ARTICLES

Ultrafast Twisting Dynamics of Photoexcited Auramine in Solution

P. Changenet, H. Zhang, M. J. van der Meer, and M. Glasbeek*

Laboratory for Physical Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

P. Plaza and M. M. Martin

Laboratoire de Photophysique Moléculaire du CNRS (A3361), Bât. 213, Université Paris-Sud, 91405 Orsay Cedex, France

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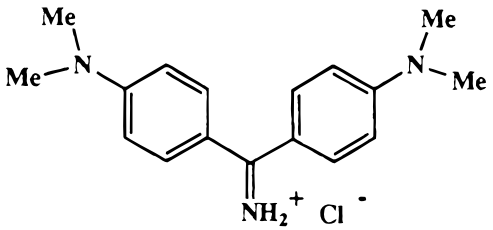
Subpicosecond fluorescence up-conversion and transient absorption spectroscopy is applied to study the excited-state dynamics of auramine, a diphenylmethane dye, in liquid solutions. The fluorescence decays, on a time scale of a few picoseconds to a few tens of picoseconds, are found to be nonexponential and solvent viscosity dependent. They can be fitted as a sum of two exponentials in ethanol and three exponentials in decanol with a larger average lifetime in the more viscous solvent. The decays exhibit wavelength-dependent time constants, whereas the fluorescence rise time is instrument limited (150 fs) at all wavelengths. The average decay time increases with the wavelength across the steady-state emission spectrum. The spectral reconstruction indicates a few hundred wavenumbers dynamic Stokes shift accompanied by a drop in the intensity in both solvents. From transient absorption experiments, the fluorescent state population is shown to decay to an intermediate dark state and then to the ground state, with a viscosity-dependent rate. 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, is proposed to explain the wavelength-dependent nonexponential fluorescence decays. Both fluorescence and transient absorption data are discussed in support of an adiabatic photoreaction involving internal twisting and charge shift.

1. Introduction

Oster et al. reported that auramine, a substituted diphenylmethane cationic dye (Scheme 1), is weakly fluorescent in water and in low-viscosity solvents and highly fluorescent in the presence of DNA[1] and polymeric acids[2] or in viscous solvents.[3] Auramine forms a highly fluorescent complex with some proteins such as the horse liver alcohol dehydrogenase (1000 times more fluorescent than in water[4]) or the Ca^{2+}-liganded calmodulin.[5] It is used as a fluorescent probe for investigating protein structure and function[4−6] and also physical aging of polymers[7,8] or dye adsorption on powdered solids.[9]

SCHEME 1



Auramine

To explain the fluorescence properties of auramine, Oster and Nishijima[3] suggested an internal conversion process via the rotational diffusion of the phenyl rings, the mobility of these large groups being affected by the surroundings. In solutions of increasing viscosity (η), they reported a linear change in the reciprocal of the fluorescence yield versus T/η. Förster and Hoffmann[10] reported that the fluorescence yield of substituted triphenyl compounds such as the triphenylmethane (TPM) dyes exhibit a sublinear increase with the solvent viscosity ($\eta^{2/3}$). They proposed that rotational diffusion of the phenyl rings occurs along a barrierless potential, with a nonradiative decay rate that depends on the twist angle. They developed a theory that describes the evolution of the excited-state population like a Brownian particle on a harmonic surface and were able to reproduce the observed viscosity effect on the fluorescence yield. More recently, Bagchi, Fleming, and Oxtoby[11,12] (BFO) developed a theory describing the excited-state population decay by a coordinate-dependent sink for the nonradiative decay and a coordinate-independent sink for the radiative decay. One of the major predictions of the BFO theory is the nonexponential character of the excited population decays, with decay functions that depend on the initial conditions. The theory also predicts fractional viscosity dependence of the fluorescence yield and viscosity effects on the nonradiative decays that depend on the form of the sink function. It is worth noting that TPM dyes were extensively investigated (see references in refs 11−19 and in the detailed review[20]), these molecules being considered as model compounds for the study of barrierless reaction,[11,12,14]

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whereas only few[19] time-resolved spectroscopic studies of auramine in liquid solution have been performed, in particular on the very short time scale.

