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On Charge Carrier Generation by Exciton–Exciton and Exciton–Photon Interactions in Crystalline Anthracene

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Two processes for photogeneration of carriers in Anthracene crystals, which have been proposed, among others, are the interaction of two singlet excitons created by light, and the ionization of one singlet or triplet exciton by absorption of a photon. Their relative importance is still controversial.

They are considered in at least two kinds of experiments:

(1) The light from a Q-spoiled Ruby Laser generates charges whose density is proportional to the cube power of the light intensity.[1–3] The favored mechanism is the ionization by a laser photon of a singlet exciton,[4] itself generated by a transition using two laser photons,[5] although not everybody agrees on this mechanism (see [1]). It can indeed be shown that barring a "catastrophe" in the transition dipole moment involved, exciton–photon (e–p) process should by far dominate over exciton–exciton (e–e) processes.[6]

(2) The light of $\lambda \sim 4300$ Å corresponds to the tail of the first allowed singlet–singlet electronic transition and is weakly absorbed ($\epsilon \sim 10^{-1}$ to 10 cm^{-1}). It generates singlet excitons in the bulk of the crystal, and triplet excitons by intersystem crossing from these singlets. At the same time, a photocurrent is observed which—when space-charge and trapping effects are avoided—is proportional to the square of the light intensity.[7] This had been initially attributed to exciton–exciton interactions, but the experiments with lasers have led some to question this interpretation.[4] The present note reports results bearing on this question.

Principle—The e–e and e–p processes cannot be separated by their light-intensity dependence, but they can be if their *temperature* dependence is investigated in proper experimental conditions.

Let n_s and ϕ the singlet exciton and photon densities, assumed constant throughout the crystal at a given time. This is true in our experiments as $\epsilon \lesssim 1$ and the crystals are ~ 2 mm thick. Let N_{ee} and N_{ep} the charge densities created by e–e and e–p processes respectively.

Pulsed light is actually used, so that trapping is unimportant. We assume a light pulse of constant intensity I and duration τ (much shorter than any transit time). The initial value of the current is simply related to the carrier density N.

We have $N_{ee} = \alpha_{ee} n_s^2 \tau$ and $N_{ep} = \alpha_{ep} n_s \phi \tau$, when the α's are the rate constants; bulk recombination can be neglected at the low charge densities where we work. In addition, ϵ, and therefore n_s, which is proportional to $\epsilon\phi$—its lifetime being assumed constant here—are exponential functions of the temperature T, with an activation energy E. But, as always $\lesssim 20\%$ of the photons are absorbed, ϕ is independent of T anywhere in the crystal.

If $N \propto \exp -E/kT$, then $N \sim N_{ep}$; but if $N \propto \exp -2E/kT$, then $N \sim N_{ee}$, provided the *actual* density of created charges is measured.

Experiments and Results

The carriers were generated by 2 μs flashes of unpolarized light from a high-pressure mercury lamp (BH6). A saturated $NaNO_2$ solution filtered out all $\lambda < 4200$ Å; the useful light was essentially the 4358 Å band. The current transients had the characteristic "triangular" shape of bulk-generated photocurrents.[2, 7] Other details have been given elsewhere.[8] *After the variation with T of the mobilities has been taken into account,* one finds:

$$N \propto \exp -\frac{0.26 \pm 0.02 \text{ eV}}{kT}$$

between 20 and 150°C.

The extinction coefficients were measured using a prism monochromator and unpolarized light. ϵ is first measured to be $\simeq 0.5$ at 20°C, in agreement with other results;[9] reflection and scattering losses have to be considered, but the final result is only weakly dependent on their actual values. Assuming the losses to be constant, ϵ is then determined at the other temperatures and one finds:

$$n_s \propto \exp - \frac{0.13 \pm 0.01 \text{ eV}}{kT}$$

between 20 and 150°C.

Discussion

(1) These results are easily understood if e–e processes are dominant in the present experimental conditions, and if an electron generated with 2 eV kinetic energy has above 20°C a temperature-independent probability of recombining with the hole generated in the same ionization process.

However, if the exciton photoionization is an activated process, and if its activation energy is 0.13 ± 0.03 eV, our results are also compatible with e–p processes. The equality or near equality of the activation energies would be in that case a coincidence. This should be compared to the 0.16 eV activation energy found by Kepler[2] for the photoionization of singlets by Ruby laser light.

No definite choice in the alternative is possible by now, but we would like to develop some considerations on the origin of this activation energy for exciton photoionization.

(2) *Discussion of the origin of an activation energy for singlet photoionization*

To explain his observations Kepler has proposed a model based on geminate or initial recombination, a process well known, for instance, in dense gases.[11] This hypothesis implies some transport properties in the wide band which make it unlikely. It implicitly assumes that, whatever the disposable energy, the carriers relax

immediately to the lowest conducting state; e–e and e–p interactions involve energies of 6.3 and 6 eV (at 4350 Å) respectively, much larger than the gap of 4 to 4.3 eV. For the Coulomb attraction to be so effective as to limit the current by initial recombination of almost all pairs, the electron must relax down to its lowest state in a distance much shorter than the radius of diffusive coulombian capture ($\lesssim 120$ Å). This implies a very strong coupling with intramolecular vibrations, if the excitation of an anthracene molecule to a triplet state by the electron is negligible, for example for energetic reasons: the mean energy of such a vibration is ~ 0.2 eV (or less) so that > 10 emission processes have to take place in much less than a 120 Å straight path, implying a free path of $\ll 20$ Å (random walk) and a scattering time of $\ll 2 \cdot 10^{-15}$ s if $m*1$ at 2 eV kinetic energy. This is much smaller than the smallest theoretical time computed by Choi and Flauss for these processes involving a 1 eV electron in benzene crystals: $2 \cdot 10^{-14}$ s; the mean value of this scattering time being $5 \cdot 10^{-13}$ s at 1 eV.[12]

The loss mechanism should therefore be investigated before the latter proposal is considered likely.

