3.1. INTRODUCTION

Traditionally, a chemical reaction is described as the passage of the reactants over an activation barrier (Eₐ) to form the products. In the case of reactions conducted in solution, solvent friction plays a very important role in both the cases of the reactions either with a finite barrier (Eₐ > kT) or no barrier (Eₐ ≤ kT ~ 1 kcal mol⁻¹), i.e. barrierless reactions.¹ - ³ The case with a sizable internal barrier has been discussed extensively from both the experimental and theoretical viewpoints following the classic work of Kramers.⁴ - ⁷ However, a large number of important chemical and biological reactions in solution occur without the intervention of any potential barrier and the dynamics of a barrierless chemical reaction differs considerably from those having an activation barrier.⁸ - ³⁵ In the absence of a barrier between the reactants and the products, there is no separation of timescales between the motion in the reactive region and in the rest of the potential energy surface (PES). Therefore, these reactions are generally characterized by high reaction rates (occurring in pico and sub-picosecond time scales), exhibit temperature dependence, which is distinctly different from that of the high barrier reactions and are often strongly coupled to solvent viscosity. Actually, the viscosity dependence of the yield or the rates of the reaction have often been used to identify and characterize the mechanism of these reactions (vide infra).

As early as in the beginning of the last century, it was noticed that some diphenylmethane (DPM) and triphenylmethane (TPM) dyes do not fluoresce in low viscosity solvents, but are strongly fluorescent in highly viscous solvents.¹⁰, ¹¹ Among these classes of dyes, Auramine, a dimethylamino substituted DPM cationic dye (Scheme I) has been considered to be a representative of that class of compounds, which show a single fluorescence band with a little solvent effect on the spectral position but a large viscosity effect on the fluorescence quantum yield. Oster and Nishijima measured the fluorescence yield of
Auramine in glycerol at various temperatures and in dextrose-glycerol-water mixtures at constant temperature. They found that the reciprocal of the fluorescence intensity was proportional to T/\(\eta\) (where \(\eta\) is the shear or macroscopic viscosity of the solvent). To interpret these results, they suggested a theoretical model for the barrierless reactions for the first time. They assumed two local sink functions, through which the population leaks away with the diffusion controlled rate. However, the excited state potential energy is independent of the torsional angle of the dimethylanilino groups and twisting only contributes to the broadening of the excited state population by diffusion over a flat potential. They also calculated that the phenyl rings needed to rotate by at least 2° relative to one another during the quenching process.

Förster and Hoffman reported a \(\eta^{2/3}\) dependence of the fluorescence yield and an \(\exp(-at^3)\) time-dependence of the relaxation rate in alcoholic solvents. On the basis of their results, they proposed another theoretical model predicting that the rotation of the phenyl rings in the excited state was driven by the downhill of a parabolically shaped potential energy surface to a minimum or a sink, which was responsible for the torsional coordinate dependent radiationless decay to the ground state. The \(\eta^{2/3}\) dependence of the fluorescence yield on the viscosity received experimental support in the older literature, but was disputed later. However, the functional form of the fluorescence decay predicted has never been observed experimentally.

Later, Bagchi, Fleming and Oxtoby proposed a generalized model to describe the twisting motion of the phenyl groups in TPM dyes on the parabolically shaped excited state potential energy surface with a position dependent or nonlocal sink function. Unlike in the case of Förster and Hoffman theory, which predicts only dynamic Stokes shift without emission band broadening, according to the Bagchi, Fleming and Oxtoby theory, both the dynamic Stokes shift and the emission band broadening is expected during the excited state relaxation process.

During the last three decades, a large number of experimental studies have been carried out using transient absorption and time-resolved fluorescence spectroscopic techniques to understand the ultrafast radiationless deactivation mechanism and the dynamics of the phenyl group twisting in DPM and TPM dyes, since they are prototypes for models of barrierless chemical reactions in solution, which can be initiated by photoexcitation.
Main aim of most of these studies reported in the early nineties of the last century was to understand the viscosity dependent nature of the radiationless deactivation mechanism of the excited state. General features of the photophysics of the TPM dyes, which came out from these studies, can be summarized as follows. The overall viscosity dependence of the excited state absorption and fluorescence decays of the TPM dyes in normal alcohols at different temperatures and pressures (to vary the viscosity) is linear.\textsuperscript{25, 26} However, non-linear viscosity dependence of fluorescence quantum yield has also been observed in similar kinds of solvents as a function of pressure, which has been tentatively attributed to pressure dependence of the radiative rate. Solvent dependence of the relaxation rate in TPM molecules cannot, as usually is done, be described by a viscosity dependence only. Because of solvent dependence of the shape and shifts of the excited state potential energy surface, different values of the activation energy and viscosity dependence is obtained in the various n-alcohols.\textsuperscript{23, 24} Although a linear viscosity dependence is observed in low viscosity alcohols ($\eta < 5$ cP), in which the relaxation is largely controlled by the barrierless rotational diffusion, the relaxation process is mainly controlled by the potential energy barrier in higher alcohols. Solvent dependent torsional dynamics has also been observed in aprtoic solvents and solvent mixtures too.\textsuperscript{29} Therefore, the reaction may not be considered barrierless in the strictest sense and this is considered as one of the main reasons for the failure of the existing theories in explaining the experimental results.

In recent years, improvement in the time resolution of the spectroscopic techniques down to the sub-picosecond and femtosecond time domain could reveal the evidence for the formation of an intervening transient state following a barrierless or a small barrier activated process from the locally excited (LE) state.\textsuperscript{31 - 37} Martin and coworkers studied the photoinduced processes in different kinds of flexible donor – acceptor complexes containing aniline groups as the electron donor, including Auramine and described the excited state relaxation is a two-state barrierless process.\textsuperscript{31 - 35} The transient state was characterized as an emissive charge transfer (CT) state in some cases, but non-emissive or a dark state in other cases. However, no direct information regarding the structural changes occurring during the relaxation processes could be obtained from the observed viscosity effect.

Nagasawa et. al. reported the results of pump-probe measurements on two TPM dyes, namely malachite green and crystal violet, with the time resolution of 30 fs and discussed
Ultrafast Twisting Dynamics in the Excited State of Auramine

the viscosity dependent aspects of the dynamics in order to understand the difference between bulk viscosity and microscopic viscosity, which a molecule actually feels.\textsuperscript{40} The pump – probe signals were analyzed using three exponential decay or growth functions and all the three components, including the component with the lifetime of a few tens of femtosecond showed viscosity dependence. These observations were explained with a combined effect of microviscosity and intramolecular relaxation. However, due to the complexity of the decay dynamics, no attempt was made to correlate the data with any of the existing theoretical models, as well as no spectral or structural dynamics were discussed.

Glasbeek and coworkers studied the dynamics of the excited states of Auramine in two alcoholic solvents, namely, ethanol and decanol, using both the fluorescence upconversion and pump-probe transient absorption spectroscopic techniques in the 400 – 650 nm region with subpicosecond and picosecond time resolution, respectively.\textsuperscript{34, 35} The authors interpreted the transient absorption – stimulated emission data by postulating the decay of the fluorescent LE state to an intermediate dark state and then to the ground state, with a viscosity dependent rate. The model predicted the occurrence of the photoreaction along a excited state potential energy surface resulting from the adiabatic electronic coupling between the LE state and the dark state, which was considered to be the characteristic of a twisted photoproduct with charge shift or a TICT state. The fluorescence decays were found to be nonexponential and dependent on the macroscopic viscosity, which was varied by changing the temperature of the solution.\textsuperscript{25} They could be fitted to two exponentials in ethanol and three exponentials in decanol with a larger average lifetime in the more viscous solvent. The decays exhibited wavelength dependent dynamics, although the fluorescence rise time was seen to be instrument response time limited (\textasciitilde150 fs) at all wavelengths. The average decay lifetime was seen to increase as the wavelength was tuned towards the red region across the steady-state emission spectrum. The time-resolved fluorescence spectra indicated a dynamic Stokes shift by a few hundred wave numbers (within the first 10 ps) accompanied by a drastic drop in the intensity to about 10\% of the initial value in both the solvents. They also could detect a residual long-lived component of fluorescence decay with the lifetimes of about 30 ps in ethanol and 130 ps in decanol, predicting that the relaxed excited state is really not a dark state, but weakly emissive. The wavelength dependent nonexponential fluorescence decay was assigned to a barrierless or
quasi-barrierless photoreaction involving the rotational diffusion of the phenyl rings, with a change in the radiative transition rate along the reaction path.

