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Charge-Transfer-Induced Twisting of the Nitro Group

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Excited-state relaxation dynamics of 2-amino-7-nitrofluorene (ANF) and 2-dimethylamino-7-nitrofluorene (DMANF) has been investigated in two aprotic solvents, namely acetonitrile and DMSO using femtosecond transient absorption spectroscopic technique. Following photoexcitation to the highly dipolar excited singlet (S_1) state, ANF and DMANF undergo mainly two concomitant relaxation processes, namely dipolar solvation and conformational relaxation via twisting of the nitro group to an orthogonal configuration with respect to the aromatic plane. Viscosity dependence of the relaxation dynamics of the S_1 states of both ANF and DMANF suggests no involvement of the twisting motion of the amino or dimethylamino group in the charge-transfer process. The twisting of the nitro group is found to be a friction affected diffusive motion, which does not associate with any further charge transfer. The results presented in this paper resolve experimentally the dynamics of the twisting motion of the nitro group for the first time.

Introduction. During the last two decades, dynamics of intramolecular charge transfer (ICT) in the excited states of numerous aromatic molecules of the type D−Ar−A (where D and A represents the electron donor and acceptor moieties, respectively, and Ar is an aromatic system linking D and A through π conjugation) have been the subject of extensive theoretical and experimental investigations.[1,2] The most controversial phenomenona in chemical science has been the formation of the twisted intramolecular charge transfer (TICT) state in which the π-orbitals of the donor and the acceptor moieties exist in orthogonal conformation.[1,3] There are two important consequences of formation of the TICT state. First, following photoexcitation, the locally excited singlet S_1(LE) state relaxes to the highly polar S_1(TICT) state and emission may be observed from both these states (dual emission).[3−7] Subsequently, the S_1(TICT) state undergoes preferential stabilization in polar solvents via solvent reorganization, called dipolar solvation, which is revealed by large Stokes shifts of the fluorescence emission in more polar solvents.[8,9] In the TICT model, both the intramolecular twisting and solvation dynamics are considered as friction affected and these two processes are supposed to be coupled.[10] Several models have been proposed to explain the solvent influence on the intramolecular charge transfer and twisting processes.[1−11]

The simplest and the most well studied molecule of the type D−Ar−A is dimethylaminobenzonitrile, $(CH_3)_2N-Ph-CN$, which shows a very distinct TICT behavior.[1,3] Among a large number of molecules substituted with different kinds of donor and acceptor moieties, nitroanilines have also been considered as potential candidates for TICT formation in the excited state. However, a very few studies have been directed toward understanding the excited-state properties of nitroaromatics because the usual fluorescence techniques cannot be applied to study their photophysical properties due to typically fast intersystem crossing (ISC) to the triplet state.[12−19] Recently, Ernsting and his co-workers investigated the relaxation dynamics of the S_1 state of *p*-nitroaniline (pNA) using ultrafast transient absorption spectroscopic technique and semiempirical theoretical calculation for both the ground and excited states.[17−19] Geometry optimization of the ground state along the $-NH_2$ waging and $-NO_2$ twisting coordinates revealed the fact that the NO_2 group rotates freely in the ground-state and the charge-transfer absorption band is broadened because of distribution of $-NO_2$ conformers around the coplanar conformation of the benzene moiety. However, in the excited electronic state, the NO_2 group is oriented orthogonal to the benzene ring. Ultrafast relaxation of the S_1 state of pNA taking place in the sub-1 ps time domain following photoexcitation by using a 400 nm light pulse was shown to consist of several consecutive processes such as vibrational relaxation, solvation, nitro twisting, and internal conversion. However, the dynamics of the twisting motion of the nitro group and the internal conversion process could not be resolved, but two distinct maxima of the stimulated emission (SE) bands prompted the authors to assume the presence of two different conformers of PNA in the excited state. They concluded that the internal conversion process was governed by the twisting of the nitro group to the perpendicular conformation toward the deep minimum of the potential energy surface (PES) along the twisting coordinate.

