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Dynamics of photochromism in salicylideneaniline: A femtosecond spectroscopic study

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Excited state intramolecular proton transfer (ESIPT) of salicylideneaniline enol and subsequent isomerization of the proton transferred keto structure to the final long-lived photochromic product has been studied in different solvents using femtosecond transient absorption and picosecond fluorescence spectroscopy. Three different types of transient absorption have been identified, *viz.* (a) from initially excited enol form, (b) proton transferred keto form and (c) corresponding to the final photochromic product. The ESIPT rate was determined from the rise time of the characteristic transient absorption originated from the proton transferred keto form and was found to be in the order of $(200–300\ \text{fs})^{-1}$ in most of the solvents. Photochromic product formation is completed within a few tens of picoseconds. The time dependent spectral change observed at the early time delay after excitation was considered to be due to cooling of the vibrationally "hot" proton transferred keto form towards the formation of the final photochromic product. The cooling process leads to the formation of some "metastable" state within a few hundred of femtoseconds in the ground state potential energy surface of the final *trans* product.

Introduction

Molecular systems having photochromic behavior are the target of considerable interest both from a fundamental and a technical point of view. As explained in the definition of photochromism, the ground state stable structure of these systems can be "switched" into some other form under photon excitation which returns back again to the ground state either by a thermal (T-type) or photochemical (P-type) process, thereby completing the reversible cycle. The reversible cyclic nature of the photochromic reactions and the existence of structurally different forms (in most cases different isomers) in the ground and excited states led to their importance in diverse applications such as optical data processing and storage devices.[1,2]

N-(2-Hydroxy benzylidene) aniline, hereafter abbreviated as salicylideneaniline (SA), has been known to exhibit photochromism both in its crystalline and solution phases.[3–7] It is generally agreed that photo excitation of SA is followed by a rapid proton transfer along the intramolecular hydrogen bond of the *o*-hydroxyl group to the imine nitrogen to form the "*cis*" proton transferred product which isomerizes to the more stable "*trans*" form by subsequent rotation around the C1–C7 and C=N bonds. So far, two different structures have been proposed for the final photoproduct. The first one is originated from the full transfer of the proton (or more specifically, hydrogen) from the initial enol structure to give "*cis*" and "*trans*" keto forms, whereas, the other involves only a partial transfer to "*cis*" and "*trans*" zwitterionic structures (Scheme 1). However, the most notable difference in the photochemistry of SA in fluid solution from that in the solid state is the transient existence of the photocolored species in the former in comparison to the later, where the photocolored product is relatively more stable. Even though a number of studies have been reported on the structure of the transient photoproduct in solution, the subject is still controversial now.[8,9] Recently sub-microsecond time resolved infra-red spectroscopic measurements showed that the final transient species of SA is a hybrid of the quinoid and zwitterionic structures and the relative contribution of the individual forms depend on the solvent characteristics.[10]

Considering the possibilities of photochromic salicylideneaniline type molecules in data storage application,[11] further study of the dynamics of photochromism seems justified. So far, almost all reports concern only the primary aspects of SA photochromism, *i.e.*, the mechanism of the process and/or the structure of the final photoproduct. However, studies on the dynamical aspects of photochromism are relatively scarce. Barbara *et al.*[6] studied the fluorescence kinetics of the ESIPT process of SA to report that it occurs on an ultrafast time scale and the rate was found to be limited within their instrument limit (<5 ps). Nanosecond laser flash photolysis studies on SA and its derivatives have been reported[12] in combination with steady state spectroscopy and semi-empirical theoretical calculations based on AM1 and INDO/S-CI methods. The lifetime of the final photoproduct is determined to be 5 ms in butyronitrile although relatively scattered data on this subject are available in the literature.[7] Recently we applied the combination of femtosecond transient absorption and picosecond time-resolved fluorescence spectroscopies to the solution phase dynamics associated with the photochromism in SA.[13] It was reported that the dynamics of both ESIPT and the final photochromic product formation occurs in the femtosecond time limit. Here, we extend our observations in a number of solvents to study the dynamics of this process in