In this paper, we present results of time-resolved spontaneous fluorescence and transient absorption measurements of auramine in liquid solutions. Fluorescence up-conversion and pump-continuum probe techniques, with subpicosecond resolution, were employed. Ethanol and decanol were used as the solvents in order to test the solvent viscosity effect. The fluorescence decays are interpreted by a solvent-viscosity dependent photoreaction, similar to that reported for TPM dyes. Furthermore, the results reveal wavelength-dependent decays without change in the fluorescence rise time. Such a behavior was previously reported for compounds that undergo barrierless or low energetic activated trans−cis isomerization in the first excited state, as for example in the cases of bacteriorhodopsin,[21] *all-trans*-retinal,[22] and, more recently, photoactive yellow protein.[23,24] The transient absorption experiments on auramine exhibit the rise of a nonemissive state population, concomitant with the rapid relaxation of the emissive first-excited-state population. It is discussed that the results support the previously proposed model of Martin et al.[19] in which diffusive twisting motions of the auramine phenyl rings cause a relaxation of the population of the emissive locally excited state into a dark excited charge-transfer state along an adiabatic potential.

2. Experimental Section

2.1. Femtosecond Fluorescence Up-Conversion Setup. Fluorescence decays of auramine were measured using the femtosecond fluorescence up-conversion setup described previously.[25] A CW Ar^+ laser pumps a Tsunami Ti:sapphire laser producing pulses, at 840 nm, with a duration of 60 fs, at a repetition rate of 82 MHz and with an output energy of about 10 nJ/pulse. The pulses are focused onto a 1 mm BBO crystal to generate the second harmonic. After splitting the pulses by a dichroic beam splitter, they are used as the pump ($\lambda = 420$ nm) and the gating pulses (fundamental frequency). The pump beam was focused onto a 1 mm cell containing the auramine solution. The sample holder is moved back and forth, perpendicular to the excitation beam, to prevent heating of the sample. The photoinduced auramine fluorescence was focused together with the gating beam onto a 1 mm BBO crystal (type I phase match). The up-converted signal was filtered by an UG 11 Schott filter (with a band-pass from 260 to 380 nm), focused on the entrance slit of a monochromator (spectral resolution <5 nm) and detected by means of a photomultiplier (EMI 9863 QB/350) connected to a photon counting system. The fluorescence decays were measured under magic angle conditions to avoid the effects due to rotational diffusion of the molecule. The up-converted signal was accumulated for 1 s, for each time-delay step. Decay measurements were performed using typical step sizes of 6.6, 66, or 264 fs. The instrumental response was estimated to be roughly 150 fs (fwhm) from the cross-correlation function of the gating and pump pulses.

2.2. Pump−Probe Setup. Time-resolved transient absorption and gain spectra were measured applying the pump−probe technique. The subpicosecond laser source was a non-mode-locked dye laser system developed at Orsay.[26] The basic system produces 500 fs pulses (400 μJ/pulse) at 610 nm from a single seeded Q-switched Nd:YAG laser (6 ns, 10 Hz). Tunable high-power subpicosecond pulses at wavelengths between 400 and 800 nm are produced by focusing the 500 fs red pulses into a 2 cm water cell. The generated white light continuum is filtered at the desired wavelength and then amplified in dye amplifiers pumped by the second or the third harmonic of the Nd:YAG laser. In this study, a first beam at 425 nm (700 fs, 20 μJ) was used to excite the sample and a second beam at 700 nm (300 fs, 200 μJ) was used to generate the continuum probe. The probe was split into two beams; one was sent through the sample, while the other passed through a reference cell. Then, the transmitted beams were focused on the entrance slit of a polychromator (Jarell-Ash, entrance slit 150 μm) through 2.50 m long optical fibers (diameter = 600 μm) and were simultaneously analyzed with a computer-controlled double-diode array detector (Princeton Instruments Inc.). The polarization of the pump light was set at the magic angle relative to the polarization of the probe light. Data were typically accumulated over 500 laser shots. The auramine solutions were contained in 1 mm flow cell, and the concentration was such as to obtain an optical density of about 0.5 at the excitation wavelength. The spectra were corrected for the chirp (group velocity dispersion) of the probe pulse using the data of a two-photon absorption experiment in 1-chloronaphthalene.

