.2 and 4.5 eV, but the magnitudes were different, being within a factor of about 2 of the results shown in Fig. 1.

The values for $\epsilon$ were taken from Bree and Lyons,[7] there being some uncertainty in the $\epsilon$ values between 4.2 and 4.5 eV. At this point, a comment must be made about the proper value to take for $\epsilon$. In some cases, $\epsilon$ will depend strongly on the direction of polarization of the incident light. In our case, we used unpolarized light, and since we were concerned only with the amount of light absorbed within 100 Å of the surface of the crystal, we took an arithmetic average of the values of $\epsilon$ given for each polarization at the incident light wavelength. This is equivalent to assuming that the incident light intensity can be divided into two portions of equal intensity in each direction of polarization.

TABLE 1 Wavelength Dependence of Double-Quantum Photoelectric Emission in Anthracene

| Exciting light wavelength (Å) | Relative light intensity $(I_0)^a$ | Relative extinction coeff. $(\epsilon)^a$ | $(I_0\,\epsilon)^{2\,a}$ | Relative emission rate $(J)^a$ | $\dfrac{J}{(I_0\,\epsilon)^{2\,a}}$ |
|---|---|---|---|---|---|
| 3130 (3.98 eV) | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| 2980 (4.18) | 0.43 | 0.7 | 0.09 | 1.6 | 17 |
| 2900 (4.29) | 0.18 | 0.4 | 0.005 | 0.9 | 170 |
| 2800 (4.45) | 0.20 | 0.6 | 0.014 | 1.7 | 120 |
| 2650 (4.72) | 0.07 | 3.6 | 0.06 | 0.4 | 6 |
| 2550 (4.88) | 0.06 | 3.4 | 0.04 | 3.4 | 90[b] |
| 2480 (5.03) | 0.12 | 3.6 | 0.19 | 22.2 | 120[b] |

[a] Normalized to 3130 Å. Arithmetic average of $\epsilon_a$ and $\epsilon_b$ taken from Bree and Lyons.[7]

[b] Linear with light intensity and is therefore not a double-exciton process.

In the previous paper dealing with the CT exciton in tetracene,[1] the $\epsilon$ data were taken from Perkampus.[24] In the addendum to that paper,[1] we made a statement to the effect that the proper way to calculate the effective $\epsilon$ is to take the average of the squares of $\epsilon$ in each polarization direction. This *statement* is incorrect, but the value *used* for $\epsilon$ in the addendum was the *correct* arithmetic average. Furthermore, we stated in ref. 1 that one should observe a plateau in the plot of the efficiency of CT exciton generation as a function of the energy of the exciting light. There are several theoretical reasons why this need not be so, and in fact, the tetracene data show a peak at 3.7 eV, and not a plateau.

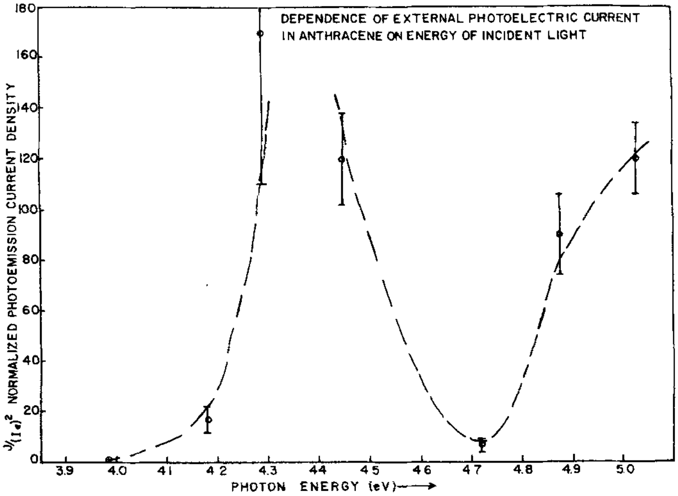

Figure 1.

