

## Photoinduced intramolecular charge transfer of TICT and related compounds in femtosecond–nanosecond time regime

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**Abstract.** The dynamics of photoinduced intramolecular electron/charge transfer of the model compounds with different degrees of electronic interactions between combined donor–acceptor groups in polar solvents have been investigated using femtosecond–picosecond time resolved absorption and fluorescence spectroscopy. In the systems showing a simple one-electron transfer from the excited state localized in the acceptor to the intramolecular ion–pair state, time dependencies of the electron transfer reaction were expressed by an extended exponential function, although the main part of the reaction can be approximated by an exponential function, from which we can estimate the approximate electron transfer time of the compounds. In some compounds, the approximate electron transfer times are found to be faster than the solvation time and the longitudinal dielectric relaxation time of the solvents. The possible mechanisms responsible for the extended exponential behavior are discussed.

In the strongly interacting donor–acceptor systems, the electronic delocalization interaction in the TICT state is affected by the solvent orientational motion as well as the geometrical structure between donor and acceptor.

**Keywords.** TICT; intramolecular charge transfer; electron transfer time; extended exponential behaviour.

### 1. Introduction

Time resolved absorption and fluorescence spectroscopy have recently been extensively used for understanding of the dynamics and mechanisms of photoinduced electron transfer reactions which is the most fundamental problem in the photophysical and photochemical primary processes in condensed phase. The electron transfer rate is considered to be determined by the following factors: (a) the magnitude of the electronic interaction responsible for the electron transfer between an electron donor (D) and an acceptor (A), (b) the Franck-Condon factor which is related to the free energy gap between the initial and final states of reaction, (c) the reorganization energies of solutes and solvent molecules in the surrounding, and (d) microscopic solvation dynamics in a broad range of solvents (Marcus 1959, 1965; Mataga 1981; Maroncelli *et al* 1990; Rips 1990).

When the electronic interaction between an electron donor and an acceptor is sufficiently strong and the energy gap relations are also favourable, the activation barriers in electron transfer reaction become very small. In the case of barrierless or very small barrier electron transfer reaction, it is believed that the orientational motions of polar solvent molecules or polar groups in the surrounding donor and acceptor molecules, of which the time dependencies are characterized by the longitudinal dielectric relaxation time  $\tau_L$  under a continuum model of solvent, play

an important role in the course of electron transfer processes (Sumi and Marcus 1986). In this work, we focus on measuring the dynamics of electron transfer in excited intramolecular D–A systems using femtosecond–picosecond time resolved absorption and fluorescence spectroscopy. The combination of the absorption and emission measurements provide us with a precise time profile for the electron transfer process affected by solvent orientation dynamics in large dynamic range and wide time scale.

Time-resolved fluorescence Stokes shift of polar fluorescent probe molecules has also been extensively studied for understanding of the microscopic relaxation processes

