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Charge-Carrier Generation in Anthracene by the Singlet-Singlet Collision-Ionization Process and the Singlet Photoionization Process

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Charge-Carrier Generation in Anthracene by the Singlet-Singlet Collision-Ionization Process and the Singlet Photoionization Process

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The numbers of photocarriers for the singlet–singlet collision-ionization and the singlet photoionization processes are separately determined at wavelengths between 400–430 nm by making use of the difference between the a- and b-polarized absorption coefficients. The relative number of carriers generated by the singlet photoionization process increases with an increase of wavelength. The contributions of the two processes balance at about 410 nm. The singlet-photoionization cross-section at 423 nm is estimated at $3 \times 10^{-(18 \pm 1)}$ cm^2.

1 INTRODUCTION

It is accepted that when the anthracene crystal is irradiated at the first singlet absorption band, charge carriers are intrinsically produced by two double-quantum processes: one is the singlet–singlet collision-ionization (SC) process[1,2] and the other the singlet photoionization (SP) process.[3,4] According to Braun,[1] the dominant carrier-generation in the wavelength range below 390 nm is due to the SC process, while Kepler[3] pointed out that carrier generation in the range of 410–440 nm could be reasonably explained by the SP process, rather than by the SC process. The interval of 390–410 nm, therefore, can be considered to be an intermediate range where the observed number of carriers is the sum of the carriers produced by the SC and SP processes.

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There has been no attempt to determine the number of carriers for each process in this wavelength range. There is a distinct difference between the SC and SP processes in the dependence of the carrier generation on the penetration depth of the incident light.[5] Therefore, the determination of the carrier number for each process can be made by analyzing the carrier number in terms of the absorption coefficient of the crystal k at a fixed excitation wavelength. It is achieved by making use of the difference between k values for the a- and b-polarized lights. In the present paper, we first present a method for separately determining the carrier numbers for the two processes and then present the spectral distribution of the ratio of the number of carriers produced by each process to the total number of carriers observed in the range 400–430 nm.

2 EXPERIMENTAL

The anthracene single crystals were kindly supplied by I. Nakada. A method for preparing the crystals was described previously.[6] Photoconductivity measurements were made at room temperature by the same method as described by Nakada *et al.*[6] The crystal was sandwiched between two transparent blocking electrodes in an argon atmosphere.

Light pulses were obtained from an air-spark flash lamp. The duration of each pulse was about 1 μsec. Relative light-intensity was measured with a phototube (Toshiba PV 34). The light intensity was changed by neutral density filters. Monochromatic lights with half widths of about 10 nm were obtained using interference filters.

Charge carriers were produced when a monochromatic light pulse was incident on the cleaved ab-face of the crystal through one of the electrodes. A voltage appeared across a serial loaded resistor R of several tens of kilo-ohm under the applied field of about 10^3–10^4 volt/cm. The time dependence of this voltage was displayed on an oscilloscope (Iwatsu MS 5013). All measurements were made with the illuminated side of the crystal at a negative potential. The number of carriers produced N can be expressed as $N = vt_t/eR$, where t_t is the transit time of electrons, e the electric charge and v the initial voltage estimated by the extrapolation of the voltage-time trace to the onset.

3 DETERMINATION OF THE CARRIER NUMBER FOR EACH PROCESS

In this section, let us confine discussions to the framework of the double-quantum generation, which is of interest to us.

When a monochromatic light-pulse is incident on the crystal and the light-pulse duration t_d is much longer than the singlet exciton lifetime t_f ($\simeq 2 \times 10^{-8}$ sec),[7] the density of singlet excitons $n(x)$ in steady state is expressed by[1]

$$n(x) = kt_f L(1 - W)\exp(-kx), \tag{1}$$

where L is the light intensity in photons/cm^2 sec, W the crystal reflectivity[8] and x the depth measured from the illuminated surface of the crystal. The numbers of carriers generated by the SC and SP processes, denoted as N_{SC} and N_{SP}, respectively, are given by the following expressions:[5]