In the present chapter, we will discuss the investigation of the relaxation dynamics of the excited singlet ($S_1$) state of Auramine in varieties of solvents in a wider wavelength region (430 – 1000 nm) using the transient absorption – stimulated emission spectroscopic technique with the time resolution of about 120 fs. Because of wider wavelength region used in this study as well as due to better sensitivity of the spectrometer, it has been possible to resolve the emission bands of the excited states with different conformational geometries. In addition, better time resolution of our transient absorption spectrometer and an extensive analyses of the temporal profiles recorded through the entire wavelength region have helped us to resolve the spectral and temporal dynamics of the transient states, which are formed during the course of relaxation of the excited state of Auramine. Earlier studies did not make any attempt to identify the processes associated with the multiexponetial decay of fluorescence, but was assigned to nonexponential viscosity dependence of the relaxation process. In addition, because of limitation of the time resolution of the transient absorption spectrometer (~1 ps) used in the earlier studies, it was not possible to identify the multiexponential and wavelength-dependent decay of the transient absorption signal.

Scheme I: bis-[4-(dimethylamino)-phenyl] methaniminium chloride (Auramine).

3.2. RESULTS AND DISCUSSION

3.2.1. Steady State Absorption and Fluorescence

Steady state absorption and fluorescence spectra of Auramine have been recorded in several kinds of solvents of different polarities andproticities. In each of these solvents, the absorption spectrum shows two strong and well resolved absorption bands in the 350 - 500 nm region. These bands are assigned to the $S_2 \leftrightarrow S_0$ and $S_1 \leftrightarrow S_0$ transitions. In acetonitrile and PC, the absorption maxima for these two transitions appear at ca. 370 and
441 nm, respectively. However, in DMSO and ethanol, the maximum of the lowest energy band is blue-shifted to 434 and 431 nm, respectively. The hypsochromic shift of the lowest energy band in these two solvents can possibly be explained by predicting weak intermolecular hydrogen bonding interaction between the solvent molecules and auramine in the ground state.

The wavelength of the emission maximum and the shape of the fluorescence spectrum of Auramine are more or less independent of the solvent characteristics. The fluorescence maximum appears at ca. 496 nm in acetonitrile, DMSO and PC but it is a little blue shifted to ca 492 nm in ethanol. In addition, the width (FWHM) of the fluorescence spectrum in ethanol is also much narrower (2800 cm$^{-1}$) than that in other solvents (3080 cm$^{-1}$). Lack of polarity dependence of the characteristics of the fluorescence spectra, particularly in aprotic solvents, suggests the non-polar character of the emissive state. This state is expected to be less polar than the ground electronic ($S_0$) state due to neutralization of the positive charge on the nitrogen atom because of intramolecular charge transfer (ICT) from the dimethylanilino groups to the methaniminium or imidocarbonyl group (vide infra).

Another important feature of the fluorescence spectrum recorded in each of these solvents is the presence of a weak but long tail to the main fluorescence band extended beyond 800 nm. While the more intense emission band with the maximum appearing at about 495 nm can be assigned to the LE state, the presence of the weak emission observed in the lower energy region possibly suggests the formation of conformationally relaxed weakly emissive excited state(s) (vide infra).

![Figure 3.1. Steady state absorption and fluorescence ($\lambda_{exc} = 400$ nm) spectra of Auramine in a few organic solvents.](image-url)
3.2.2. Transient Absorption Study

3.2.2a. Aprotic Solvents

Steady state absorption spectrum in each of the solvents used here suggests that photoexcitation using 400 nm laser light excites the molecules either to the $S_2$ state or to the higher vibrational levels of the $S_1$ state. The time-resolved transient absorption spectra constructed following photoexcitation of Auramine in DMSO have been shown in Figure 3.2. The transient spectrum recorded at 0.2 ps delay-time is characterized by an intense negative absorption band in the 470 - 630 nm region with a maximum at ca 510 nm and a shoulder at ca 565 nm, as well as a weak but broad excited state absorption (ESA) band in the 630 – 1000 nm region. Comparing the shapes of the steady state absorption and fluorescence bands of Auramine in this solvent (Figure 3.1), the negative absorption band appearing in the 470 – 630 nm region is assigned to stimulated emission (SE), and not to the ground state bleaching.

Both the SE and ESA bands are short-lived and show significant evolution in the sub-5 ps time-domain (Figure 3.2A). In this time-domain, decay of the SE band in the 470 – 630 nm region leads to the development of an ESA band with the maximum at ca 480 nm. While two new SE bands appear in the 630 – 1000 nm region following the decay of the ESA band. The intensity of the SE band in the 600 – 750 nm region with maximum at ca 715 nm attains maximum at the delay-time of about 1.5 ps. Whereas, the SE band in the 760 – 1000 nm region with the maximum at 830 nm continues to rise up to about 3.5 ps delay time. The occurrence of these SE bands is a new and important feature observed in the present work for the first time. With further increase in the delay time beyond 3.5 ps, all these SE and ESA bands decay (Figure 3.2B) but the decay of the SE band in the near IR (NIR) region (i.e. 700 – 1000 nm region) is accompanied by a dynamic shift of the maximum towards the lower energy region and the emission maximum shifts to 920 nm after the delay time of 20 ps. Therefore, the pattern of the time evolution of the transient spectra presented in Figure 3.2 reveals the possible involvement of three kinds of transient species or excited states, which are characterized by the SE bands in the 470 – 630 nm, 630 – 750 nm and 750 – 1000 nm regions and these three states are consecutively formed following photoexcitation of Auramine in DMSO using 400 nm light.
Figure 3.2. Time-resolved absorption spectra of the transient species formed following photoexcitation of auramine in DMSO using 400 nm laser pulses. The spectra shown in this figure recorded at the following delay times (ps): (A): 0.2, 0.25, 0.3, 0.35, 0.45, 0.55, 0.7, 1, 1.2, 1.5, 2, 2.5 and 3.5; (B) 4, 5, 6, 7, 8, 9, 12, 14, 16, 22, and 30.

Each of the temporal profiles recorded in the 470 – 1000 nm wavelength region could be fitted with a three or a four exponential function. The temporal profiles recorded at a few selective wavelengths along with the best fit multi-exponential functions have been presented in Figure 3.3. The lifetimes associated with the best fit functions are given in Table 3.1 and they have been found to show systematic wavelength dependence (vide infra). In this table (and also in the Table 3.3), the lifetime, designated as $\tau_1$, $\tau_2$ or $\tau_3$, which represents the wavelength dependent dynamics associated with a particular transient state, has been placed in the same column. In this table, however, we have not shown an additional component of the decay of ESA, the lifetime of which is longer than 500 ps and can be associated with a product state, which has not been characterized in this work. The analyses of the temporal profiles support our prediction regarding the involvement of at least three kinds of processes or transient states in the time evolution of the transient spectra presented in Figure 3.2.