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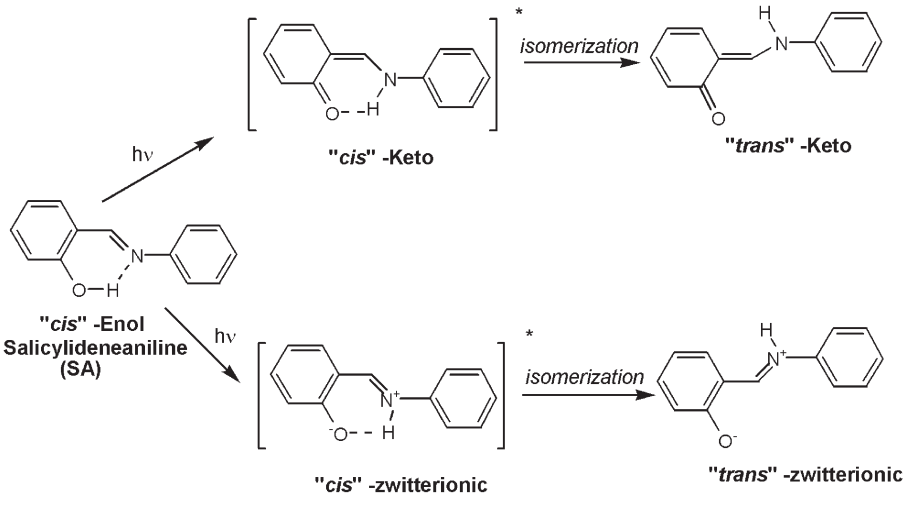


Scheme 1

more detail with the intention of understanding the mechanism of photochromic reaction.

Experimental

Salicylideneaniline (SA) was purchased from Tokyo Kasei and recrystallized from methanol. The solvents cyclohexane, ethanol, acetonitrile, butanol (all spectroscopic grade from Chameleon Reagent), cyclohexanol (99%, Chameleon Reagent) and butyronitrile (99%, Tokyo Kasei) were used as received. Concentration of the sample for transient absorption spectra was kept $\sim 8 \times 10^{-4}$ mol dm^{-3}. All experiments were carried out at 294 ± 2 K.

Steady state absorption and fluorescence spectra were recorded in U-3210 (Hitachi) and FluoroMax-2 (JOBINYVON-SPEX) spectrometers, respectively. Emission spectra were corrected for the spectral sensitivity of the instrument.

The sample was excited by the second harmonic (360 nm) of the fundamental (center wavelength 720 nm, pulse width ~200 fs FWHM) output of a femtosecond dye laser (Coherent, Satori 774) and a dye amplifier (Continuum, RGA 60-10 and PTA 60) at a repetition rate of 10 Hz. The dye laser was pumped with a cw mode-locked Nd:YAG laser (Coherent, Antares 76S). A femtosecond supercontinuum probe pulse was generated by focusing a part of the amplified fundamental output in a 1 cm H_2O cell. The details of transient absorption spectral data acquisition, one wavelength rise and decay curves and fluorescence decay measurements are mentioned in our earlier report.[13]

The instrument response function for the fluorescence decay measurements was about 30 ps FWHM. The fluorescence decay and one-wavelength rise and decay curves were analyzed by a non-linear least-square iterative convolution method based on Marquardt algorithm.[14,15]

Results

(a) Steady state spectra of salicylideneaniline

Fig. 1 shows the steady state absorption and fluorescence spectra of salicylideneaniline (SA). The absorption band at 345 nm is considered to be due to the hydrogen bonded enol tautomer of SA. Excitation at this band gives a broad and weak fluorescence at ~545 nm.

(b) Femtosecond transient absorption spectroscopic studies

We measured the transient absorption spectra of SA excited with a 200 fs FWHM laser pulse at 360 nm in a subpicosecond time delay. The photon energy of excitation at 360 nm ($\sim 2.78 \times 10^4$ cm^{-1}) is well below the ground state absorption maxima for SA in solution (345 nm, $\sim 2.90 \times 10^4$ cm^{-1}). So we can consider that the laser excitation leads to population of the lowest vibrational level of the S_1 electronic state of the enolic form of SA. Fig. 2 shows the transient absorption spectra of SA in butanol at different time delays after excitation. The time evolution of the spectral characteristics can be separated into different distinct parts.

