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Detrapping of Holes by Singlet Excitons or Photons in Crystalline Anthracene†

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Abstract—Hole detrapping has been studied through photoenhanced currents obtained under pulsed illumination of crystalline anthracene. Detrapping by singlet excitons is observed above 260 °K, and direct photodetrapping below this temperature. The rate constant for hole detrapping by singlets is $\sim 10^{-8}$ cm^3 s^{-1}. No evidence is found of an anomalously large rate constant. The cross section for photodetrapping using photons $4300 < \lambda < 5500$Å is of the order of 10^{-17} cm^2. Hole detrapping and electron detrapping appear to be very similar processes.

The interaction of trapped carriers, electrons or holes, with excitons or photons in crystalline anthracene has been studied by now in a number of cases. This interaction can be approached experimentally in two ways: either by looking at its effect on the exciton or photon—quenching, or absorption—and measuring a rate constant γ for this process, or by studying the resulting conductivity due to carrier detrapping, and the corresponding rate constant α.§

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§ $\gamma = \alpha$ only when every quenching leads to ionization. In such a case, the exciton or photon energy is always transferred to the trapped charge, and never directly dissipated in vibrations or phonons, as would be the case for instance if the vicinity of the trapped charge enhances intersystem crossing $T_1 \rightarrow S_0$ at a distance where energy transfer from the triplet to the charge is still negligible. Even so, an additional condition is that no retrapping takes place. If the carrier was trapped in a very distorted region of the crystal, retrapping may be highly probable. Even if this is not the case, the excited carrier will thermalize again in the vicinity of the trap—say within 100Å—and retrapping by simple random diffusion may take place. But the probability of such a process is not very high, and in actuality, γ and α are not measured to sufficient accuracy for this to be important. Such effects would

Triplet exciton-trapped electron interaction has been studied by Weisz *et al.*,[1] through its effect on the triplet lifetime, triplet–triplet interactions being negligible. They deduce a rate constant $\gamma_{TE} = 3.2\ 10^{-11}\ cm^3\ s^{-1}$. Similarly, holes are detrapped by triplets and quench them, the corresponding rate constants γ_{TH} and α_{TH} being of the order of $3 \pm 2\ 10^{-11}\ cm^3\ s^{-1}$.[2] These values are very similar to the triplet–triplet interaction rate constant $\gamma_{TT} \sim 3.10^{-11}\ cm^3\ s^{-1}$,[3] showing that interaction has a high probability at any encounter and suggesting that the different structures of the valence and the conduction bands, such as the existence of a wide band, play no role.†

Electron photodetrapping has also been studied in Ref. 1 and the corresponding cross sections measured from 1 to 2.8 eV.‡ Hole photodetrapping has not, but we would expect it not to be very different, judging from the results with triplets. We then expect fairly large cross sections (up to a few $10^{-17}\ cm^2$).

It has been also known for some time that singlet excitons can detrap holes,[4] but only recently have the corresponding rate constants been measured, with conflicting results. Wakayama and Williams[5] observed the quenching of delayed fluorescence under high intensity red excitation (6328 Å), in the presence of a current, in conditions where carrier–triplet interactions are negligible. They

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make $\gamma > \alpha$. On the contrary, if carriers are trapped at sites which would, even neutral, quench excitons or absorb photons, the presence of the charges will not be seen when the fate of excitation is studied, but the existence of the interaction will lead to conductivity, hence in this case $\gamma < \alpha$, as was apparently first understood by M. Pope (cf. Ref. 6).

Therefore, one should exercise some care when comparing experiments where, either γ, or α, is measured.

However, in real life γ and α are measured by macroscopic experiments, and errors in the assumed distribution of the trapped carriers may lead to sizeable errors, especially on α. In our case, where the whole volume is excited, this is not expected to give rise to very large errors.

† Triplet exciton–free electron interaction was studied by W. Helfrich (*Phys. Rev. Letters* **16**, 401 (1966)). The corresponding $\gamma \sim 10^{-9}\ cm^3\ s^{-1}$ (there is obviously no corresponding α). Again, this is almost a diffusion-limited value, determined by the diffusivity of the free carrier. This shows that in this case also the structure of the conduction band plays no role in exciton quenching. But we do not know whether this quenching is due to energy transfer or to intersystem crossing.