2.3. Samples. Auramine, 4,4′-(imidocarbonyl)-bis(*N*,*N*-dimethylaniline) monohydrochloride, was purchased from Aldrich (80%) and purified by several sublimations to eliminate a fluorescent impurity that could be detected when auramine solutions were excited near 350 nm. The solvents used were UV spectroscopy grade ethanol (Merck, $\epsilon = 24.5$, $\eta = 1.08$ cP) and 99% decanol (Janssen, $\epsilon = 8.1$, $\eta = 14.3$ cP). The absence of detectable impurity in decanol was checked by steady-state fluorescence measurements. The sample concentration was chosen to be larger than 10^{-4} M in order to avoid deprotonation of auramine. In fluorescence decay experiments, we checked that the results were not affected when the solutions were diluted by a factor of 2. All measurements were carried out at room temperature.

3. Results

3.1. Time-Resolved Spontaneous Fluorescence. Representative fluorescence up-conversion decays measured for auramine in ethanol and decanol are shown in Figures1 and 2. As illustrated by the transients of these figures, the fluorescence decays are dependent on the wavelength at which the emission is detected. Each fluorescence decay could be fitted to a multiexponential decay function convoluted with the system response function. The data for various wavelengths over the 465−600 nm spectral range are collected in Table 1, for auramine dissolved in ethanol (a) and decanol (b). It is seen that the weighted average lifetime increases gradually when the detection wavelength is increased. The variation of the two time constants for the fluorescence decay of auramine in ethanol over the whole spectral range is from 0.7 ps up to about 1.9 ps and from 2.7 ps up to 4.6 ps, respectively. In decanol, three time constants are required, the ranges of which are given as 0.9−1.1, 15−50, and 50−130 ps. Thus, for the fluorescence decay components, the lifetimes (as well as the amplitudes) are wavelength-dependent: the contribution of the fastest decay decreases progressively when the detection wavelength is increased. In the more viscous solvent, decanol ($\eta = 14.3$ cP), for wavelengths longer than 560 nm, the fastest decay component has disappeared. Also, the weighted average lifetime is longer than in the low-viscosity ethanol ($\eta = 1.08$ cP). In all fluorescence transients, the initial rise was determined by the system response function; i.e., the fluorescence rise following the laser pulse is faster than the time resolution of the experiments (150 fs). No change in the lifetimes (or the amplitudes) was observed when the excitation wavelength was

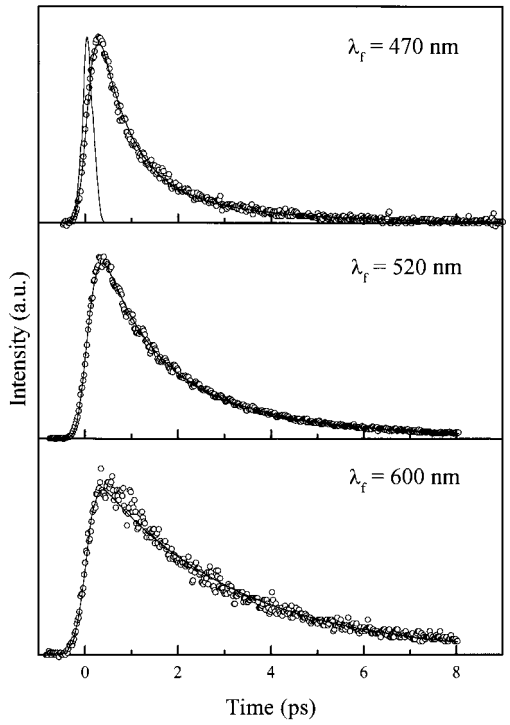

Figure 1. Representative fluorescence decays of auramine in ethanol at room temperature, after 80 fs pulsed excitation, at 420 nm, at three different detection wavelengths. The apparatus response function is included in the figure.