Initially, just after the excitation we can observe a very broad band covering the wavelength region 400–500 nm with a maximum at about 450 nm. This band may be explained as originating from the $S_n \leftarrow S_1$ absorption of the enolic form of SA. As we reported earlier,[13] this is the first observation of the $S_n \leftarrow S_1$ absorption originating from the initially excited enolic form of SA before proton transfer. The strong, sharp negative absorption at 410 nm can be considered as the stimulated Raman scattering originating from the solvent.

The broad band corresponding to $S_n \leftarrow S_1$ absorption is replaced by a sharp and intense absorption very rapidly. This new band is blue-shifted from the initial band. The time evolution of this band is rather interesting and relatively complicated. A number of distinct features can be observed within a few picoseconds. A broad shoulder centered around 485 nm is observed along with the sharp band at 420 nm. Again a very broad negative absorption with a maximum at about 620 nm is observed just after the appearance of the shoulder.

Another important observation is that along with these spectral changes, the 420 nm shifts to the blue edges as

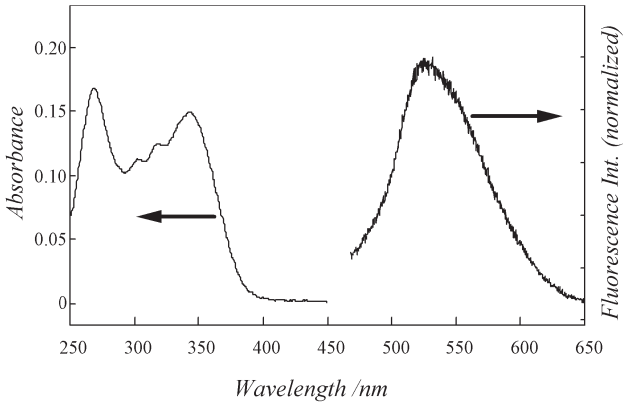


Fig. 1 Steady state absorption and fluorescence spectra of a 2.5×10^{-5} mol dm^{-3} solution of salicylideneaniline in cyclohexane. Fluorescence emission spectra were taken at the excitation wavelength 345 nm.

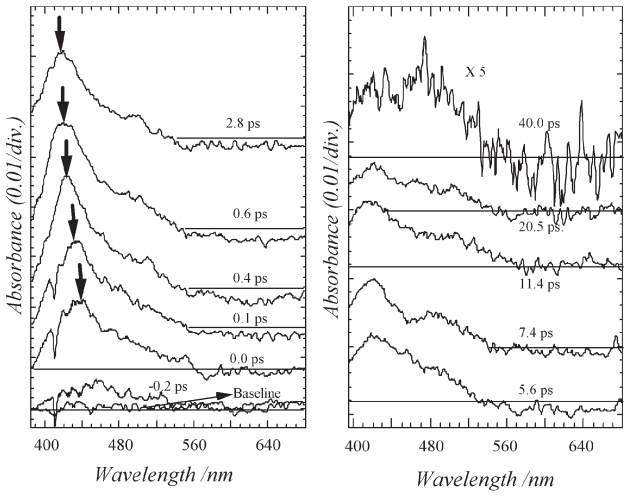


Fig. 2 Transient absorption spectra of salicylideneaniline in butanol at different time delays. The time delays are indicated in the figure. Vertical arrows guide the eye in the direction of spectral shift in the initial time region.

indicated by the vertical arrows in Fig. 2. After a few picoseconds, the intensity of the 420 nm absorption band starts decreasing. The intensity of the stimulated emission also vanishes within a few to a few tens of picoseconds depending on the solvent. At a longer time delay, the spectral features change completely and again a very broad absorption spectrum in the range of 425–550 nm corresponding to the final photoproduct[12a] is observed within a few tens of picoseconds which persists over 3 ns (the maximum limit of our measurement system). The evolution of transient absorption spectral properties of SA is similar in different solvents. Fig. 3 shows the transient spectra of SA in acetonitrile. From this figure the rapid spectral change of the SA transient absorption at the early time region becomes clearer.

