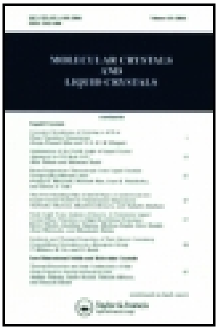

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Autoionization and Exciton Annihilation in Anthracene

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Autoionization and Exciton Annihilation in Anthracene

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Abstract—Evidence is presented that the intrinsic carrier generation process in anthracene is one of autoionization (AI) rather than a band-to-band transition. These results are also consistent with the assertion that at least at 6.3 eV, the AI intermediate state is the same, regardless of whether the energy is delivered by a single photon, or by an exciton–exciton process. We have shown that in many cases of "pure" anthracene crystals, there exist impurities that have an effective surface concentration of $\sim 5 \times 10^{-5}$ mol fraction, as indicated by exciton quenching properties. These impurities are presumed to be oxygen. The effective exciton lifetime in the surface region is about 5×10^{-9} sec.

We have also indicated how the Millikan condenser technique can be used to measure a variety of properties of the exciton.

In previous papers,[1, 2, 3, 4] we outlined arguments that supported our view that intrinsic carrier generation in anthracene is an autoionization (AI) process. We present here a more detailed experimental verification of this hypothesis. In addition, we use some of the results of our work to discuss some questions raised in the work of Kepler and Merrifield,[5] and Hoesterey and Letson.[6] Thus, our work shows why singlet exciton–exciton annihilation in the surface region of the usual crystal is not important, relative to exciton dissociation in the surface region. We also explain why anthracene doped with tetracene in the concentration of 40 ppm shows the same quantum efficiency for carrier generation as does pure anthracene.

Finally, we show how the Millikan condenser technique can be used to determine exciton–exciton annihilation coefficients, exciton diffusion lengths and concentration of quenching centers in the surface region.

Autoionization Study

By AI we mean a process in which a bound molecular state in the crystal is produced, that has an energy higher than its ionization energy in the crystal and that then acts as an intrinsic source of free carriers. Thus, if we consider the following equations, where $h\nu$ is equal to twice the singlet exciton energy, A^*,

$$\begin{aligned} h\nu + A &\longrightarrow [A^{**}] \xrightarrow{\gamma} A^+ + e^- \\ A^* + A^* &\xrightarrow{\beta'} [A^{**}] \xrightarrow{\gamma} A^+ + e^- \end{aligned} \qquad (1)$$

the first case represents the formation of A^{**} the AI state following the absorption of a photon, whereas the second case represents the collision of two excitons to form the *same* AI state, which has the *same* probability of ionizing in either case. In other words, upon absorption of a photon of energy greater than 4 eV in anthracene, for example, the individual molecule in the crystal becomes excited to an energy level *above* that required to produce a pair of free carriers. Nevertheless, the molecule does not ionize with high probability; in fact, most of the time the molecule decays to the ground state without ionizing. However, when the molecule does ionize, the free electron and hole travel in the conductivity band system that is characteristic of the crystal. Thus the AI states are embedded in a crystal continuum in the same way that discrete molecular and atomic levels have been observed in the continua of the molecular and atomic spectra.[7] These states have also been referred to as super-excited states,[8] and pre-ionization states.[7]

As indicated in previous papers,[3, 9] the external photoelectric current produced by singlet exciton–exciton (X–X) annihilation can be written

$$J_{xx} = \frac{l(1-\sigma)}{6} \beta' \gamma (kI_0 \tau')^2_{xx} \qquad (2)$$

where J_{xx} is the observed current, l is the escape depth of the emitted electrons and is assumed to be less than 300 Å,[3] the fraction 1/6 is an approximate geometric factor, σ is the reflection factor for electrons moving from the interior for the crystal to the exterior, β' is the X–X annihilation coefficient, γ is the fraction of the AI states produced by X–X annihilation that results in energetic (energy greater than I_c, the ionization energy of the crystal) free electrons, k is the absorption coefficient, I_0 is the incident light intensity, and τ' is the lifetime of the exciton in the region from which the emitted electrons come.