‡ The values quoted in the article implicitly assume $\gamma_{TE} = \alpha_{TE}$ (see footnote † on p. 23). If it were not, their values of σ_{TE} should be multiplied by α/γ.

deduce from their results $\gamma_{SH} \sim 5.10^{-5}$ cm^3 s^{-1}, a very large value for the rate of singlet quenching by charges in the bulk. Pope, Burgos and Wotherspoon[6] have studied the electric field modulation of the fluorescence excited by strongly absorbed (3650 Å) light, from which they deduce $\alpha_{SH} \sim 8.10^{-10}$ cm^3 s^{-1} (called γ'_{SH} in their paper), which would mean a small probability of hole detrapping by singlet excitons near a Au electrode.†

We have conducted similar experiments on anthracene crystals excited with weakly absorbed light (in the Urbach tail of the first singlet absorption) and longer wavelength. Hole detrapping by singlet quenching and photon absorption are both observed. Our results indicate that hole or electron detrapping are very similar processes, further substantiating the idea that band structure (for instance the presence of wide band) is not the important factor for the rates. We also find, as expected, that singlet–singlet and singlet-trapped hole interactions have comparable rates, apparently in disagreement with the results of Ref. 5.

1. Experimental Conditions

We have studied the current transients generated by illumination of anthracene crystals with pulses of very weakly absorbed light. The crystals, 1 to 3 mm thick, were tightly pressed between two SnO_2-coated glass plates. SnO_2 is a hole injecting electrode and a trapped space-charge of holes builds up in the crystal.‡ The crystals were placed, under vacuum, in a sample holder permitting the temperature T to be varied between 230 and 380 °K, the voltage V being permanently applied.

The light pulses were generated by a Xe-flashlamp. Their temporal shape was approximately triangular, with a risetime 6 μs, and a total

† One may also mention that an upper limit of γ_{SH} in the related material tetracene is given by L. Peter and G. Vaubel (*Phys. Stat. Sol.* **b48**, 587 (1971)), $\gamma_{SH} \lesssim 10^{-7}$ cm^3 s^{-1}. In tetracene γ_{SS} is not known, but one can expect $\gamma_{SS} \gtrsim \gamma_{ST}$ and $\gamma_{ST} \sim 2.2\,10^{-7}$ cm^3 s^{-1} (Ern, V., Saint-Clair, J. L., Schott, M. and Delacote, G., *Chem. Phys. Letters* **10**, 287 (1971)).

‡ SnO_2 in thin film is a degenerate semiconductor with a very large work function (~ 5.6 eV), it is not surprising that hole injection occurs. Indeed, large hole currents can be injected into anthracene ($\geqslant 10^{-6}$ A/cm^2) with no appearance of saturation. In all our experiments, we are never in a situation where the current is injection limited.

duration $\sim 15\ \mu s$. An elliptical mirror was used to increase the light flux on the sample. The spectral output between 4000 and 10,000 Å, measured using a grating monochromator shows no significant structure (at 20 Å resolution) smoothly decreasing toward long wavelengths. The light flux on the crystal has been measured using a calibrated photodiode and found to be slightly less than 10^{17} photons/cm^2 s Å near 4500 Å. The illuminated area was $\simeq 0.2$ cm^2.

In pulsed photoenhanced current experiments, various filter combinations were used. The corresponding transmissions are shown on Figs 1 and 2.

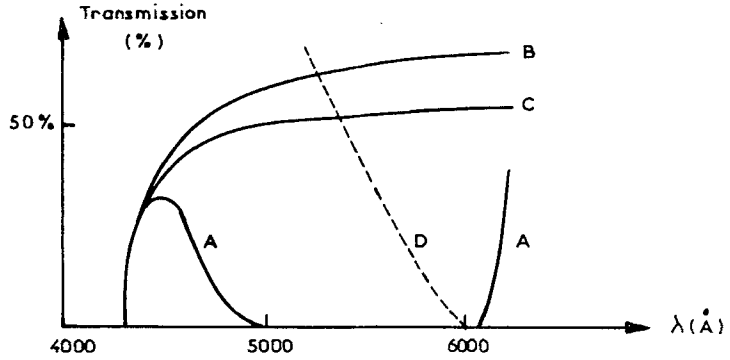

Figure 1. Transmission of the filter combinations used in this work: A—Three 2E and one 34A filters; B—Four 2E filters; C—Three 2E and one neutral density filter; D—1 cm $CuSO_4$ saturated water.