Two distinct wavelength regions, namely 470 – 570 nm and 590 – 1000 nm, could be identified as representing the dynamics of similar kinds of processes. A careful
examination of the trend in variation of the lifetimes of the different components with the monitoring wavelength is expected to provide a better insight about the processes involved in the excited state relaxation dynamics. For each of the temporal profiles recorded in the 470 – 570 nm region, the SE emission rises with the instrument response time (~120 fs) and then decays biexponentially leading to the growth of the ESA band. Subsequently, ESA decays with the lifetime, $\tau_3(d)$, of about 11 ± 3 ps. The rise times of both the components, i.e. $\tau_1(g)$ and $\tau_2(g)$, are more or less wavelength independent (except the value of $\tau_1(g)$ (0.25 ps) measured at 470 nm, possibly because of overlapping of the SE band with the maximum at 510 nm and the ESA band with the maximum at 480 nm) and the average values are 0.6 ± 0.2 and 2.3 ± 0.5 ps, respectively.

Each of the temporal profiles recorded in the 610 – 870 nm region has also been fitted using three exponential functions, consisting of an ultrafast rise of SE (represented by $\tau_2(d)$), the rise of the ESA (represented by, $\tau_3(g)$) and a long-lived component representing the decay of ESA. Because of very small amplitude of the third component in this wavelength region, the lifetime of this component could not be determined accurately and hence this value has not been given in Table 3.1. However, to obtain a good fit of the temporal curve, introduction of this component has been found essential. The values of both $\tau_2(d)$ and $\tau_3(g)$ have been found to be dependent on the monitoring wavelength and as the wavelength is tuned from 610 nm to 870 nm, $\tau_2(d)$ increases from 0.2 ps measured at 610 nm to 1.7 ps at 870 nm, whereas $\tau_3(g)$ increases from 2.2 ps at 610 nm to 10 ps at 870 nm. Analyses of the temporal profiles recorded in the 900 - 1000 nm region, however, reveals the presence of a short-lived rising component, $\tau_1(g)$, and the lifetime of this component increases marginally from 0.3 to 0.5 ps as the wavelength is tuned from 900 – 1000 nm. In this region, the lifetimes of the other two components remain more or less constant with the values of $\tau_2(d)$ ~2.7 ± 0.5 ps and $\tau_3(g)$ ~ 11 ± 1 ps.
Figure 3.3. Temporal profiles (circles) recorded at a few selective wavelengths following photoexcitation of Auramine in DMSO. The decay (d) and rising (r) components associated with the best fit functions (red lines) are given in Table 3.1.

It is important to observe that the decay time of ESA ($\tau_3(d) = 11 \pm 3$ ps) determined in the 470 – 530 nm region agrees well with the decay time of the SE band measured in the 900 – 1000 nm region ($\tau_3(g) = 11 \pm 1$ ps). This lifetime can be assigned to the decay time of the fully relaxed $S_1$ state to the ground electronic state and we assign this as the transient state II or TS II. In addition, the ultrafast decay component of the SE with the average lifetime $\tau_1(g)$ of about 0.6 ps, has the concurrent one, representing the ultrafast rise of ESA with the lifetime $\tau_1(g)$ of about 0.5 ps, measured at 1000 nm. This component can obviously be assigned to the Franck-Condon (FC) or the LE state and not to the $S_2$ state or the vibrational relaxation process (vide infra, Section 3.2.2c). This discussion clearly reveals that the process of conversion of the LE state to the fully relaxed TS II state takes place.
through another transient intermediate species, which has been designated here as the TS I state, with the lifetime of about 2.5 ps.

**Table 3.1:** Lifetimes of three components obtained by fitting the temporal profiles, recorded at different wavelengths following photoexcitation of Auramine in DMSO, using a multiple exponential function.

<table>
<thead>
<tr>
<th>Wavelength, nm</th>
<th>τ₁, ps</th>
<th>τ₂, ps</th>
<th>τ₃, ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>470ᵃ</td>
<td>0.25 (g)</td>
<td>2.7 (g)</td>
<td>13 (d)</td>
</tr>
<tr>
<td>490ᵃ</td>
<td>0.5 (g)</td>
<td>1.8 (g)</td>
<td>14 (d)</td>
</tr>
<tr>
<td>510ᵃ</td>
<td>0.4 (g)</td>
<td>2.0 (g)</td>
<td>8.5 (d)</td>
</tr>
<tr>
<td>530ᵃ</td>
<td>0.8 (g)</td>
<td>1.8 (g)</td>
<td>9 (d)</td>
</tr>
<tr>
<td>550ᵃ</td>
<td>0.7 (g)</td>
<td>2.8 (g)</td>
<td>9 (d)</td>
</tr>
<tr>
<td>570ᵃ</td>
<td>0.5 (g)</td>
<td>2.5 (g)</td>
<td>9.5 (d)</td>
</tr>
<tr>
<td>590ᵃ</td>
<td>0.2 (d)</td>
<td>1.8 (g)</td>
<td></td>
</tr>
<tr>
<td>610ᵃ</td>
<td>0.2 (d)</td>
<td>2.2 (g)</td>
<td></td>
</tr>
<tr>
<td>630ᵃ</td>
<td>0.17 (d)</td>
<td>2.3 (g)</td>
<td></td>
</tr>
<tr>
<td>650ᵃ</td>
<td>0.23 (d)</td>
<td>2.5 (g)</td>
<td></td>
</tr>
<tr>
<td>670ᵃ</td>
<td>0.35 (d)</td>
<td>2.4 (g)</td>
<td></td>
</tr>
<tr>
<td>690ᵃᵇ</td>
<td>0.32 (d)</td>
<td>2.9 (g)</td>
<td></td>
</tr>
<tr>
<td>710ᵃᵇ</td>
<td>0.45 (d)</td>
<td>4.35 (g)</td>
<td></td>
</tr>
<tr>
<td>750ᵃᵇ</td>
<td>0.45 (d)</td>
<td>4.2 (g)</td>
<td></td>
</tr>
<tr>
<td>790ᵃᵇ</td>
<td>0.6 (d)</td>
<td>5.7 (g)</td>
<td></td>
</tr>
<tr>
<td>830ᵃᵇ</td>
<td>0.8 (d)</td>
<td>6.5 (g)</td>
<td></td>
</tr>
<tr>
<td>850ᵃᵇ</td>
<td>1 (d)</td>
<td>7 (g)</td>
<td></td>
</tr>
<tr>
<td>870ᵃᵇ</td>
<td>1.7 (d)</td>
<td>10 (g)</td>
<td></td>
</tr>
<tr>
<td>905ᵇ</td>
<td>0.34 (d)</td>
<td>3.5 (d)</td>
<td>10.2 (g)</td>
</tr>
<tr>
<td>920ᵇ</td>
<td>0.3 (g)</td>
<td>3.1 (d)</td>
<td>10 (g)</td>
</tr>
<tr>
<td>950ᵇ</td>
<td>0.4 (g)</td>
<td>2.5 (d)</td>
<td>10.5 (g)</td>
</tr>
<tr>
<td>1000ᵇ</td>
<td>0.5 (g)</td>
<td>2.5 (d)</td>
<td>11.5 (g)</td>
</tr>
</tbody>
</table>

ᵃThe best-fit function for the temporal profile recorded at this wavelength is associated with an instrument response time limited growth of SE or ESA (not given in the table). ᵇThe best-fit function for the temporal profile recorded at this wavelength is associated with a long-lived (lifetime > 500 ps) decay component of ESA. Letter ‘g’ or ‘d’ given inside the bracket indicates that the component is associated with the rise or decay of transient absorption, respectively.