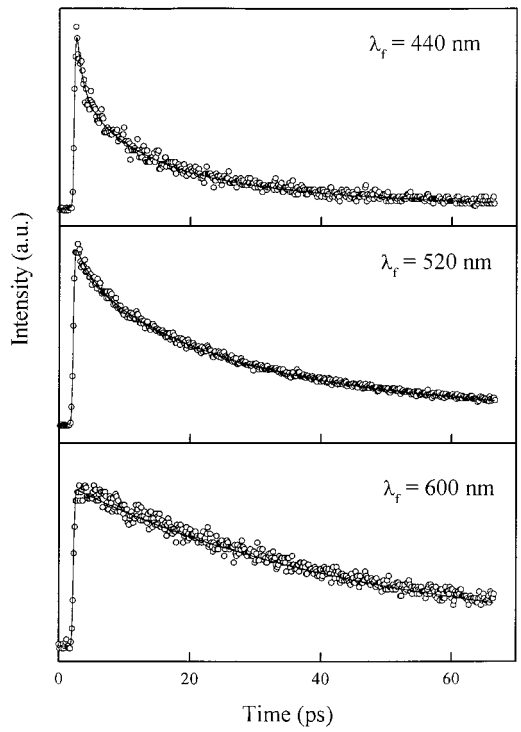

Figure 2. Representative fluorescence decays of auramine in decanol at room temperature, after 80 fs pulsed excitation, at 420 nm, at three different detection wavelengths.

tuned to higher energy, i.e., to 400 nm instead of 420 nm. Using the spectral reconstruction method of Maroncelli and Fleming,[27] the time-resolved fluorescence spectra displayed in Figure 3were obtained for auramine. The spectra in this figure show the best-fit results of the point-to-point reconstructed spectra to a log-normal function at various times after the excitation pulse.

TABLE 1: Fluorescence Exponential Decay Components for Auramine Dissolved in (a) Ethanol and (b) Decanol

λ_f, nm	τ_1, ps (%)	τ_2, ps (%)	τ_3, ps (%)
	(a) In Ethanol		
465	0.7 (75)	2.7 (25)	
490	0.8 (65)	2.8 (35)	
515	1.4 (65)	3.8 (35)	
545	1.9 (55)	3.3 (45)	
570	1.7 (65)	4.3 (35)	
600	1.5 (55)	4.6 (45)	
	(b) In Decanol		
465	0.9 (35)	16.5 (40)	51.5 (25)
490	1.1 (25)	19.5 (40)	52.0 (35)
515	1.1 (15)	22.0 (40)	51.0 (45)
545	1.1 (10)	25.5 (50)	65.5 (40)
570		31.0 (55)	79.0 (45)
600		49.5 (80)	131.5 (20)

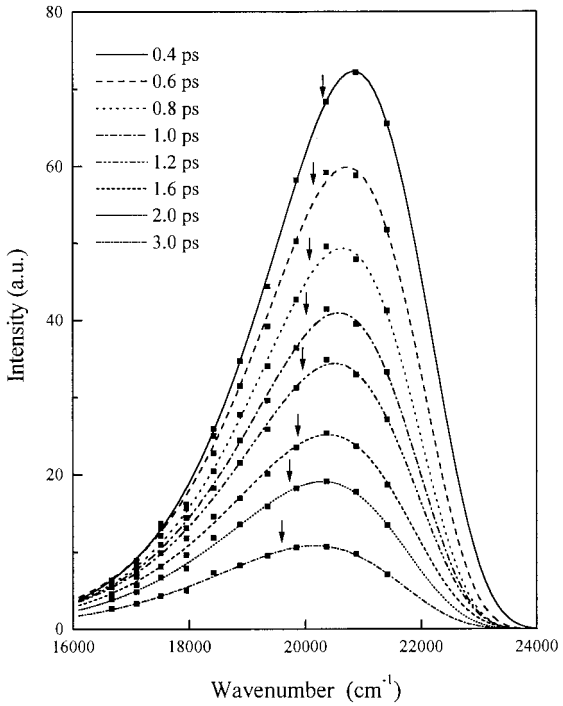

Figure 3. Log-normal fits to the reconstructed spectra of auramine in ethanol from fluorescence decays. Dots represent the reconstructed intensity data points from the experimental fluorescence transients. Arrows indicate position of first moment of the frequency.

3.2. Time-Resolved Absorption, Bleaching, and Gain Spectra. The pump−probe spectra, measured for auramine in decanol in the 370−650 nm spectral range after excitation at 425 nm with a 700 fs pulse, are given in Figure 4for several pump−probe delays between 2 and 300 ps. The steady-state absorption and fluorescence spectra are also shown in the figure. The spectral changes in the differential optical density (ΔD) look similar to those reported previously for auramine in ethanol,[19] except that in decanol the changes occur on a longer time scale.