Ernsting and his co-workers also investigated the relaxation dynamics of 2-amino-7-nitrofluorenone (ANF) (Scheme 1) in acetonitrile using femtosecond transient absorption spectroscopic technique in sub-1 ps time-domain.[18] A large and ultrafast

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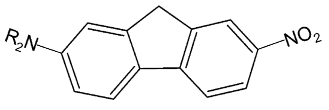
SCHEME 1: Molecular Structures of ANF and DMANF



R = H : ANF

R = CH_3 : DMANF

dynamic Stokes shift of the SE band maximum was assigned to dipolar solvation process. An important aspect of this work was to unravel the oscillatory behavior in the dynamic Stokes shift of SE band for the first time. However, the results reported here did not reveal anything relating to the conformational relaxation of ANF in the excited state.

In the present letter, we report the preliminary results of our investigation on the relaxation dynamics of ANF and its dimethyl-substituted derivative, namely 2-(4-*N*,*N*-dimethylamino-7-nitrofluorenone (DMANF) (Scheme 1) in polar aprotic solvents. This investigation provides, for the first time, an experimental proof of a few hypotheses made earlier regarding the relaxation dynamics in the excited states of nitroaromatics.[12−16] First, unlike in numerous *p*-substituted *N*,*N*-dimethylaniline derivatives, the ICT process in the excited states of *N*,*N*-dimethylamino-substituted nitroaromatics does not involve the twisting of the dimethylamino group (i.e., no involvement of the TICT process). Second, in addition to dipolar solvation, the energy of the ICT state of the nitroaromatics is further stabilized by twisting of the nitro group to an orthogonal configuration with respect to the aromatic ring. However, the twisting of the nitro group is not associated with further charge transfer, and hence this cannot be considered as the TICT process.

Experimental Section. ANF and DMANF have been prepared and purified following a standard procedure.[20] All the solvents (Spectrochem, India) were of UV spectroscopic grade and were used as received without further purification. Steady-state absorption spectra were recorded on a Shimadzu model UV-160A spectrophotometer. Fluorescence spectra, which were corrected for wavelength dependence of the instrument response, were recorded using a diode array based optical multichannel analyzer (Spectroscopic Instruments, Germany) following photoexcitation by using 355 nm laser pulses from a picosecond Nd:YAG laser (Continuum). The emission spectra in rigid matrices at 77 K were recorded by freezing the sample solutions, which were taken in a round quartz tube of 4 mm diameter, in liquid nitrogen put in a quartz dewar.

Temporal dynamics of the transient species created following photoexcitation using 400 nm laser pulses were recorded in the 470−1000 nm wavelength region using a femtosecond pump−probe transient absorption spectrometer, which has been described in detail elsewhere.[21] The overall time resolution of the absorption spectrometer is about 120 fs. The temporal profiles recorded using different probe wavelengths were fitted with up to four exponentially decaying or growing components by iterative deconvolution method using an sech^2 type instrument response function with fwhm of 120 fs and were also used for constructing the time-resolved differential absorption spectra.

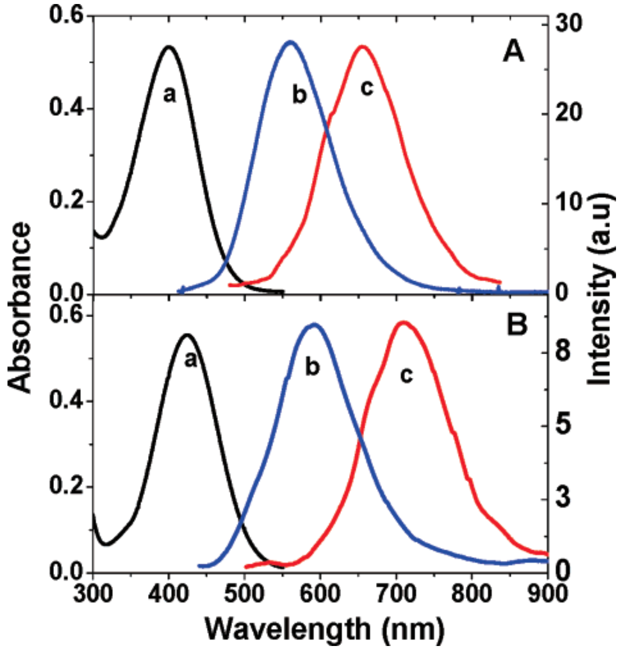


Figure 1. Steady-state absorption (a) and fluorescence spectra (b and c) of ANF (A) and DMANF (B) in acetonitrile recorded in rigid matrices at 77 K (b) and in solution at 298 K (a and c).