The dynamical behavior of the spectra is depicted in Fig. 4, where we show the rise and decay dynamics of the transient absorption at some selected wavelengths. The time profiles for the absorption part could be reproduced well by fitting the experimental points with a sum of three exponential function (eqn. (1)) as judged by the statistical parameters like reduced chi-square (χ_R^2) and visual inspection of the distribution of weighted residuals.

$$A(t) = \sum_{i=0}^{2} a_i \exp\left(-\frac{t}{\tau_i}\right) \quad (1)$$

The first term, with a negative pre-exponential factor, indicates the rise part followed by two decay components. The longest component (>3 ns) of the fitted parameters may be due to the long lived final photochromic product. The photophysics occurring at this time window is beyond our detection limit, so we confine our discussion only on the first two components. However, the stimulated emission part can be reproduced by a single exponential decay only. We were unable to fit the rise part of the stimulated emission due to the very weak transient intensity and rather bad signal to noise ratio (Fig. 4, 620 nm). The fitted values of the rise and first decay components for the absorption and the single decay component for the stimulated emission are listed in Table 1. It is observed that both the absorption bands at 420 nm and 485 nm have relatively similar kinetic parameters. The rise time of the 420 nm absorption band is a few hundred femtoseconds, which varies in different solvents. It is clear that for the stronger hydrogen bonding alcoholic solvents like ethanol, the time constant for the rise component is higher than that in other solvents, however, any direct correlation of this parameter with solvent polarity and viscosity could not be observed. The first decay component

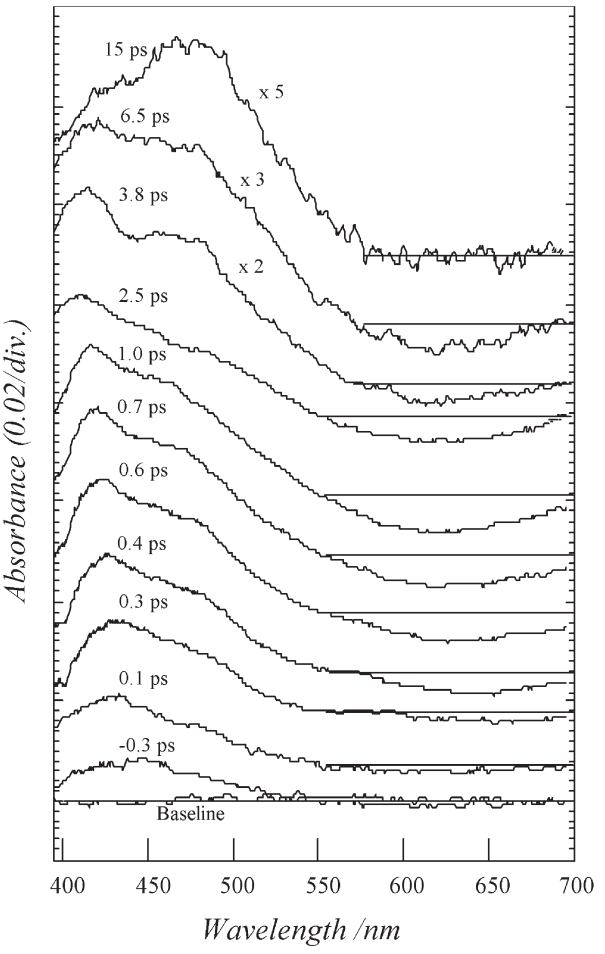


Fig. 3 Transient absorption spectra of salicylideneaniline in acetonitrile at different time delay.

varies within a few picoseconds in different solvents. The decay parameter obtained from the fitting of the stimulated emission is also of the order of a few picoseconds, which is in good agreement with the picosecond time-resolved fluorescence decay parameters (see below).

(c) Picosecond time-resolved fluorescence studies

We have analyzed the time dependence of the fluorescence decay profile of SA in different solvents measured by picosecond laser pulse (30 ps FWHM). The time profile was collected at the emission maximum of the steady state fluorescence (540 nm). Representative fluorescence traces are shown in Fig. 5 for different solvents. The decay profiles could be fitted well with two exponential functions, however, the relative contribution of the long decay component is very low ($<0.1\%$) in all cases except for cyclohexanol. So we can consider a two component decay for cyclohexanol whereas for other solvents, fluorescence decay consists of effectively a single component. In Table 2, we have summarized the fluorescence decay times along with the pre-exponential factors.

