JETP LETTERS VOLUME 10, NUMBER 5 5 SEPTEMBER 1969

PHOTOIONIZATION OF SINGLET MOLECULAR EXCITATIONS IN SOLUTIONS OF AROMATIC CARBOHYDRATES

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Submitted 8 July 1969; resubmitted 7 August 1969
ZhETF Pis. Red. 10, No. 5, 205 - 209 (5 September 1969)

The use of giant laser pulses has made it possible to investigate processes in which short-lived molecular states interact with photons. In [1, 2] they observed the ionization of singlet excitons in anthracene crystals by ruby-laser photons; the cross section of this ionization was 10^{-21} cm^2, in satisfactory agreement with the cross section of the transition to the conduction band. In the case of solutions, ions can be produced both by optic transitions to the solvent band and by optic transitions from the lowest excited singlet level to the higher ones, with subsequent nonradiative ionization, if the levels of the higher singlet excitations lie above the bottom of the conduction band.

To study this process, we investigated simultaneously the fluorescence and the photoeffect in a solution of pyrene in tetrahydrofuran under the influence of giant ruby-laser pulses. Pyrene solutions of 3×10^{17} cm^{-3} concentration were excited by pulses of 30 nsec duration with peak intensity from 4×10^{24} to 2×10^{25} cm^{-2} sec^{-1}. The solution preparation procedure will be described in another article. The fluorescence pulses were measured with the aid of a microsecond signal accumulator described in [3]. The photocurrent pulses were registered with an ordinary oscilloscope. The excitation, fluorescence, and photocurrent pulse waveforms are shown in Fig. 1. The electric field intensity was chosen to be high enough to eliminate the recombination of the formed molecular ions. The fluorescence intensity was proportional to the square of the light intensity ($I \sim L^2$), and the photocurrent was $i_{ph} \sim L^n$, with $n = 2.6 \pm 0.3$ (Fig. 2). The fluoresence decay time, 300 ± 50 nsec, was in good agreement with the lifetime of the lowest singlet excitation [4]. The peak concentration of the singlet excitations, determined from the fluorescence intensity, amounted to $(1 - 5) \times 10^{11}$ cm^{-3}. The production of these excitations, according to [5], is due to two-photon absorption. The coefficient of this absorption, obtained from the given value of the concentration, equals $\delta = (1.5 \pm 1.0) \times 10^{-50}$ cm^4 sec^{-1}, which agrees with measurements of δ in anthracene [6]. The carrier density determined from the value of i_{ph} and from the mobility ($\mu = 2 \times 10^{-4}$ cm^{2}V^{-1} sec^{-1}) equals $(1 - 1.5) \times 10^{10}$ cm^{-3} at maximum intensity. Since the light pulse duration (t_u) is shorter than the lifetime of the singlet excitations, their concentration is equal to:

$$n_s = \delta n_0 L^2 t_u, \tag{1}$$

where δ is the coefficient of two-photon absorption and n_0 is the concentration of the molecules in the solution. Assuming that the carriers are produced by photoionization of singlet excitations, their density equals

$$n = (1/2) \delta \sigma_s n_0 (F^3/t_u), \tag{2}$$

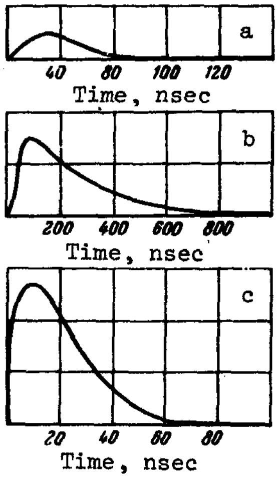

Fig. 1. Excitation (a), fluorescence (b), and photocurrent pulses (c). The photocurrent decrease time corresponds to the time of flight.

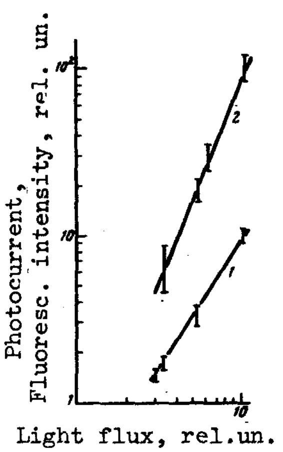

Fig. 2. Fluorescence intensity (1) and photocurrent maximum (2) vs. light intensity.