Results and Discussion. Figure 1A shows the steady-state absorption and fluorescence spectra of ANF in acetonoitrile solution at room temperature as well as in rigid matrix at 77 K. The broad absorption band is assigned to the ICT band and excitation using 400 nm light produces the molecules in the S_1(ICT) state directly. The fluorescence spectrum recorded in solution at room temperature has a large bandwidth (2900 cm^{-1}) and a large Stokes shift (9800 cm^{-1}) with maximum at 655 nm, and it can be assigned to the emission from the S_1(ICT) state, which is a highly polar excited state. Earlier studies revealed a large solvatochromic behavior of the dye due to a large change in the dipole moment following photoexcitation of ANF to the S_1(ICT) state ($\Delta\mu = 25$ D) and the dipole moments of the ground and excited states have been determined to be 7 and 32 D, respectively.[22−27] In a rigid matrix, in which the reorientation of the solvent molecules is much slower than the lifetime of the excited state, the S_1(ICT) state remains nearly unsolvated and also no significant change in geometrical conformation can take place. The fluorescence spectrum recorded at 77 K has a much smaller Stokes shift than the shift observed in the fluorescence spectrum recorded in solution. The fluorescence spectra recorded in solution (at 298 K) and rigid matrix (at 77 K) of methylcyclohexane are nearly identical, and both have the maximum at 560 nm (not shown in the figure). Stokes shifts measured in benzene−acetonitrile solvent mixtures are linearly correlated to the dielectric properties of the solvents according to the modified Lippert equation.[28] These observations suggest that the dual emission feature, which is the characteristic of the TICT process, is not observed in the relaxation of the S_1 state and the solvent polarity-dependent Stokes shift results from the increased solvation energy in more polar solvents due to dipolar solvation. The solvation energy, which is calculated from the difference in energy of the fluorescence maxima observed in rigid matrix (550 nm) and in solution (655 nm), is as large as about 2600 cm^{-1} in acetonitrile.

Absorption and emission spectra of DMANF in acetonitrile solution at room temperature as well as the emission spectrum recorded in rigid matrix of the same solvent at 77 K are shown in Figure 1B. In this case, both the absorption and fluorescence maxima show bathochromic shifts comparable to those observed for ANF in the same solvent. The fluorescence maxima appear at 590 and 710 nm in rigid matrix and solution, respectively, and hence the Stokes shift and solvation energy have been calculated to be about 2850 and 9500 cm^{-1}, respectively. The values of both these parameters are comparable to those determined in the case of ANF in acetonitrile solvent and suggests that the intramolecular charge-transfer characteristics