The meaning of τ' must be dealt with at greater length because we feel that it contains an explanation of a wide variety of behavior. It has been customary in dealing with the singlet exciton lifetime to use a value of 2×10^{-8} sec. It is known that the lifetime of the singlet exciton in the bulk of thick crystals can be as high as 3×10^{-8} sec, and for very thin crystals ($\sim 0.1\ \mu$) it can drop into the nanosecond range.[10] The fact that the lifetime diminishes as the surface to volume ratio increases has been attributed to the quenching effect of the surface. The surface is not to be considered as a geometrical construct, but rather a region in which the properties attributed to the surface attenuate rapidly. Thus, Khan-Magometova[11] postulates a surface containing an exponentially decreasing concentration of quenching centers. We feel that this model is effective not only in explaining the fluorescence behavior of anthracene, but also the electrical properties in the surface region. By surface region, we shall mean at least within 300 Å from the geometrical boundary.

In other words, it is not proper to use the value $\tau = 2.6 \times 10^{-8}$ sec for the exciton lifetime,[5] unless it has been so measured in the region of interest. That this is not a trivial point will be appreciated shortly when it be shown that an error of a factor of at least 30 is introduced by neglecting this point.

For external electron emission produced by a single photon (X) absorption, we have

$$J_x = \frac{l(1-\sigma)}{6}\gamma(kI_0)_x \tag{3}$$

where J_x is the observed current, and the other quantities are as defined previously. The essence of the AI hypothesis lies in the correlation of J_x with the excitation of the bound state characterized by the optical absorption coefficient k, and having an efficiency of ionization γ. The same correlation would exist between J_x and a band-to-band transition, if the major part of k was represented by such a transition. This is not the case however, since the absorption spectrum of anthracene can be explained on the basis of excitation of bound states.[16] Furthermore, in (2) and (3), if the energy delivered to the molecule by the single photon excitation is equal to that delivered by the X–X excitation, then γ will be the same in (2) and (3). Finally, $l(1-\sigma)$ will be the same in both processes under these conditions.

With these assumptions, one can now combine (2) and (3) to produce

$$\beta' = \frac{J_{xx}}{J_x}[(kI_0)_x/(kI_0\tau')^2_{xx}] \tag{4}$$

The usefulness of (4) lies in the fact that questions of geometry or ambient conditions are not relevant as far as the emerging electron is concerned because only a comparison between the X and X–X process is considered. This is particularly important for us since we use the Millikan condenser technique,[12] and it is often difficult to determine the precise geometry of the particle. The evaluation of β' is thus seen to depend critically on τ'.

In our previous paper,[3] we gave general reasons why we expected τ' to be in the nanosecond range rather than in the tens of nanoseconds. It is possible, however, to arrive at an unequivocal evaluation of both τ' and β'. It is well known[13] that the addition of tetracene to an anthracene crystal can result in a radical change in the fluorescence emission from the characteristic blue of anthracene, to the green of tetracene. Tetracene acts as an efficient exciton trap, and in so doing, decreases the effective lifetime of the characteristic blue fluorescence of anthracene. This process has been well studied, first by Schmillen[14] and later by Wendel and Hartig.[15] These workers measured the blue fluorescence lifetime in anthracene as a function of tetracene content. We therefore added tetracene to our anthracene crystals so that we *determined* τ' in advance, instead of trying to deduce what it might be in the pure crystal we measured. The addition of tetracene had no effect on the J_x process in the concentration range studied; this was to be expected since this process does not involve exciton migration, and the emerging electron has a vanishingly small chance of hitting a tetracene molecule in its short trip to the exterior of the crystal. On the other hand, the addition of tetracene, *above certain concentrations* had a marked effect on J_{xx}. These results are shown in Table 1. For each concentration studied, four or five crystals were used. The data shown in the J_{xx}/J_x column show the spread of the results, and the corresponding values of β'. The solid solutions were made by adding purified tetracene (sublimed eight times) to synthetic anthracene (Eastman H-480) pumping to 10^{-4} mm for several hours, and then sealing in the vacuum. For concentrations of tetracene less than 10^{-3} mol/mol, a benzene solution was used. The mixture was then melted and slowly cooled overnight. Samples were transferred in the presence of a safelight and the normal room atmosphere, and placed inside the Millikan chamber containing the usual argon atmosphere. The following data are applicable: $I_x(1980\ \text{Å}) = 2.2 \times 10^{10}$ cm^{-2} sec^{-1}; $I_{xx}(3650\ \text{Å}) = 4.6 \times 10^{15}$ cm^{-2} sec^{-1}; $k_x^{16} = 3.5 \times 10^5$ cm^{-1}, $k_{xx} = 8 \times 10^4$ cm^{-1}. Two points should

