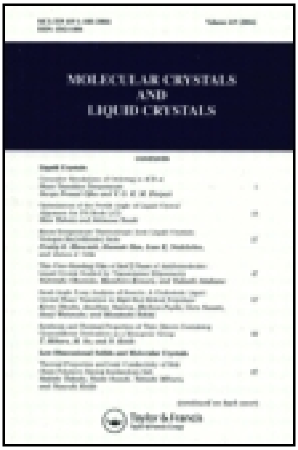

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ON TEMPERATURE DEPENDENCE OF CHARGE PHOTOGENERATION IN MOLECULAR CRYSTALS

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Abstract A simple analytical expression for the charge photogeneration yield (ϕ) is derived which is based on the Onsager theory of geminate recombination. The expression shows non-Arrhenius temperature (T) dependence $\phi \sim \exp(-A/T^{1/2})$ with $A=2(e^2\alpha/4\pi\epsilon\epsilon_0 k)^{1/2}$, where α is a characteristic parameter in the spatial (r) distribution function of thermalized electron-hole pairs $g(r) = (\alpha/4\pi r^2)\exp(-\alpha r)$. The values of α obtained on its basis from the literature experimental data for anthracene crystals are interpreted in terms of collision cross section for primary carriers. The discrete photon energy dependence of α can be explained by crystal anisotropy for the carrier motion.

INTRODUCTION

The charge photogeneration efficiency (ϕ) in molecular crystals is limited by geminate recombination, in which an electron and a hole created in a single ionization event recombine with each other. The usual theory applied to this phenomenon is due to Onsager[1,2] who gave a rigorous analysis of the diffusive motion of a pair of oppositely charged particles in the presence of an external electric field. Although Onsager's analysis is strictly applicable to isotropic media, the

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theory has been applied to highly anisotropic molecular crystals such as anthracene.[3-9] Moreover, despite, generally, non-Arrhenius temperature dependence of ϕ resulting from Onsager's formulation, the Arrhenius type functions have been applied to describe the experimental results.[8,9] The activation energy (E_a) has been ascribed to the Coulombic well of the two attracting carriers. Such an interpretation, justified with the assumption that the pair distribution is described by the δ function $g(r) = (1/4\pi r_o^2)\delta(r-r_o)$, required introduction of an effective, much shorter, thermalization length $r_o = \langle r\rangle = e^2/4\pi\epsilon\epsilon_o E_a$ in the case of more realistic exponential and Gaussian forms of $g(r)$.[8] In addition, two discrete values of E_a in different photon energy ranges must have been discussed in terms of autoionization from specific fixed electronic levels after intramolecular vibronic relaxation.[8,10,11] The importance of analyzing photoionization phenomena within the framework of the distribution functions $g(r)$ allowing a range of thermalization lengths $\langle r\rangle$ has been already pointed out and a complex analytic expression for ϕ derived with an exponential form of $g(r) = (\alpha/4\pi r^2)\exp(-\alpha r)$.[12] Non-Arrhenius type of temperature (T) dependence of ϕ has been found by computation of the infinite series appearing in the solution for ϕ . The steepness of the function $\phi(T)$ increased with the dispersion parameter (α) increasing. The computations have not been compared with experiment and the exponential shape of $g(r)$ not rationalized in terms of physical processes. In the present paper, we derive a much simpler analytic expression for $\phi(F,T)$ in low-field (F) approximation which allows direct determination of the dispersion parameter α from experimental data on temperature dependence of the photogeneration efficiency. Having thus determined the values of α for different photon energy ranges, we speculate on the origin of their discretization. We assume that the exponential distribution $g(r)$ results from hot carrier scattering out of the carrier flux, α^{-1} being the scattering mean free path. Due to anisotropy of the microscopic collision cross section for the carriers the mean free path takes discrete values reflecting anisotropy of the crystal.

