

Time-resolved photoconductivity in the phenanthrene-PMDA CT complex: Evidence for thermal dissociation of singlet CT excitons^{a)}

Marek Samoc,^{b)} Elizabeth L. Kennell and Charles L. Braun
Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

(Received 29 June 1987; accepted 24 September 1987)

A multitude of physically and biologically important processes involve separation of a charge pair created on nearby molecules. Examples of such processes include photostimulated charge transfer across an interface and, as in the present case, optical production of charge transfer (CT) excited states. The intermediate in each process is a charge transfer pair consisting of an electron localized on an acceptor molecule and a hole on the donor molecule. Such CT pairs may be formed either by direct absorption or by energy transfer from higher energy states of locally excited donor or acceptor molecules.

It has been pointed out recently¹ that the photogeneration of free charges from heteromolecular CT pairs may differ from that in one-component materials.^{2,3} Because such CT states are often the lowest energy singlet electronic excitations of the system, their lifetimes can be as long as 10^{-8} s and more. The long-lived CT states are formed by relaxation of the vibrationally or electronically excited states produced by light absorption or energy transfer. It has, however, been argued that *nonrelaxed* CT states are more likely precursors of photocarriers than the *relaxed* states because the excess energy of the former may be used to facilitate dissociation. Yokoyama *et al.*⁴ proposed that a higher excited CT state plays a dominant role in photogeneration in doped poly-*N*-vinylcarbazole. Sebastian *et al.*⁵ assumed that nonrelaxed CT state thermalization is the pathway to producing large radius geminate pairs in anthracene-like photoconductors.

We approached the question of unrelaxed versus relaxed precursors by investigating the kinetics of the photocurrent rise upon pulse excitation in the 1:1 complex phenanthrene-PMDA which is known^{6,7} to be photoconductive. We measured a CT exciton lifetime of 11 ns; all nonrelaxed excited states should be much shorter lived. One may thus expect that a measurement of photocurrent risetime with nanosecond resolution should unambiguously indicate whether the relaxed exciton is the precursor of any photocarriers which are observed.

The experiment used a Molelectron DL-II dye laser pumped by a Molelectron UV24 nitrogen laser as the source of pulses of 7 ns half-width. Phenanthrene-PMDA samples were prepared as polycrystalline thin films⁶ between quartz disks equipped with SnO_x conducting strips. A simple FET follower was used for driving the cable connecting the sample holder to a Tektronix 2467 scope fitted with a DS01 digitizing camera. An IBM XT personal computer collected the data as well as performed most of the fitting procedures. In order to keep the electronics risetime below about 2 ns, it was necessary to limit the input resistance of the FET follower to values in the range 100 to 400 Ω depending on the capacitance of the sample. Signals were averaged by collecting a

certain number (usually 12) of single-shot photocurrent transients and the same number of transients with the light path blocked. The photocurrent signals were then added together and the background signals subtracted.

To interpret the experimental transients we assume that an intermediate *S* is produced upon absorption of a light pulse of intensity $I(t)$ and that this intermediate, characterized by a lifetime τ_S , dissociates to give charge carriers whose lifetime is τ_c . Solutions of the appropriate system of two differential equations were used to fit the values of the parameters τ_S and τ_c to the transients obtained for phenanthrene-PMDA at wavelengths in the range 337 to 520 nm. The $I(t)$ dependence needed for the convolution was measured using a fast photodiode.

Figure 1 shows a transient recorded using 440 nm light and the best-fit theoretical curve. As can be seen, the least-squares lifetime of the intermediate ($\tau_S = 10.9$ ns) is in very good agreement with the 11 ns lifetime of the lowest CT singlet of phenanthrene-PMDA. In a series of measurements over the whole spectral range, we observed about 20% scatter of τ_S but no obvious wavelength dependence. Similar transients were obtained for both negative and positive voltages applied to the front electrode, i.e., for predominant transport of electrons and of holes. Thus, these measurements provide direct evidence that the photogeneration process in phenanthrene-PMDA involves dissociation of the *relaxed* CT singlet. Even at photon energies more than 1 eV above the energy of the relaxed CT state as well as for excitation of the local donor singlet state, radiationless decay of the lowest CT state and subsequent CT state dissociation appear to prevail over ionization of unrelaxed states.

We also observed fast risetimes of the photocurrent in

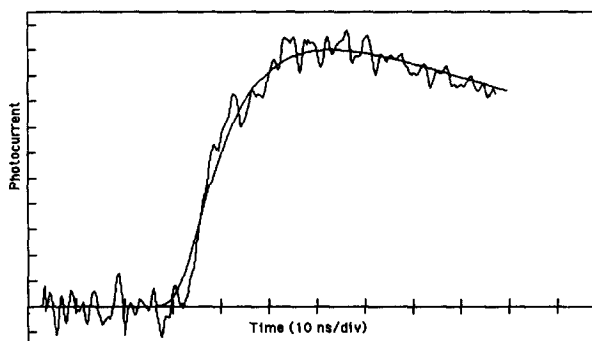


FIG. 1. Photocurrent transient obtained at room temperature for an approximately 80 μm thick phenanthrene-PMDA sample excited at 440 nm with a 500 μJ pulse (about 10^{24} photons/cm² s). — 400 V was applied to the front electrode. The peak photocurrent is about 83 μA . The smooth line is the least-squares fit with the parameters $\tau_S = 10.86$ ns and $\tau_c = 149.7$ ns.