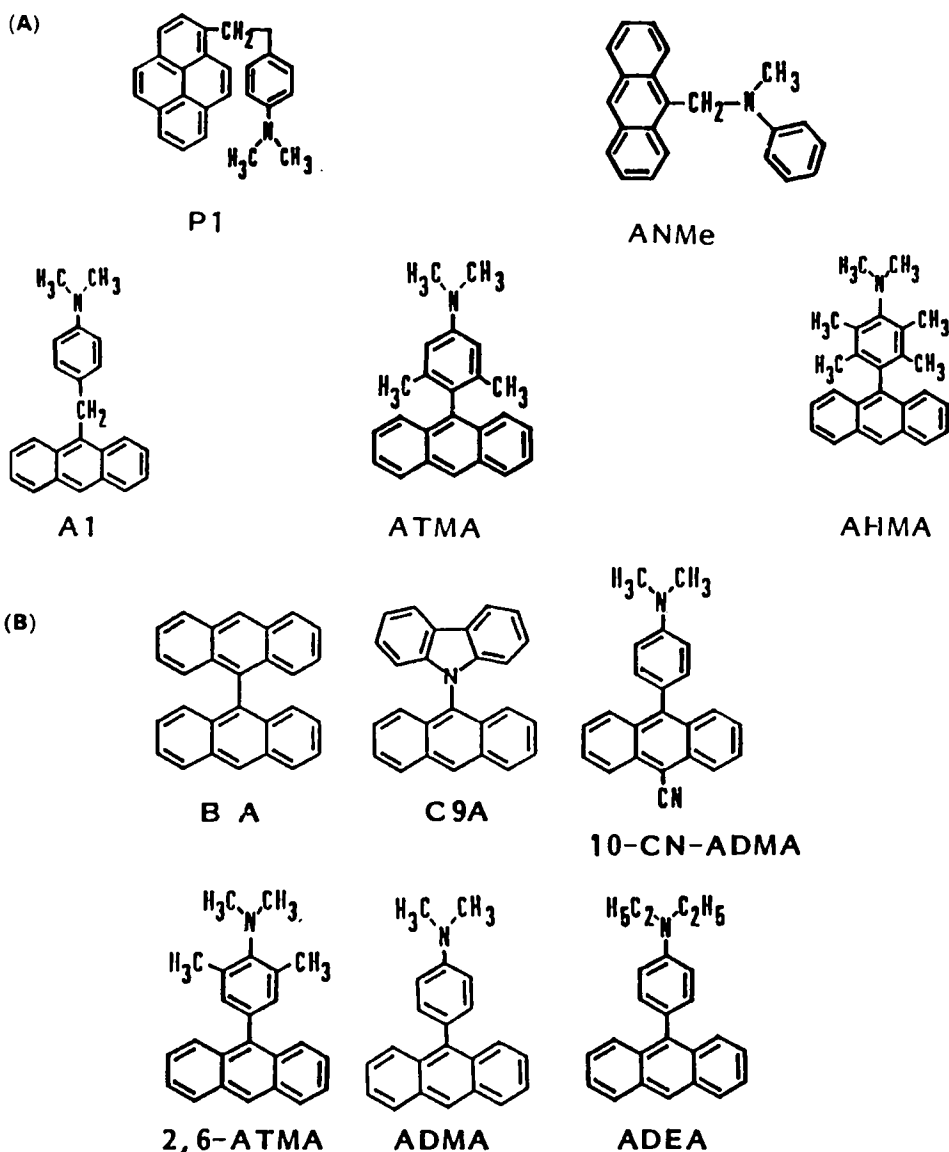


Figure 1. Molecular structures for the intramolecular D–A compounds studied here. (A) D–A systems showing simple electron transfer in the excited state. (B) Strongly interacting D–A systems in the excited state.

of the solvent in the environment of the probe (Maroncelli and Fleming 1987; Nagarajan *et al* 1987; Jarzeba *et al* 1991). The important experimental results for the solvation dynamics show that the time scales observed for solvation are usually larger than  $\tau_L$  and the solvent relaxation function is not predicted using bulk dielectric relaxation times of the neat solvent and the continuum solvent description model. However, the systematic studies on the photoinduced electron transfer affected by solvent relaxation dynamics are very few and these studies have been investigated mainly by means of time resolved fluorescence measurements (Nagarajan *et al* 1987; Barbara and Jarzeba 1990).

In the present report, we have examined the following systems (figure 1) with different degrees of electronic interactions between combined D–A groups which seem to be appropriate for the elucidation of the polar solvent dynamics associated with the electron transfer reaction. In the compounds denoted group A in the figure 1, there is no appreciable change of absorption spectra due to the electronic interaction between donor and acceptor groups both in the ground state and in the excited state immediately after laser excitation. The transient absorption spectra of these systems show the simple electron transfer from the state localized in the pyrenyl or anthryl part (LE state) to the intramolecular ion-pair state (IP state) (Okada *et al* 1987; Mataga *et al* 1990). The electron transfer in the excited state in polar solvent seems to take place easily when the surrounding solvent orientations are favorable.