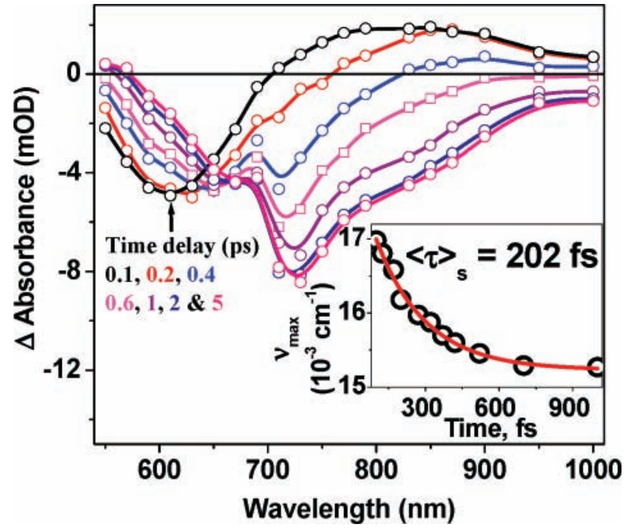


Figure 2. Time-resolved differential absorption spectra of the transient species formed following photoexcitation of ANF in acetonitrile using 400 nm laser pulses of 50 fs duration. Inset: Time-correlation curve of the dynamic shift of the stimulated emission band observed in the 500−750 nm region. Exponential fitting of this curve provides the average lifetime of dipolar solvation, $\langle\tau\rangle_{\text{solv}}$, in this solvent.

of these two molecules are very similar, in spite of the fact that the $N(CH_3)_2$ group has larger electron donating ability than that of the NH_2 group.

Figure 2 presents the time-resolved differential absorption spectra of the transient species produced due to photoexcitation of ANF in acetonitrile solution at room temperature using 400 nm laser pulses of 70 fs duration. The transient spectrum constructed for 0.1 ps delay-time shows the presence of a SE band with maximum at ca. 600 nm and a broad excited-state absorption (ESA) band in the 700−1000 nm region. With increase in delay time, the maximum of the SE band gradually shifts toward the lower energy region without any change in intensity of the band. The wavelength maximum of this SE band shifts from 600 nm observed at 0.1 ps to ca. 675 nm at 1 ps delay time. However, the most important feature to observe in the time-resolved spectra presented in Figure 2 is the concomitant development of another distinct emission band in the 700−1000 nm region with a maximum at ca. 725 nm. Unlike the SE band that appears in the 500−700 nm region, the maximum of this new SE band shows very little dynamic shift of the SE maximum during the course of its development. It is interesting (and somewhat surprising, too) to note that this SE band has no analogue in the steady-state emission spectrum of ANF in acetonitrile (Figure 1A).

Temporal dynamics recorded in the 470−750 nm region is dependent on the probe wavelength because of the dynamic Stokes shift of the SE band as well as the development of the new SE band. However, the temporal profiles recorded in the 750−1000 nm region do not show wavelength dependence, and each of them could be fitted with a triexponential function having the lifetimes independent of the probe wavelength (Figure 3). While the details of the solvent and wavelength dependence of the dynamics of the excited states of ANF and DMANF will be discussed in another paper, we will present here only the analysis of the temporal dynamics at 830 nm in the polar aprotic solvents, namely acetonitrile and DMSO. The fit function consists of two exponential decay terms with the lifetimes of τ_1(d) and τ_2(d) and one exponential growth term with the lifetime of τ_3(g). The ultrafast decay component with the lifetime of τ_1(d) arises due to the decay of the ESA band in the 700−1000 nm region, and the other decay component, τ_2(d), in reality, arises because of the growth of the SE band in this region. The growing component with a longer lifetime, τ_3(g), arises because of the decay of the intensity of stimulated emission. The values of τ_1(d), τ_2(d), and τ_3(g) have been evaluated to be 0.3, 1.0, and 76 ps in acetonitrile and 1.0, 9.7, and 99 ps in DMSO, respectively.