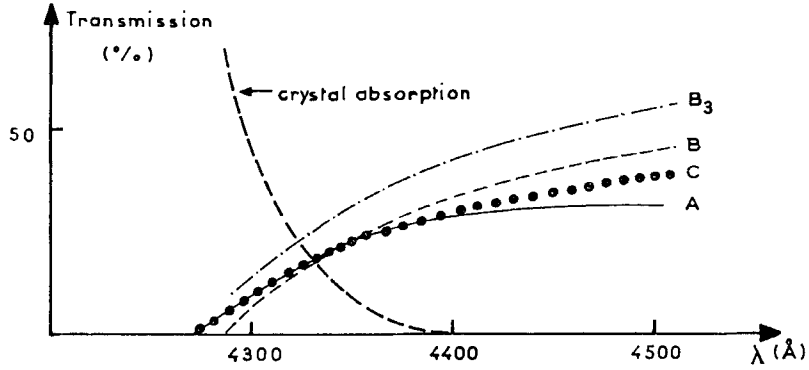

Figure 2. Transmission in the range 4300–4500Å of the same combinations as in Fig. 1 plus B3—three 2E Wratten filters only.

Surface generated currents are negligible. Indeed, the absorption coefficients are small ($\epsilon < 10\ \mathrm{cm}^{-1}$) at all temperatures for all the wavelengths transmitted by the filters.

The current transients were fed into a Keithley 102B amplifier (bandwidth 1 Hz to 200 KHz or 1 MHz depending on the experiments) and displayed on an oscilloscope. The peak current I was measured. As the transit times—determined by the apparent mobility—are much longer than t_1 (except at the highest voltages and highest temperatures) I is related to the number of charges set in motion by light in a simple way. If K is the rate of carrier production, by whatever mechanism, and the light pulse is approximated by a square pulse of duration t_1, the number of charges in motion at maximum current is Kt_1 in the absence of trapping and $K\tau_p$ for a carrier whose trapping time τ_p would be $\ll t_1$. Experimentally, electrons are only slowly trapped ($\tau_p{}^- \sim 100\,\mu\mathrm{s}$) and holes are trapped by tetracene (concentration 10^{-8}) with a $\tau_p{}^+ \sim 10\,\mu\mathrm{s} \sim t_1$.† Therefore, the peak current is only weakly dependent on variations of transport properties of the carriers and proportional to the rate of carrier production. This is not true, of course, of the current shape after the peak.

2. Results

The following properties of the peak current I have been observed:

(*a*) I is proportional to V^2 and is well below the SCL current value. At the highest temperatures and at high V, I seems to increase slightly less rapidly than V^2, but then the transit times are no more

† From the observed T-dependence of the apparent μ^+, measured on the same crystals in strongly absorbed light, we can deduce a tetracene density of $10^{14}\ \mathrm{cm}^{-3}$. Using the trapping parameters measured by other authors (Hoesterey, D. C. and Letson, G. M., *J. Phys. Chem. Solids* **24**, 1609 (1963) and Schmillen, A. and Falter, W. W., *Zeits. Phys.* **218**, 401 (1969)), one can calculate a value for $\tau_p{}^+ \sim 5\,\mu\mathrm{s}$ in good agreement with our observed value.

In addition, our crystals contain a low concentration of deeper, permanent traps with $\tau_p \sim 100\,\mu\mathrm{s}$. Before illumination, almost all the space charge resides in these traps, not in the tetracene traps, and the dark current is very small. After pulsing the flashlight, $\sim 10^{-2}$ of the space charge is in the shallow traps, and return to the deep traps in a time comparable to the hole residence time on tetracene, which is always very much shorter than the time between two experiments.

longer than t_1 and carrier exit at the electrodes should be taken into account accordingly (Fig. 3).

(b) From ~260 to ~370 °K, $I \propto \exp(-0.30 \pm 0.02\ \mathrm{eV}/kT)$. This has been verified throughout only with filter combination B. With the others, study has been restricted to low temperatures (Fig. 4).