On the other hand, the electronic delocalization interaction between D and A in the excited state may be much stronger in the compound group B. In those strongly interacting systems, the time resolved absorption spectra change their band shapes gradually over the delay times, indicating the gradual change of electronic structure accompanied by the conformational change between donor and acceptor groups in the course of the solvation process. From the above experimental results of transient absorption measurements, we can conclude that there exist many states with different degrees of charge transfer and, accordingly, with different degrees of solvation and twisting between two moieties in the excited state (Okada *et al* 1987).

## 2. Time resolved absorption and fluorescence measurements

A femtosecond laser photolysis system was used for the measurement of time-resolved absorption spectra in subpicosecond to tens of picosecond regions. The output of a synchronously pumped pyridine-1 (710 nm) or rhodamine 6G (590 nm) dye laser was amplified to several hundreds of  $\mu\text{J}/\text{pulse}$ . The amplified pulse with several hundred femtoseconds was frequency doubled and used for exciting the sample. The rest of the fundamental pulse was focused into  $\text{D}_2\text{O}$  to generate a white light probe pulse. Two sets of multichannel photodiode detectors were used to observe wide-band transient absorption spectra. When necessary, the observed spectra were corrected for the chirping of the monitoring probe pulse.

The probe light is amplified, in general, by the induced fluorescence emission (stimulated emission) when the transition probability is not so small. In fact, the laser action of ADMA has been found in nonpolar and slightly polar solvents (Nakashima *et al* 1973). The effect of the stimulated emission may be given by the following equation.

The increase  $dI$  of the probe light intensity  $I$  incident on the medium at distance  $dx$

containing excited molecules of concentration  $c$  can be written as

$$dI = Ac dx + B Ic dx - \epsilon Ic dx, \quad (1)$$

where  $A$  and  $B$  are Einstein's coefficients and  $\epsilon$  is the extinction coefficient of  $S_n - S_1$  absorption. The total light intensity measured by a photodiode in the wavelength region without absorption of the ground state molecules may be written as follows under the assumption of uniform distribution of the excited molecules.

$$I = I_0 \exp(B - \epsilon)cx + \{ \exp(B - \epsilon)cx - 1 \} A / (B - \epsilon). \quad (2)$$

The second term on the right-hand side of (2) represents the emission intensity in the absence of probe light ( $I_0 = 0$ ). By subtracting this emission intensity from the observed transient absorption, one can obtain the  $(B - \epsilon)$  spectrum instead of the  $\epsilon$  spectrum ( $S_n - S_1$  absorption), in the absorption region where strong fluorescence is observed.

Time-resolved fluorescence was measured by using a correlated single photon counting technique with a synchronously pumped, cavity dumped dye laser. The observed pulse width of the exciting laser pulse was about 40 ps (FWHM). Fluorescence was detected under the optics setting at the magic angle. Fluorescence decay curves were analyzed by using ACOS 1000 system of the Computation Center, Osaka University. Sample solutions were deaerated by freeze-pump-thaw cycles or by flushing  $N_2$  stream.

### 3. Dynamical behaviors in simple one electron transfer systems

#### 3.1 Time resolved absorption spectra

Time resolved absorption spectra of P1(A) and ANMe(B) in hexanenitrile are indicated in figure 2. In the case of P1, one can see the rapid rise of the characteristic sharp absorption band at 500 nm (pyrene anion) and around 460 nm (N, N-dimethylaniline cation and pyrene anion) due to the intramolecular ion pair state. Time resolved absorption spectra of ANMe show the rise of a cation (480 nm) and an anion ( $> 630$  nm) band and the decay of absorbance of 600 nm which is ascribed to the  $S_n - S_1$  transition localized in the anthracene part. The photoinduced charge separation process in polar solvents for every system indicated in figure 1A can be analyzed by a simple one-electron transfer as a two-state model of LE to IP (Okada *et al* 1987; Mataga *et al* 1990). The main part of the rise curves of the ion-pair state absorbance can be expressed approximately by an exponential function, though the rise curve obtained by more precise measurements shows non-exponential behavior as described later. The obtained approximate rise times in alkanenitriles are listed in table 1 together with  $\tau_L$  of the solvent and solvation time  $\tau_s$ , determined by the measurement of the time dependent Stokes shift of fluorescence (Kahlow *et al* 1988).