As in the case with tetracene,[1] anthracene also shows a peak in its photoemission, and in the case of anthracene, this peak appears between 4.3 and 4.43 eV. There is also a peak in the photoconductivity of anthracene near 4.4 eV which has been associated with an energy gap for bulk generation of carriers.[8] The appearance of the peak in the photoconductivity[8] and the peak in the photoemission at about 4.4 eV could mark the onset of a conductivity state, and for reasons to be given elsewhere in this paper, we believe that this would be an upper conductivity state. It is also possible that the peaks are produced by the onset of a new competing optical transition that reduces the efficiency of producing carriers. Such a transition is the ${}^1B_b$ transition, which is observed at 4.60 eV in anthracene,[25] and which may begin at 4.4 eV. This transition has been analyzed by Ham and Rudenberg[26] who describe it in terms of a configuration interaction of two states of nearly equal energy. One state involves a transition from the highest filled $\pi$ orbital to the second vacant excited $\pi$ orbital ($S_0 \rightarrow S_2$). The other state involves a transition from the penultimate filled $\pi$ orbital to the first vacant excited $\pi$ orbital ($S_{-1} \rightarrow S_1$). Since the latter configuration involves an $S_1$ level, which is a poorer level for carrier production, this may be a reason for the decreased ionization efficiency. In our tetracene study[1] we noted a peak in the external electron emission efficiency at 3.7 eV. In tetracene, there is also a ${}^1B_b$ transition that starts near 3.7 eV, and this transition seems to decrease the ionization efficiency in tetracene also. We will discuss these transitions in a forthcoming paper.

This brings us to an examination of our results. As is seen in Fig. 1, there is a peak near 4.4 eV similar to that observed by Castro and Hornig.[8] In view of the existence of the ${}^1B_b$ transition in anthracene close to 4.4 eV, the peak in the photoconductivity curve observed by Castro and Hornig[8] and the peak in our curve cannot be attributed to the lower edge of a broad upper conductivity band. That there is an upper conductivity band at all is supported by our observation that electroluminescence can occur in anthracene as a result of impact ionization produced by accelerated electrons.[9] These electrons could not have been accelerated in a narrow band, and the normal conductivity level in anthracene has been shown to be a narrow band.[10] In view of the fact that the bulk photoconductivity observed by Castro and Hornig[8] starts sharply near 4 eV, and the efficiency of producing CT excitons in anthracene rises sharply beyond 4 eV, we would place the lower edge of the broad continuum at 4 eV.

Our reasons for believing that the 4 eV value refers to $E_c$ rather than $E_c'$ are based on the following: The energy of the CT state relative to the ground state of the crystal can be approximated by the expression[6]

$$E(\mathrm{CT}) = I_g - A_g - C - P(\mathrm{CT}) \tag{2}$$

where $I_g$, $A_g$, $C$ and $P(\mathrm{CT})$ are respectively the ionization energy of the free molecule in the gas, the electron affinity of the molecule in the gas, the Coulomb energy of the interaction of the ion-pair, and $P$ is the lattice polarization energy due to the ion-pair. A similar expression exists for the energy of the lowest conduction state, and is given by[4]

$$E_{c'} = I_g - A_g - (P_e + P_h) \tag{3}$$

where $P_e$ and $P_h$ are respectively the lattice polarization energies of the separated electron and hole. By subtracting (2) from (3) we get

$$E_{c'} - E(\mathrm{CT}) = C + P(\mathrm{CT}) - (P_e + P_h) \tag{4}$$

From Ref. (6) we take $C = 2.5$ eV, and $P = 1$ eV; these values, when combined with the values given in Ref. (6) for $I_g$ and $A_g$, yield a value for $E(\mathrm{CT})$ of 3.4 eV $\pm$ 0.5 eV, which is very close to our experimentally observed value. Since $A_g \cong 0.5$ eV in Ref. (6), the high values assumed for $A_g$ by Lyons do not seem to be justified. The problem then becomes to evaluate the expression $P_e + P_h$. One can assume that either $P_e = P_h$ or, if they are not equal that most likely $P_e < P_h$ because the electron density should be higher around a hole (positive ion) than around the negative ion. In either case, there should not be a large difference in energy between $P_e$ and $P_h$ in anthracene. According to a calculation by Lyons,[11] $2P_h \cong 3.48$ eV; the same value is obtained experimentally from the relation $I_g - I_c = P_h$. Using (4), this would put $E_{c'}$ either at or close to $E(\mathrm{CT})$. It is not likely that $E_{c'} - E(\mathrm{CT}) < 0.1$ eV because one would see a distinct increase in the negative carrier photoconductivity in this energy range (3.45 eV). This has not been observed. Thus it is probable that $E_{c'} \geqslant 3.6$ eV in anthracene, but not greater than 4 eV. Furthermore, if we take $E_c = 4$ eV, then $P_e = P_h$. Using the approximation of Lyons, $I_c - E_c = P_e$, one gets $P_e = 1.7$ eV.