(c) Below 260 °K, the variation of I with T is much less pronounced, tending toward an activation energy less than 0.1 eV.

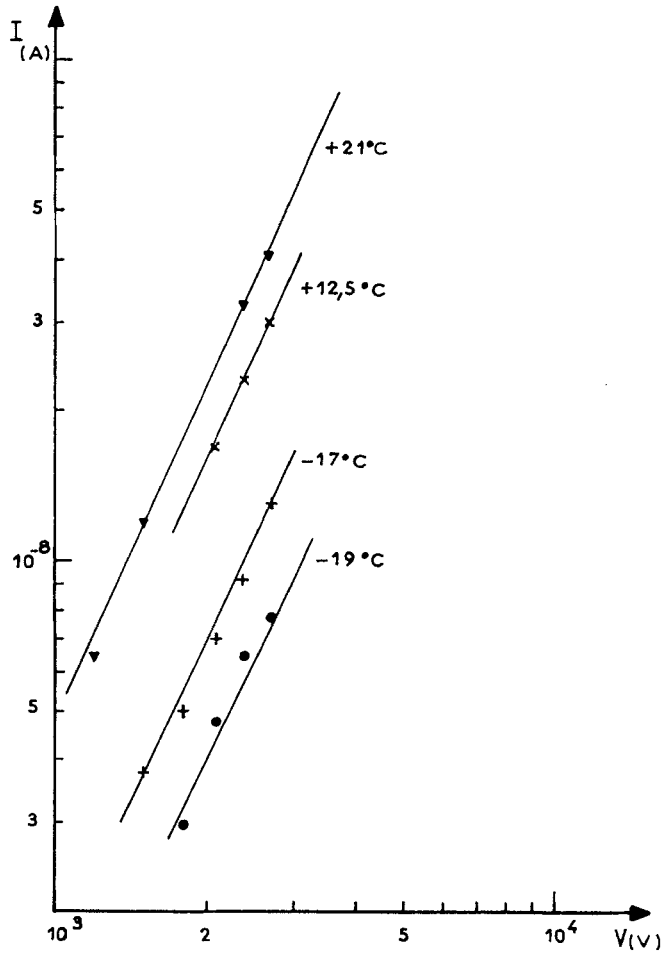

Figure 3. Voltage dependence of I at different temperatures. Points: experimental; Lines: $I \propto V^2$ dependence.