Many of the values listed in table 1 were obtained by excitation at 355 nm which corresponds to the excitation up to the acceptor LE state with excess vibrational energy of thousands of wavenumbers. We have also carried out investigations using 295 nm laser pulse as an excitation light as indicated in the table. Although the irradiation at 295 nm corresponds to the excitation of the donor part, we could not

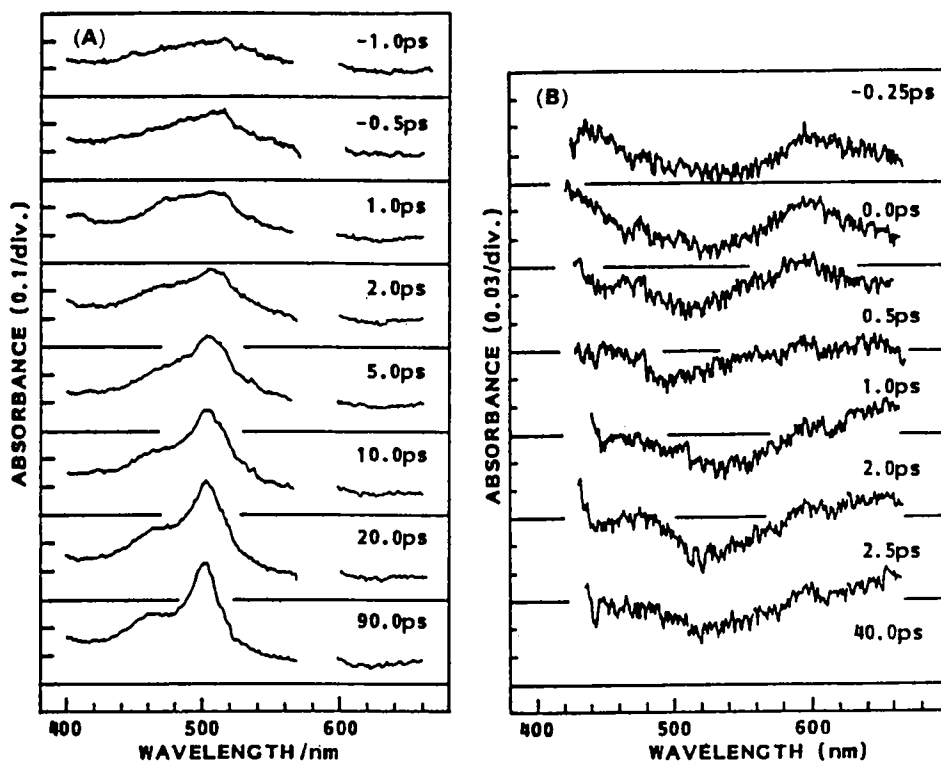


Figure 2. Time resolved absorption spectra of PI (A) and ANMe (B) in hexanenitrile at room temperature.

Table 1. Approximate rise time of the ion pair state in alkanenitriles at room temperature and  $\tau_L$  and  $\tau_s$  of the solvents.

Solvent	Acetonitrile (ps)	Butyronitrile (ps)	Hexanenitrile (ps)
AI	0.65	1.0	1.4
PI	1.7	2.5	1.6 <sup>a)</sup> 4.5 4.5 <sup>a)</sup>
ANMe			0.7
ATMA	0.6		1.5
AHMA	1.5		12.5
$\tau_L$	0.19	0.53	0.98–1.1
$\tau_s$	0.4–0.9	1.5–2.1	3.5–4.5

<sup>a)</sup> Rise time obtained by excitation at 295 nm

detect the rise of the  $S_n \leftarrow S_1$  absorption of the anthracene or pyrene moiety and the electron transfer times obtained were the same as those obtained by 355 nm excitation within experimental error. Since the time scale of the cooling process of a vibrationally hot molecule in solution is about tens of picoseconds (Green 1979; Sealimeyer and

Kaiser 1988; Laemer *et al* 1989), the electron transfer should take place from the state with excess vibrational energy.

