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Detection of the Triplet State of Some Organic Molecules Adsorbed on Cellulose Substrate by Diffuse Reflectance Laser Photolysis Method

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Absorption spectra and decay processes of the triplet states of sodium 1-pyrenylsulfonate, phenanthrene, and p-terphenyl adsorbed on cellulose filter paper have been measured directly by a nanosecond diffuse reflectance laser photolysis method.

Flash and laser photolysis methods have made a great contribution to the studies on photophysical and photochemical processes of molecules and molecular assemblies. Direct measurements of excited states and transient species in microsecond to picosecond time regions provide detailed mechanistic information and make it possible to determine rate constants of primary processes. Most of the systems studied are optically homogeneous and transparent, gas or solution phase. This laser photolysis technique has been extended to optically scattering powder systems such as molecular and inorganic crystals, semiconductors, polymers, molecules adsorbed on silica gel, and so on. Namely, Wilkinson et al. developed diffuse reflectance laser photolysis method on 1981 and applied it to various kinds of solid materials.1) Subsequently, we have improved its time-resolution up to 10 ps and revealed intersystem crossing process of molecular crystals.2)

Cellulose substrate (filter paper) is an optically good scattering material and adsorbs various kinds of molecule. This is indispensable in chemical purification and a prototype of thin layer in chromatography. Phosphorescence measurement of adsorbates on this substrate is possible at room temperature and is now deemed to be a practical and powerful analytical tool. Recently,

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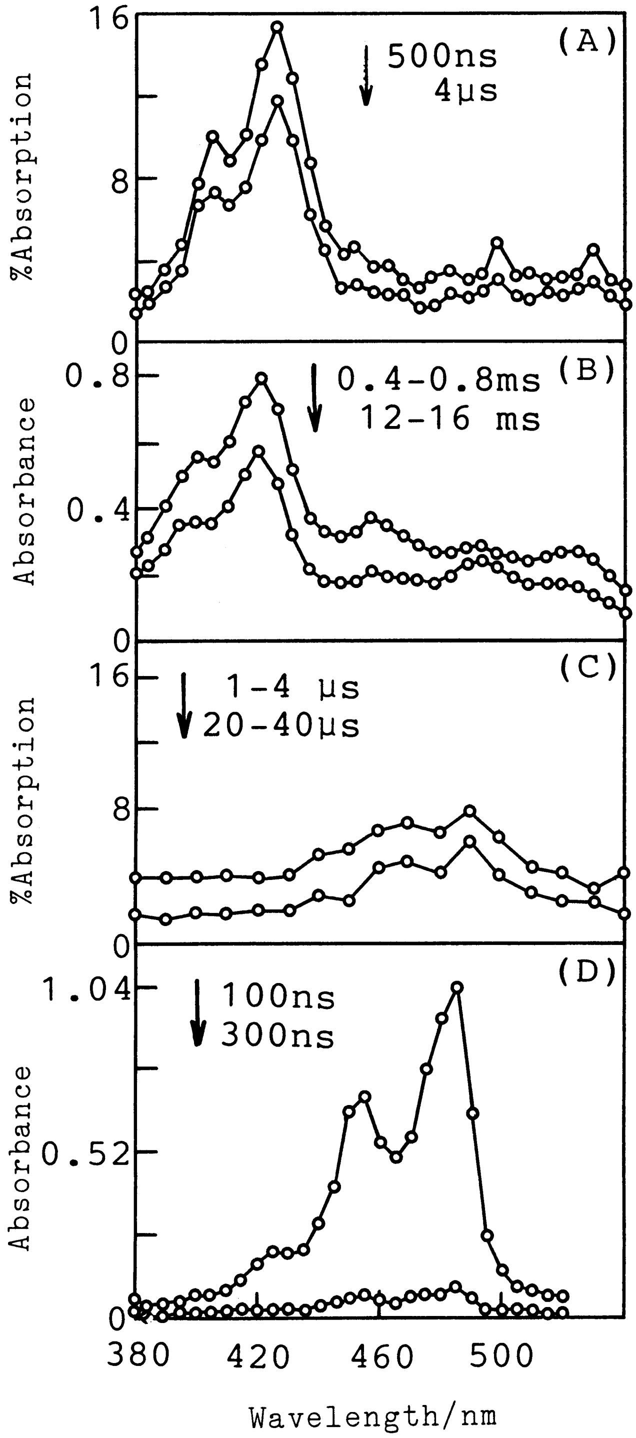

Fig.1. Transient absorption spectra of sodium 1-pyrenylsulfonate (A) and phenanthrene (C) adsorbed on cellulose substrate. The respective reference triplet spectra are given in (B) and (D).

spectroscopic attention has been focused on the aromatic-molecular adsorbates, and their phosphorescence band widths are considered in terms of electron-phonon coupling.$^{3)}$ In the present work, we have applied nanosecond diffuse reflectance laser photolysis to molecules adsorbed on cellulose paper and measured for the first time their triplet absorption spectra.