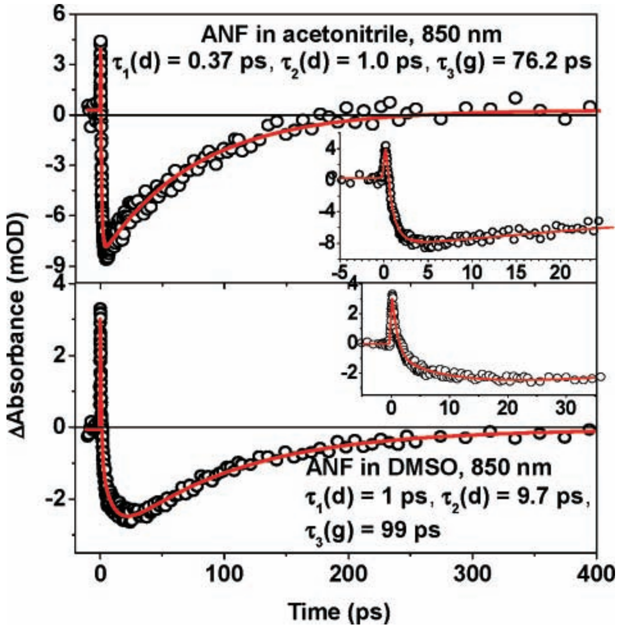


Figure 3. Temporal dynamics of the transient species recorded at 850 nm following photoexcitation of ANF in acetonitrile. Solid lines represent the best-fit three exponential fit functions obtained after iterative deconvolution of the experimental temporal profiles with the sech^2 type instrument response profile with fwhm of 120 fs. Inset: Temporal profiles at shorter time scales.

We mentioned earlier that Ernsting et al. also studied the excited relaxation dynamics of ANF in acetonitrile with 40 fs time resolution and monitored the complete evolution of this SE band in the 400−750 nm region in the sub-200 fs time domain.[19] They concluded that the time-dependent Stokes shift of the SE band was determined by pure solvation of the S_1(ICT) state, supporting the conclusion of Hallidy and Topp.[24] The maximum of the SE band was seen to appear at 550 nm at 40 fs delay time. This emission maximum matches with that of the fluorescence spectrum of ANF recorded in the rigid matrix of acetonitrile and corresponds to the unsolvated S_1(ICT) state of ANF. In our experiment, we observe the maximum of the SE band at 600 nm at 0.1 ps delay time, when the S_1 state has already been partially solvated. Combining the information obtained from the steady-state and the time-resolved experiments and following the suggestion of Ernsting and co-workers, evolution of the SE band in the 500−700 nm region is assigned to the dipolar solvation of the S_1(ICT) state formed following photoexcitaion. Because the total solvation process is nonexponential and 60% of the solvation process, which is known as “inertial solvation”, is complete within 200 fs,[19] only the average solvation time could be determined in the present case by exponential fitting of the time correlation curve for the dynamic shift of the SE maximum (inset, Figure 2). The lifetime of the average solvation time, $\langle\tau\rangle_s$, obtained from this fitting, is about 0.2 ps, which agrees well the average solvation time predicted from a simple continuum calculation, but a little shorter than those values experimentally determined earlier using other fluorescence probes.[29,30,31]

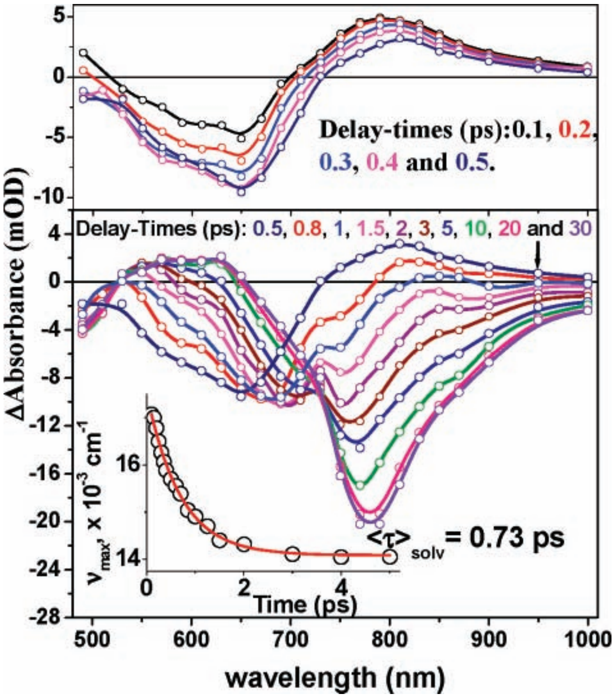


Figure 4. Time-resolved differential absorption spectra of the transient species formed following photoexcitation of DMANF in acetonitrile using 400 nm laser pulses of 50 fs duration. Inset: Exponential fitting of the time-correlation curve of the dynamic shift of the stimulated emission band observed in the 500−750 nm region provides the average lifetime of dipolar solvation, $\langle\tau\rangle_{solv}$, in this solvent.