The approximate electron transfer times of D–A systems studied here are rather close to the solvation time  $\tau_s$ , but longer than the longitudinal dielectric relaxation time  $\tau_L$  of solvents except in the case of ANMe. In the case of AHMA, the tetramethyl–phenyl ring acts as a spacer between donor (dimethylamino) and acceptor (anthryl) and, therefore, the electronic interaction between two groups is much smaller compared to that of 3,5-ATMA. Actually, we can not observe the dimethylaniline cation bands around 500 nm in the IP state of AHMA, while the cation band maximum at 500 nm is clearly observed in the case of 3,5-ATMA in polar solvents. The observed results suggest that the photoinduced electron transfer process is possibly controlled by the solvent orientation dynamics, especially in the systems of A1, ATMA, and ANMe. It is noted here that the electron transfer time of ANMe in hexanenitrile is faster than  $\tau_L$ . Because of this rapid electron transfer time of ANMe, the electronic interaction responsible for the electron transfer reaction between D and A in ANMe seems to be stronger than that in A1, since the charge density on the N atom of N,N-dimethylaniline is much larger than that on the C atom at *p*-position. It is plausible that the contribution of intramolecular vibrations to electron transfer process will enhance the reaction rate. It is also plausible that some pre-solvated solvent molecules close to the N atom exist in the case of ANMe, because the bulky chromophores connected to the N atom may prevent random fluctuational motion of solvent molecules, leading to the increase of electron transfer rate. The results might be ascribed to the fact that the solvent dielectric response on the electron transfer dynamics for the compound ANMe can not be treated with a homogeneous continuum model of solvent, though the detailed mechanism is not clear now.

### 3.2 Decay curves of LE fluorescence

Time-resolved absorption method has a subpicosecond time resolution but the dynamic range of this method is rather poor. More precise information on the time dependencies of the electron transfer rate were obtained by time resolved fluorescence measurements by means of a single photon counting method (Okada *et al* 1990). The fluorescence decay curves monitored at the fluorescence band of pyrene or anthracene moiety were non-exponential and could not be analyzed by two or three exponential functions. We have analyzed the decay curves by means of an extended exponential function,

$$F(t) = A \exp[-(t/\tau)^\beta] + B \exp(-kt), \quad (3)$$

where the second term is due to the contribution from the photoproducts, the amount of which was about 0.1% in a fresh sample.

The temperature dependencies of the decay curve of LE fluorescence of A1 in 1-butanol are shown in figure 3. The decay curves are fitted successfully by (3). The time scale per channel is different between two panels in the figure and both time scales are indicated for the decay curve measured at 246 K for the comparison of the time profiles in the wide time range. The value of  $\beta$  and  $\tau$  obtained are summarized in table 2. The correlation time  $\tau$  increases and  $\beta$  decreases with decreasing temperature. The smaller  $\beta$  value may reflect the broader distribution of solvent orientational relaxation times, indicating the enhancement inhomogeneity of the systems.