We distinguish three stages, displayed in Figure 4a−c. Following the excitation pulse, the differential optical density (ΔD) is negative (Figure 4a, $\Delta t = 2$ ps) in the whole spectral range. Below 450 nm, the spectrum is dominated by the bleaching of the sample absorption. Above 470 nm, where fluorescence is expected and where the ground state does not absorb, the negative ΔD values show that gain is dominant over the contributions (to the differential absorption) of excited-state absorption in this wavelength region (vide infra). For $\Delta t =$ 2−50 ps, a fast decrease of the gain signal below 500 nm occurs

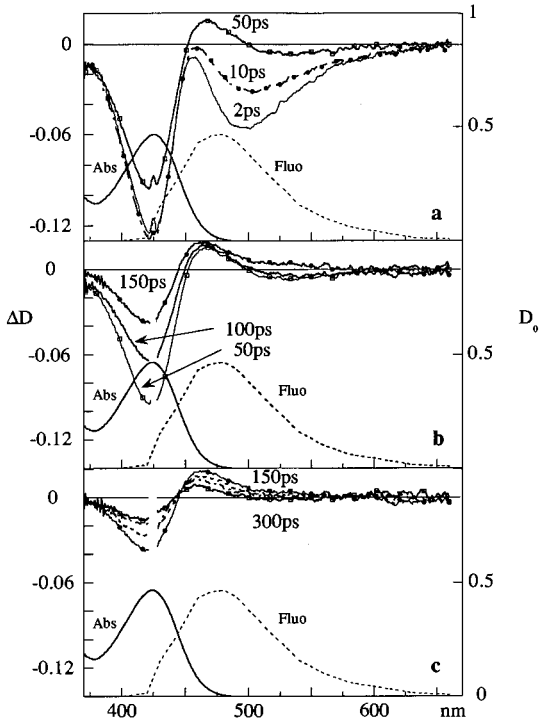

Figure 4. Time-resolved differential absorption (ΔD, left scale) of auramine in decanol at room temperature after 700 fs pulsed pumping at 425 nm. Pump−probe delays are included; (a) 2−50 ps, (b) 50−150 ps, and (c) 150−300 ps. The right scale refers to the steady-state absorption D_0 and emission spectra of auramine in decanol (normalized).

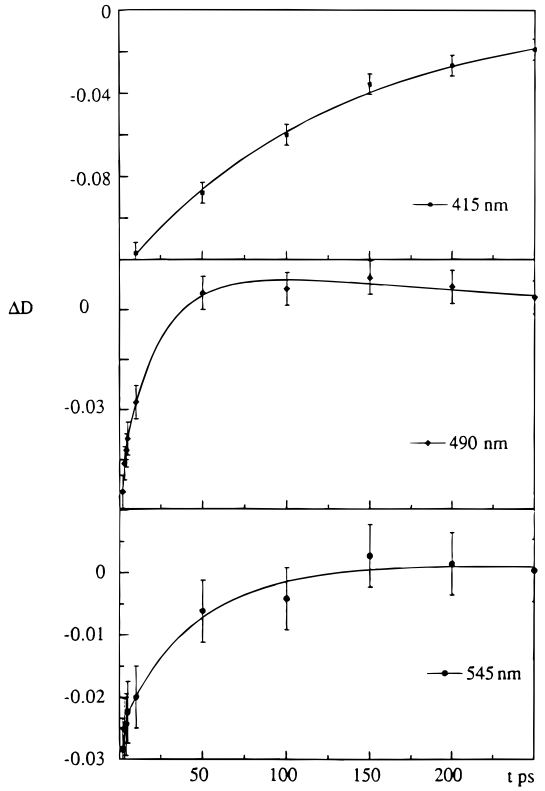

Figure 5. Kinetics of the time-resolved differential absorption $\Delta D(t)$ measured at 415, 490, and 545 nm, for auramine in decanol after excitation with a 700 fs pulsed excitation at 425 nm. At 415 nm, after a lag of 10 ps, the fit gives an exponential decay of the bleaching with a time constant of 130 ps. The fits shown for 490 and 545 nm were done by using a four-exponential function and fixing one time constant at 130 ps and using the data obtained from the fluorescence decay at the same wavelength (Table 1b) for the three other ones.