A summary of the above results, with some additional energy values is given in Table 2, the estimated values being in parentheses.

The establishment of a value for $E(\mathrm{CT})$ places a lower limit on the value for $E_{c'}$. Furthermore, it can be concluded that all activation energies for dark conductivity in anthracene hitherto measured have not referred to an intrinsic bulk carrier generation process. Our value for $E(\mathrm{CT})$ also confirms the conjecture of Berry *et al.*[14] and Kearns[12] that $E(\mathrm{CT}) > E$ (singlet exciton).

TABLE 2 Energy Levels in Anthracene Crystal

| | |
|---|---|
| $I_g$ | 7.4 eV[13] |
| $I_c$ | 5.65[4, 5] |
| $E_c$ | (4) |
| $E_{c'}$ | (3.7) |
| $E(\mathrm{CT})$ | 3.45 |
| $E$ (singlet exciton) | 3.15 |
| $E$ (triplet exciton) | 1.8 |

### *Photoemission Beyond* 5 *eV*

In Fig. 1, it is seen that beyond an energy of 5 eV, the current $J$ increases rapidly. In this energy region, however, $J$ is linearly dependent on the light intensity, and cannot therefore be analyzed in the light of double-quantum processes. This is a puzzling result since it implies that $I_c$ is lower than 5.65 eV. In fact, Terenin and Vilessov[15] give two $I_c$ values for anthracene, 4.9 and 5.6 eV. We also have on occasions, measured an $I_c$ value of 4.9 eV, but only when we worked with negatively charged crystals, or in atmospheres where we suspected that there was more than a trace of oxygen. We believe that the lower value for $I_c$ is caused by the presence of small amounts of oxygen or other electronegative impurity at the surface of the anthracene. One possible explanation for the mode of behavior of the oxygen is as follows: if the crystal is positively charged, then oxygen is not adsorbed well, because the adsorption of oxygen at an insulator surface is dependent on the concentration of free electrons at that surface.[16] Consequently, the measurement of $I_c$, in the presence of small traces of oxygen, on a *positively* charged crystal,[2] is not likely to run into interference by the oxygen. This situation obtains when we measure $I_c$ using (1), and under these conditions, we obtain a value of 5.65 eV for $I_c$. If, however, we measure $I_c$ by using a negatively charged crystal, then oxygen can be adsorbed even in the dark, and under these conditions, we sometimes see a threshold for external electron emission at 4.9 eV. We think that the low value for $I_c$ is caused by *the emission of an oxygen molecule-ion* from the surface. From an energetic point of view, it is easier to remove an electron from anthracene if one can place it on an oxygen molecule, thus utilizing the electron affinity of oxygen (0.46 eV[17]). Oxygen can also diminish the rate of electron emission because it can dissipate the kinetic energy of the emitted electron, making easier the recapture of the negative charge by the crystallite. Although the double-quantum experiments described in Fig. 1, are electron emission rate studies, and were performed on negatively charged crystallites, it is not likely that the results obtained at light energies less than 4.9 eV were affected by traces of oxygen. The reason for this is twofold: firstly, the exciton energy is not large enough to produce electron emission even if an $O_2$ molecule could provide its electron affinity, and secondly, the energy liberated by the annihilation of two excitons is sufficient to produce electron emission regardless of the $O_2$; in the latter case, if the $O_2$ concentration is very small, the rate of emission is not markedly reduced, especially since the concentration of excited electrons is quite low in the double-quantum case, so the probability of an impact between an electron and a surface $O_2$ molecule is small. However, when the energy of the exciting light exceeds $E_c$ then relatively large concentrations of energetic free electrons are generated inside the crystal. The probability of collision between an electron and an adsorbed oxygen ion therefore increases and eventually, as $E$ in (1) is increased, the electron energy will become large enough so that an $O_2^-$ ion can become detached from the crystal. While this mechanism seems capable of supplying energy for the electron emission, it does not completely make up the difference between 5.65 and 4.9 eV, even if we ignore the small binding energy of a neutral $O_2$ molecule to the anthracene surface, which also must be overcome. This conclusion is based on a value for $A_g$ for $O_2$ (g) of 0.46 eV,[17] which leaves a deficit of 0.25 eV. Only $10^{-4}$ of the electrons generated by light of energy 4.9 eV that strike the surface of the crystal have an energy of about 5.2 eV, the energy needed to ionize the crystal if the electron affinity of $O_2$ is utilized. The efficiency of external emission is certainly much lower at 4.9 eV than at 5.65 eV, but we have not yet measured the difference quantitatively.