The wavelength dependence of the temporal profiles recorded in the entire wavelength region presented in Figure 3.3 and the lifetimes given in Table 3.1 reveal that both the rise time, \(τ₂(d)\), and the decay time, \(τ₃(g)\), of the SE increases as the wavelength is tuned towards the longer wavelength region and attains the steady values (i.e. about 2.5 and 11 ps, respectively) in the 590 - 1000 nm region. This kind of wavelength dependent dynamics is commonly observed in the case of solvation or solvent reorganization process around a probe molecule in the excited state, in case its formation is associated with a large
In the case of polar solvation, the rise time of the SE measured at the wavelengths in the extreme red region of the emission band can be correlated with the average solvation time. We observe that the average rise time of the SE band (~2.7 ps) determined in the 900 – 1000 nm wavelength region is comparable with the average solvation time ($\tau_{\text{solv}}$) of DMSO, which has been determined using a standard probe molecule and varies in the range 1.8 – 3.3 ps. However, one should be careful to assign this process to solvation. Such a wavelength dependent SE dynamics is also expected for a barrierless reaction, since a particular monitoring wavelength probes the motion of the excited state population along the potential energy surface through a narrow observation window.

As discussed earlier, an important consequence of the wavelength dependence of the temporal profiles arising due to solvation or conformational relaxation process is the dynamic bathochromic shift of the maximum of the SE band. In order to confirm the nature of the process in the present case, we have normalized the time-resolved spectra presented in figure 3.2 with respect to the maximum of the SE band of each spectrum as shown in figure 3.4. We find the continuous bathochromic shift of the maximum of the SE band from 510 nm to 565 nm in sub-1.5 ps time domain. However, this dynamic shift may be a consequence of the development of the ESA band with maximum at 480 nm and possibly not due to solvation or any other reason.

This figure also clearly reveals the appearance of a weak SE band with maximum at 710 nm, following the decay of the SE band in the 470 – 600 nm and prior to the development of the SE band in the 750 – 1000 nm region. Dynamic shift is not evident in this region. Further, in the time domain longer than 4 ps, we observe the dynamic shift of the maximum of the SE band from 830 nm to 900 nm, but it is also possibly a consequence of the development of the ESA band with the maximum at 800 nm.
Figure 3.4: Wavelength dependence of the temporal dynamics of the transient species generated following photoexcitation of auramine in DMSO. Lifetimes of the decay (d) and growth (g) components associated with the fit functions are given in Table 3.1.

We have also normalized the maximum of the SE intensity for each of the temporal profiles recorded at different wavelengths (the normalized best fit functions corresponding to the different wavelengths are shown in Figure 3.5).
Ultrafast Twisting Dynamics in the Excited State of Auramine

Figure 3.5. (A) The best fit functions associated with the temporal profiles, which have been normalized with respect to the SE emission intensity, recorded at different wavelengths following photoexcitation of auramine in DMSO. (Inset A): Plot of the wavenumber (inverse wavelength) vs. time at which the maximum SE intensity occurs at this wavelength.

B: The time-resolved spectra of the transient obtained using the normalized best fit functions presented in (A), Delay times(ps): 0.15, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 2, 4, 6, 8, 10, 12 and 15). Inset B: Temporal dynamics of the dynamic shift of maximum frequency of the SE band.

This clearly reveals that as the wavelength is tuned towards the longer wavelength region, the maximum intensity of the stimulated emission is attained at a longer delay time. We find that the correlation between the probe frequency and the delay-time at which the maximum of SE is attained follows an exponential function with a lifetime of about 1.5 ps
Ultrafast Twisting Dynamics in the Excited State of Auramine

(inset of Figure 3.5), which, however, is shorter than the average solvation time of DMSO. In spite of the systematic wavelength dependence of the temporal dynamics, the dynamic shift of the SE maximum is not very evident in the time-resolved spectra presented in Figure 3.2 or Figure 3.4, possibly because of consecutive formation of more than one transient states during the relaxation of the S₁ state of Auramine and hence the structured SE spectra.

In order to confirm the involvement of more than one transient species or the processes, such as solvation and / or conformational relaxation, as well as to reveal their identities, we investigated the temporal dynamics of the excited states of Auramine in a few other aprotic solvents of different viscosities and solvation times (Table 3.2). The time resolved spectra of the transient species formed following photoexcitation of Auramine in PC, are shown in Figure 3.6. Characteristics of the time evolution of the transient spectra are very similar to those observed in the case of DMSO.

Figure 3.6: (A) Time-resolved absorption spectra of the transient species formed following photoexcitation of Auramine in PC using 400 nm laser pulses. (B) Transient spectra, each of which is normalized at the maximum SE intensity to -10 mOD to reveal the involvement of two transient states with the SE maxima at 740 and 870 nm.
However, in this case, the involvement of the transient species, TS I, which can be characterized by its SE band with the maximum at 740 nm, is clearly evident. To make this point more convincing, we have presented the time resolved transient spectra, each of which have been normalized (to maximum absorbance of -10 mOD) at the corresponding SE maximum, in Figure 3.6B. The time-resolved spectra presented in Figure 3.6B also reveal an apparent bathochromic shift of the SE maximum from 470 nm to 920 nm with increase in delay time from 0.15 to 20 ps. However, like in the case of DMSO, because of the presence of multiple emission bands and also overlapping of the SE and ESA bands, the correlation of the dynamic shift of the SE maximum with the delay time has not been possible.

Temporal profiles recorded at a few selective wavelengths following photoexcitation of auramine in PC, along with the best fit functions, have been presented in Figure 3.7.

Figure 3.7: Temporal dynamics at different wavelengths in PC. Lifetimes associated with the best fit functions are given in Table 3.2.

Wavelength dependence of the different lifetime components is also very similar to those observed in DMSO and the lifetimes of the components determined at different monitoring wavelengths are given in Table 3.2.
Table 3.2: Lifetimes of three components obtained by fittings of the temporal curves recorded at different wavelengths following photoexcitation of auramine in PC.

<table>
<thead>
<tr>
<th>Wavelength, nm</th>
<th>τ₁, ps (g / d)</th>
<th>τ₂, ps (g / d)</th>
<th>τ₃, ps (g / d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>480°</td>
<td>0.3 (d)</td>
<td>3 (g)</td>
<td>14 (d)</td>
</tr>
<tr>
<td>510°</td>
<td>0.7 (g)</td>
<td>3.2 (g)</td>
<td>13 (d)</td>
</tr>
<tr>
<td>530°</td>
<td>0.9 (g)</td>
<td>3.9 (g)</td>
<td>10 (d)</td>
</tr>
<tr>
<td>550°</td>
<td>1.2 (g)</td>
<td>4.0 (g)</td>
<td>11 (d)</td>
</tr>
<tr>
<td>570°</td>
<td>1.3 (g)</td>
<td>4.0 (g)</td>
<td>11 (d)</td>
</tr>
<tr>
<td>590°</td>
<td>1.3 (g)</td>
<td>4.2 (g)</td>
<td>11 (d)</td>
</tr>
<tr>
<td>630°</td>
<td>0.28 (d)</td>
<td>2.4 (g)</td>
<td></td>
</tr>
<tr>
<td>730°</td>
<td>0.3 (d)</td>
<td>5.6 (g)</td>
<td></td>
</tr>
<tr>
<td>830°</td>
<td>0.8 (d)</td>
<td>7.7 (g)</td>
<td></td>
</tr>
<tr>
<td>850°</td>
<td>0.85 (d)</td>
<td>8.2 (g)</td>
<td></td>
</tr>
<tr>
<td>870°</td>
<td>1.15 (d)</td>
<td>8.6 (g)</td>
<td></td>
</tr>
<tr>
<td>880°</td>
<td>1.3 (d)</td>
<td>9.26 (g)</td>
<td></td>
</tr>
<tr>
<td>900°</td>
<td>0.3 (g)</td>
<td>1.6 (d)</td>
<td>9.5 (g)</td>
</tr>
<tr>
<td>940°</td>
<td>0.4 (g)</td>
<td>1.65 (d)</td>
<td>9.5 (g)</td>
</tr>
<tr>
<td>1000°</td>
<td>0.7 (g)</td>
<td>2.0 ps (d)</td>
<td>10 (g)</td>
</tr>
</tbody>
</table>

