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PHOTOINDUCED CHARGE SEPARATION. DIPOLES, EXCIPLEXES AND ION PAIRS.

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Astract Depending on the system, the extent of photoinduced charge separation varies from intramolecular to intermolecular and further to ion-radical pairs of arbitrary separation. Transient dc conductivity techniques allow study of all these stages in photoinduced charge separation with subnanosecond time resolution. In the simplest case, photoexcitation of a molecule can result in intramolecular charge transfer, i.e. the creation of an excited state dipole moment, which exists only until the molecule relaxes to the ground state. In the case of an intermolecular charge transfer, there is a nonzero probability for the charges to dissociate and create free ion radicals. The larger the initial charge separation the greater is their probability of dissociation. The probability increases even more in the case of photoionization where the photoelectron thermalizes at a distance from the parent cation, creating the so called geminate ion radical pair.

I. DIPOLES (Intramolecular charge transfer)

A few examples demonstrate the diversity of the technique:

–The triad molecule MA-ANI-NI (methoxyaniline-aminonaphthalimide-dimethylphenyl-naphthalene-diimide-octane) is an example of intramolecular photoinduced multistep chargetransfer which results in a giant dipole moment (see Figure 1) of $\mu = 87 \pm 6$ D ($\approx$ 19 Å charge separation)[2]. The effect of light polarization on the DC conductivity signal allows an estimate of the ground state dipole moment ($\mu_g = 16 \pm 5$ D) and electric field dependence of the charge transfer rate constants (negligible for this system) as well. The independence of the dipole moment on excitation wavelength indicates high efficiency of intramolecular energy transfer. For this system a formation of ion radical pairs by a "partial" recombination between two of the giant dipoles has been found. The electric field assisted dissociation yield of these pairs is in good agreement with Onsager's geminate pair model.

– In systems with broken excited state symmetry such as bianthryl and tetraphenylethylene[3] (see Figure 2) the method allows not only measurement of the excited state dipole moments but also establishes the importance of excited state polarizability on the dipole formation. For molecules with zero ground state dipole moment, excitation by light polarized parallel to the electric field typically leads to a signal rising slower than for perpendicular polarization, because of the greater average rotation angle required for reaching equilibrium with the applied electric field. In these symmetrical systems where

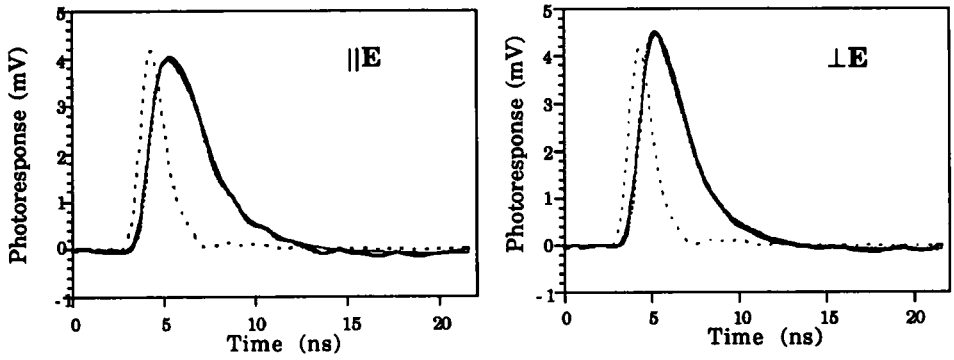

FIGURE 1 The photoresponses of MA-ANI-NI in toluene after absorption of 14 μJ at 416 nm in a cell with 1000V across a 0.6 mm gap between electrodes. Light polarizations parallel and perpendicular to the electric field give different signals because of nonzero (μ_g= 16 D) ground state dipole moment of MA-ANI-NI. Points show experimental signals, dashed lines describe laser pulse time profile and solid lines are theoretical fits with maximum dipole moment μ_2 = 87 D lasting 300 ns. Rotational time is 1.6 ns and the lifetime of intermediate state, 0.43 ns, was taken from transient absorption[1].

polarizability is responsible for dipole formation, the situation is reverse because now dipoles can be oriented along the field without rotation but by polarization, thus giving a faster rise for the signal with parallel light polarization.