THEORY

It can be shown that at low fields, where the Onsager function is truncated at the linear term in F, the carrier quantum yield can be expressed as[8]

$$\phi/\phi_i = 4\pi(1 + 2\beta q)\int_0^\infty \exp(-2q/r)g(r)r^2dr\ , \qquad (1)$$

where ϕ_i is the primary quantum yield in carrier pairs for the absorbed photon and

$$\beta = eF/kT\ , \quad \text{and} \quad q = e^2/8\pi\epsilon\epsilon_o kT\ , \qquad (2)$$

ϵ being the dielectric constant, ϵ_o - vacuum permittivity, e - elementary charge, k - Boltzmann's constant.
The exponential function g(r) leads to[12]

$$\phi/\phi_i = 2(1 + 2\beta q)(2q/\alpha)^{1/2}\,K_1[2(2q\alpha)^{1/2}]\ , \qquad (3)$$

where K_1 is the Bessel function of the first kind. If the Coulombic interaction between pair charges at the thermalization range (α^{-1}) exceeds thermal energy kT (i.e. $2q\alpha > 1$), the Bessel function can be simplified[13] and expression (3) takes the form (see Appendix)

$$\phi/\phi_i \simeq \pi^{1/2}(2q\alpha)^{1/4}(1 + 2\beta q)\exp[-2(2q\alpha)^{1/2}]\ . \qquad (4)$$

The fraction of the initial quantum yield that escapes geminate recombination at zero applied field is thus given by

$$\phi(0)/\phi_i = \pi^{1/2}(2q\alpha)^{1/4}\exp(-A/T^{1/2})\ , \qquad (5)$$

where

$$A = 2(e^2\alpha/4\pi\epsilon\epsilon_o k)^{1/2}\ . \qquad (6)$$

Since the preexponential factor is only a slightly varying function of temperature, we are justified in defining A by

$$A \simeq -\frac{d\ln[\phi(0)/\phi_i]}{d(1/T^{1/2})}\ . \qquad (7)$$

COMPARISON WITH EXPERIMENT AND DISCUSSION

Over the temperature range 200 - 300K, a plot of the experimental data of Chance and Braun[8] both in the form ln $\phi(0)$ against $T^{-1/2}$ and ln $\phi(0)$ against T^{-1} gives a straight line as shown in Fig.1.

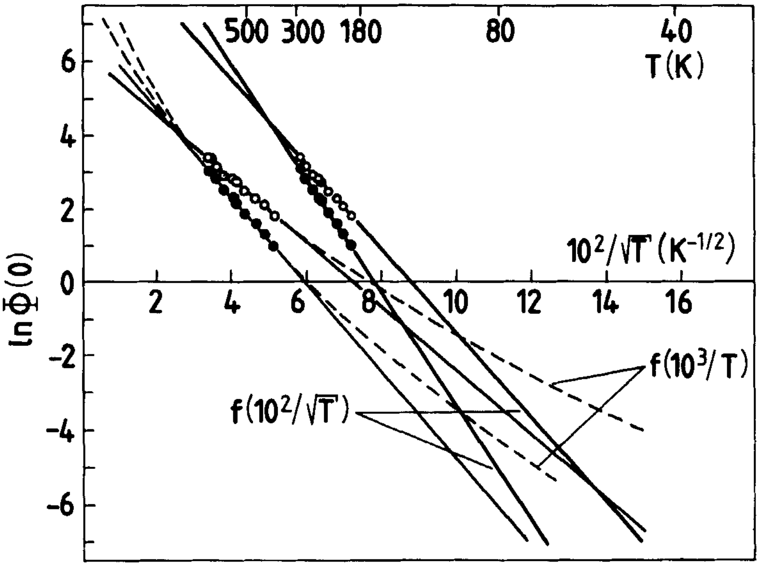

FIGURE 1 Natural logarithm of the experimental carrier yield (arbitratry units) versus reciprocal square root of the temperature f($10^2/\sqrt{T}$) and reciprocal temperature f(1000/T) for anthracene crystal. Open circles correspond to the excitation wavelength λ_{ex} = 210nm and full circles to λ_{ex} = 280 nm (From Chance and Braun[8]).