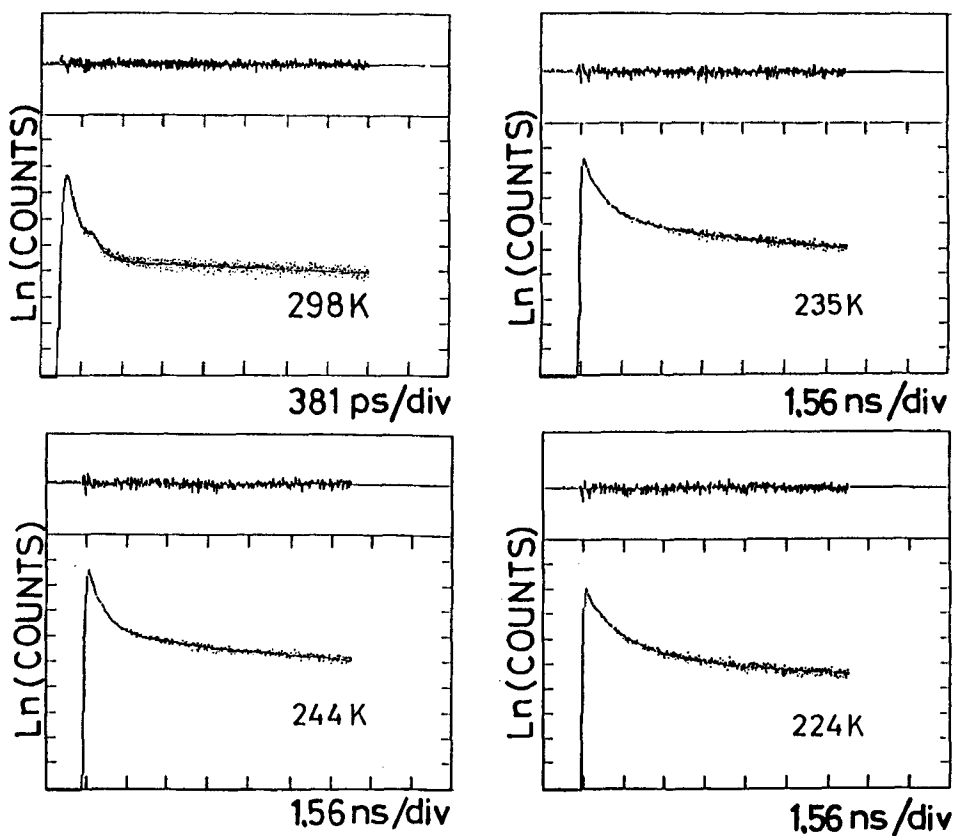


Figure 3. Temperature dependence of the LE fluorescence decay curve of A1 in 1-butanol (dotted) and the calculated curve using (3) (solid line).

Table 2.  $\beta$  and  $\tau$  values of the intramolecular D-A systems in some solvents.

	Solvent	Temperature (K)	$\beta$	$\tau$ (ps)
A1	1-Butanol	298	0.62	8.2
		244	0.46	43.5
		235	0.41	44.2
		224	0.35	38.2
	2-MethylTHF	298	0.79	9.2
P1	1-Butanol	298	0.95	86.9
		254	0.82	192
		248	0.75	243
		226	0.69	292
		206	0.74	692
	Hexanenitrile	298	0.8	5.8
ATMA	1-Butanol	298	0.52	3.6
AHMA	1-Butanol	298	1.0	86.9
		254	0.90	590
		196	0.73	2270

The values of  $\beta$  and  $\tau$  obtained depend strongly on the sample. For example, the correlation times of the observed fluorescence decay curve in the case of A1 and 3,5-ATMA in 1-butanol at room temperature are rather close to the fastest longitudinal dielectric relaxation time but close to the bulk relaxation time in the case of P1 and AHMA. It is well known that the dielectric responses of alcoholic solvents do not show a simple Debye dispersion. In this respect, the non-exponential behavior in the systems of A1 in 2-methyltetrahydrofuran and P1 in hexanenitrile, where the solvents are considered to show simple dielectric relaxation, seems very important.

The decay curve of the LE fluorescence of P1 in hexanenitrile was well analyzed by (3) with  $\beta = 0.8$  and  $\tau = 5.8$  ps. The rise curve of the ion-pair state of P1 obtained by the transient absorption measurement shown in figure 2A was reproduced very well even in the picosecond time regime by the same values of  $\beta$  and  $\tau$  obtained by the fluorescence measurement as shown in figure 4A as well as the case of A1 in 1-butanol (figure 4B), although the time resolution of our single photon counting system was about 10 ps. Other systems such as 3,5-ATMA in 1-butanol and A1 in 2-methyltetrahydrofuran were also analyzed successfully by the same manner.