While the solvation process is nearly complete within about 1 ps delay time (inset A, Figure 2), the growth of another SE band in the 700−1000 nm continues up to about 5 ps. Surprisingly, Ernsting and co-workers did not observe this feature. We assign the development of this new band due to conformational relaxation of the molecule via twisting of the nitro group to an orthogonal configuration with respect to the molecular plane of the fluorene (aromatic) moiety. Very little dynamic shift of the SE maximum during the development of this new SE band supports the prediction about the twisting of the nitro group because this process is associated with a small change in dipole moment of the molecule.[13] This conformer of the S_1(ICT) state is nonfluorescent because the molecular geometry after twisting of the nitro group reaches the sink region of the potential energy surface, where the strong anharmonicity of the molecular vibrations increases the overlap between the ground and the excited states. Consequently, a fast nonradiative relaxation rate prevails and the spontaneous emission cross-section becomes negligibly small. However, the larger SE cross section of this twisted state as compared to that of the untwisted conformer results in the appearance of the SE band, which reveals the formation of the twisted conformer (vide infra). Following these arguments regarding the evolution of the excited states of ANF, the three lifetime components, namely τ_1(d), τ_2(d), and τ_3(g), are assigned to those of dipolar solvation, the twisting of the nitro group, and the S_1 state of ANF, respectively. A larger lifetime of the nitro twisting process in DMSO (viscosity ∼ 1.99 cP) as compared to that measured in acetonitrile (viscosity ∼ 0.34 cP) suggests that it represents a friction affected diffusive motion.

Figure 4 shows the time-resolved transient spectra of DMANF in DMSO following photoexcitation using 400 nm laser light. We observe that evolution of the transient spectra follows the features similar to those observed in the case of ANF in acetonitrile (Figure 2). However, in this case, we observe that, immediately after photoexcitation, the intensity of the SE band, which appears in the 500−750 nm region, initially increases up to about 0.5 ps delay time. This fact suggests that 400 nm light excites the DMANF molecule to the LE state and the initial increase in intensity of the SE band indicates the dynamics of the conversion of the LE to the ICT state. The average lifetime of the dipolar solvation process determined from the time correlation curve of the dynamic Stokes shift of the SE maximum is about 0.73 ps (inset A, Figure 4), which is also much shorter than the average solvation time (1.4−3.1 ps) determined in this solvent using other kinds of probes.[31,32] The transient spectrum recorded for the 30 ps delay time shows the presence of the only SE band with maximum at 790 nm, and this band represents the emission from that conformer of the S_1(ICT) state, which has the nitro group orthogonally twisted with respect to the aromatic plane. In the case of DMANF, too, we have not observed the spontaneous emission from this conformer in the steady-state fluorescence spectrum recorded in acetonitrile (Figure 1B).

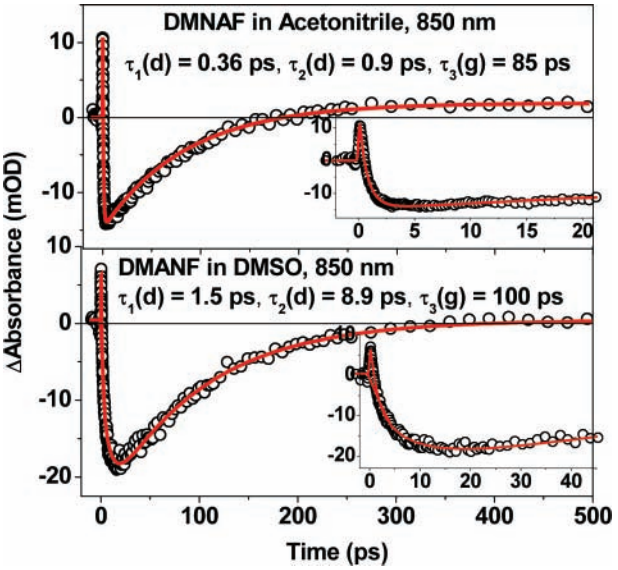


Figure 5. Temporal dynamics of the transient species recorded at 850 nm following photoexcitation of ANF in acetonitrile. Solid lines represent the best-fit three exponential fit functions obtained after iterative deconvolution of the experimental temporal profiles with the sech^2 type instrument response profile with fwhm of 120 fs. Inset: Temporal profiles at shorter time scale.