Discussion

In the ground state SA exists mainly as the hydrogen bonded enol form as suggested by NMR and IR studies.[8,9,16] Excitation with a 360 nm laser pulse leads to the formation of the S_1 state from where very fast proton transfer occurs to give the keto structure. Emission from this state results in a large Stokes shift ($>10\,000$ cm^{-1}) between the absorption and fluorescence maxima, which is a characteristic feature for the proton transfer systems and can be explained on the basis of

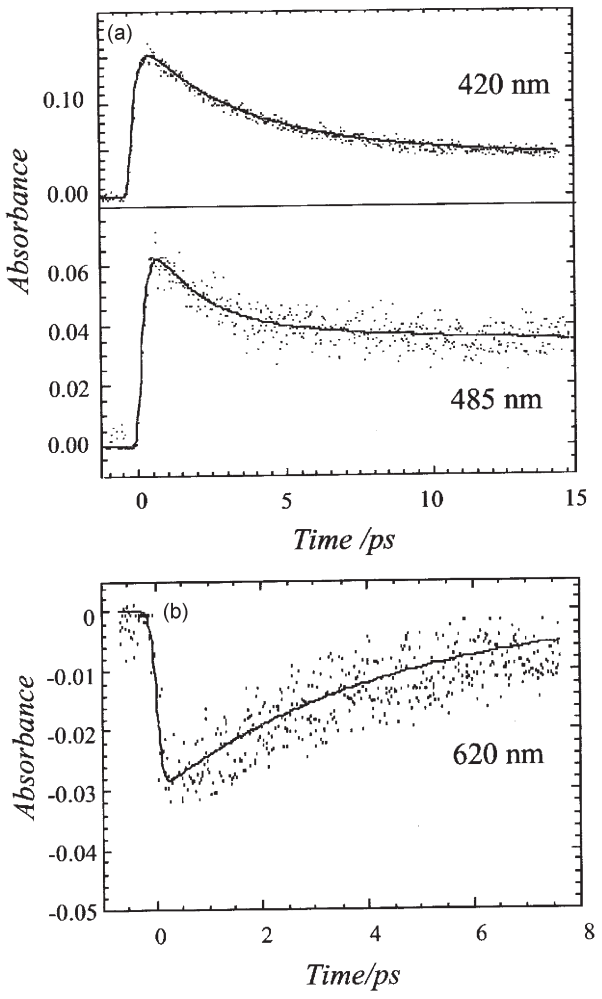


Fig. 4 Kinetics of transient absorption measured at fixed wavelengths for salicylideneaniline in acetonitrile. Corresponding wavelengths are indicated in the figure.

Förster cycle[17] for this kind of system. Although photochromism in SA has been known for more than thirty years now, understanding of the complete mechanism for this process is still unclear.

In a recent publication by Zgierski and Grabowska[18] on the mechanism of SA photochromism by *ab-initio* theoretical calculation, the unstable planar $S_1(\pi\pi^*)$ state of the initial enol tautomer was proposed as the common precursor of the fluorescent keto tautomer and photochromic transient. However, this mechanism could not explain the excitation energy dependence of the photochromic yield observed experimentally and

Table 1 Fitted parameters for the kinetic data measured at fixed wavelength transient absorption of SA in different solvents[a]

	420 nm		485 nm		620 nm[b]
Solvent	τ_{rise}[c] / fs	τ_{decay}[d] / ps	τ_{rise}[c] / fs	τ_{decay}[d] / ps	τ_{decay}[d] / ps
Cyclohexane	210(1.0)	3.9(0.8)	180(0.8)	3.5(0.6)	4.0(1.0)
Ethanol	380(0.9)	6.0(0.8)	500(0.9)	5.4(0.6)	8.3(1.0)
Acetonitrile	240(0.9)	7.9(0.6)	200(0.9)	5.6(0.6)	4.5(1.0)
Butanol	245(1.0)	24.5(0.7)	180(0.9)	30.0(0.8)	8.0(1.0)
Cyclohexanol	280(1.0)	7.0(0.7)	360(0.9)	52.2(0.6)	116.0(1.0)
		41.4(0.2)			
Butyronitrile	250(0.9)	15.3(0.6)	300(0.8)	13.6(0.8)	14.0(1.0)

[a] Values in parentheses indicate pre-exponential factors associated with each lifetime. [b] The rise part at this wavelength could not be fitted due to the poor s/n ratio. [c] Values are within ±100 fs. [d] Values are within ±1.0 ps.