### *Estimation of Value for Recombination Coefficient for CT–CT Annihilation*

An examination of Table 1 shows the interesting result that the efficiency of photoemission produced by CT–CT exciton annihilation at $E = 4.4$ eV is 100 times greater than that produced by exciton–exciton annihilation at $E = 3.98$ eV. At present, we do not know the exact contribution of the neutral exciton–exciton reaction to the electron emission rate at 3.98 eV, but for the moment, let us assume that this emission is due entirely to neutral excitons. The implications of the failure of this assumption will be discussed later in this paper. Although the emission at 4.4 eV also contains a contribution to neutral exciton–exciton annihilation, we can as a first approximation attribute all the emission at 4.4 eV to the CT–CT exciton process. Following the procedure outlined previously, we can say

$$J(\mathrm{CT}) = \frac{\rho v(1-\sigma)}{4} \qquad (5)$$

where $J(\mathrm{CT})$ is the current density of emitted electrons produced by the CT–CT exciton process, $\rho$ is the density of high energy electrons within the crystal, $v$ is the average velocity of the high energy electrons, corrected by a factor 4 to include only the electrons travelling in the direction of the surface and $\sigma$ is a reflection factor that represents the fraction of electrons that do not leave the crystal despite the fact that they are travelling in the correct direction. Assuming a double-exciton interaction,

$$\rho = \beta(\mathrm{CT})\, n^2(\mathrm{CT})\, \tau_e \qquad (6)$$

where $\beta(\mathrm{CT})$ is the recombination coefficient for the CT exciton–exciton annihilation, $n(\mathrm{CT})$ is the steady state density of CT excitons, and $\tau_e$ is the lifetime of the high energy electron. For $n(\mathrm{CT})$, we have

$$n(\mathrm{CT}) = \alpha k I \tau(\mathrm{CT}) \tag{7}$$

where $I$ is the number of quanta incident on the crystal, per unit area and time, $k$ is the absorption coefficient for the light, $\tau(\mathrm{CT})$ is the lifetime of the CT exciton, and $\alpha$ is the efficiency of forming the CT exciton with the incident light. Equations (6) and (7) are pertinent to our process regardless of whether a complex of two CT excitons is or is not a kinetic intermediate to the electron emission, because we are in a steady state condition.

If we assume that $v$, $\sigma$, and $\tau_e$ are the same for electrons generated by neutral exciton–exciton, and by CT exciton–exciton annihilation then, since similar equations to (5), (6) and (7) obtain for the neutral exciton, we get

$$\frac{J(\mathrm{CT})}{(I\epsilon)^2(\mathrm{CT})}\bigg/\frac{J}{(I\epsilon)^2} = \frac{\alpha^2\beta(\mathrm{CT})\tau^2(\mathrm{CT})}{\beta\tau^2} = 100 \tag{8}$$

Where $\epsilon$ is the extinction coefficient and $J$, $\beta$ and $\tau$ are defined as before, but apply to the neutral exciton, at an incident light energy of 3.98 eV.

Since $\alpha < 1$, we can say that

$$\beta(\mathrm{CT})\tau^2(\mathrm{CT}) > 100\beta\tau^2 \tag{9}$$

A further evaluation of $\beta(\mathrm{CT})$ depends on the establishment of a value for $\tau(\mathrm{CT})$.