In addition, there exists experimental information in contradiction with Kepler's model. Initial recombination is independent of the origin of the electron-hole pair, whether it comes from photoionization of the singlet, or of the triplet, or of the ground state, or from exciton interaction. Castro[13] has studied in his PhD thesis one-photon carrier creation from the ground state using a total energy of 4.5 eV or less. The total energy in Kepler experiments is 4.9 eV and therefore the "relaxation length" in his case should be longer than in Castro's, hence the "activation energy" smaller, contrary to observation (0.05 eV *vs* 0.16 eV).

Therefore, if Castro and Kepler results are equally trusted, the comparison of the activation energies they obtain, proves that the 0.16 eV value found by Kepler cannot be explained solely by initial recombination, but is due to another unknown property of singlet photoionization, or is even the consequence of the use of a laser.

In summary, our results can be explained by e–p processes if

these have, *for an unknown reason*, an activation energy of 0.13 ± 0.03 eV at 4358 Å.

(3) *Discussion of the possible involvement of triplets*

The fraction of singlet excitons decaying into triplets by intersystem crossing is $k_{ST}\tau_f$. The fluorescence lifetime of the singlet is only weakly temperature-dependent above 20°C but k_{ST} varies as $\exp - 0.1$ eV$/kT$,[14] and therefore the triplet density n_T varies as

$$n_T \propto \exp - \frac{0.23 \text{ eV}}{kT}$$

Our experimental results allow therefore to exclude that carrier generation via singlet–triplet interaction is dominant in the present circumstances, as it should give a generated carrier density $N \propto \exp - 0.36$ eV$/kT$. In addition, Kepler has found in carrier generation by laser light where almost exactly the same energy (4.9 eV) is utilized, an activation energy of 0.16 eV.[2] If this depends only on the total energy involved in the pair creation—as it should with initial recombination—the observed current should vary as $\exp - 0.52$ eV$/kT$ in the case of singlet–triplet interaction, or twice the observed value.

The photoionization of the triplets cannot be excluded using the temperature variation alone, if it happened that initial recombination is negligible at 4.75 eV, but let us compare it with singlet photoionization:

$$N_{Tp} \sim \tfrac{1}{2}\alpha_{Tp}[k_{ST}\tau\, \epsilon I \tau_f]\phi\tau$$

where $k_{ST}\tau_f \epsilon I \tau$ is the triplet density at the end of the flash, neglecting triplet decay during the flash.

$$N_{Sp} = \alpha_{Sp}[\epsilon I \tau_f]\phi\tau$$

$$\frac{N_{Tp}}{N_{Sp}} = \frac{\alpha_{Tp}}{\alpha_{Sp}}\frac{k_{ST}\tau}{2} \sim \frac{\alpha_{Tp}}{\alpha_{Sp}} \qquad \text{at } 20°\text{C}$$

because $\tau \sim 2 \cdot 10^{-6}$s in our experiments. For longer flashes the situation should be more favorable. But from Silver's results[15] $\alpha_{Tp} \lesssim 10^{-1}\, \alpha_{Sp}$ and triplet photoionization should be negligible *vs* singlet photoionization, and a fortiori *vs* singlet–singlet interaction.

(4) A further experimental check for choosing between e–e and e–p processes would be, for instance, to increase ϕ and/or lower n and try to observe an activation energy for N of 0.13 eV (in weakly absorbed light), or conversely decrease ϕ and/or increase n and try to observe an activation energy of ~ 0.4 eV. In the former case, this would indicate that e–e processes were dominant here and that initial recombination is unimportant. In the latter, the contrary would be indicated.

(5) If e–e processes are indeed dominant, it is possible to deduce from these experiments an upper bound for the photoionization of singlets at 4358 Å. This value depends on the singlet–singlet interaction rate constant, which is of the order of $10^{-11\pm1}$ cm^3 s^{-1}. Using Silver's old value of $5 \cdot 10^{-12}$,[7] one finds $\sigma_{ep} < 3 \cdot 10^{-20}$ cm^2. Using his new value of $8 \cdot 10^{-11}$,[14] one finds $\sigma_{ep} < 5 \cdot 10^{-19}$ cm^2. The *absolute* photon flux in our experiment was not known well enough to allow us to refine on these numbers.

In conclusion, the present results are just a piece of information which has to be taken into account, but does not allow by itself to distinguish between energetically similar processes. On the whole, however, they support the idea that bulk generation of carriers through singlet–singlet interaction indeed exists where proper experimental conditions are realized, and that initial recombination is not very important for electrons with more than 1 eV kinetic energy.

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