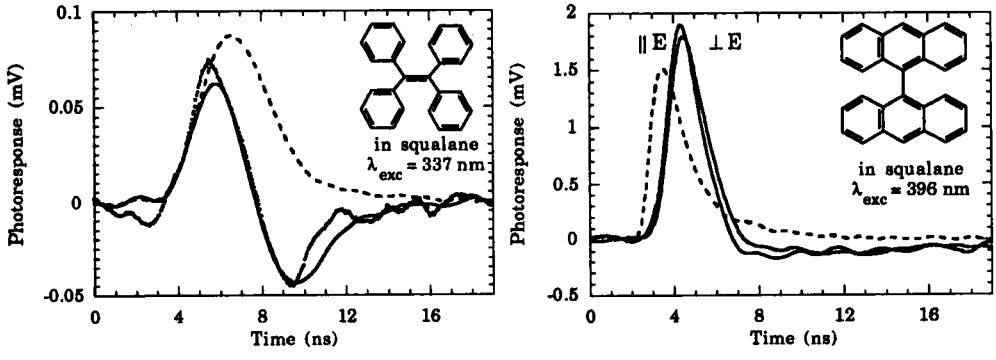

FIGURE 2 Photoresponses for tetraphenylethylene (left) and bianthryl (right) solutions in squalane after excitation at specified wavelengths in a cell with 1100 V applied across 0.5 mm gap. Dipole moments/life times are 7.8 D/1.1 ns and 5.9 D/15 ns, respectively. In the case of bianthryl, two polarizations of the 396 nm laser excitation make a profound difference associated with anisotropic polarizability of this molecule.

– Diphenylcyclopropenone (DPCP), shown in Figure 3, illustrates the situation in which a dipole moment is lost in a photochemical reaction. Upon excitation cleavage of CO

leads to an overall decrease in dipole moment from 5.1 D of DPCP to negligibly small dipole moments of CO and diphenylacetylene[4].

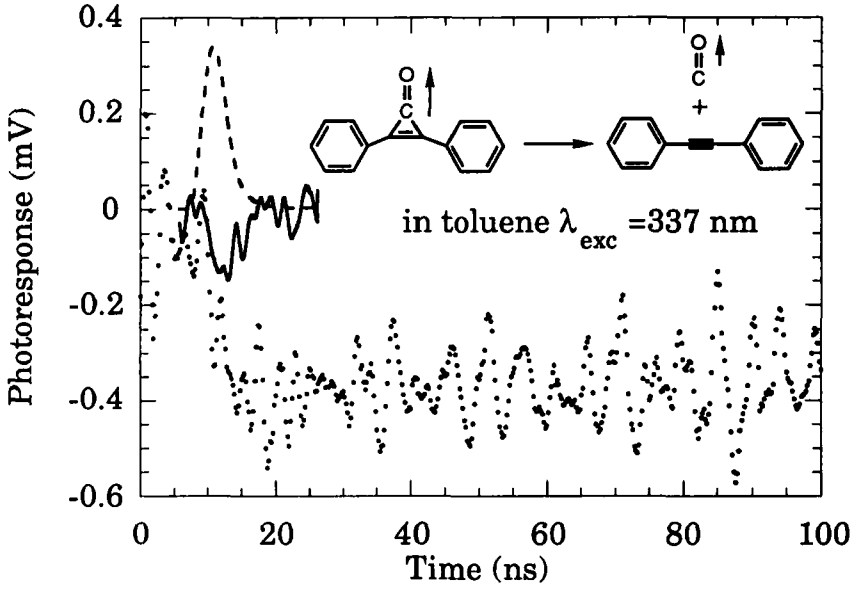

FIGURE 3 Photoresponse for diphenylcyclopropenone solution in toluene after absorption of 19 μJ at 337 nm in a cell with 1000 V applied across a 0.4 mm gap. Solid line shows signal in a displacement current mode (50 Ω load resistor) and points for a charge displace-ment mode (100 k Ω load). Dashed line shows laser pulse time profile. Best fit (not shown) gives a ground state dipole moment of 5.5 D with the assumption of zero dipole moment after excitation.