Following the same arguments as presented in the case of DMSO solvent, the average lifetimes of the three transient states involved in the conformational relaxation of the excited state of Auramine in PC have been determined as $1.1 \pm 0.4$ ps, $3.5 \pm 1$ ps and $11 \pm 3$ ps. In this case too, the correlation between the probe frequency and the delay time, at which the maximum of the SE intensity is attained, follows an exponential function with a lifetime of about $1.2$ ps, which is also shorter than the solvation time of PC ($<\tau>_{\text{solv}} \sim 3$ ps) shown in figure 3.8.
Temporal dynamics at a few selective wavelengths have also been investigated in acetone, acetonitrile, dimethylformamide (DMF) and formamide and the average lifetimes of the three transient states or conformers formed in these solvents are given in Table 3.3.
Table 3.3: Lifetimes of three transient species involved in the excited state dynamics of Auramine in different kinds of solvents. $\tau_1$, $\tau_2$ and $\tau_3$ are assigned to the lifetimes of the LE, TS I and TS II states, respectively (see text).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\varepsilon_0$ a</th>
<th>$\pi^*$ value b</th>
<th>$&lt;\tau&gt;$ sol (ps) c</th>
<th>$\eta$ (cP)</th>
<th>$\tau_1$ (ps)</th>
<th>$\tau_2$ (ps)</th>
<th>$\tau_3$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>20.6</td>
<td>0.68</td>
<td>0.83</td>
<td>0.62</td>
<td>0.20</td>
<td>1.0</td>
<td>8</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>35.8</td>
<td>0.71</td>
<td>0.5</td>
<td>0.34</td>
<td>0.25</td>
<td>1.0</td>
<td>5</td>
</tr>
<tr>
<td>DMF</td>
<td>36.7</td>
<td>0.88</td>
<td>0.92</td>
<td>0.8</td>
<td>0.35</td>
<td>1.6</td>
<td>8</td>
</tr>
<tr>
<td>DMSO</td>
<td>46.4</td>
<td>1.00</td>
<td>1.8</td>
<td>1.99</td>
<td>0.60</td>
<td>2.5</td>
<td>12</td>
</tr>
<tr>
<td>PC</td>
<td>64.9</td>
<td>0.83</td>
<td>3.0</td>
<td>2.65</td>
<td>1.10</td>
<td>3.5</td>
<td>12</td>
</tr>
<tr>
<td>Formamide</td>
<td>111</td>
<td>1.12</td>
<td>5</td>
<td>3.3</td>
<td>0.45</td>
<td>2.3</td>
<td>4.5</td>
</tr>
<tr>
<td>Methanol</td>
<td>32.5</td>
<td>0.59</td>
<td>5</td>
<td>0.55</td>
<td>0.50</td>
<td>2.2</td>
<td>10</td>
</tr>
<tr>
<td>Ethanol</td>
<td>24.3</td>
<td>0.54</td>
<td>16</td>
<td>1.08</td>
<td>1.4</td>
<td>3.5</td>
<td>17</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>20.4</td>
<td>0.53</td>
<td>26</td>
<td>1.94</td>
<td>2.0</td>
<td>8.1</td>
<td>28</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>18.4</td>
<td>0.41</td>
<td>63</td>
<td>2.57</td>
<td>3.5</td>
<td>10.5</td>
<td>50</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>14.0</td>
<td>-</td>
<td>103</td>
<td>3.51</td>
<td>4.0</td>
<td>16</td>
<td>57</td>
</tr>
<tr>
<td>EG</td>
<td>37.7</td>
<td>0.93</td>
<td>15.3</td>
<td>13.8</td>
<td>1.0</td>
<td>8</td>
<td>30</td>
</tr>
</tbody>
</table>

aTaken from ref. (47); b Taken from ref. (82); c Taken from ref. (83).

3.2.2b. Protic Solvents

The excited state dynamics of Auramine has been extensively studied by the earlier workers in ethanol and decanol solvents using both the transient absorption as well as the fluorescence spectroscopic methods. However, these studies have been limited in the wavelength region of 350 – 650 nm. So we have investigated the dynamics of the excited state of Auramine in the series of normal alcoholic solvents (methanol to 1-pentanol) as well as in ethylene glycol (EG) with a better time-resolution and in a much wider wavelength region (e.g. 430 – 1000 nm region). The time-resolved spectra of the transient species generated following photoexcitation of Auramine in ethanol have been presented in Figure 3.9. The characteristics of the time evolution of the transient spectra and the temporal dynamics recorded in this solvent have been observed to be very similar to those observed in aprotic solvents. However, in this case, the broadening of the SE band in the 470 – 650 nm region, which is assigned to the LE state, and the dynamic bathochromic shift of the emission maximum are more clearly evident. In addition, formation of the other two transient states with the SE maxima at 710 and 850 nm is also evident. However, in this case too, because of structurally resolved SE spectra of the transient states and
overlapping of the SE and ESA bands, the correlation of the frequency shift with the delay time has not been possible.

Figure 3.9: Time-resolved differential absorption spectra of the transient species formed following photoexcitation of Auramine in ethanol using 400 nm laser pulses.

In Figure 3.10, we have shown a few typical temporal profiles along with the best fit functions to show the wavelength dependent dynamics of the excited state of Auramine in ethanol.
Figure 3.10: Temporal profiles (circles) of the transient species generated following photoexcitation of Auramine in ethanol. Lifetimes of the components associated with the best fit functions (red lines) are given in Table 3.3.

The variation of the lifetimes of the three components with the change in wavelength is shown in Table 3.4. Like in the cases of aprotic solvents, in spite of strong wavelength dependence of the lifetimes, the involvement of three different conformational states in the dynamics of the excited states of Auramine is clearly evident. The wavelength dependence of the lifetimes of the three components is very similar to that observed in the case of aprotic solvents. Therefore, following the same arguments as presented in the case of the aprotic solvents, the lifetimes of the three transient species responsible for the evolution of the time-resolved spectra presented in Figure 3.5, have been determined as 1.4 ± 0.3, 3.5 ± 0.3 and 17 ± 3 ps.
Table 3.4: Lifetimes of the components obtained by three or four exponential fittings of the temporal curves recorded at different wavelengths following photoexcitation of Auramine in ethanol.

