CHEMISTRY LETTERS, pp. 235-239, 1974. Published by the Chemical Society of Japan

A NEW METHOD FOR MEASURING $S_n \leftarrow S_1$ ABSORPTION SPECTRA

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A new method for measuring absorption spectra of transient species in the nanosecond time scale was developed. It is applicable to highly fluorescent systems and gives accurate results in spite of its rather simple optical alignment. The method was applied to the 1,2,4,5-tetracyanobenzene-methyl-substituted benzene and 1,4-dicyanobenzene-pyrene systems.

Absorption spectra of such short-lived species as aromatic molecules in excited singlet states were measured by several authors with the aid of nanosecond time-resolved spectroscopy techniques, laser induced spark$^{1)}$ and pulsed emission from some scintillators$^{2)}$ or from a Xe lamp$^{3,4)}$ being used as spectro-flash for the absorption measurement. There are some difficulties, however, in obtaining well resolved spectra by these methods using singly-pulsed photolysis and spectro-flashes, because the signal to noise ratio (S/N) is usually small for the transient absorption measurement and strong fluorescence caused by the laser excitation often overlaps the absorption bands due to the transitions from excited singlet states.

In the present study, we develop a new method for measuring absorption spectra of transient species in the nanosecond time scale, a pulsed N_2 laser in repetitive operation being used both for the excitation of samples and for the excitation of a dye solution which induces super-radiant fluorescence used as spectro-flash for the measurement of transient absorption spectra. The high S/N value can be obtained by integrating the signals induced by the repetitively-pulsed flashes with a boxcar integrator. Furthermore, by using the super-radiant flash as the light source for the absorption measurement, it is possible to locate a detection part including a monochromator far from a sample and therefore to remove the effect of the fluorescence upon the observed absorption spectra.

Several authors have studied the $S_n \leftarrow S_1$ absorption spectra of weak charge-transfer complexes as well as exciplexes and found that they are composed of the bands pertinent to the anion of acceptor and/or the cation of donor.$^{5-7)}$ It should be emphasized that the slight difference between the absorption spectrum of the donor-acceptor complex in the lowest excited singlet state and that of the cation or the anion deduced from the component molecule can clearly be recognized by the aid of the newly developed method.

Experimental

The experimental set-up is shown in Fig. 1. A light beam from a repetitively-operated nitrogen gas laser of the cross field type (Avco Everett model 1000; peak power ~100 kW; pulse width ~10 ns) is focused to a line on the inside wall of a dye cell (DC) and of a sample cell (SC) with a cylindrical lens. DC and SC contain dye and sample solutions, respectively.

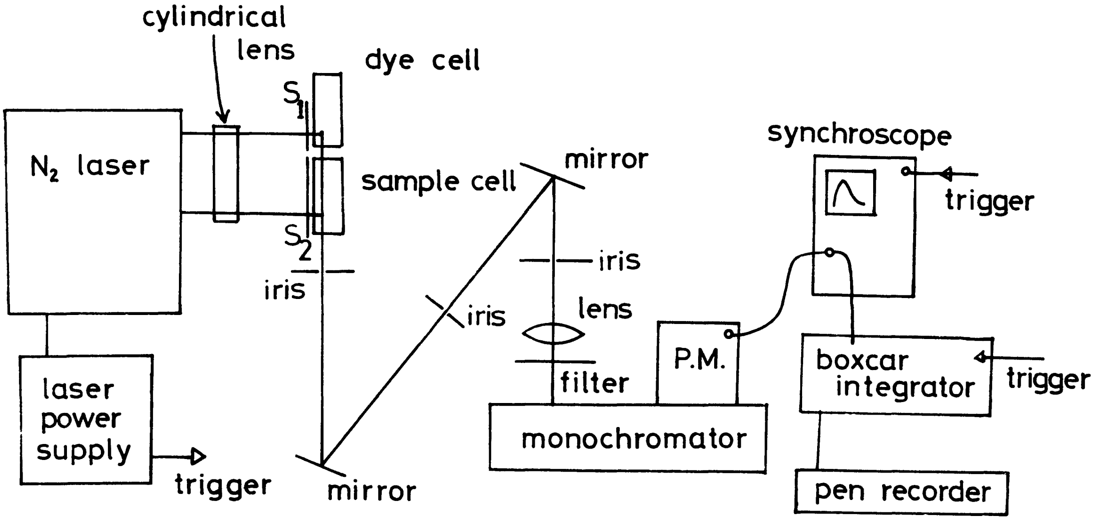

Fig. 1. Block diagram of the apparatus for the time-resolved absorption measurement.

The rectangular output beam of the nitrogen laser is well suited for dye laser pumping. The super-radiant fluorescence with small divergent angle and with wide spectral bandwidth ($\gtrsim$ 1500 Å) emitted from the transversely-pumped dye solution passes through the excited region of the sample solution. Hence the super-radiant fluorescence from the dye solution is effectively absorbed by excited specimens in the sample solution. The optical alignment of the light source, sample, detector, and other parts employed in this experiment is very easy, since the colinearity can be obtained without any special effort.