### *Estimation of Value for $\tau(CT)$*

We know from our electroluminescence studies[9] that the recombination of holes and electrons produces the same light as in normal fluorescence. Therefore, an examination of the decay of light produced by highly ionizing radiation in anthracene should provide some information on the time constant for the decay of a CT exciton. Two such studies are those of Schmillen[18] and Gibbons, Northrop and Simpson;[19] Schmillen studied the $\alpha$-particle problem and Gibbons *et al.* studied the $\alpha$, $\beta$, $\gamma$ and UV induced fluorescence. Schmillen finds at least three time constants in the fluorescence decay of anthracene excited by an $\alpha$-particle: 18.8, 160, and $2100 \times 10^{-9}$ sec. The ratios of the total fluorescent energy found in these components is respectively 1:0.23:0.12. Gibbons *et al.* also find at least two identical components in all types of excitation, one in the $10^{-7}$ sec region, and a tail that is in the microsecond region, and give convincing evidence that the component that produces this $10^{-6}$ sec emission is a complex consisting of two excitons. Gibbons *et al.* rule out the involvement of ionized states in the formation of this complex by carrying out their experiment in the presence and absence of a field of $3 \times 10^4$ V/cm; they state, however, that their field experiments were preliminary, and our delayed electroluminescence studies[9] show that this field strength will not significantly alter the recombination of holes and electrons, probably because of internal fields that tend to neutralize the external field, but that higher fields will alter the fluorescence produced by ionization. In our view, the complex described by Gibbons *et al.* is a double CT-exciton complex, even in the case of UV excitation, because the high intensity spark UV light source they used undoubtedly had components in the 3000 Å region and below. In any event, the $10^{-6}$ sec component is not a single exciton. The 19 nsec lifetime is that of the normal singlet exciton. The intermediate lifetime, $1.6 \times 10^{-7}$ sec we feel represents a lifetime of the nearest neighbor CT exciton.

One can estimate an upper limit for $\beta$(CT) by calculating the maximum, or Coulomb capture cross-section for the CT exciton. $\beta(\mathrm{CT}) = \sigma v_i$ where $\sigma$ is the capture cross-section and $v_i$ is the velocity of the exciton. Assume for simplicity that the two CT excitons are approaching end on, for which the potential energy as a function of distance $r$ is

$$V(r) = -\frac{2e^2 a^2}{4\pi\epsilon\epsilon_0 r^3} \qquad (10)$$

where $a = 5$ Å is the distance of closest approach of the hole and electron. Following Rose,[20] we find the minimum in the probability distribution of a CT exciton around another CT exciton. The probability distribution is given by

$$P(r) \propto 4\pi r^2 \exp\left(-\frac{V(r)}{kT}\right) \tag{11}$$

for which one calculates the minimal condition

$$2 - \frac{r}{kT}\left(\frac{dV(r)}{dr}\right) = 0 \tag{12}$$

and from (10), using $\epsilon = 4$, and $a = 5$ Å

$$r \simeq 2 \times 10^{-7} \text{ cm.} \tag{13}$$

from which we get a capture cross-section of about $1.3 \times 10^{-13}$ cm$^2$ for the CT exciton–exciton interaction. Theoretical estimates of the velocity of an exciton vary from $10^4$ to $10^5$ cm/sec.[21] Assume a velocity $v_i$ for the CT exciton of $10^4$ cm/sec, which gives $\beta(\text{CT})(\text{calc}) \cong 1.3 \times 10^{-9}$ cm$^3$ sec$^{-1}$. Using the value for $\beta = 2.6 \times 10^{-12}$ cm$^3$ sec$^{-1}$,[29] we get

$$\beta(\text{CT}) < 500\beta \tag{14}$$

If $v_i$ is smaller than $10^4$ cm/sec, then $\beta(\text{CT})$ will be smaller than in (14).