$$N_{\text{SC}} = Apt_f k,\ N_{\text{SP}} = Aq, \tag{2}$$

where

$$A = \tfrac{1}{2}t_f t_d SL^2(1 - W)^2(1 - \exp[-2kd]). \tag{3}$$

Here, p and q are the rate constant for the SC process and the cross-section for the SP process, respectively, and S and d the illuminated surface area and the thickness of the crystal, respectively. The total number of carriers generated by the double-quantum processes N_d is given by the sum of simultaneous contributions from the SC and SP processes:

$$N_d = N_{\text{SC}} + N_{\text{SP}}. \tag{4}$$

The ratio of each contribution to N_d is simply given by a function of q/p and k:

$$r_{\text{SC}} = 1 - r_{\text{SP}} = \frac{N_{\text{SC}}}{N_d} = \left(1 + \frac{q}{pt_f k}\right)^{-1}. \tag{5}$$

Hence, it can be calculated using a known value of k[9] if q/p is determined.

Let us denote N_d for the a- and b-polarized lights as N_d^{a} and N_d^{b}, respectively. If q and p are both independent of the polarization of the incident light, they are expressed by $N_d^{\text{i}} = A^{\text{i}}(pt_f k^{\text{i}} + q)$, where i = a and b, respectively, and $A^{\text{i}} = (1/2)t_f t_d SL^2(1 - W^{\text{i}})^2(1 - \exp[-2k^{\text{i}}d])$. Here, W^{i} is the reflectivity for an i-polarized light. Accordingly, it follows that

$$\frac{p}{q} = \left(k^{\text{b}}\frac{N_d^{\text{a}}}{A^{\text{a}}} - k^{\text{a}}\frac{N_d^{\text{b}}}{A^{\text{b}}}\right)t_f \bigg/ \left(\frac{N_d^{\text{b}}}{A^{\text{b}}} - \frac{N_d^{\text{a}}}{A^{\text{a}}}\right). \tag{6}$$

Here, p and q are given as follows:

$$p = \left(\frac{N_d^{\text{b}}}{A^{\text{b}}} - \frac{N_d^{\text{a}}}{A^{\text{a}}}\right)\bigg/ t_f(k^{\text{b}} - k^{\text{a}}),\ q = \left(k^{\text{b}}\frac{N_d^{\text{a}}}{A^{\text{a}}} - k^{\text{a}}\frac{N_d^{\text{b}}}{A^{\text{b}}}\right)\bigg/(k^{\text{b}} - k^{\text{a}}). \tag{7}$$

Thus, q/p can be determined if the values for N_d^i/A^i, (i = a, b) are obtained experimentally in an arbitrary unit. The value of q/p obtained permits us to separate the observed N_d into the two parts N_{SC} and N_{SP} according to the following equation:

$$N_{SC} = N_d - N_{SP} = N_d r_{SC} = N_d\left(1 + \frac{q}{pt_f k}\right)^{-1}. \tag{8}$$

It might be necessary here to discuss the assumption that p and q do not depend on the polarization of the excitation light. In the first singlet-exciton band of the anthracene crystal, the light absorption produces excitons in the a- and b-polarized electronic states separated by the Davydov splitting.[10] Two relaxation processes should be considered.[11] One is the vibrational-relaxation process within the a- or b-polarized state and the second the radiationless-transition process between the a- and b-polarized states. Both these processes take place in a time much shorter than the radiative decay time of the singlet exciton t_f.(11–14) The Davydov splitting is known to be about 190 cm^{-1} at most between the a- and b-polarized states relaxed vibrationally.[8] Therefore, the two relaxations will quickly lead to the population of singlet excitons in the thermal equilibrium between these two relaxed polarized states during the radiative exciton-decay.[13] In the SC process, two singlet excitons in the thermal equilibrium collide to yield a pair of free electron and free hole. It is reasonable to assume that the rate constant for the SC process p is independent of the polarization of the excitation. On the other hand, in the SP process, singlet excitons in the equilibrium state are optically ionized. The cross-section for ionizing these excitons by the a-polarized light is not necessarily identical with that by the b-polarized light. The state to which the singlet excitons are optically excited, however, corresponds to the very high-energy level close to the crystal-ionization state and will be a broad continuum in a fairly isotropic crystal state.[15] Therefore, the cross-section for the SP process q should be practically independent of the polarization.

