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Mono- and Bi-photonic Ionization of Aromatic Molecules in Liquid Solutions by the 347 nm Light Pulse

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The photoionization of aromatic molecules constitutes a primary step of growing importance in photochemical processes. Richards *et al.* observed the absorption spectra of the pyrene cation radical which was produced by the biphotonic absorption of the 347 nm light pulse.[1] The ionization of perylene was found to occur by a biphotonic process.[2] Recently, a monophotonic ionization of perylene has been suggested when the excitation is below 230 nm.[3] However, the monophotonic ionization of aromatic molecules in liquid solutions by the excitation with the 347 nm light pulse has not been reported.

We have confirmed by means of the laser photolysis and transient photoconductivity measurements that the ionization of *N*,*N*-diphenyl-*p*-phenylenediamine (DPPD) and phenothiazine in an acetonitrile solution occurs by monophotonic excitation at 347 nm.

The second harmonics of a Q-switched ruby laser (Japan Electron Optics, JLR-02A) was used as an exciting light pulse. The produced ion radicals were observed by measuring the photocurrent induced by laser excitation. Details of the measurement are given elsewhere.[4] For examining the effect of the excitation light intensity on the photocurrent, the intensity of the laser pulse was reduced by using neutral filters composed of wire gauzes. Relative values of the exciting intensity were monitored by measuring the intensity of light partially reflected by means of a beam splitter with a photomultiplier. The absolute value was determined by a ballistic thermopile TRG model 100 (Hadron).

The samples were purified in the usual way. All the solutions for the measurment were deaerated completely by repeated freeze-pump-thaw cycles.

The effects of the exciting light intensity on the peak photocurrent of the acetonitrile as well as the tetrahydrofuran (THF) solutions of the aromatic molecules at room temperature are shown in Figs. 1 and 2, respectively.

One can see from Fig. 1 that the ionization process of phenothiazine as well as that of DPPD in acetonitrile are monophotonic. Since the curves of the photocurrent consist of the exponential rise curve and the hyperbolic decay curve which varies with the initial

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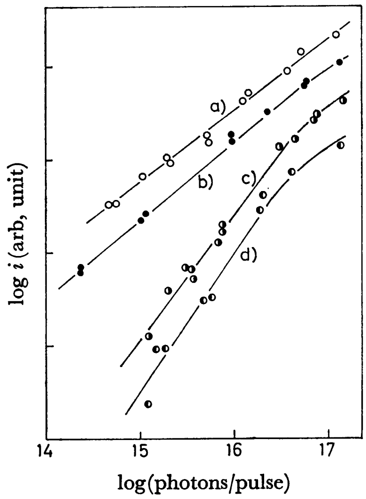

Fig. 1. The effects of the exciting light intensity on the peak photocurrent in acetonitrile solutions. (a) phenothiazine (10^{-3} M), (b) DPPD (10^{-3} M), (c) pyrene (10^{-3} M), (d) perylene (saturated).

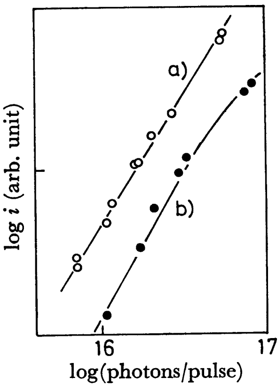

Fig. 2. The effects of the exciting light intensity on the peak photocurrent in THF solutions. (a) phenothiazine (10^{-3} M), (b) DPPD (10^{-3} M).

concentration of ions, *i.e.*, the decay is more remarkable at higher exciting light intensity, the observed value of the peak photocurrent appears to be somewhat smaller than the true value at high light intensity. Therefore, the slopes of the straight lines in Figs. 1 and 2 seem to give slightly smaller values than the real ones. Contrary to this, both ionization processes of the phenothiazine–THF and the DPPD–THF systems are not monophotonic but biphotonic as indicated in Fig. 2. We have confirmed also that the photoionization process of DPPD by the 347 nm pulse is biphotonic in nonpolar solvents.

It has been suggested from a detailed kinetic study that the photo-oxidation of DPPD originates from the upper excited singlet state.[5] Then, the photoionization of DPPD may occur from the upper excited singlet state, since it seems to be certain that the intermediate of the photo-oxidation is a DPPD cation radical.[5] In relation to the above statement, we have observed the laser-induced photocurrent with the rise and decay curves quite similar to the laser pulse in the case of the DPPD-nonpolar as well as moderately polar solvent systems.[6] Although the details of the result will be given elsewhere, the laser-induced photocurrent with very short lifetime might be ascribed to the electrons with a quite large mobility produced by the ionization from the excited Franck-Condon state.

Now, the photoionization process in a considerably polar solvent such as acetonitrile is monophotonic as described above, although the ionization potential of DPPD in the gas phase may be much larger than the energy of 347 nm excitation. However, the energy required for the separation of cation and electron may be compensated by the solvation energies for them. The circumstance in the case of the monophotonic ionization of phenothiazine may be quite similar to that of DPPD. One might suppose that acetonitrile forms a molecular complex with the solute in the ground state and the complex ionizes in the excited state. We have, however, confirmed that there is no indication of such a complex formation in the absorption spectra of these molecules in acetonitrile. Since the solvation energy of THF for the cation and an electron may be much smaller than that of acetonitrile, the monophotonic ionization cannot take place in a THF solution.

We have confirmed that both of the photoionization processes of pyrene and perylene in acetonitrile by the 347 nm pulse are biphotonic as shown in Fig. 1. Of course, the photoionization processes of these molecules in a THF solution are biphotonic. However, it seems to be rather difficult at the present stage of investigation to determine whether the biphotonic ionization process involves excited singlet or triplet state as photoactive intermediate. It might be possible also that both of excited singlet and triplet states are involved in the process as the intermediates.

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