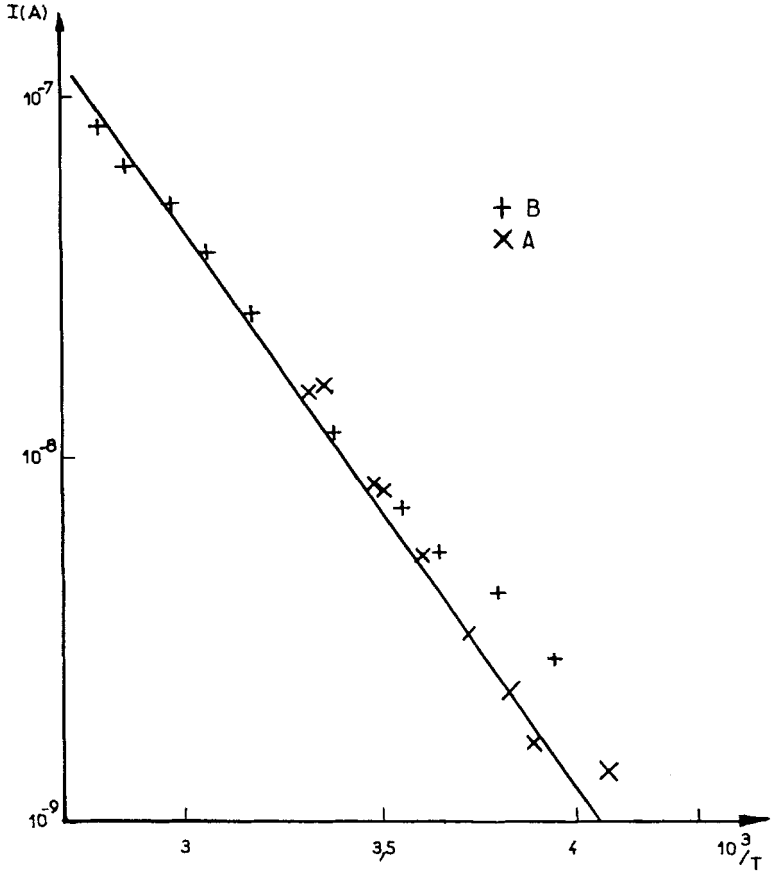

Figure 4. Temperature dependence of the peak current for A and B. Voltages are chosen to give equal currents at high temperature. Straight line: $\exp -0.30\ \mathrm{eV}/kT$.

(d) At room temperature, the ratio $I(A)/I(C)$ of the currents obtained with filter combinations A and C is ~ 0.8. With decreasing I, this ratio decreases, and is ~ 0.4 at lower temperatures (Fig. 5).

(e) If a 1-cm thick water cell is added to any combination, and water then replaced by a saturated solution of $CuSO_4$ (absorption on Fig. 1), the observed currents are not dependent of the presence or absence of $CuSO_4$ (within 10%).

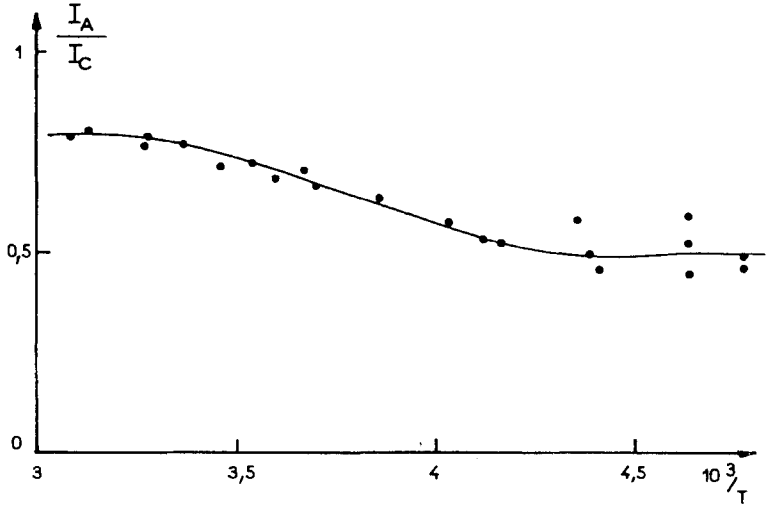

Figure 5. Ratio of peak currents obtained with filter combinations A and C. Dots: experimental ratios.

(f) $I(B3)$ with filter combination $B3$ is 2.1 times $I(B)$. In combination $B3$, one $2E$ filter has been removed from combination B.

(g) If neutral density filters are added to $B3$, I is proportional to their transmission, between 60 and 100% transmission. Due to the relatively small value of I, measurement has not been pushed to higher O.D.

3. Discussion

With high intensity weakly absorbed light, as was used here, two kinds of processes may be important. Double quantum carrier generation processes by singlet–singlet, singlet–triplet, singlet–photon or triplet–photon interactions. Or carrier release, that is, in our case hole detrapping by a singlet (SH), a triplet (TH) or directly a photon (Hϕ). The first four processes would give currents proportional to the square of the light flux, in contradiction with result (g). This check however is not good enough, but these processes may also be rejected on other grounds, using result (a).

The rates of double quantum generation processes have been shown in all cases where this has been verified, to be almost indepen-

dent of the applied field in the range ($<10^4$ V/cm) used here.† One should therefore expect a current $I \propto V$ as long as the duration of carrier generation t_1 is much shorter than the transit time. The $I \propto V^2$ dependence then shows that the carrier generation process is by hole detrapping, from a pool of trapped holes whose total number $N \propto V$ as expected of a space charge.[4]