simultaneously with the rise of a transient absorption band around 465 nm, indicating the formation of a transient state from the fluorescent state. At longer delays (Figure 4b) the remaining part of the gain band above 500 nm vanishes, and a weak transient absorption band is seen below 550 nm when $\Delta t \cong 150$ ps. This change, from gain to transient absorption, looks similar to that observed at 465 nm but at a slower rate, in agreement with the results obtained in the fluorescence up-conversion experiments when detection is at the red edge of the fluorescence band. The bleaching signal remains practically constant during the first 10 ps after excitation; subsequently, it shows a decay (Figure 4a,b). Finally, for $\Delta t = 150-300$ ps (Figure 4c), both transient absorption and bleaching signals decay, and an isosbestic point around 450 nm with $\Delta D \approx 0$ is obtained, showing that the transient-state population is relaxing to the ground state.

Kinetics are illustrated in Figure 5at three probe wavelengths: one in the bleaching band (415 nm) and two in two different regions of the gain band (490 and 545 nm). It is seen that the decay of the bleaching signal, i.e., the ground-state repopulation, measured at 415 nm, for $\Delta t > 10$ ps, is well described by a single-exponential function with a time constant of 130 ps. At 490 and 545 nm both the decay of the fluorescent state and the rise and decay of the transient state are assumed to be probed, although the contribution of the latter is almost negligible at 545 nm. It is seen that the time-resolved differential optical density $\Delta D(t)$ is well fitted as a sum of four exponentials, by fixing the values of the time constants equal to the three fluorescence decay components given at these wavelengths in Table 1b (although the fastest component of $\approx$1 ps does not have much meaning for a fit without convolution of the instrumental time response), plus the 130 ps component measured at 415 nm. The fit gives, as expected, a different sign for the preexponential factor of the 130 ps transient-state decay component and a weaker contribution of this component at 545 nm. Also, the fit confirms that this transient state is formed through the fluorescent-state decay. By fixing only the 130 ps component, a rough biexponential fit gives an average first time constant of 19 $\pm$ 3 ps at 490 nm and 40 $\pm$ 15 ps at 545 nm, in reasonable agreement with the weighted average fluorescence decay times measured at these wavelengths.

4. Discussion

4.1. Nonexponential Fluorescence Decays. The fluorescence up-conversion experiments allow a direct observation of the relaxation of the locally excited state without any interference of the ground-state and excited-state absorptions. The fast nonexponential decays of the spontaneous emission and the strong viscosity effect on the lifetimes (Figures 1 and 2, Table 1) suggest that a barrierless photoreaction similar to that reported in the early studies for TPM dyes[3,10] occurs in auramine. In detail, there are some differences, however. In decanol, which is roughly 13 times more viscous than ethanol, the weighted average lifetimes at the selected wavelengths (Table 1a,b) are increased by a factor of about 14 $\pm$ 3, except at 600 nm where the disappearance of the fastest component leads to a larger effect. This increase is about twice that found for the TPM dyes ethyl violet[15,17] and crystal violet[14] in the same solvents. On the basis of the BFO theory,[11,12,19] the difference in the observed viscosity effects would indicate that the sink functions, i.e., the reaction coordinate dependence of the nonradiative decay rate, are different. However, the BFO theory predicts an excitation wavelength dependence of the excited-state relaxation dynamics, which was not observed for TPM dyes

(see references in refs 12 and 16) and has not been found here for auramine, either. The absence of an excitation wavelength effect also allows us to exclude that the observed dynamics are complicated by concurrent vibrational redistribution.

4.2. Wavelength-Dependent Fluorescence Decays. The experiments reveal that the weighted average fluorescence lifetime of auramine, in both solvents, increases with the emission wavelength; a rise in the red wing of the fluorescence spectrum remained unobserved. Nonexponential and wavelength-dependent decay behavior of the spontaneous fluorescence was also reported for compounds that undergo barrierless or low energetic activated trans−cis isomerization in the first excited state, as for example the 1,1′-diethyl-4,4′-cyanine dye,[28,29] bacteriorhodopsin,[21] *all-trans*-retinal,[22] and, more recently, photoactive yellow protein.[23,24] No variation of the lifetime with the emission wavelength was observed in the case of the *cis*-stilbene isomerization,[30] however. The absence of a temporal rise in the red wing of the fluorescence band of auramine is similar to the results for the trans−cis isomerization studies cited above,[21−24] but unlike that for the 1,1′-diethyl-4,4′-cyanine dye molecule for which a rise in the red part of the emission was found.[28,29]