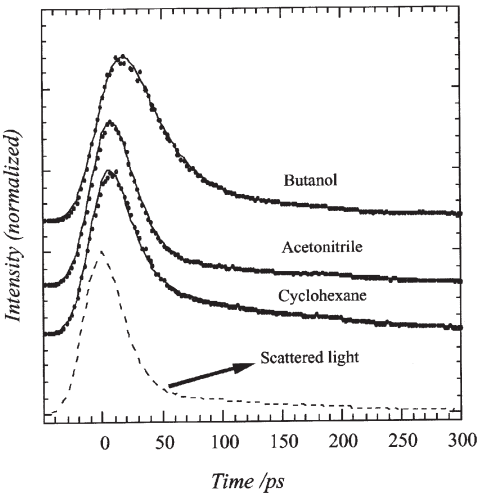


Fig. 5 Fluorescence decay profile of salicylideneaniline in different solvents measured at 540 nm and excited with 360 nm with 30 ps FWHM laser pulse. The normalized decay (dashed line) and simulated (solid line) profiles are shifted vertically for clarity.

needs to be investigated in more detail. In a classic paper by Rosenfeld *et al.*,[19] it was shown that the yield of the final photochromic product is inversely proportional to the quantum yield of fluorescence and the ratio of these two yields depends on the excitation wavelength. These observations can be explained as follows. An adiabatic proton transfer from the excited enol to the keto form leads to population of the "hot" vibrational state *ca.* 3000 cm^{-1} above the vibrationally "cold" state.[20] It was proposed that the vibrationally "hot" keto tautomer resulting from the very fast proton transfer is the common precursor to form the vibrationally "cold" fluorescing state and the final photochromic product.[6,13,19]

Nanosecond laser flash photolysis studies reported earlier[12] could not follow the fast processes of photochromic reaction of SA and its derivatives. However, femtosecond spectroscopic experiments enable us to study the processes that may proceed in the time interval between the population of the initially excited "hot" keto form and the population of the vibrationally relaxed "cold" fluorescing state and/or the final photochromic product.

The sharp and intense absorption around 420 nm is considered to be due to the proton transferred keto species from the excited enol form. The very broad band just after excitation is due to $S_n \leftarrow S_1$ excitation of the enol form. The proton transfer time can be followed with the rise time of the 420 nm band. As shown in Table 1, PT occurs on an ultrafast time scale and depends on the nature of the solvent. As reported for many other systems, ESIPT occurs on an ultrafast time scale in both solution and solid phases even at very low temperature[21] up to 4 K. Recently, ESIPT in 2-(2′-hydroxyphenyl)-4-methyloxazole (HPMO) was found to occur with a time constant much

Table 2 Fluorescence decay parameters of SA in different solvents measured by a picosecond TCSPC technique

Solvent	τ_{decay}[a] / ps	Pre-exponential factor
Cyclohexane	5	0.97
Ethanol	11	0.99
Acetonitrile	7	0.99
Butanol	27	1.00
Cyclohexanol	48	0.80
	130	0.20
Butyronitrile	18	0.99

[a] Values are within ±1.0 ps.

less than 300 fs.[22] It is seen from Table 1 that the proton transfer process is relatively slow in stronger hydrogen bonding solvents like ethanol ($\tau_{PT} = 380$ fs) compared to cyclohexane ($\tau_{PT} = 210$ fs) or acetonitrile ($\tau_{PT} = 240$ fs). The ESIPT process is a direct consequence of the pre-formed hydrogen bond in the molecule and in protonic solvents the transfer rate decreases due to the competition of possible formation of an "intermolecular" hydrogen bond with the solvent. However, as observed in most cases, there is no direct correlation of the ESIPT time with solvent polarity and viscosity.

The decay components for the transient absorption and the stimulated emission are very close to each other and may be considered to be the same within the experimental error. So we can consider that both these arise from the same species *i.e.*, the proton transfer keto tautomer. Steady state spectroscopy shows that the tautomeric fluorescence of SA appears at 540 nm. However, in femtosecond transient absorption spectra, we get a very broad stimulated emission having a maximum at *ca.* 620 nm. This shift in the band maximum may be due to the spectral overlap of the transient absorption and the stimulated emission. Transient absorption at 420 nm along with the shoulder at 485 nm is considered to have originated from the proton transferred keto form (Scheme 2). The vibrationally very "hot" state produced just after the proton transfer and the "relaxed" fluorescing states are vibronically coupled so that transient absorption arises from these states before relaxation to the photochromic product. As we mentioned in our earlier report[13] and also in the foregoing section, the time dependent spectral evolution in the initial time region after excitation is due to vibrational relaxation of the "hot" keto tautomer to the vibrationally "cold" fluorescing state and the photochromic product. To determine the spectral evolution during this time more accurately, we simulated the transient absorption part of the spectra with the following function