One of the possible mechanisms responsible for the extended exponential behavior of the intramolecular electron transfer reaction in polar solvents may be saturation effects of solvation dynamics in nearby solvents strongly coupled to the charge distribution in the excited D-A systems. Such a solute-solvent interaction will give a radial distribution of the orientational relaxation time of the solvent. Another possibility may be related to a relaxation dynamics of the initial distribution of solvation. When the relaxation time between solvation modes is longer than the rapid electron transfer time in a solvation mode favorable for intramolecular electron transfer reaction, the distribution of solvation may be deviated in the course of the reaction from that of a equilibrium one, leading to the observed non-exponential behavior of the fluorescence decay curve.

#### 4. Charge transfer in strongly interacting systems

##### 4.1 ADMA and related compounds

Time-resolved absorption spectra of ADMA and 10-CN-ADMA in hexanenitrile are indicated in figure 4. A depression of the absorbance spectrum of ADMA was observed around 459 nm at 0.2 ps and shifted toward longer wavelengths with increase of the delay times owing to the dynamic Stokes shift of the stimulated fluorescence emission as described in §2. It is noted that the absorbance spectrum detected at  $-0.2$  ps is similar to the  $S_n - S_1$  absorption of anthracene or 9-phenylanthracene itself. The transient spectra change in shape gradually with increase of the delay time (Okada *et al* 1987). The rise time of charge transfer state of ADMA in hexanenitrile obtained at 660 nm where the effect of the stimulated emission on the spectra seems to be negligible was 0.6 ps followed by small rise with longer time scales, although the transient spectra cannot be analyzed by the simple two state model of LE to IP.

In the case of 10-CN-ADMA in hexanenitrile, broad and structureless spectra were detected. The effect of the stimulated emission was hardly observed (slightly observed around 570 nm at 0.8 ps spectrum), indicating that the electronic structure of charge