The light passes through several irises and is reflected by mirrors, and is focused with a lens through appropriate filters in front of the slit of a grating monochromator (SPEX model 1604) attached with a photomultiplier (P.M., EMI 6256S).

The spectral distribution of the super-radiant emission suffered or free from the transient absorption is obtained with or without a screen on the side wall of SC, respectively. The method is extraordinarily useful for the highly fluorescent system, since the super-radiant fluorescence from the excited dye molecules has small divergent angle while the fluorescence from the sample greatly diverges and, therefore, the latter becomes weak much faster than the former with the increase of the distance from the sample. The repetitive operation of a nitrogen gas laser enables us to improve the S/N value by the method of signal integration with the aid of a boxcar integrator (PAR model 160).

Results and Discussion

The $S_n \leftarrow S_1$ absorption spectra were measured with the TCNB complexes with benzene, toluene, and mesitylene by using the acidic ethanol solution of 4-methylumbelliferone as a monitoring light source. The results are shown in Fig. 2, together with the spectrum observed with the chemically prepared TCNB anion.[5,6] These spectra are similar to each other with the peaks at 467, 467, 465, and 462 nm,[8] for the TCNB complexes with benzene, toluene, and mesitylene, and the chemically prepared anion, respectively. This is the first time to point out that there are significant differences between the peak positions of these spectra; this indicates that the complexes in the lowest excited singlet states are, strictly speaking, a little different from the free TCNB anion in their electronic structures, although their similarities have hitherto been pointed out.[6]

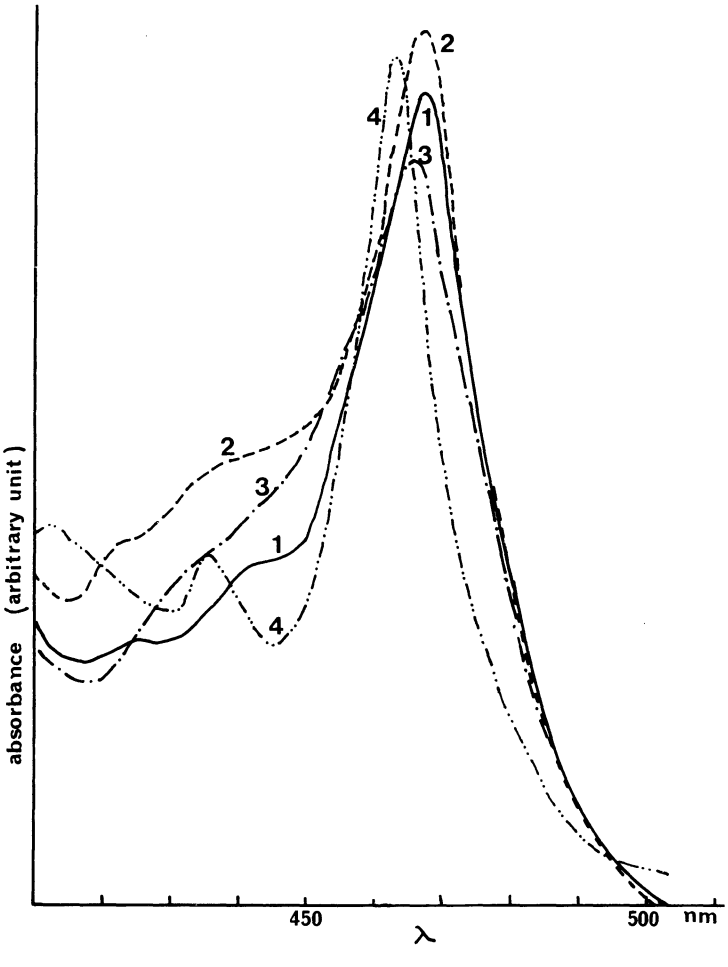

Fig. 2.
$S_n \leftarrow S_1$ absorption spectra measured for the TCNB-benzene (curve 1), TCNB-toluene (curve 2), and TCNB-mesitylene (curve 3) complexes at room temperature. Curve 4 is the absorption spectrum of the chemically prepared TCNB anion. The concentrations of TCNB are $\sim 1 \times 10^{-3}$ M for the benzene, toluene, and mesitylene solutions.