4 RESULTS AND DISCUSSION

Charge carriers (i.e., free electrons) were generated by illumination of polarised, monochromatic light pulses at several wavelengths between 400–430 nm. Photocarriers often include those produced by extrinsic single-quantum processes such as the singlet-surface process.[16] The change in the observed carrier number N with attenuating the incident light was analyzed in order to exclude a contribution from the single-quantum generation from N. If N/r is plotted against r, the value of N_d, which we need, can be obtained from the gradient of the N/r versus r curve, because $N/r = N_d r + N_s$. Here

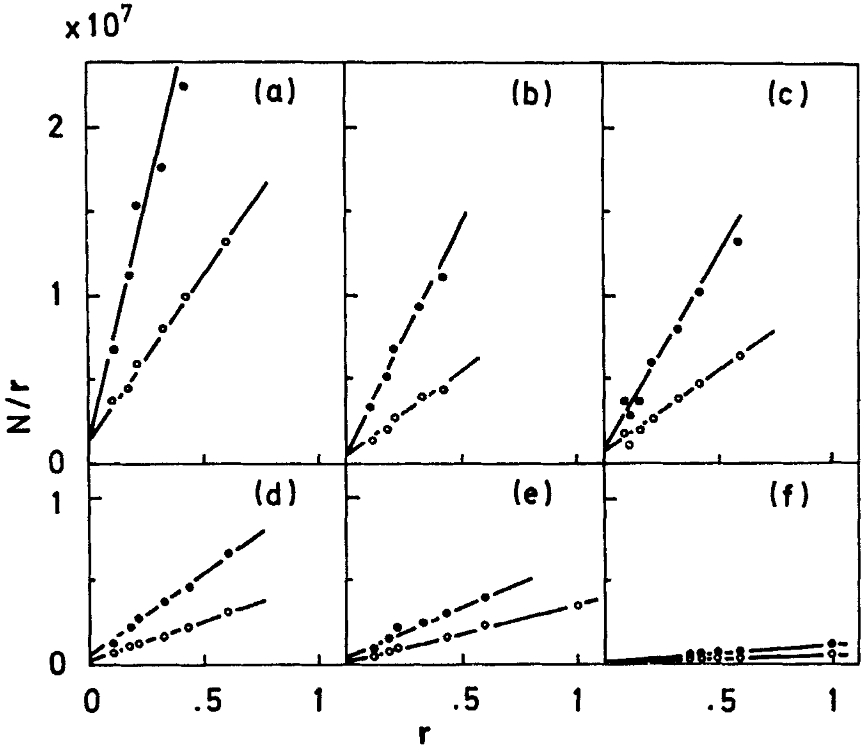

FIGURE 1 The plots of N/r against the attenuation factor r for the a- (filled circles) and b-polarizing directions (open circles) of monochromatic lights: (a) λ = 401.4 nm; (b) 407.0 nm; (c) 410.1 nm; (d) 412.8 nm; (e) 415.6 nm; (f) 422.0 nm.

r is the attenuation factor by which the incident light is reduced and N_d and N_s the numbers of carriers for $r = 1$ generated by the double- and single-quantum processes, respectively. Experimental N/r versus r curves obtained for an 0.044 cm thick crystal, are shown in Figure 1. The wavelength of the incident light λ was estimated as the reciprocal of the average wave-number of photons absorbed within the crystal.