II. EXCIPLEXES (Intermolecular charge transfer)

Intermolecular charge transfer has been studied using the exciplex systems with cyanosubstituted anthracenes as acceptors and methyl substituted benzenes as donors[5].

– The results reveal a correlation between the magnitude of charge separation and the driving force of electron transfer ($-\Delta G_{et}$).

– The magnitude of the dipole moments does not reach the value of 15 - 16 D calculated for 100% charge transfer over 3.4 Å (see Table 1). We speculate that because of a substantial polarizability of acceptor anions, center of negative charge is pulled toward the donor molecule thus reducing the dipole moment. Indeed, between two acceptors we used, TCA(tetracyanoanthracene) and DCA (dicyanoanthracene), maximum dipole moments are achieved for TCA which has greater electron affinity, *i.e.* smaller polarizability.

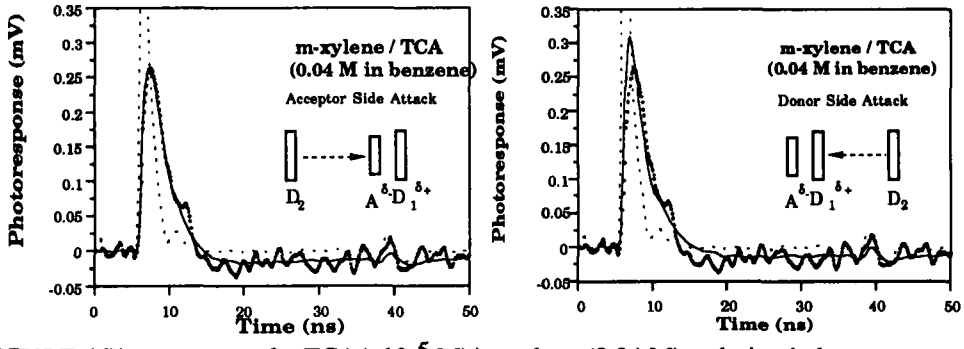

FIGURE 4 Photoresponse for TCA($\approx 10^{-5}$ M)/m-xylene (0.04 M) solution in benzene after excitation at 416 nm (57 μJ of absorbed energy) with 600 V applied across 0.4 mm gap. Two alternative fits are presented: "Donor side attack" where TCA/m-xylene exciplex newly formed by quenching of TCA/benzene exciplex has parallel dipole moment and "Acceptor side attack", in which dipole moment nverts The assumption of acceptor side atack fits the data. In both cases dipole moment of TCA/benzene was 3.4 D and from best fit (solid lines) for TCA/m-xylene's dipole moment of 8 D lasting 55 ns was found. Rotational time of 0.4 ns and a quenching time of 2.2 ns were measured independently.

TABLE I. Dipole Moments in Neat Donor Solvents (μ_{neat}) and Dilute Solutions of Donor Molecules in Benzene (μ_{dilute})

Donor/Acceptor	I_{ion}(eV)	μ_{neat}(D)	μ_{dilute}(D)
1,3,5-TMB/DCA	8.39	2.8	
1,2,4-TMB/DCA	8.27	5.6	
Benzene/TCA	9.25	3.4	
Toluene/TCA	8.81	8.9	
m-Xylene/TCA	8.59	13.9	8.0
p-Xylene/TCA	8.44	12.3	
1,3,5-TMB/TCA	8.39	19.5	9.6
1,2,4-TMB/TCA	8.27	14.3	10.0
Durene/TCA	8.02		10.1
HMB/TCA	7.85		10.5

– From kinetics of exciplex quenching by greater donor molecules, mechanism of donor molecule exchange can be extracted. In the case TCA/benzene exciplex quenched by m-xylene, an acceptor side attack (see Figure 4) seems to be more efficient. But if the quencher is hexamethylbenzene (HMB), a quenching radius exceeds a contact radius and

no side preference is observed. Instead, initially formed dipole moment of the distant TCA/HMB[6] pair which is higher than in an exciplex, relaxes to the equilibrium value.