As said above, the variation with T of the apparent hole mobility does not affect I. The observed temperature dependence is then solely due to the generation step, the quantum yield is $\propto \exp -(0.30\ \text{eV}/kT)$. We do not expect the H$\phi$ process to be temperature dependent to that extent: the trap is left neutral by hole release, and back-trapping is not aided by coulomb forces as in the case of geminate recombination. Also, as Hϕ process could, in principle, be due to absorption of photons in a wide wavelength range, no Urbach-type temperature dependence of the absorption is expected (absorption will be dependent upon the oscillator strength of a whole transition).‡ The known value of α_{TH} also makes process HT unable to explain the observed currents. Neglecting any triplet decay during the flash we get n_t^{max}, the maximum triplet density attained $n_t^{max} = k_{st} t_1 \epsilon_s F_s \tau_f$, ϵ_s being the average absorption coefficient of the light, of flux F_s, transmitted by the filters and able to generate singlets i.e. absorbed to some extent. τ_f is the fluorescence lifetime. With a trapped hole density $n_p \sim 5\ 10^{10}$ cm^{-3} (a 3-mm thick crystal with 2750 V applied),§ the HT process falls short by 2 orders of

† This has been verified in details by the present authors for the SS process (unpublished). Verification of this point is generally not explicitly mentioned in other works. The variation of α_{SS} with electric field is small, and would be compatible with geminate recombination, as observed by Batt *et al.* for one-photon photoionization of the ground state (Batt, R. H., Braun, C. L. and Hornig, J. F., *Appl. Opt. Suppl.* **3**, 20 (1969)).

‡ Result (b), and also result (d) would imply that, for some reason, only the photons where a 2E filter has a transmission ~ 0.5 are effective. The corresponding flux $\lesssim 10^{19}$ cm^{-2} s^{-1}. From the observed I and τ_p, this would imply $\sigma_{H\phi}$ (4300Å) $\sim 10^{-15}$ cm^2 plus an Urbach type variation, a clearly irrealistic value.

§ This figure assumes a homogeneous space charge. In one-carrier trap-free space charge current flow, the *free* carrier density is proportional to $x^{-1/2}$ (see Ref. 4, p. 9). We expect the *trapped* and free carrier densities to vary similarly in the presence of a homogeneous density of trapping centers (nowhere saturated). In this case, the simple formulae used here are good to within a factor of 2. If the trapping center density is very inhomogeneous, for instance

magnitude to account for the experimental value $n_c \sim 2.10^8$ cm^{-3}.†

The observed currents, except possibly those at the lowest temperatures, are therefore due to process SH. The density of free holes n_c is with this process:

$$n_c \sim \alpha_{SH} n_s n_p \tau_p \sim \alpha_{SH} \epsilon_s F_s \tau_f n_p \tau_p$$

$\epsilon_s F_s$ is deduced from the measured photon flux and filters transmission and the unpolarized absorption spectrum of anthracene.[7] The active wavelengths lie between 4270 and 4400 Å for which $\epsilon_s F_s$ is estimated to be $\sim 2.10^{18}$ cm^{-3} s^{-1}. This figure is the most uncertain of all the numbers quoted here (one order of magnitude) from which we deduce the order of magnitude of $\alpha_{SH} \sim 10^{-8}$ cm^3 s^{-1}. α_{SH} could be measured with better accuracy only in an experiment where both the light flux and the space charge would be precisely known.

Process SH explains result (a) as all detrapping processes do. Result (b) is explained by the temperature dependence of ϵ_s. Indeed, the 0.30 eV dependence corresponds to $\lambda = 4300$ Å, precisely where one 2E filter absorbs 50% of the light. This is in agreement with result (f) as combinations $B3$ and B are made of stacks of 3 and 4 $2E$ filters respectively. At the same wavelength of 4300, the transmittance of filter A is 80% of that of C, in agreement with result (d) at room temperature.

However, results (c) and (d) *at low temperature* are not explained in this way. Process TH and all double quantum processes remaining excluded, the only process left is hole photodetrapping, that is a

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very large near the electrodes, then we overestimate n_p in the bulk, and consequently we may underestimate the rate constants, although this will be in part corrected by the fact we are dealing with the whole thickness of the crystal. In our case however, there is no sign of such a thing: current transients are typical of bulk generation, and surface trapping does not show up on the strongly absorbed light signals either. Pope *et al.* (Ref. 6) assume a very large inhomogeneity, all the trap charge being concentrated in a region less than 1000Å thick. This might lead then to an underestimated α_{SH}.