phenanthrene-PMDA. At light intensities higher than those used to obtain Fig. 1, the signal shape changes and is characterized by a much faster rise time. Attempts to fit those transients usually produce values of 1 to 4 ns as the lifetime of the intermediate, i.e., values near the time resolution capability of our circuitry. Such signals appear to be composed of two components: a slow component which is described by a rise-time equal to that of the low-intensity signals and a fast component (some contribution of this fast component can also be seen in the rising part of the transient shown in Fig. 1). We tentatively attribute the fast risetime component to a two-photon process. Lowering the light intensity (even by defocusing the light pulse and keeping the number of photons constant) reduces the magnitude of the fast component much faster than it does the total charge produced. The presence of the fast photogeneration process is obviously a complication that reduces considerably the range of light intensities at which useful measurements can be performed. At the same time, however, observation of the fast component proves that the time resolution of our system is sufficient to resolve accurately the slower risetimes of the signals at lower light intensities.

The shape of the decaying part of the photocurrent signal depends both on the light intensity and on wavelength. We thus conclude that the calculated carrier lifetimes τ_c do not reflect only first-order trapping but are more likely controlled by recombination of charge carriers. Indeed, in some

cases (especially at high light intensities), better fits could be obtained by assuming that the carrier population decays according to second order kinetics.

In conclusion, our measurements provide clear evidence that thermal dissociation of relaxed, singlet CT excited states is the dominant charge carrier photogeneration process in the phenanthrene-PMDA system. Preliminary data for other two-component systems indicate that such behavior is not unique to phenanthrene-PMDA.

^{a)} Grant DE-FG02-86ER13592 from the Department of Energy provided partial support for this work.

^{b)} On leave from Institute of Organic and Physical Chemistry, Technical University of Wrocław, Poland.

¹C. L. Braun, *J. Chem. Phys.* **80**, 4157 (1984); M. Samoc and D. F. Williams, *ibid.* **78**, 1924 (1983).

²R. R. Chance and C. L. Braun, *J. Chem. Phys.* **64**, 3573 (1976); K. Kato and C. L. Braun, *ibid.* **72**, 172 (1980).

³M. Pope and C. Swenberg, *Electronic Processes in Organic Crystals* (Oxford University, London, 1982); E. A. Silinsh and A. J. Jurgis, *Chem. Phys.* **94**, 77 (1985).

⁴M. Yokoyama, Y. Endo, A. Matsubara, and H. Mikawa, *J. Chem. Phys.* **75**, 3006 (1981); M. Yokoyama, S. Shimokihara, A. Matsubara, and H. Mikawa, *ibid.* **76**, 724 (1982).

⁵L. Sebastian, G. Weiser, G. Peter, and H. Baessler, *Chem. Phys.* **75**, 103 (1983).

⁶H. Moehwald, D. Haarer, and G. Castro, *Chem. Phys. Lett.* **32**, 433 (1975).

⁷D. Haarer, *Festkoerperprobleme*, **20**, 341 (1980).

Dynamics and spectroscopic manifestations of two-photon bound-bound absorption through a repulsive intermediate state

Leping Li, Robert J. Lipert, Haiyoon Park, William A. Chupka, and Steven D. Colson
Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut 06511

(Received 28 August 1987; accepted 29 September 1987)

The work by Heller *et al.*¹ on the time-dependent theory of Raman scattering provides a simple physical picture which separates the static effects, due to the coordinate dependence of the electronic transition dipole, from the dynamic effects that arise from wave packet propagation on the Born-Oppenheimer surfaces. These concepts have been aptly applied by Kinsey and his co-workers to the study of emission spectroscopy of dissociating molecules as a means of probing details of dynamics in extremely short-lived species.²

Both the theory and experiment can be extended to two-photon absorption between two bound states through a repulsive intermediate state, since Raman scattering is just a special case of a two-photon process. In this extension, the wave packet dynamics on the repulsive potential surface will be probed by projection of the evolving wave packet into the discrete levels of an excited, instead of ground, state. At the

same time, the wave packet propagation on the repulsive potential surface will enable us to obtain information about excited bound states in regions which are normally inaccessible due to unfavorable Franck-Condon factors.

To apply this idea we have recently carried out an experiment on the Cl₂ molecule by a 2 + 1 multiphoton ionization process in which the first photon falls into a fairly strong repulsive continuum but far from any effective bound transfer state. A detailed spectroscopic analysis will be given in a separate paper.³ Here we focus on the role of the repulsive state as an intermediate in a two-photon, bound-bound transition, and illustrate a conceptually intuitive connection between the spectroscopic features and the underlying wave packet dynamics on the repulsive potential surface.

The experiment was performed in a time-of-flight mass spectrometer under collision-free conditions in a cw free jet of a 1% Cl₂/He gas mixture. The molecular beam was