In the preceding paper we reported that the contribution of the charge transfer configuration in the lowest excited singlet state are 96.7, 96.7, and 99.7 % for the TCNB-benzene, -toluene, and -mesitylene complexes in fluid solution at room temperature,[9] respectively. This order of magnitude of the charge-transfer character is closely related with the observed peak wavelengths of the $S_n \leftarrow S_1$ absorptions of the complexes. That is, the absorption maximum shifts to shorter wavelengths with the

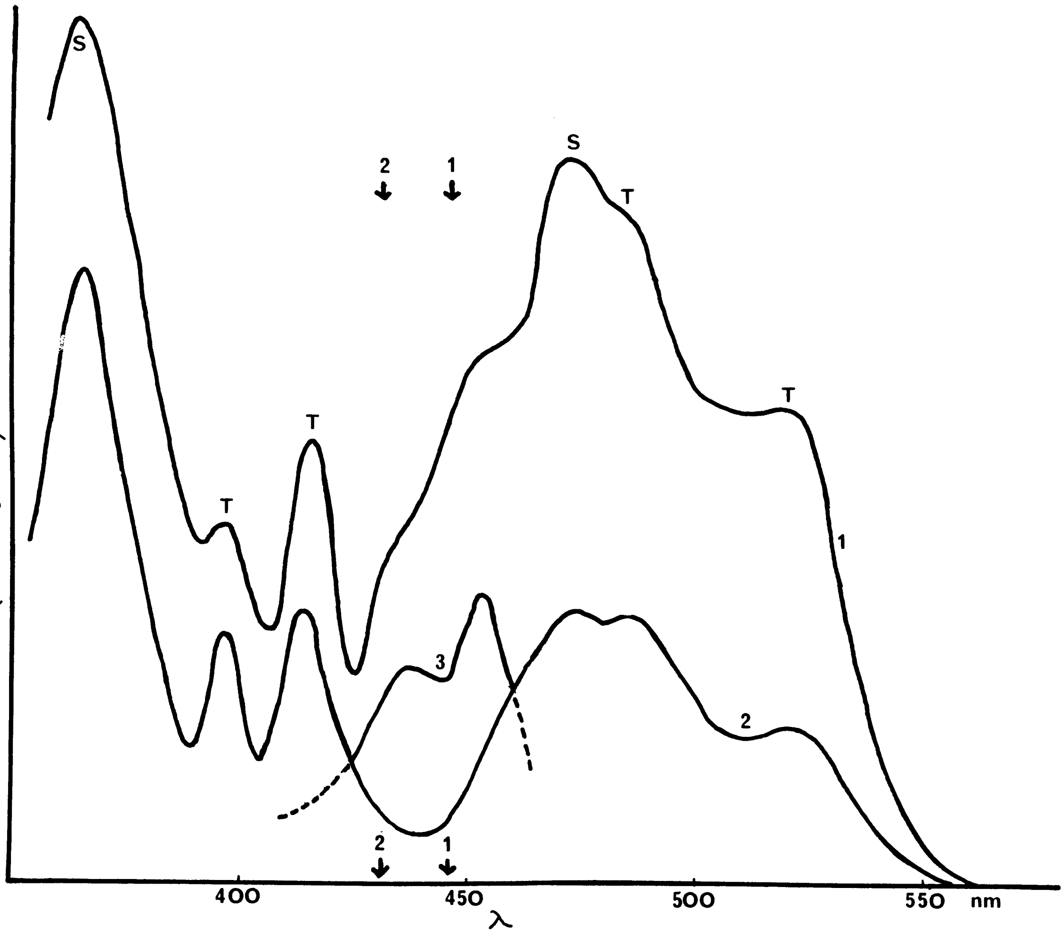

Fig. 3. Transient absorption spectra measured for the DCNB (1.0×10^{-2} M)-pyrene (3.2×10^{-6} M)-toluene (curve 1) and pyrene (3.2×10^{-6} M)-toluene (curve 2) systems. S and T indicate the $S_n\leftarrow S_1$ and $T_n\leftarrow T_1$ transitions of the pyrene molecule.

increasing charge-transfer character in the lowest excited singlet state of the complex. This tendency is consistent with the fact that the absorption maximum of the chemically prepared TCNB anion appears in the shorter wavelengths than that of the TCNB-mesitylene system.

The transient absorption spectra of the 1,4-dicyanobenzene(DCNB)-pyrene-toluene and pyrene-toluene systems are shown in Fig. 3. Toluene solutions of phenylbiphenyloxadiazole and 2,5-diphenyloxazole, ethanol solutions of α-naphthyloxazole, 3-cyano-4-methylumbelliferone, and fluorescein, and acidic ethanol solution of 4-methylumbelliferone were used as spectro-flash light sources. As is shown in Fig. 3, the transient spectrum for the pyrene-toluene system is composed of the $S_n\leftarrow S_1$ and $T_n\leftarrow T_1$ transitions of the pyrene molecule,$^{10-13)}$ which are indicated by S and T, respectively. Curve 3 obtained as the difference in the transient spectra normalized at 500 nm between the DCNB-toluene and DCNB-pyrene-toluene systems exhibits the $S_n\leftarrow S_1$ transition of the DCNB-pyrene complex. In this spectrum, the maxima appear at 436 and 453 nm while the chemically prepared pyrene cation(14) and DCNB anion(15) have the maxima at 431 (arrow 2) and 446 nm (arrow 1), respectively. It is concluded from this accurate measurement that the $S_n \leftarrow S_1$ absorption bands of the complexes under consideration slightly shift to the lower frequencies compared with those of the corresponding component cations or anions.

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(Received December 26, 1973)