The value for q/p can be now calculated at each wavelength from Eq. (6). In order to take into account the spectral broadness of the incident light, the effective values for A^i and k^i were evaluated by integrating over the energy spectrum of the incident light. The values for q/p obtained are plotted against λ in Figure 2, together with the values for p and q obtained from Eq. (7). It appears that p is nearly constant over the wavelength range and q and q/p increase with a decrease of λ. The spectral distributions of r_{SC} and r_{SP} were determined from Eq. (5) using the plot of q/p versus λ (Figure 2) and the

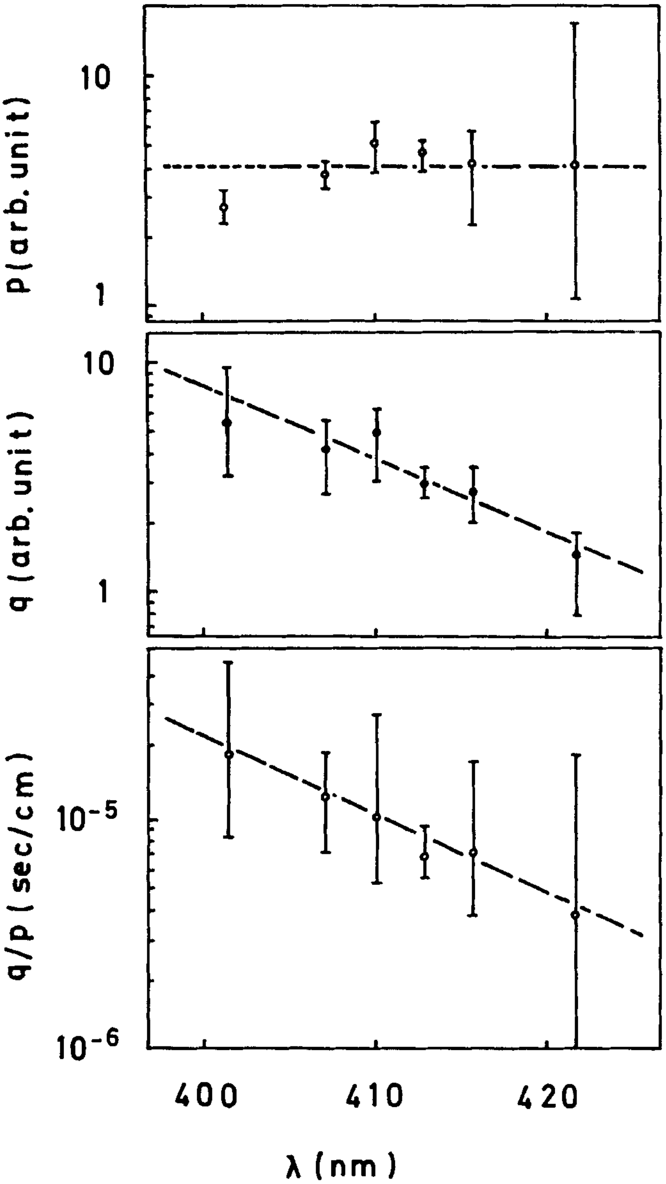

FIGURE 2 The plots of p, q and q/p against wavelength λ, where p and q are the rate constant for the SC process and the cross-section for the SP process, respectively.

values for k^a and k^b.[9] Figure 3 shows the values for r_{SC} thus obtained. Here, the expression of r_{SC} for the unpolarized light was derived by using $n(x) = (\frac{1}{2})t_f L \sum_i^{a,b} (1 - W^i)k^i \exp(-k^i x)$ in place of Eq. (1). In this case, the value for r_{SC} varies slightly with d·in the longer wavelength range. The following results were then obtained: (1) the relative contribution of the SP process r_{SP} to the double-quantum generation increases with an increase of the wavelength; (2) r_{SC} is of the comparable order of magnitude with r_{SP} in the