TABLE 1 Determination of Exciton–Exciton Annihilation Coefficient in Anthracene

Concentration of tetracene mol/mol	J_{xx}/J_x	τ'[a] sec × 10^9	$\beta' \times 10^9$ cm^{3}sec^{-1}
0[b]	2.5–1.5		
10^{-5}	2.5–1.5	4.8	6–4
10^{-4}	1–0.7	3	6–5
10^{-3}	0.15–0.10	1.3	5–3
	Average $\beta' = 5 \times 10^{-9}$ cm^{3}sec^{-1}		

[a] Values for τ' taken from reference 15.

[b] Zone-refined anthracene used for this experiment.

be made: the value of k for the X–X process is not known with sufficient precision for our purposes. Thus, the value we use, 8×10^4 cm^{-1} is taken from Lyons and Morris;[16] a value $k = 5 \times 10^4$ is given by Steketee and de Jonge.[17] Depending on which value one takes, the value of β' will vary from 0.5×10^{-8} to 1.3×10^{-8} cm^3 sec^{-1}. The constancy of β' over a fourteen-fold variation in $(\tau')^2$ and its agreement with values measured by Bergman[18] *et al.* (1×10^{-8} cm^3 sec^{-1}) and Hasegawa and Yoshimura[19] (0.6×10^{-8} cm^3 sec^{-1}) is excellent, and gives strong support to our hypothesis that the ionization produced by the direct photon absorption and the indirect X–X process proceed through the same intermediate state, and that this is an AI state.

This result corroborates previous conclusions[2, 4] made in this laboratory that the intrinsic carrier generation process in anthracene is AI.

