BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 997—998 (1973)

Rise Times of Triplet-Triplet Absorptions of Some Aromatic Hydrocarbons

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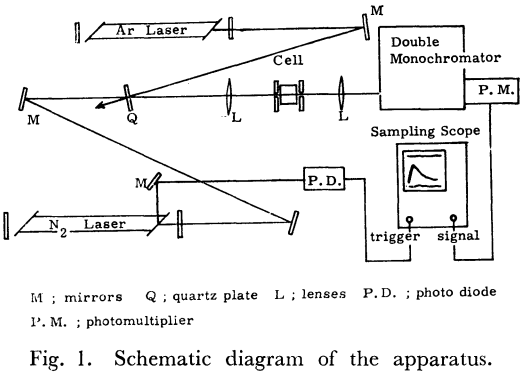
(Received July 4, 1972)

Recent development of lasers has given the chemist short-lived sources of excitation which are powerful enough to observe excited singlet species by absorption spectroscopy.[1-5] This technique has been called "laser photolysis" and applied to know higher excited singlet levels. Analyses of the growth rate of triplet state and the decay process of singlet state which occur during scores of nanoseconds are possible by the similar technique and give informations about dynamic behavior of energy relaxation. Especially, if the rate constant of the growth of the triplet state is determined, it provides information on the initial state of the relaxation process to the triplet state. In this note we report the rise times of the triplet states of phenanthrene, 3,4-benzpyrene and 1,2,3,4-dibenzanthracene in 2-methyltetrahydrofuran at room temperature. The transient spectra and the decay times of the singlet states of these compounds were already reported by Porter and Topp.[4] In order to make a comparison, we also measured the decay times of their excited singlet states on the same experimental condition for the triplet states.

A coaxial type pulsed N_2 laser constructed in our laboratory was used as a pumping source. A 12 nsec, 0.2 mJ. pulse of light of wavelength of 3371 Å is produced with a repetition rate of *ca.* 30 Hz. In spite of the small peak power of our N_2 laser used here, sufficient amount of excited singlet molecules for observation of the transient process can be accumulated by focusing the laser beam on a very small area.

A probe light must be intense on account of the low sensitivity of wide band detection system. When fluorescence overlaps S–S or T–T absorption region, monitoring light has to be more intense than the fluorescence by the order of two or more. A CRL 52B cw Ar ion laser which has total output power of 4 W was used for this purpose. This laser has eight lasing lines between 4579 Å and 5145 Å and the molecules studied here have both S–S and T–T absorptions in this region.[4] The two laser beams were made to coincide strictly by employing the experimental setup shown in Fig. 1. The greater part of the light from N_2 laser passed through a quartz plate Q, while a portion



M ; mirrors Q ; quartz plate L ; lenses P.D. ; photo diode
P.M. ; photomultiplier

Fig. 1. Schematic diagram of the apparatus.

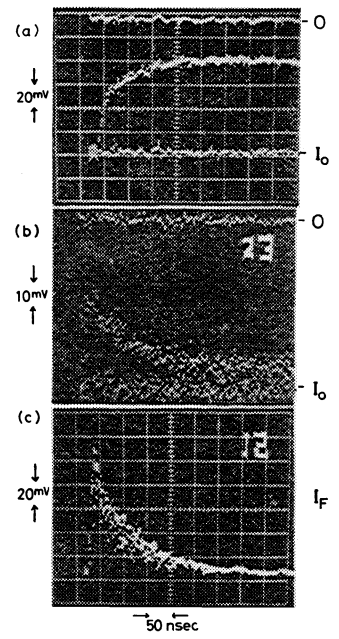


Fig. 2. Oscilloscope tracings (50 ns/div.) of 5×10^{-3} mol/l phenanthrene in 2-methyltetrahydrofuran. (a) Rise of the T_1–T_n absorption at 4880 Å. (b) Decay of the S_1–S_n absorption at 5145 Å. (c) Decay of the fluorescence at 4200 Å.