Sodium 1-pyrenylsulfonate (PyS) was synthesized in this laboratory. Phenanthrene (Tokyo Kasei, zone refine grade, 100 passes) was used without further purification. p-Terphenyl (Dotite scintillation grade) was zone refined (100 passed). These molecules were adsorbed by dipping filter paper (Whatman 4) in aqueous or methanol solution with ca 10^{-3} mol dm^{-3} chromophore concentration for 12 h. After drying them in the dark, spectral measurements were performed. The absorption as well as fluorescence spectra were almost the same as those of molecules in solution, indicating no appreciable interaction with the cellulose substrate. A microcomputer-controlled diffuse reflectance laser photolysis system was used, the details of which are described in elsewhere.$^{4)}$

The obtained transient absorption spectra and the reference triplet bands measured in dilute hexane solution by transmittance laser photolysis method are summarized in Fig. 1. Although the peak position showed the 5 nm red-shift, we consider that these are due to the triplet state, because their spectral shape is similar to that of the corresponding T_n-T_1 absorption band. In the case of phenanthrene absorption spectra are very broad and a weak band is superposed around 420 nm. As the triplet excimer of phenanthrene has a structureless band in the latter wavelength,5) this may be responsible for the present tail.

In order to confirm this assignment, effects of co-adsorption of closed-shell heavy metal ions such as Tl^+, and Pb^{++}, and Ag^+ were examined. The absorption and fluorescence spectra of aromatic molecules were not modified to a great extent by Tl^+ and Pb^{++}. In the system containing Ag^+, a red-shift and a broadening of the spectra were detected, indicating rather strong complex formation in the ground state. By the co-adsorption, fluorescence was quenched, and phosphorescence originally not detected was enhanced. The phosphorescence bands of the Ag^+ quencher systems became again broader compared to the Tl^+ and Pb^{++} systems. Transient absorption spectral shape of adsorbed molecules with these metal ions were similar to those of quencher-free system, and their peak position is red-shifted by 5 nm. It is worth noting that absorption intensity was also enhanced by a few times. These behavior can be interpreted in terms of intersystem crossing enhanced by the external heavy-atom effect due to co-adsorbed heavy metal ions. This is quite reasonable, because it was confirmed by picosecond and nanosecond transmittance laser photolysis study in solution that quenching of aromatic hydrocarbon by Tl^+, Pb^{++}, and Ag^+ is ascribed to nonfluorescent complex formation followed by rapid intersystem crossing.6)

One may point out a possibility that molecules form microcrystals on the substrate, which can be denied by the result on p-terphenyl. Microcrystalline p-terphenyl gives the triplet band at 480 nm, while the band of doped molecule in polymer and in solution is around 450 nm.7) Since the present case

Table 1. Half-life of sodium 1-pyrenylsulfonate systems on cellulose substrate

	PyS	PyS + Tl^+	PyS + Pb^{++}
in solution	7.5 μs	7.3 μs	-
on filter paper	27.0 ms	2.5 ms	7.5 ms

correspondes to the latter wavelength, molecules are adsorbed separately on the cellulose paper.

As the decay curves of the triplet state complex and do not obey a simple first- or/and second-order decay kinetics, the half-life of the triplet decay was examined. Some results on PyS systems are listed in Table 1. The triplet absorption on cellulose decayed very slow compared to the solution system. This is because the diffusion-controlled process, leading to the T-T annihilation, is completely suppressed by adsorption. The enhancement factor of the intersystem crossing rate to the ground state by Tl^+ is about a few, which is again interpreted as induced by the heavy metal ions. Similar experimental results were obtained for phenanthrene with and without quencher, and we consider that the present behavior under adsorption is quite general.

It is interesting that the half-lives of the triplet phenanthrene and p-terphenyl on cellulose are a few tens of μs and shorter than that of PyS. This difference may be ascribed to the presence of sulfonic ion in the former system. This substituent has a role of anchor and molecular motion leading to deactivation is completely suppressed.

In conclusion, the triplet state absorption spectra and their dynamics have been measured by diffuse reflectance laser photolysis. Separation of a small amount of chemical species by filter paper is quite common and practically important, so that the present work means that this laser photolysis method is quite fruitful in elucidating photochemical reactions of such species.

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