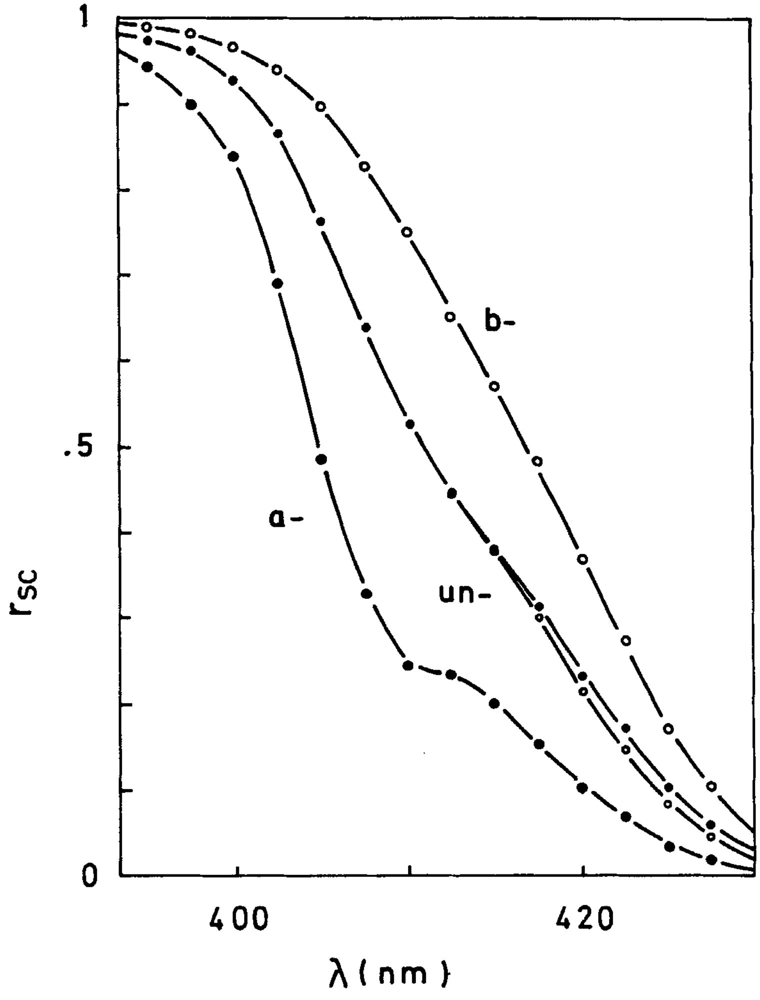

FIGURE 3 The spectral distribution of the relative contribution of the SC process r_{SC} to the double-quantum generation: ○ for the a-polarized light; ● for the b-polarized light; ◦ for the unpolarized light, d = 1 cm; • for the unpolarized light, d = 0.01 cm.

range of about 400–420 nm; (3) the wavelength where the contributions of the two processes balance is about 405–415 nm; (4) for the unpolarized light, r_{SC} exceeds 90% in the range where $\lambda \lesssim 400$ nm, while r_{SP} exceeds 90% in the range where $\lambda \gtrsim 425$ nm.

The p value obtained by Braun[1] has been reported as $0.9 \times 10^{-(12 \pm 0.4)}$ cm^3/sec for $\lambda < 390$ nm. Applying this p value to the present result of q/p (Figure 2), we can estimate the q value. The value q obtained from $q/p = 3.8 \times 10^{-(6 \pm 0.8)}$ sec/cm at $\lambda = 423$ nm is about $3 \times 10^{-(18 \pm 1)}$ cm^2. This value q agrees with the values (0.5×10^{-8} cm^2) evaluated previously by Kepler[3] at 425 nm and by Strome[17] at 421 nm.

As is shown in Figure 2, the rate constant for the SC process p is practically independent of the excitation wavelength. In order to obtain this result, we have assumed that p and q do not depend on the polarization of the excitation light. We introduced this assumption on the basis of the argument that the light absorption always results in the identical thermal population of singlet excitons between the two polarized electronic state regardless of the excitation energy and its polarization (see the Section 3). If this argument is reasonable, it leads to a natural consequence that p does not depend on the excitation wavelength as well as on its polarization. Therefore, the above result for p might imply that our assumption is reasonable.

We have shown the method for separately determining the carrier numbers for the SC and SP processes. Carrier generation by the double-quantum process has been often observed not only in the anthracene crystal but also for example in the α-sulphur crystal.[18] The present method proposed is applicable to the latter crystal if only the following assumption is valid for this crystal: p and q are both independent of the polarization of the excitation.

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