The result in (14), together with the estimate for $\tau(\text{CT})$ of $1.6 \times 10^{-7}$ sec can be placed back into (8) giving for

$$\alpha \geqslant \frac{10}{22} \cdot \frac{\tau}{\tau(\text{CT})} \simeq 0.04 \tag{15}$$

Thus, we have an efficiency of generating CT excitons at 4.4 eV that must be larger than 4%. Since the CT excitons are presumed to be formed mostly by the recombination of free holes and electrons, this must also be the approximate bulk ionization efficiency at 4.4 eV. From (15) and (7) one gets the surprising result that the steady state density of CT excitons is $\geqslant 40\%$ of the steady state density of neutral excitons, at 4.4 eV. Since the quantum efficiency for fluorescence in the vacuum UV is still high, the CT excitons must decay efficiently via the singlet state; but with a time constant of $10^{-7}$ sec. This is how we interpret the $10^{-7}$ sec component in the UV induced fluorescence reported by Gibbons *et al.*[19]

The efficiency of generating CT excitons by $\alpha$-particle bombardment must be greater than 4% relative to normal singlet state production. In fact, the work of Schmillen[18] shows that the ratio of the total energy that appears with a $1.6 \times 10^{-7}$ sec time constant, to that with the $2 \times 10^{-8}$ sec (normal singlet state) time constant is 0.23. Since the total emitted energy is proportional to the number of excited states produced at time $t = 0$ by the $\alpha$-particle, we get an efficiency of producing the $10^{-7}$ sec state, which we conjecture is the lowest energy CT state, of about 20%.

It is possible that the efficiency of CT exciton production under $\alpha$-particle bombardment is greater than this, because it is conceivable that there is also a "triplet" CT exciton[6] in the sense that the spin of the excess electron is the same as the spin of the electron next to the hole. The decay of a "triplet" CT exciton would go via the triplet manifold and thus would not be seen as fluorescence. The maximum efficiency for CT exciton generation would thus be at least 40%.

### *Delayed Scintillation Fluorescence in Anthracene*

We would like to suggest that the $10^{-6}$ sec component reported in Schmillen's work is, following Gibbons *et al.*, an exciton complex, with the exception that it is a CT exciton-dimer. Since the ratio of the total fluorescent energy in the $10^{-7}$ sec state to the $10^{-6}$ sec state is 2:1, and since we assume that the dimer is produced only by association of CT excitons, we must find the concentration of CT excitons that will give the observed ratio. We shall assume that the formation of the dimer takes place in a time interval that is short compared with the lifetime of either the CT exciton or its dimer, namely $10^{-8}$ sec. This is also the time beyond which the decay of the scintillation pulse is exponential.[22] Under these conditions

$$\frac{dN_1}{dt} = -2\beta(\mathrm{CT})\,n_1^2 \tag{16}$$

$$\frac{dN_2}{dt} = \beta(\mathrm{CT})\,n_1^2 \tag{17}$$

where $n_1$, and $n_2$ are respectively the densities of the CT exciton and its dimer, $\beta(\mathrm{CT}) \cong 10^{-9}$ cm$^3$ sec$^{-1}$.

When solved with the appropriate boundary conditions, we get

$$\frac{n_2}{n_1} = \tfrac{1}{2} = \beta(\mathrm{CT})n_1^0 t \tag{18}$$

where $n_1^0$ is the CT exciton concentration at $t = 0$. From (18) we get

$$n_1^0 = \frac{1}{2\beta(\mathrm{CT})t} \cong 5 \times 10^{16}/\mathrm{cm}^3 \qquad \text{for CT excitons} \tag{19}$$

Let us now see if this density is reasonable. The fluorescence conversion efficiency of anthracene under $\alpha$-particle excitation is about 1 photon emitted per 1000 eV,[23] or $5.3 \times 10^3$ photons per 5.3 MeV $\alpha$-particle. Using Schmillen's ratio of $10^{-8}$ to $10^{-7}$ sec components, we should expect $N(\mathrm{CT}) = 10^3$. The range of an $\alpha$-particle in anthracene is about 30 $\mu$ [23] and in a time of $10^{-8}$ sec, which is half the lifetime of the neutral exciton, the distance covered by the exciton should be about 500 Å.[20] The distance covered by a CT exciton would not be greater than this because its diffusion coefficient should be smaller than that of the neutral exciton. The volume of the channel should therefore be about $2.5 \times 10^{-13}$ cm$^3$, and $n(\mathrm{CT}) \geqslant 4 \times 10^{15}/\mathrm{cm}^3$. Considering the crudeness of this calculation, this is reasonable agreement with (19); in fact, since the value of $n_1^0$ in (19) depends inversely on the time $t$, and on the inverse square of the time in the channel calculation, it is evident that at slightly shorter times or with more slowly moving CT excitons, there could be coincidence between the two calculations. This coincidence is even more likely if one uses an estimate of the channel radius of about $10^{-7}$ cm.[28] In the channel of excitation produced by the $\alpha$-particle, it is not only possible to produce CT exciton dimers, but trimers as well. These poly-CT excitons should be almost immobile and could act as quenching centers.