Temporal evolution of the transient species recorded at 850 nm in acetonitrile and DMSO solvents are shown in Figure 5. Following the same arguments as presented earlier in the case of ANF, the lifetimes of the dipolar solvation, twisting motion of the nitro group, and the S_1(ICT) state of DMNAF have been evaluated to be 0.3, 0.9, and 79 ps in acetonitrile and 1.5, 8.9, and 100 ps in DMSO, respectively. A comparison of these values with those for ANF reveal that the lifetimes of all three processes are nearly the same for both these molecules in the corresponding solvents in spite of the fact that the viscosity of DMSO (∼1.99 cP) is about six times larger than that of acetonitrile (∼0.34 cP).[33] The amino or the dimethylamino group does not twist to facilitate further charge transfer, but only wags about the aromatic plane. Therefore, we conclude that the conventional TICT process is not observed in this molecule and the charge-transfer dynamics in the S_1(ICT) state is nearly independent of the size as well as the electron-donating ability of the donor group. Following creation of the S_1(ICT) state, in which the charge is transferred from the amino or the dimethylamino group to the nitro group, mobility of these functional groups changes. Dobkowski et al. investigated the possibility whether *p*-nitro-*N*,*N*-dimethylaniline (*p*-NDMA) would show a relaxation to the TICT state in polar solvents.[13] Experimental results and quantum chemical calculation performed by this group established that, in contrast to numerous derivatives of *p*-substituted *N*,*N*-dimethylaniline, *p*-NDMA, following photoexcitation in fluid polar solvents, did not relax to the TICT state generated by the rotation of either the dimethylamino group or the nitro group. This result is consistent with the suggestion of Cowley and Peoples that, for strong acceptors, such as nitrobenzene, TICT formation cannot be observed.[14] The dynamical behavior of the excited state of pNA is also in contrast with the conventional concept of twisting of the dimethylamino group, which has been found crucial in many common photoinduced charge-transfer dynamics.[1]

While the solvent reorientation takes place due to creation of a large dipole following photoexcitation, transfer of charge from the donor to the acceptor group induces the twisting of the nitro group to its perpendicular configuration with respect to the aromatic plane. Sinha and Yates made theoretical calculation and electro-optical absorption measurements on differently substituted nitroaromatics.[12] They found that the twisting about the single bond connecting the donor (an aromatic ring) and the acceptor (the nitro group) had a tremendous effect on the charge distribution both in the ground state and in the Franck−Condon (FC) excited state. However, they revealed an important fact that a twist of the nitro group is accompanied by a very small change (∼2D) of the dipole moment, and this cannot be considered as a TICT process and hence further solvation would not be required for the new conformer of the S_1(ICT) state. This fact is supported by the absence of dynamic shift of the maximum of the SE band assigned to the new conformer formed following twisting motion of the nitro group. However, the viscosity dependence of the lifetime of the nitro group twisting suggests that the process is a friction affected diffusive motion.

Conclusion. We report the dynamics of solvation and conformational relaxationof ANF and DMANF in aprotic solvents. The S_1(ICT) state, which is created following photoexcitation using 400 nm light and has a large dipole moment, shows strong solvatochromic behavior revealed by a large dynamic shift of the stimulated emission maximum in the time-resolved transient spectra. Concomitant with the solvation process, it also undergoes the conformational relaxation only by twisting of the nitro group, whereas the amino or dimethylamino group only wags about the aromatic plane. Because this conformational relaxation does not accompany any further charge transfer in the S_1(ICT) state, it cannot be considered as the conventional TICT process.

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