It is evident that a difference between Arrhenius f(1000/T) and non-Arrhenius f($100/T^{1/2}$) behaviour of $\phi(0)$ could be apparent below 200K, that is behind the lower limit of the temperature range possible from the existing experimental data. According to Eqn.(7) the slope of the straight line plot of f($100/T^{1/2}$) can be obtained and α determined using Eqn.(6). A - and therefore α - is essentially a constant over two substantial ranges in photon energy 4.4 - 5.2 eV (280 - 240 nm) and 5.4 - 6.2 eV (230 - 200 nm) (see Table I). We suggest these results as arising from the anisotropy of the carrier motion. If $\alpha^{-1} = \Delta$ is identified with the mean free

TABLE I Measured and calculated model parameters

Wavelength range	Calculated quantity / Measured quality	$\frac{1}{\alpha} = \Delta$ [Å]	$\sigma = \frac{1}{N_o\Delta}$ [Å²]	σ_{mol} [Å²]
I (200-230nm)	$\alpha_1 = 6.6\times10^8\ m^{-1}$	15.2	15.7	14.6
II (240-280nm)	$\alpha_2 = 1.2\times10^9\ m^{-1}$	8.3	28.7	29.2

path for carrier collision with anthracene molecules, the microscopic collision cross section $\sigma = (N_o\Delta)^{-1}$ can be defined, where $N_o = 4.2\times10^{21}$ cm^{-3} is the average concentration of the molecules. The two values of Δ: Δ_1 and Δ_2 correspond to different values of σ characteristic for the area screened by the molecular projections on the c' and b crystallographic directions, respectively. They are strictly related to the dimensions of anthracene molecule:[14] $\sigma_{1mol} \simeq 3.4\times4.3$ Å² = 14.6 Å² and $\sigma_{2mol} \simeq 3.4\times8.6$ Å² = = 29.2 Å² (see Table I). We note that the preferential directions of the carrier motion are determined by both intermolecular distance and σ; the probability for the carrier transmission along the particular crystallographic directions in anthracene are given by $P(a) = \exp(-a/\Delta_a) = \exp(-8.56$ Å$/6.5$ Å$) = 0.27$, $P(b) = = \exp(-b/\Delta_b) = \exp(-6.04$ Å$/8.3$ Å$) = 0.73$ and $P(c) = \exp(-c/\Delta_c) = = \exp(-11.16$ Å$/15.2$ Å$) = 0.48$. $\Delta_i = (N_o\sigma_i)^{-1}$ with $i = a,b,c$ has been used in the above evaluation. Due to energy reasons the motion of hot carriers along the b direction prevails in excitation region I and along c' direction in excitation region II. Such a picture of the carrier thermalization process justifies an exponential shape of the distribution function g(r) which corresponds to the exponential decay of the primary current that results from carrier scattering out of the hot carriers flux.

APPENDIX

In deriving Eq. (4), we have approximated the Bessel function[13]

$$K_1(z) = (\pi/2z)^{1/2}\, e^{-z} \left[\sum_{k=0}^{n-1} \frac{1}{(2z)^k} \frac{1}{k!} \frac{\Gamma\left(\frac{3}{2} + k\right)}{\Gamma\left(\frac{3}{2} - k\right)} \right] \tag{A1}$$

by

$$K_1(z) \approx (\pi/2z)^{1/2} \exp(-z) \ , \tag{A2}$$

where $z = 2\sqrt{2q\alpha}$ and Γ denotes the gamma Euler function. Such an approximation is possible for $z \gg 1$ and $k = 0$, when the $k > 0$ terms in the series on the right-hand side of Eq. (A1) can be neglected. The condition $z \gg 1$ requires $\alpha \gg \pi\epsilon\epsilon_0 kT/e^2$ which for anthracene (ϵ = 3.2) and at room temperature ($kT \approx 0.025$ eV) gives $\alpha \gg 1.4\times10^5$ cm^{-1} or $\Delta = \alpha^{-1} \ll 700$ Å. This limiting value of Δ is much larger than the Onsager radius (~200 Å) and thus the approximation can be safely applied for $T < 300$ K.

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