<table>
<thead>
<tr>
<th>Wavelength, nm</th>
<th>( \tau_1 ), ps (g / d)</th>
<th>( \tau_2 ), ps (g / d)</th>
<th>( \tau_3 ), ps (g / d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>470</td>
<td>0.53 (g)</td>
<td>3.8 (g)</td>
<td>19.3 (d)</td>
</tr>
<tr>
<td>480</td>
<td>0.5 (g)</td>
<td>3.6 (g)</td>
<td>20 (d)</td>
</tr>
<tr>
<td>490</td>
<td>0.71 (g)</td>
<td>3.1 (g)</td>
<td>16.9 (d)</td>
</tr>
<tr>
<td>510</td>
<td>1.4 (g)</td>
<td>3.7 (g)</td>
<td>20.4 (d)</td>
</tr>
<tr>
<td>520</td>
<td>1.5 (g)</td>
<td>3.5 (g)</td>
<td>12 (d)</td>
</tr>
<tr>
<td>530</td>
<td>1.4 (g)</td>
<td>3.7 (g)</td>
<td>12.0 (d)</td>
</tr>
<tr>
<td>590</td>
<td>0.26 (d)</td>
<td>3.3 (g)</td>
<td></td>
</tr>
<tr>
<td>630</td>
<td>0.29 (d)</td>
<td>4.0 (g)</td>
<td></td>
</tr>
<tr>
<td>650</td>
<td>0.45 (d)</td>
<td>6.8 (g)</td>
<td></td>
</tr>
<tr>
<td>710</td>
<td>0.5 (d)</td>
<td>8.5 (g)</td>
<td></td>
</tr>
<tr>
<td>730</td>
<td>0.52 (d)</td>
<td>8.2 (g)</td>
<td></td>
</tr>
<tr>
<td>770</td>
<td>0.6 (d)</td>
<td>11 (g)</td>
<td></td>
</tr>
<tr>
<td>790</td>
<td>0.1 (d)</td>
<td>1.2 (d)</td>
<td>14.5 (g)</td>
</tr>
<tr>
<td>830</td>
<td>0.27 (d)</td>
<td>2.5 (d)</td>
<td>14.5 (g)</td>
</tr>
<tr>
<td>900</td>
<td>0.3 (d)</td>
<td>3.9 (d)</td>
<td>20 (g)</td>
</tr>
<tr>
<td>950</td>
<td>0.4 (g)</td>
<td>3.6 (d)</td>
<td>18 (g)</td>
</tr>
<tr>
<td>1000</td>
<td>0.7 (g)</td>
<td>3.4 (d)</td>
<td>14 (g)</td>
</tr>
</tbody>
</table>

The superscripts, ‘a’ and ‘b’, have the same significance as those in the case of Table 3.1.

In Figure 3.11, we have shown the wavelength dependence of the delay time at which the maximum of the SE intensity appears and also the correlation of the frequency shift with the delay time, which follows an exponential function with a lifetime of about 1.4 ps, which is much shorter than the average solvation time of ethanol (<\( \tau >_{\text{solv}} \) ~ 16 ps) but comparable with those determined in aprotic solvents of comparable viscosities (Table 3.2).
Figure 3.11. Best fit functions for the normalized temporal curves recorded at different wavelengths following photoexcitation of Auramine in ethanol. This presentation reveals clearly the continuous evolution of the transient species in the entire wavelength region. Inset: Correlation between the probe frequency and the delay-time, at which the maximum of stimulated emission is attained, follows an exponential function with a lifetime of about 1.4 ps.

This confirms the fact that the dynamic frequency shift observed in the present study does not represent the solvation, but possibly the conformational relaxation process.

We have also determined the lifetimes of the three transient states with different conformations involved in the relaxation of the excited state of Auramine in other alcoholic solvents following photoexcitation using 400 nm light as shown in Figure 3.12. and they have been compared with the corresponding values determined in other aprotic and protic solvents in Table 3.2.
Figure 3.12. Temporal dynamics in alcoholic solvents recorded at 480 and 1000 nm.

3.2.2c: Dynamics of Bleach Recovery:
Because of overlapping of the different ESA and SE bands in the 470 – 1000 nm region, we observe wavelength dependence of the lifetimes of the three transient species. For further establishment of the involvement of three transient states and to ensure the accuracy of the lifetime values given in Table 3.2, we have also recorded the dynamics of the ESA monitored at 435 nm in a few selective solvents and the results have been presented in Figure 3.13. Considering the fact that the monitoring wavelength (435 nm) is nearly coincident with that of the ground state absorption maximum, the transient
Ultrafast Twisting Dynamics in the Excited State of Auramine

differential absorption signal is expected to be negative because of the ground state bleaching, which should show instrument response time limited rise followed by multiexponential bleach recovery dynamics with the lifetime values similar to those presented in Table 3.2 for the corresponding solvents. However, in contrary to our expectation, we observe the appearance of an ESA signal with the instrument response time-limited rise instead of a negative absorbance signal. Further, the time evolution of the transient absorption signal could be fitted with a four exponential decay and / or rise function. The first component represents the ultrafast decay of the ESA leading to the rise of the bleaching signal followed by the double exponential bleach recovery leading to the rise of another ESA. The decay time of this ESA is longer than a few hundred picosecond and it can be assigned to that of the long-lived product state.

In spite of the fact that the rise of the stimulated emission signal recorded at 480 or 500 nm, which coincides nearly with the maximum of the steady-state fluorescence spectrum, is instrument response time limited (vide supra), we find that, in each kind of solvents, the rise of the bleaching signal monitored at 435 nm is not limited by the instrument response time but rises with a lifetime, which is dependent on the solvent characteristics. Hence, it is obvious that in this wavelength region, the bleaching band is overlapped with an ESA band of the LE state, which is produced following photoexcitation of Auramine. We find that the rise time of the bleaching signal in each of the four solvents is nearly in agreement with the value of $\tau_1$ measured in the corresponding solvent (Table 3.2). These arguments also suggest that the molecules excited to the $S_2$ state or the higher vibrational levels of the $S_1$ state using 400 nm light undergo ultrafast relaxation to the zero vibrational level of the $S_1$ (LE) state, with a lifetime, which is faster than the instrument response time. Further, the lifetimes of the two rising components, which represent the bleach recovery processes, also agree well with the values of $\tau_2$ and $\tau_3$, respectively, presented in Table 3.2. These facts confirm our prediction regarding the involvement of three kinds of processes or excited states in the relaxation dynamics of the $S_1$ state of Auramine.

One important observation in the present study is the residual long-lived ESA at several probe wavelengths, which could be assigned either to the triplet state or the FC ground state corresponding to the TS II state. Considering the fact that there is no experimental evidence that the ground state recovery due to the decay of the FC ground state corresponding to the TS II state is slower than that of the $S_1$ state, it is assumed that this
process is very fast. Therefore the long-lived ESA may possibly be assigned to the triplet state.

Figure 3.13. Temporal profiles (circles) recorded at 435 nm in four solvents. The lifetimes associated with the best fit functions (red lines) are given in the insets.

3.3. Potential Energy Surface (PES) Diagram: Considering the above arguments presented in the preceding sections, we propose the over-simplified PES diagram presented in Figure 3.14 to illustrate the relaxation behavior of the $S_1$ state of Auramine. The experimental results led us to predict the involvement of three transient states, namely the LE, TS I and TS II states. Following photoexcitation to the LE state, which has an emission maximum at ca 510 nm, the Auramine molecule undergoes the conformational relaxation with the lifetime of $\tau_1$ to form the TS I state. This state, which has an emission maximum at ca 710 nm, undergoes another
conformational change with the lifetime of $\tau_2$ to form the geometrical conformer TS II. This conformer undergoes mainly nonradiative relaxation to the ground electronic state, but its formation has been easily identifiable by its SE band with the maximum at ca 870 nm.

Figure 3.14: Over-simplified potential energy surface (PES) diagram for the configurational relaxation of Auramine in the $S_1$ state.
3.4. Solvent Effect on the Lifetimes of the Relaxation Processes:

As explained in the earlier sections that wavelength dependent SE dynamics observed here may be attributed to either conformational relaxation via twisting of the dimethylanilino groups or solvation of the TICT state, we intend to correlate the lifetimes of the transient species given in Table 3.2 with two important solvent parameters, namely macroscopic viscosity (\(\eta\)) and average solvation times (\(\langle \tau \rangle_{\text{sol}}\)). Both these parameters control the dynamics of barrier crossing processes. While the diffusive motion of the chromophoric groups in a molecule leading to configurational relaxation is mainly controlled by the viscosity of the solvent, solvation may change both the height of the barrier as well as the shape of the potential energy surface.\(^1\),\(^51\),\(^52\) As mentioned earlier, the effect of solvent on the relaxation dynamics of both the DPM and TPM dyes has been the subject of intense discussion, and it has repeatedly been emphasized that solvent dependence of the relaxation rate in TPM molecules cannot be described by a viscosity dependence alone, because of the solvent dependence of the shape of the potential energy surface. Therefore, we have chosen advertently about a dozen of solvents, each of which belongs to one of two classes, namely aprotic and alcoholic, in order to vary the solvation times by about two orders of magnitude to show that possibly solvation plays a more important role in the relaxation dynamics of the excited state of Auramine than the viscosity.