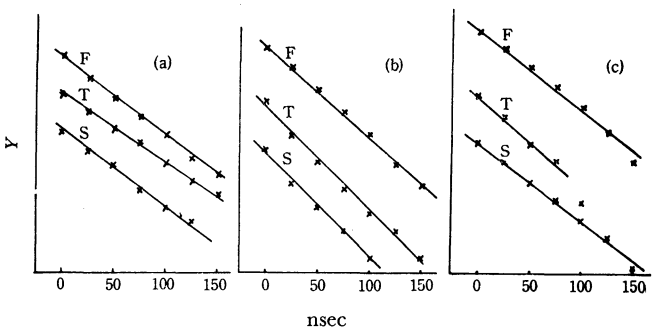


Fig. 3. First order decay curves of the singlet absorption (S); $Y=\log(\text{O.D.})^{S-S}$ and the fluorescence (F); $Y=\log I_F$, and first order increase of the triplet absorption (T); $Y=\log((\text{O.D.})^{T-T}_{max}-(\text{O.D.})^{T-T})$. (a): phenanthrene, (b): 3,4-benzopyrene, (c): 1,2,3,4-dibenzanthracene.

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Table 1. Rise times of triplet–triplet absorption, decay times of singlet–singlet absorption, and lifetimes of fluorescence in 2-methyltetrahydrofuran

		Rise time of T–T absorption	Decay time of S–S absorption	Decay time of fluorescence
Phenanthrene	This work	78 ns (4880 Å)	74 ns (5145 Å)	71 ns (4200 Å)
	Porter and Topp[a,c]		65 ns	67.2 ns
3,4-benzpyrene	This work	53 ns (4765 Å)	53 ns (5145 Å)	60 ns (4140 Å)
	Porter and Topp[b,c]		49.1 ns	57.5 ns
1,2,3,4-dibenzanthrecene	This work	62 ns (4579 Å)	71 ns (4880 Å)	71 ns (4100 Å)
	Porter and Topp[b,c]		51.2 ns	53.5 ns
	Lavalette *et al.*[a,d]	58 ns	56 ns	61 ns

a) In polymethyl methacrylate. b) In cyclohexane. c) Ref. 4. d) Ref. 6.

of the Ar ion laser beam was reflected and the two beams were adjusted to coincide exactly. Although the reflectivity of the quartz plate is low, reflected Ar ion laser beam was still intense enough. After adequate diaphragms the two beams were focused through the sample cell and refocused onto the entrance slit of a Nalumi 0.3-m double monochromator.

The repeated pulsed N_2 laser enabled us to employ sampling technique which is suitable for high speed phenomena. A probe beam emerging from the exit slit of the monochromator was detected by a 1P28 photomultiplier with a load resistance of 50 Ω. The output of the photomultiplier at a centain time after triggering was displayed on a Tektronix 564A sampling oscilloscope.

Fig. 2 shows the rise curve of the T–T absorption of 5×10^{-3} mol/l deaerated solution of phenanthrene in 2-methyltetrahydrofuran taken at 4880 Å and decay curve of the S–S absorption at 5145 Å. Upper traces are with the monitoring light off and lower traces are with the exciting light off. Assuming first order processes, triplet rise time and singlet decay time are determined by plotting log $((\text{O.D.})^{\text{T-T}}_{\text{max}}-(\text{O.D.})^{\text{T-T}})$ and log $(\text{O.D.})^{\text{S-S}}$ *vs.* time, respectively. Fig. 3 shows that they are described well as first order processes and the results are tabulated in Table 1. The rise times of the T–T absorption and the decay times of the S–S absorption coincide with each other within experimental errors and also agree well with the fluorescence lifetimes. These agreements apparently show that the initial states of the energy relaxation process of these molecules to their triplet states are the fluorescent states. In this table, the rate times obtained in this work are somewhat different from those of the literatures.[4,6] It is probably due to the difference of the solvent used.

The method described here is considered to be of wide applicability to the study of the dynamic behaviors of the excited state molecules. For example, intermediate species formed after the photolysis can be detected, and the rate of formation can be determined. Recently it has been suggested that intersystem crossing of electron-donor-acceptor complex[7] or photoionization of organic molecules[8] may occur from excited Franck-Condon state, not from fluorescent state. Such problems can be dissolved by the comparison of the rise time of triplet state or ionized molecules with the decay time of singlet state, both of which are determined with high accuracy by this technique.

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