Lifetime of Exciton in Pure Anthracene

An examination of Table 1 shows that tetracene affects J_{xx} *only* when C is equal to or greater than 10^{-4} mol fraction. This means that in the normal, "pure" anthracene, the effective concentration of impurities in the surface region is somewhere between 10^{-5} and 10^{-4} mol fraction! In anthracene, this corresponds to a density of 10^{17} cm^{-3}. (At this impurity density, the dark conductivity would certainly be surface impurity dominated.) It is also seen that the effective exciton lifetime in the region from which the electrons emerge, $\tau' = 4.8 \times 10^{-9}$ sec. This is calculated by using the constant calculated value of β' and the measured value of J_{xx}/J_x for a pure crystal. This value of τ' is appropriate for a tetracene mol fraction of about 3×10^{-5}. Let us now digress to the work of Hoesterey and Letson[6] who measured the photogeneration of carriers in anthracene doped with tetracene and excited by near UV light, they found to their surprise that the *quantum efficiency* of carrier generation η, was independent of tetracene content up to the maximum tetracene concentration they studied, 40 ppm or about 3×10^{-5} mol fraction. The carrier mobility μ was however, markedly affected by the added tetracene. Hoesterey and Letson explained the decrease in μ on the basis of the trapping of the carrier by the tetracene. We suggest the following explanation for the constancy of η: The diffusion length of the singlet exciton in anthracene is about 450 Å.[25] Using the average absorption coefficient[5] of 3×10^4 means that the ratio of diffusion length to absorption depth is 0.15 and that the role of diffusion of excitons to the surface from the interior of the crystal is not very important; those excitons generated close to the surface will be most effective in creating carriers. However, if there is an effective impurity concentration in this thin surface region, then the density of excitons *in this region* will be diminished, mainly affecting η. Since this surface region is narrow, and diffusion to the surface is not of great importance, the normal *fluorescence* behavior of the pure material is not as markedly affected as is η. But if an impurity such as tetracene is added in increasing concentration to the anthracene, the fluorescence of anthracene will be affected by the tetracene long before η is affected, because η is determined by the larger surface impurity concentration. We therefore suggest that despite the fact that Hoesterey and Letson did a thorough job of purifying and crystallizing their material, they eventually washed the surface of the crystal in air (albeit in the presence of a safelight), introducing oxygen and surface defects in a thin surface region. If the effective surface concentration was *more than* 3×10^{-5} mol fraction, then the addition of tetracene would not change the density of surface quenching centers until the tetracene density exceeded 3×10^{-5} mol fraction. This concentration checks very well with the figure we obtained in our work. (There is also recent evidence[20] that even in the absence of oxygen, there are crystal defects that, in the surface region, grow in concentration under the influence of highly absorbed light to an extent that can lead to crystal disruption if the crystal is thin enough.)

Exciton–Exciton Annihilation and Exciton Dissociation

Let us now consider the paper by Kepler and Merrifield[5] (KM) in the light of the above findings. In that paper KM described the results they obtained in a pulse-type photoconductivity experiment in which they used highly absorbed, near UV light and analyze them from the point of view of an X–X process and also a surface generation process. KM showed that the X–X process can produce an abundance of carriers but that recombination was necessary to give the equations for the observed linear light intensity dependence of the carrier density. Our work shows that the value of $\tau = 2.6 \times 10^{-8}$ sec used by KM should be 4.8×10^{-9} sec instead. This would diminish the calculated carrier density by a factor of at least 30. Using the most recent values for the hole-electron[21, 22] recombination coefficient, the calculated carrier density is far below the measured density. One can safely conclude that the X–X process does not compete effectively with the surface generation process when highly absorbed light is used at least in the case of a crystal with a surface that has been in contact with oxygen, or has another efficient surface quenching mechanism[20] for excitons.

We therefore conclude that the carrier generation mechanism for this wavelength light is that of exciton dissociation at impurities or at the surface. We also suggest that the carrier recombination process is first-order, as indicated in previous work.[1, 2, 4, 23] The impurities can act both as recombination centers and as traps.

As for the surface generation process, we suggest that the appropriate steady state equation representing the exciton density in the surface region for strongly absorbed light is that of Khan-Magometova[11]

$$D\frac{d^2 n}{dx^2} - rCn - \frac{n}{\tau} + kI = 0 \tag{5}$$

where D is the exciton diffusion coefficient, r is the exciton-impurity interaction coefficient, $C(x)$ is the density of impurity. Following Khan-Magometova,[11] $C(x) = C_0 \exp(-\alpha x)$, and as usual, $I = I_0 \exp(-kx)$. At $x = 0$, $C = C_0$, and C_0 is chosen so that $1/rC_0 = \tau' = 4.8 \times 10^{-9}$ sec, the measured value. By referring to the data of Wendel and Hartig,[15] $C_0 \sim 2 \times 10^{17}$ cm^{-3} and $r \sim 1.0 \times 10^{-9}$ cm^3 sec^{-1}. $\tau = 3 \times 10^{-8}$ sec, the exciton lifetime in the bulk of the crystal.[10] The value taken for r means that the bimolecular rate constant for exciton-impurity interactions is about 1/5 to 1/10 of that of the X–X interaction rate constant β'. The fact that both partners move in the X–X process accounts for part of this factor; the larger effective radius of the exciton, relative to that of the impurity should account for some of the rest.