The best-known model for accounting the solvent dependence of the rate of an activated barrier crossing process by the configurational relaxation via rotation about a double bond in the trans-cis isomerization reaction or twisting of the dimethylamino or the dimethylanilino group about a single bond in a TICT process, is that of Kramers and the rate of decay (\(k\)) of the excited state undergoing twisting or rotational motion is dependent on viscosity and temperature.\(^4\),\(^5\)

\[
k = F(\eta) \exp\left(-\frac{E_a}{RT}\right)
\]

and \(F(\eta)\) is given by the one-dimensional Kramers model.\(^4\)

\[
F(\eta) = \frac{A\eta}{B} \left\{\left[1 + \left(\frac{B}{\eta}\right)^2\right]^{\frac{1}{2}} - 1\right\}
\]

Where \(A\) and \(B\) are parameters related to the well and barrier frequencies, respectively. At the high friction limit, the Kramers model approaches to Smoluchowski approximation,\(^5\)

81
Ultrafast Twisting Dynamics in the Excited State of Auramine

\[ F(\eta) = C\eta^{-1} \quad (3) \]

Where ‘C’ is a constant, which is not dependent on viscosity. However, experimental results show that, in most of the cases, Kramers equation (3) does not hold good and the decay rate can be fitted fairly well to a power-law function, \(^{53-61}\)

\[ k = Z \eta^{-\alpha} \exp\left(-\frac{E_a}{RT}\right) \quad (0<\alpha<1) \quad (4) \]

\[ \ln(k) = -\alpha \ln(\eta) + \ln(Z) - \left(\frac{E_a}{RT}\right) \quad (5) \]

where \(Z\) is a preexponential factor. Therefore, at a particular temperature, in a series of similar kind of solvents, in which the barrier height may be assumed to remain more or less unchanged, a linear correlation between \(\ln(k)\) and \(\ln(\eta)\) is expected in case the twisting dynamics control the relaxation of the \(S_1\) state. There is a general correlation among the parameters of equation (4) that for smaller barriers \((E_a)\), the pre-exponential factor \(Z\) decreases, while \(\alpha\) increases. \(^{61}\)

In Figure 3.15, we have presented the viscosity dependence of the lifetimes of the three transient states in both aprotic and protic solvents. Considering the error in determining the lifetimes of the transient states, we find that all three lifetimes follow a linear relationship with the viscosities of the solvents. However, the functional forms (i.e. slopes and intercepts of the best fit lines) are different in these two kinds of solvents. It is important to note that EG do not follow the behavior of the linear alcohols but of the aprotic solvents. Let us first discuss the viscosity dependence of \(\tau_1\) and \(\tau_2\), which represent the conformational relaxation processes in the \(S_1\) state corresponding to the consecutive conversions of the LE state to the TS I state and then to the TS II state, respectively. The process with the lifetime of \(\tau_3\) is really not related to any conformational relaxation process but the internal conversion from the \(S_1\) state to the \(S_0\) state. In spite of this fact, \(\tau_3\) shows viscosity dependence and needs to adopt different mechanism to explain it (vide infra).
Figure 3.15: **A.** Viscosity dependence of the lifetimes of the three transient states determined in twelve solvents (Table 2). In the case of each of the lifetime components (a, b and c represents the viscosity dependence of $\tau_1$, $\tau_2$ and $\tau_3$, respectively). The best fit line has different slopes in linear alcohols (solvents 7 - 11) and other solvents, say, aprotic solvents (1 – 6), as well as ethylene glycol (12). The values of the three parameters obtained by the linear fit, (intercept, slope and adj. $R^2$), are given in the insets.

**B.** Correlation between the decay lifetimes of the excited states with the average solvation times, $<\tau>_{sol}$ of the solvents. The values of the three parameters obtained by the linear fit, (intercept, slope and adj. $R^2$), are given in the insets. Curves a, b and c represents the lifetime components $\tau_1$, $\tau_2$ and $\tau_3$, respectively.

**Solvents:** acetone (1); acetonitrile (2); dimethylformamide (3); DMSO(4); PC (5); formamide (6); methanol (7); ethanol (8); 1-propanol(9); 1-butanol(10); 1-pentanol (11); EG (12).

In this chapter, we have studied the twisting dynamics of Auramine in the solvents having a narrow viscosity range ($\eta < 5$ cP), except that in EG ($\eta \sim 13.8$ cP). Firstly, in aprotic solvents and in EG, the $\alpha$ values for $\tau_1$ and $\tau_2$ have been determined as 0.44 and 0.58,
respectively. The fractional viscosity dependence of barrierless isomerization reactions have been studied using the mode coupling theory, which finds the value of $\alpha$ in the range of $0.5 - 0.8$. Therefore our value (i.e. 0.58) determined for $\tau_2$ is in close agreement with the theoretical prediction and reveals $\eta^{-2/3}$ or $\eta^{0.66}$ dependence of viscosity, as predicted and observed by Förster and Hoffman. But that for $\tau_1$ (i.e. 0.44) is smaller than the theoretically predicted values.

Although a quantitative understanding of the origin of equation (4) is still lacking, several possible explanations for the origin of the fractional viscosity dependence of the rates have been given, such as breakdown of Stokes-Einstein relation, multidimensionality of the potential energy surface, time-dependent friction, existence of specific solute-solvent interactions, etc. In the present case, the contribution of the first factor may be neglected because of the smaller size of the solvents used here as compared to that of the solute, but the contribution of other three factors should be considered. The twisting coordinate of two dimethylanilino groups is possibly not simply one dimensional but other modes may also be involved in the reaction increasing the overall rate of the relaxation process.

Time-dependent friction, a non-Markovian dynamics, arises from the fact that the solute–solvent coupling through friction depends on the relative time scale of the processes. According to the mode coupling theory, the viscosity of the solvent is decomposed into fast and slow response components.

$$\eta(t) = \eta_F(t) + \eta_L(t)$$  \hspace{1cm} (6)