$$\text{Absorption}(\bar{\nu}) = A + \sum B \exp\left[-1.204\left(\frac{\bar{\nu} - \bar{\nu}_n^{\max}}{\bar{\nu}_n^{\text{FWHM}}}\right)^2\right] \quad (2)$$

where, 'n' varies from 1 to 2 for the first (420 nm) and second (485 nm) band, respectively. 'A' and 'B' are constants. The terms 'max' and 'FWHM' indicate the position and the full width at half maxima (in cm^{-1}) for the respective bands. The time dependent shift of the spectral position and narrowing of the band width was reproduced with a single exponential function. Measured time constants are about a few hundred femtoseconds for both cases. Fig. 6 shows the time dependent blue shift of the 420 nm transient absorption band of SA in cyclohexane. The time evolution of the transient absorption spectra may be the result of several factors. Of these, the following three are the most important (a) the decay originating from the internal conversion (IC) of the higher excited electronic state, (b) the cooling process of the vibrationally unrelaxed state (IVR), and (c) the excess energy transfer to the surrounding solvent medium. Both of the first two processes are known to occur within a few tens to a few hundreds of femtoseconds for large organic molecules in solution, whereas, the last phenomenon occurs with a time constant of 5 to 50 picoseconds,[23] depending on the solvent and the excess vibrational energy. However, for SA, we can neglect the first possibility because the proton transfer occurs from the first excited enol form to the keto form. So, the time dependent transient absorption spectral change during the early time delay may be regarded as *due to the intramolecular vibrational relaxation (IVR)* of the "hot" proton transferred keto tautomer simultaneously to the photochromic product and the vibrationally "cold" fluorescing state. Corresponding values for different solvents are given in Table 3 along with the solvent parameters like viscosity (η) and the static dielectric constant (ε). In large molecules like SA in solution, the density of vibronic states is very high and the relaxation of excess vibrational energy within a few hundred of femtoseconds is reasonable to understand. However, the other possible factor which can contribute to this very fast vibrational energy redistribution is that the final photochromic product of SA has a *trans* configuration. The initially formed *cis*-keto structure after proton transfer undergoes a simultaneous rotation around the C1–C7 and C=N bonds to form the final photoproduct. Earlier reports suggest that IVR is faster for systems having large molecular flexibility.[24] Rotation induces a Coriolis force in the molecule which can couple with vibrational modes to give a faster IVR rate.[25] A close look in Table 3 shows that the photochromic product formation time (τ_{PC}) is rather scattered for different solvents and no direct correlation can be made with solvent polarity and/or viscosity parameters. In recent studies it is confirmed that the extent of IVR may be controlled by solvents[26] and coupling of some specific solvent modes with

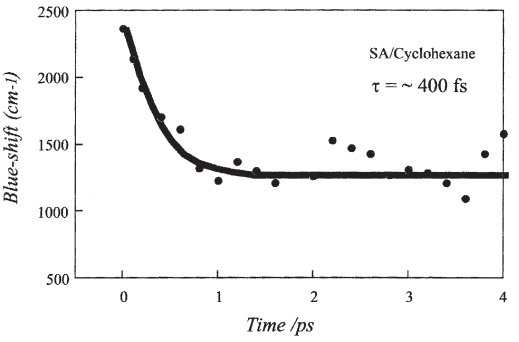
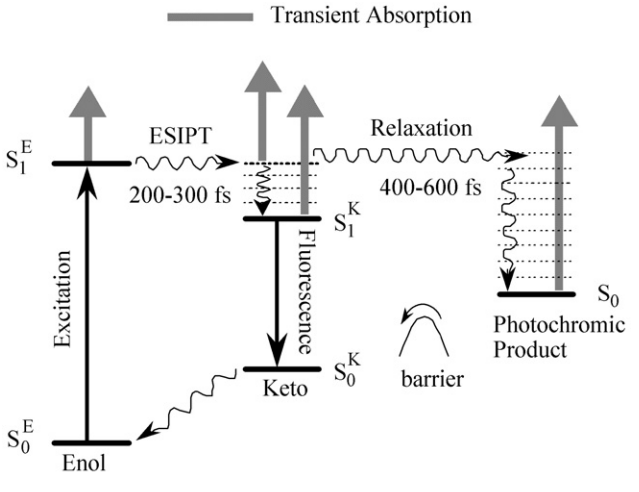


Fig. 6 Time dependent spectral shift of 420 nm transient absorption band of salicylideneaniline in cyclohexane at the initial time region after excitation.