– In neat solvents measured dipole moments are greater because of triplex formation. Triplexes are complexes between an acceptor and a cation dimer. Positive charge in a triplex is located between two donor molecules, thus increasing the extent of charge separation (dipole moment). Correlation between dipole moments and $-\Delta G_{et}$ for triplexes is not absolute (see Table 1). This reflects geometric restriction in dimer formation for different substituted methylbenzene.

III. GEMINATE ION PAIRS.

Photoionization of TMPD (N,N'-tetramethylparaphenylenediamine) and TMAE (tetramethylaminoethylene) was used to study the kinetics of geminate recombination. A few qualitative conclusions have be reached despite the early stage of this work.

– In cyclohexane and fluorobenzene photocurrent signals are indistinguishable from the laser time profile (FWHM 1.6 ns) but in squalane (where the electron mobility is low) recombination is slow enough to be analyzed (see Figure 5)

– Nearly quadratic dependence of the signal on laser intensity (not shown) in in the wavelength range studied (longer than 266 nm) confirms a two photon ionization origin of the signals.

– Absence of a signal sign change at longer times is consistent with (at least for the two photon ionization conditions) a long tail in the distribution function of thermalized electron separations. Signal independence on the light polarization confirms that the distribution function has nearly spherical symmetry.

– Current goals in this project are to achieve one photon ionization conditions where analysis of the signal (time dependence and light polarization variation) should give the information about the electron-cation spatial distribution function.

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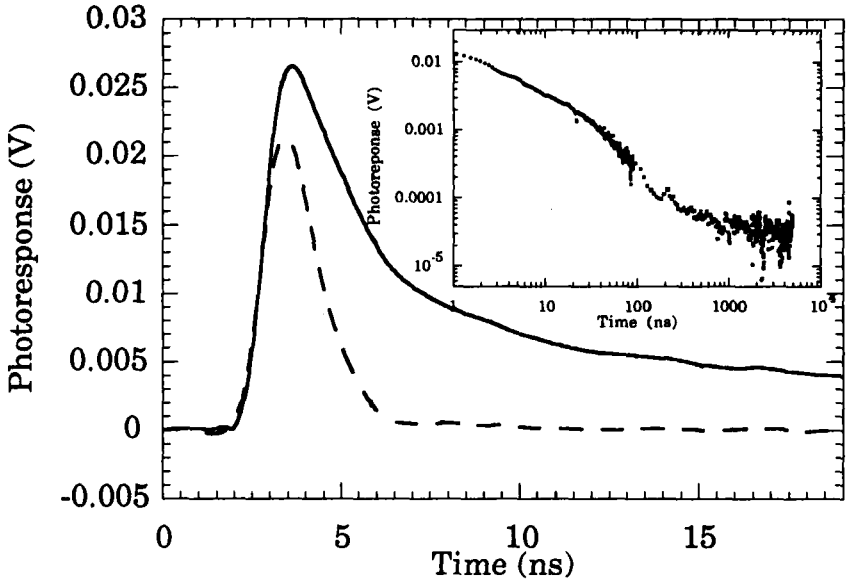

FIGURE 5 Transient dc conductivity of geminate electron/cation recombination in squalane after two photon ionization of TMPD (solid line) at 299 nm. Signals for parallel Dashed line shows the excitation laser pulse time profile. The insert log-log plot of the signal combined from traces on different time scales shows that there is no negative current observed.

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