† The HT process can also be rejected for two other reasons: (1) It would lead to delayed carrier generation; below room temperature where the macroscopic mobility μ^+ is small, the current returns rapidly to a very low value, and no delayed generation is visible. (2) As $k_{ST} \propto \exp -0.1$ eV$/kT$, result (b) would mean that $\epsilon_s \propto \exp(-0.18$ eV$/kT)$ corresponding to a λ where 2E filters absorb, hence in further contradiction with result (f).

temperature-independent absorption by *ionized* localized center.† Result (e) then implies that photons of $\lambda > 6000$ Å are much less effective in detrapping holes than those of shorter wavelengths. Assuming that $\sigma_{\phi H}$ and $\sigma_{\phi E}$ have similar energy dependence,[1] knowing the transmissions of filters and the wavelength dependence of the lamp flux, the ratio I_A/I_C of the hole photodetrapping currents using A and C filters respectively is calculated to be 0.35. This value is to be compared with the 0.4 found (result (d)).

From our results, we can estimate an approximate value of $\sigma_{\phi H}$, from the current at the temperature (260 °K) where ϕH and SH contributions are comparable, the observed current being twice that predicted by SH alone:

$$\alpha_{SH}\,\epsilon_s F_s \tau_f = \overline{\sigma_{\phi H}}\,\phi$$

where $\overline{\sigma_{\phi H}}$ is a " mean " cross section for all wavelengths in the range 4300–5500 Å. From $F_s/\phi \sim 0.2$ we get $\overline{\sigma_{\phi H}} \sim 5\ 10^{-18}$ cm². This value is less uncertain that our value of α_{SH}, because it does not

† One might argue that low-temperature currents are still due to SH, Urbach tail absorption being at these T negligible compared to temperature-independent absorption by *neutral* localized centers (impurities or imperfections) where singlet excitons are created. But the singlets created by such absorptions are trapped and they first must be detrapped in order to move and interact with the trapped hole. This detrapping is an *activated* process, and as the binding energy is > 0.25 eV (because all higher energy photons are absorbed by the filters) even this process will have a temperature dependence similar to the above considered SH process. In addition, one must assume that the effective wavelengths are those where 34A transmits only a fraction of ND 80% in order to have an overall ratio ~0.4. Hence long wavelengths $\gtrsim$ 4650Å or 2.67 eV would be dominant. The binding energy of such centers for a singlet exciton would then be $\gtrsim$ 0.4 eV, corresponding to a residence time at 250 °K so long that the singlet will never be free and cannot diffuse to a trapped hole.

Energy transfer from the singlet to the hole might also be imagined to proceed through a temperature independent resonance (Forster) process. Assuming that all molecules within 30Å of a hole will transfer their energy to it, each " transfer sphere " contains approximately 400 molecules and around $n_p = 5.10^{10}$ cm^{-3}, these spheres occupy 5.10^{-9} of the total volume. Assuming further that interaction with the hole distorts the energy spectrum of these molecules and depresses their singlet levels strongly enough to raise the absorption coefficient of all these molecules to the unrealistic value of 10^5, the equivalent apparent ϵ is only 5.10^{-4} cm^{-1}, too small to account for the observed currents.

Process SH being unable to explain our results, only process Hϕ can do.

contain the uncertainty on $\epsilon_s F_s$ but only on ϕ (the ratio n_c/n_v is fairly well known).

4. Conclusion

We have shown that trapped holes are made free by photon absorption and singlet quenching in our experiments. The rate constant α_{SH} of hole detrapping by singlet quenching is $\sim 10^{-8}$ cm^3 s^{-1}. This is larger than quoted in Ref. 6, where the presence of a surface barrier may have influenced the results. This is much less than found in Ref. 5. Our results could be reconciled with Ref. 5 only by assuming that $\gamma_{SH}/\alpha_{SH} \sim 5\,10^3$. α_{SH} is, within experimental accuracy, equal to γ_{SS}.

As for photodetrapping, our average value is very similar to that obtained in Ref. 1 for electrons, further evidence of an essentially similar behaviour of hole and electron detrapping. Either the details of the valence and conduction bands structure play no role in the processes studied here, or these structures are very similar.

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3. See Avakian, P. and Merrifield, R. E., *Mol. Cryst.* **5**, 37 (1968).
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