Scheme 2

Table 3 The corresponding time (τ_{PC}) for vibrational relaxation of the 'hot' proton transferred state of SA to the ground state of the final photochromic product in different solvents[a]

Solvent	η/mN s m^{-2}	ε	τ_{PC}/fs
Cyclohexane	0.980	2.02	400 ± 100
Ethanol	1.078	24.55	600 ± 50
Acetonitrile	0.375	37.5	380 ± 80
Butanol	0.455	13.4	350 ± 100
Cyclohexanol	41.07	15.0	460 ± 75
Butyronitrile	0.624	20.3	530 ± 50

[a] Solvent viscosity (η) and static dielectric constant (ε) parameters are taken from ref. 30.

the vibrational mode may lead to solvent dependent IVR.[27] Previous observation on SA showed that the yield of photochromic product increases with an increase in excitation energy confirming the involvement of the vibrationally "hot" proton transferred keto form in the formation of the final product.[6,19] However, as observed in our study, the vibrationally "hot" state has an expected lifetime of about a few hundred femtosecond. We note that we could not observe any solvent viscosity dependence in this relaxation process. So, the direct conversion of the vibrationally "hot" *cis* structure to the corresponding *trans* form in the ground state within this short time limit seems ambiguous.

It is reasonable to believe that some metastable *trans* isomer in the ground state potential energy surface (PES) of the final photochromic product is formed *directly from the vibrationally "hot" state of proton transferred cis keto form*. Spectral narrowing and the blue shift of the 420 nm transient absorption band in the early time region (Fig. 2) is a clear indication of vibrational relaxation from the 'hot' state. Recent *ab-initio* theoretical calculations[18] also showed that the vibrationally hot proton transferred *cis* keto form is prone to undergo a twist of around 80° to give an energetically more stable conformation, which is very well prepared to adopt the *trans* configuration. We believe that such an intermediate is formed from the proton transferred keto form within 500 ± 100 fs, which is obtained from the fitting of the spectral blue shift (Fig. 6). As observed in the photochromic reaction of some spiroxazine derivatives[28,29] reported earlier, the metastable isomer formed in the PES of the final product as a consequence of rapid vibrational energy redistribution could not be identified even in femtosecond pump–probe experiments mentioned in this study. The τ_{PC} values in Table 3 are almost the same within the error limit of the determination procedure, except for the case of ethanol, for which the observed value is almost one and half to twice that in other solvents. This time constant could not be correlated with the longitudinal relaxation times (τ_L) of the solvent. So solvent relaxation does not play an important role in this process. However, ultrafast transient absorption experimental results suggest that the relaxation of the vibrationally "hot" proton transferred *cis* keto tautomer to the twisted metastable *trans* isomer originates from the progression of some specific vibrational mode in the multidimensional wave packet. Then the metastable *trans* isomer is converted to the energetically favorable final photochromic product (Scheme 2).

Conclusion

The dynamics of salicylideneaniline photochromism have been studied using femtosecond transient absorption and picosecond fluorescence spectroscopy. It is observed that at least three transients are formed at different time delays during the photochromic reaction pathway having distinct absorption maxima. The dynamics associated with the formation of proton transferred keto structure from the initially excited enol form occurs within ~200 fs. The rate of proton transfer is observed to be almost half in hydrogen bonding solvents like ethanol compared to that in non-polar solvents like cyclohexane. The spectral shift observed in the pump–probe experiments in the initial time region after excitation is due to the relaxation of the hot proton transferred keto form to the final photochromic product and vibrationally cold fluorescing state. Vibrational relaxation of the "hot" *cis* keto tautomer leads to the formation of some twisted metastable *trans* isomer in the ground state potential energy surface within 500 ± 100 fs that eventually relaxes to the final photochromic product.

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