The time-dependent viscosity effect has been explained by the hierarchy structure of the solvation shell. In the present case, the ultrafast molecular motion, which has the lifetime $\tau_1$, is associated with a smaller amplitude motion, e.g. wiggle or small flip of the phenyl rings, and hence does not feel fully the mechanical friction contributed by the solvent motion, but coupled to the first term, $\eta_F(t)$, which represents the inertial motion of the solvent. Thus the effective friction acting on the solute motion becomes less than the bulk value, the static (or zero-frequency) friction. On the other hand, the longer component of the transient decay, $\tau_2$, is associated with a large amplitude diffusive rotational motion of the phenyl groups, which needs to replace a larger number of solvent molecules and is mainly coupled to the component, $\eta_L$, representing the bulk viscosity of the solvent.
Comparing the nearly isoviscous solvents, namely DMSO and ethanol and also PC and 1-propanol, the corresponding lifetime values are much longer in protic solvents. In addition, the slopes of the best fit lines representing the viscosity dependency of $\tau_1$ and $\tau_2$ in the case of the alcoholic solvents are near unity and are larger than those in the case of aprotic solvents. This is also in perfect agreement with the observation of Sundström and Gilbro in the case of the lower alcohols with $\eta < 5$ cP.\textsuperscript{22 - 23} They suggested that the potential barrier in these solvents is very close to zero and the relaxation characteristics are reminiscent of the Oster – Nishijima model. Therefore, the slower decay rate in an alcohol as compared to that in an aprotic solvent of comparable viscosity suggests a larger barrier originated completely from the solvent properties. Since the viscosity-dependence of both $\tau_1$ and $\tau_2$ in alcoholic solvents is very similar, the multidimensionality of the potential energy surface or the time-dependent viscosity or hierarchy structure of the solvation shell are not the only contributing factors but other factors such as the intermolecular hydrogen bonding between the excited state and the solvent as well as the energy of activation for the viscosity of the alcoholic solvents may be the important factors contributing to the slower twisting dynamics of auramine in alcohols. However, the longer lifetimes of the $S_1$ state of Auramine in alcohols as compared to those measured in aprotic solvents of comparable viscosity and polarity (Table 3.2), suggest that the effect of intermolecular hydrogen bonding is not an important factor in this case, since hydrogen bond stretching vibration provides an efficient radiationless deactivation mechanism for the excited state and the lifetimes are expected to be reduced significantly.\textsuperscript{75 - 77} However, the reason for nearly equal slopes, which are near unity, for the best fit lines representing the viscosity dependence of $\tau_1$ and $\tau_2$, as presented in Figure 3.15, should be rationalized and more specific interpretation is needed to obtain a correct description of the effect of solvent viscosity on the conformational relaxation process. The observed viscosity effect on the decay rate constants in linear chain alcohols can be explained by taking the free volume concept into consideration.\textsuperscript{40, 73} When microscopic friction is taken into consideration, the rotational and translational diffusion processes associated with the twisting motion should include two processes: (a) a process by which the surrounding solvent makes free volume, and (b) a process by which the dimethylanilino group moves into the free space created by the solvent molecules. The process (a) should strongly
Ultrafast Twisting Dynamics in the Excited State of Auramine

depend on the viscosity of the solvent and the process (b) should depend on the interaction between the solvent and the solute molecule as well as the intramolecular activation barrier. The activation energy of viscosity of the ethanol solvent have been calculated by the fluorescence depolarization method as 15.5 kJ mol$^{-1}$. Similar viscosity dependence of both the lifetime components, $\tau_1$ and $\tau_2$, and also the barrierless nature of the twisting processes in Auramine, $^{23-29,31,34,35}$ suggest that the rates of these processes are mainly governed by the activation energy of viscosity of the alcohol. Actually, the data presented in Figure 3.15A, only reveals the linear dependence of activation energy of viscosity on the length of the alkane chain of the linear alcohol, not related to the relaxation behavior of the excited state of Auramine.

The increase of the decay lifetime $\tau_3$, which represents the decay of the twisted TS II state to the ground state, with increasing solvent viscosity, was already reported in Auramine and other TPM dyes.$^{29,31-36,40}$ Do the solvent viscosity dependence of $\tau_3$ indicates a further large amplitude motion? Earlier, we showed that the lifetimes of the TICT states of the molecules like Michler’s ketone$^{78}$ decrease with increase in the polarity of the solvents. This fact was explained by the energy gap law.$^{78-81}$ Since the fluorescence yield from the TS II state is negligibly small, the inverse of the lifetime can be equated to the rate of the internal conversion process, $k_{IC}$. The relation between $k_{IC}$ and the energy of the $S_1$ state, $E'(S_1)$ can be expressed in a quantitative form in terms of the energy-gap law [Eq. (7)].$^{80,81}$

$$k_{IC} = \exp \left( -\gamma \frac{E'(S_1)}{h\omega_M} \right)$$

(7)

Where $h\omega_M$ is the energy of the characteristic accepting mode and $\gamma$ is a constant. The potential energy of the TICT state decreases with increase in polarity of the solvent, because of larger solvation energy in solvents of larger polarity, leading to a decrease in the energy gap between the $S_1$ and $S_0$ states and hence increasing the rate of the nonradiative process from the $S_1$ state. However, in this case we could not find any such correlation between $\tau_3$ and the polarity parameter ($\pi^*$) of the solvents used here. Hence the same argument cannot be applied in the case of Auramine.

Martin et. al. also proposed a molecular relaxation scheme, in which the TICT state decays to the ground state via an internal conversion process involving intramolecular high frequency modes ($\omega_M$), in addition to the phenyl group twisting motion, as in the case of electron transfer reaction in Marcus inverted region.$^{31}$ However, Rettig and his coworkers
found some drawbacks and difficulties with this explanation while comparing the internal conversion rates of the julolidino analogue of crystal violet with those of other TPM dyes.\textsuperscript{33} They postulated the existence of a conical intersection (or a photochemical funnel) on a multidimensional reaction hypersurface, leading to a surface touching of the $S_1$ and $S_0$ adiabatic states resulting in ultrafast internal conversion process. According to this model, formation of the photochemical funnel also needs further rotation around a chemical bond. However, this fact is yet to be supported by experimental and theoretical studies.

Surprisingly, we could also find a reasonably good linear correlation between all the three lifetimes and $\langle \tau \rangle_{\text{sol}}$ (Figure 3.15 B). In this case, both the aprotic and protic solvents, except EG, follow the same linear functional relationship. It is also interesting to observe that the slopes of the best fit lines in all the three cases are very similar. Therefore, we may conclude that not only the diffusional twisting motion but also the solvation of the TICT state possibly control the overall dynamics of the relaxation of the $S_1$ state of Auramine.

3.5. CONCLUSION

Steady state absorption and fluorescence as well as the sub-picosecond time-resolved absorption – stimulated emission spectroscopic techniques have been applied to study the excited state relaxation dynamics of Auramine in different kinds of solvents following photoexcitation at 400 nm light. Our experimental results led us to predict the involvement of three transient states, namely the LE, TS I and TS II states, which are geometrical conformers formed via two consecutive processes following photoexcitation. Characteristics of the time evolution of the transient spectra and wavelength dependence of the temporal dynamics are very similar in different kinds of solvents used here. The LE state, which has the steady state fluorescence maximum at ca 495 nm, is easily identifiable by the SE band appearing at 510 nm immediately after the excitation laser pulse. TS I and TS II states have been characterized by their SE bands with maximum at ca 710 and 830 nm. Fractional viscosity dependence of the lifetimes of the LE and TS I states ($\tau_1$ and $\tau_2$, respectively) in aprotic solvents suggests that conformational relaxation processes in the excited state of Auramine are nearly barrierless processes. $\eta^{0.58}$ dependence of viscosity of $\tau_2$ in aprotic solvents confirms the fact that it is associated with a large amplitude diffusive rotational motion of one of the phenyl groups and is mainly coupled to the bulk viscosity.
of the solvent. But $\eta^{0.44}$ dependence of viscosity of $\tau_1$ suggests that it is possibly associated with a smaller amplitude motion, e.g. wiggle or small flip of the phenyl rings, and hence does not feel fully the mechanical friction contributed by the solvent motion, but coupled to the inertial motion of the solvent. In normal alcohols, slower twisting dynamics or $\eta^1$ dependence of both $\tau_1$ and $\tau_2$ has been explained by the relatively large activation energy of the solvent viscosity. To explain the viscosity dependence of the decay lifetime of the TS II state, which undergoes an efficient internal conversion process to the ground state, the possibility of occurrence of different mechanisms, such as, energy gap law, involvement of intramolecular high frequency modes as well as the phenyl group twisting motion on a potential energy surface having a photochemical funnel, have been discussed.

3.6. REFERENCES


(4) Kramers, H. A. Physica, 1940, 7, 284.


Ultrafast Twisting Dynamics in the Excited State of Auramine


Ultrafast Twisting Dynamics in the Excited State of Auramine