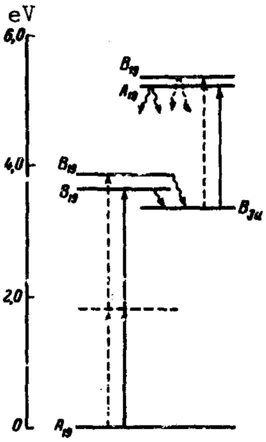

Fig. 3. Scheme of carrier production in pyrene solution under the influence of laser pulses.

where F is the total number of photons per pulse and σ_s is the photoionization cross section. According to (2), the carrier density is inversely proportional to the light pulse duration at equal energy. Different values of t_u were obtained by varying the generation conditions (the optical density of the passive shutter and the resonator length). When t_u was changed from 30 to 80 nsec, the value of n/F^3 decreased by a factor 1.5 - 2.5, which is in satisfactory agreement with the hypothesis that the carriers are generated by photoionization of singlet excitations.

For another generation mechanism, namely direct three-photon ionization ($n \sim (F^3/t_u^2)$), this decrease whould be larger by 2.5 - 3 times. In a third possible generation mechanism, photoionization of triplet excitations produced by ST conversion, n is independent of t_u:

$$n = (1/6)\phi_T \delta \sigma_T n_0 (F^3/\tau_s)\,, \tag{3}$$

where ϕ_T is the quantum yield of the ST conversion and σ_T is the cross section for the photoionization of the triplet excitations. When the laser operates in the free running mode (total pulse energy 20 times larger than in the Q-switching mode, pulse duration 5 x 10^{-4} sec, and $\tau_T > t_u > \tau_s$)(the lifetime of the triplet excitations in these solutions is 1.2 x 10^{-3} sec), we have for this mechanism

$$n > (1/2)\phi_T \delta \sigma_T n_0 (F^3/t_u). \tag{3'}$$

The > sign is due to the presence of spikes in the laser pulse in this mode, causing the true illumination time to be shorter than t_u. According to (3) and (3'), the photocurrent in the free-running mode should be more than 15 times the current in the Q-switching mode. The experimentally observed current, however, was smaller by a factor of 5, which also corresponds to photoionization of singlet excitations.

The cross section σ_s for the ionization of singlet excitations, obtained from (2), amounts to (0.5 - 2) x 10^{-18} cm^2, which is much higher than the corresponding value for anthracene. According to a calculation of the levels of the pyrene molecule [2], two-photon transitions to the B_{1g} levels are allowed. The lifetimes at these levels are quite small compared with t_u. It follows also from the fluorescence spectra [5] and from the fluorescence decay time, that in the case of two-photon absorption excitations are accumulated at the lower singlet excited level of symmetry B_{3u}. Single-photon transitions from this level are allowed at the levels A_{1g} and B_{1g}. The energy of the ruby-laser quantum is close to the energy difference between B_{3u} and these levels. Consequently, the corresponding transitions are possible and have cross sections close to the resonance ones. Judging from the fact that the ion production is observed in triplet-triplet annihilation (the energy of the lowest triplet state of pyrene is 2.1 eV), the energy of production of molecular ions in tetrahydrofuran does not exceed 4.2 eV. The obtained values of the ionization cross section show that the probability of production of molecular ions by nonradiative deactivation of the higher excited states of pyrene with approximate energy 5 eV is quite high. The complete scheme of the process is shown in Fig. 3. The fact that the indicated singlet transitions are allowed, together with the large probability of the subsequent ionization, accounts for the high value of σ_s.

Such values of σ_s make it possible, in principle, to change the relative concentrations of the molecular ions and of the excited molecules by changing the intensity of the light. If these states are active centers that realize various chemical-reaction channels, then it is possible to obtain directed chemical transformations with the aid of lasers.

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CONCERNING AN EXPERIMENTAL VERIFICATION OF THE SELF-CONSISTENT POTENTIAL FOR 4f ELECTRONS OF RARE-EARTH ATOMS

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Submitted 8 July 1969
ZhETF Pis. Red. 10, No. 5, 209 - 213 (5 September 1969)

In the case of the 4f electrons in the rare-earth region, self-consistent calculations of many-electron atoms, performed within the framework of the Hartree [1], Hartree-Fock-Slater [2], and Dirac-Slater [3] methods, lead to effective potentials (self-consistent + centrifugal) with two minima (Fig. 1). These correspond to two possible states of the 4f electron, with nearly equal energies but with greatly differing (by an approximate factor of 20) mean radii (external and internal "collapsed" states [1]). This situation, which is curious in itself, explains many unusual properties of rare-earth metals, particularly the so called isomorphic phase transition in cerium. At the same time, although the models used to obtain the results