Determination of Exciton Diffusion Lengths

The Millikan condenser technique should be applicable to the problem of measuring the diffusion length of the CT exciton in the same way as was indicated by Mulder[25] for the normal exciton, if we treat the CT exciton movement as a hopping process, in which each contact between the CT exciton and an impurity destroys the CT exciton. Under such assumptions, one would expect that in tetracene-doped anthracene crystals,

$$(l/l_0)_x = 1/(1+CH_0)^{1/2} \tag{6}$$

where H_0 is the number of hops taken by the exciton in its lifetime in the pure crystal, C is the effective cmol ratio of impurity (tetracene for example), and $(l/l_0)_x$ is the ratio of the diffusion length in the x direction of the exciton in the doped crystal, relative to the pure crystal. On a random walk model, $l=\sqrt{H}\ A_0$ where A_0 is an average lattice distance, for example, 4 Å. Since $H \propto \tau$, we can write

$$\tau/\tau_0 = 1/(1+CH_0) \tag{7}$$

The ratio τ/τ_0 for the CT exciton in doped anthracene can be obtained by measuring J_{xx} for a CT–CT exciton annihilation process in a series of doped anthracene crystals. A plot of τ_0/τ against C should give H_0 and hence l_0 for the CT exciton.

The data in Table 1 should be capable of being analyzed using (7), but they are not. Equation (7) is valid only if the impurity is *uniformly* distributed as a solid solution throughout the anthracene and the anthracene lattice is not seriously distorted by the inclusion of the impurity. If any of the impurity precipitates because of solubility saturation, then the *effective* impurity concentration is *less* than the nominal concentration, the precipitate representing large clusters of pure tetracene. The formation of such islands has previously been observed.[13]

Determination of X–X Annihilation Coefficients

It is also apparent that we can use the techniques outlined in this paper to measure the value of β' for X–X processes in other crystals, if the efficiency of generating the exciton is known. Furthermore, one can use the known value of β' in anthracene to measure the exciton lifetime in anthracene doped with other impurities such as acridine. If acridine is more soluble in anthracene than is tetracene, then it will be possible to study the implications of (5) with greater confidence.

Conclusion

We have given additional evidence herein that the intrinsic carrier generation process is one of autoionization rather than a band-to-band transition.[22, 24] We have also shown that our results are consistent with the assertion that at least at 6.3 eV, the AI intermediate state is the same, regardless of whether the energy is delivered by a single photon, or by an X–X process. We have shown that in many cases of "pure" anthracene crystals, there exist impurities that have an effective surface concentration of $\sim 5 \times 10^{-5}$ mol fraction, as indicated by exciton quenching properties. These impurities are presumed to be oxygen. The effective lifetime in the surface region is about 5×10^{-9} sec.

We have also indicated how the Millikan condenser technique can be used to measure a variety of properties of the exciton.

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Note Added in Proof

Another paper has recently appeared[26] dealing with the singlet exciton–exciton annihilation coefficient, β'. In this paper, a value

$\beta' = 2.5 \times 10^{-7}$ cm^3 sec^{-1} is obtained. This value was based on a normal singlet lifetime of 4.2×10^{-9} sec, in a region at least 2000 Å deep. The crystal thickness is not given, but we would guess that it is thicker than 0.5 μ.

We feel that this value of β' is in error from two points of view. In the first place, the hole-electron recombination coefficient ϕ^{27} is between 2 and 5×10^{-7} cm^3 sec^{-1}, and one would expect $\beta' \ll \phi$. Secondly, the singlet lifetime in a crystal thicker than 0.5 μ should be close to the value normally used, 2×10^{-8} sec.

Since the value of β' depends inversely on the square of the singlet exciton lifetime in the Tolstoi and Abramov paper, the effect of correcting the singlet lifetime is to make their $\beta' = 10^{-8}$ cm^3 sec^{-1} in agreement with the previously cited values for β'.

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