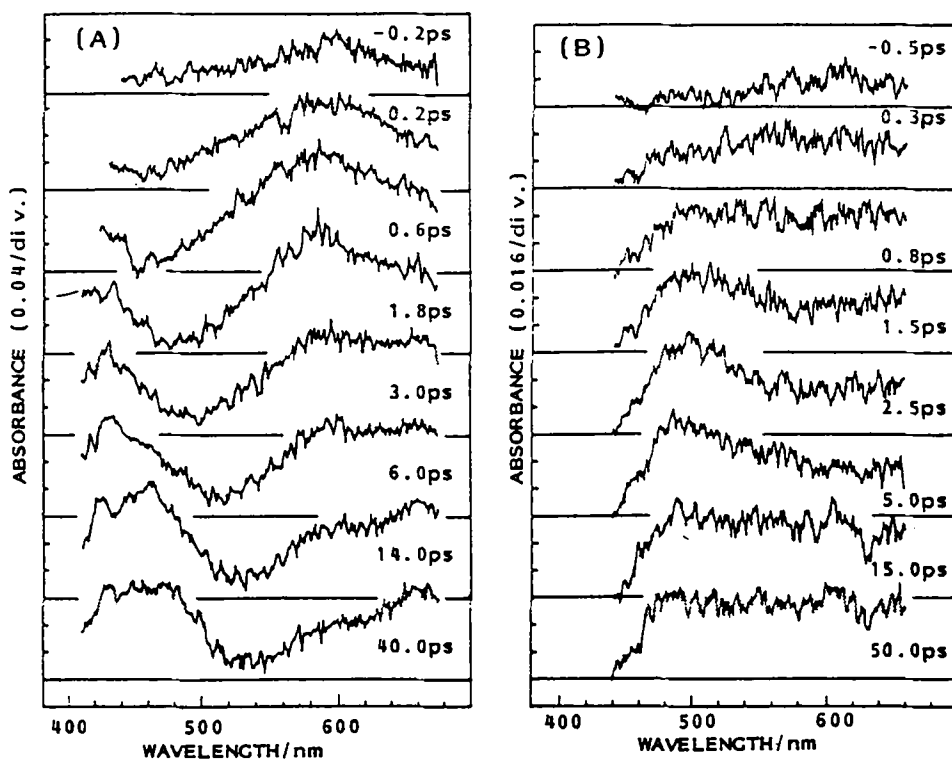


Figure 4. Time resolved absorption spectra of ADMA (A) and 10-CN-ADMA (B) in hexanenitrile at room temperature.

transfer state of 10-CN-ADMA may be more polar than that of ADMA due to the cyano-substitution, leading to decrease of the transition moment from the excited state to ground state. It is difficult again to analyze the spectra by the two state model.

On the basis of the above results of the transient absorption measurements, we may conclude that there exist many states with different electronic structures associated with different degrees of solvation and twisting angle between D and A. The electronic structure may be regulated by the intramolecular rearrangements connected nonlinearly to the surrounding solvent molecules (Masaki *et al* 1976). These results observed in the strongly interacting systems cannot be interpreted by the simple model based on the usual electron transfer theory which assumes rather weak interaction.

#### 4.2 9,9'-Bianthryl and related compounds

The fluorescence spectrum of BA in low temperature matrices is structured and quite similar to the emission of monomeric anthracene, since two anthryl planes of BA are mutually perpendicular in the ground state. In nonpolar solvents at room temperature, the fluorescence band is broadened and slightly red-shifted compared with that detected at 77 K, which indicates that the excited equilibrium state at room temperature is delocalized between two equal anthracene subunits and probably is a little inclined from a perpendicular configuration. The  $S_0 - S_1$  absorption spectra

are also different from each other between two temperatures corresponding to the difference of the fluorescence bands. The absorption spectra obtained immediately after laser irradiation is assigned mainly to the spectrum due to the ground state geometry. With increase of the delay time, the spectrum changes toward that of the equilibrium state. We can estimate the decay time of the initial configuration. The obtained decay times in alkane solvents are several picoseconds and depend only slightly upon the solvent viscosity (Okada *et al* 1990).

The formation of the charge transfer state in viscous alcoholic solvents such as 1-butanol and 1-pentanol, is reported elsewhere (Mataga *et al* 1989). The charge transfer takes place from the twisted form (relaxed fluorescent state observed in nonpolar solvents) and the observed charge transfer time is similar to the longitudinal relaxation time of the alcohols. We have also examined the charge transfer processes of BA in alkanenitriles where the solvent relaxation time is much faster than that of alcohols and have concluded that the charge transfer process competes with the relaxation process to the inclined form. The observed spectra of the charge transfer state in polar solvents are not the same as the superposition of absorption bands of anion and cation radicals of anthracene indicating some delocalization interaction between two identical components. From an analysis of the transient absorption spectra, the rise times of the charge transfer state have been estimated to be 1.8, 3.4 and 7.5 ps in acetonitrile, butyronitrile, and hexanenitrile, respectively. The obtained rise times are much longer than the solvation time and longitudinal relaxation time of solvent.

In the case of C9A in alkanenitrile, we have observed slower rise time of the charge transfer state than the case of BA, that is 3.8 and 9.0 ps in butyronitrile and hexanenitrile, respectively. The electronic delocalization interaction in the excited state of C9A may be stronger than that of BA due to the smaller steric hindrance.

One of the possible mechanisms for the slow charge transfer time may be solute-solvent interaction in the excited state, namely, the electronic structure depends upon the orientation in the surrounding solvent molecules, while the orientation of solvent causes the electronic structure of solute to decrease the delocalization interaction and to attain the more polar structure with the geometric structural change.

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