The estimates made herein for $\alpha$ and $\beta$(CT) have been conservative. The estimate of $\beta$(CT) made in (14) was based on a $v_i = 10^4$ cm/sec. If $v_i$ is less than this, then $\beta$(CT) will be smaller than has been estimated, and this in turn will cause $\alpha$ to increase. Finally, if the neutral exciton–exciton contribution to the emission current at 4.4 eV is smaller than we estimated, $\alpha$ will be even larger. A smaller $\beta$(CT) will require a higher $n$(CT) in order to justify our position that the $10^{-6}$ sec tail in the delayed fluorescence of anthracene is due to the decay of a CT exciton dimer, but the lower value for $v_i$ tends to increase $n$(CT) in the $\alpha$-particle channel.

The efficiency of generating CT excitons using light of energy 3.45 eV is certainly less than 0.1 of that at 4.4 eV, because the results summarized in (8) were obtained at 3.98 eV, at which energy CT exciton formation is much more efficient than at 3.45 eV. Since the lifetime of a higher vibrational state of the neutral exciton is of the order of $10^{-12}$ sec, one would not expect an efficiency of more than $10^{-5}$ for forming a CT state at 3.45 eV ($\tau(\mathrm{CT}) = 10^{-7}$ sec) from an excited singlet state of the same energy.

It is interesting that in both anthracene and tetracene, the position of $E_c$ seems to be close to but below the second excited singlet state level.

We wish to express our appreciation to Dr. H. Kallmann for helpful discussions. Our discussions with Dr. N. Geacintov, Dr. M. Sano, and Mr. R. Laupheimer have also been valuable. Mr. Sidney Fox assisted in making these measurements.

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## Notes added in proof

(1) A recent paper by King and Voltz[32] concerning the delayed fluorescence produced by α-particle bombardment of anthracene emphasizes the role of the triplet exciton in this phenomenon. These authors state that the triplet state is produced mainly by the recombination of holes and electrons. It must also be considered that the CT exciton may be a kinetic intermediate to the triplet state. From our delayed electroluminescence work,[9] it appears that the lifetime for decay of a CT exciton to the first excited singlet state (as deduced from the half-life of the delayed electroluminescence) is less that $10^{-6}$ sec. The CT exciton may also decay via the triplet state, and the lifetime for this process is probably different from that of the singlet state decay. There may therefore be more than one lifetime for the decay of a CT exciton.

(2) In a private communication from M. Silver, we have learned that there is an alternate method for handling the data shown in Table 1. Silver points out that while our mechanism for CT exciton formation from free electrons and holes is reasonable, the free-electron state can be created more efficiently by a direct band-to-band transition, rather than by the autoionization of an upper excited exciton state. On the basis of this model, he derives a linear dependence of $J/I_0^2$ on photon energy, and no peaks appear in this plot. Furthermore, he derives an inverse dependence of the bulk photocurrent on the extinction coefficient, which has been observed in anthracene. It is also possible to obtain a value of 4.1 eV for the free-electron band edge; this is quite close to our value in Table 1. If Silver's proposal is correct for anthracene, then our analysis that leads to an evaluation of $\alpha$ (Eqs. 8 and 15) is not valid, and any conclusions based on $\alpha$ should be held in abeyance.

(3) We have observed external photoelectric emission in naphthalene induced by light of maximum energy 3.7 eV; $I_C = 6.8$ eV for this compound. Despite the fact that the incident energy is less than that of the 0–0 singlet transition (3.96 eV) we observe a square dependence of the emission current on the light intensity. Preliminary results indicate that the annihilating states each have an

energy of about 3.9 eV. When the incident light energy extends to 5.6 eV, the annihilating states each have an energy of about 4.4 eV. These values would correspond to the singlet and CT exciton states in naphthalene. More precise values and a discussion will be presented in a forthcoming paper.

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