Alternatively, the wavelength dependence of the fluorescence transients is reflected in the temporal behavior of the emission spectrum. The position of the band maximum in the reconstructed spectra of auramine (cf. Figure 3) shows a slight dynamic red shift of about 800 cm^{-1} in ethanol (approximately 500 cm^{-1} in decanol), and the total fluorescence intensity is rapidly reduced as time progresses. In Figure 3, the dynamic Stokes shift, as represented by the arrows that show the first moment of the log-normal functional fits at the various delay times, is included. A viscosity-dependent ultrafast spectral shift of the fluorescence band was reported for the cyanine dye,[28,29] whereas a change in the amplitude of the fluorescence spectrum with a weak change in the peak position, spectral width, and shape, with time up to 5 ps, was reported for bacteriorhodopsin.[21] In the case of the photoactive yellow protein, the wavelength-dependent decays[23] and the reconstructed spectra[24] exhibit an initially fast decaying (femtosecond/picosecond) narrowed spectrum that shows a broadening and further decay in the long time range (picosecond/nanosecond) of the red edge, with very little spectral shift.

By comparison with the TPM dyes, internal twisting, through rotation of the phenyl groups, is likely to be the photoreaction that causes the observed fluorescence behavior of auramine. We consider the rapid decay component at the blue wing of the auramine emission band as typical of the motion, on the excited-state potential, of the excited-state population out of the Franck−Condon region. On the basis of the BFO theory, one could suggest that the rapid decrease in the fluorescence intensity as the dynamic Stokes shift progresses results from a rapid increase in the nonradiative decay rate as the excited-state population moves along the reaction path, i.e., as the excited molecules twist, the minimum of the excited-state potential being supposed to be strongly nonradiatively coupled to the ground state.[11,12] However, in such a case, transient absorption experiments should display multiexponential ground-state repopulation kinetics, whereas after a 10 ps time lag a single-exponential function with a 130 ps time constant is found for auramine in the present study. Moreover, an increase in the nonradiative decay as the reaction proceeds would also give rise to a shortening of the fluorescence lifetime in the long wavelength region of the emission spectrum. The opposite behavior is observed, however (cf. Table 1). As can be seen from Figure 3, the overall integrated intensity of the emission band has decreased to about 17% of its initial value after 3 ps. A slight decrease in the emission intensity is expected on the basis of the ν^3 law (Einstein's relation) for spontaneous emission, but this cannot account for the appreciable intensity decrease obtained experimentally. An alternative proposal for the fluorescence intensity decrease with time is that there is a decrease in the radiative rate while the molecule twists, as a result of the change in the degree of conjugation. Thus, the potential energy surface on which the relaxation takes place is not considered to be characteristic of a single electronic state for which the radiative character does not change with the reaction coordinate (such as in a solvation process). A decrease in the transition electric dipole moment as the relaxation takes place is expected, if the reaction path is the adiabatic curve resulting from the electronic coupling between the fluorescent locally excited state and a transient excited state of nonradiative character typical of a twisted dark photoproduct. This can indeed explain the results of the transient absorption experiments on auramine, both in the present study in decanol and in an earlier study in ethanol.[19]

The ultrafast appearance, the fast nonexponential decay, and the negligible red shift of the spontaneous emission show that auramine behaves like bacteriorhodopsin (bR)[21] and photoactive yellow protein[23,24] (PYP). For both systems it has recently been proposed that the excited-state dynamics is compatible with a three-state model in which the system very rapidly decays out of the Franck−Condon regime (<50 fs) into an almost flat potential energy surface with a small barrier[31] to form the reaction region typical of a twisted molecule. In the reactive region there is an anticrossing with another excited electronic state, and fluorescence is assumed to take place predominantly when the molecule is in the reactive region. Inhomogeneous broadening due to ill-defined surroundings is held responsible for the spread in excited-state lifetimes. A similar model could also be relevant in the case of auramine when it performs its torsional diffusion motions. We thus infer that the relaxation within the auramine molecule from the locally excited (fluorescent) state to the twisted dark state either may involve a barrierless decay along the adiabatic potential energy surface or may pass a small energy barrier and thus may be slightly energetically activated.

4.3. Transient Photoproduct. In decanol, there is almost no change in the bleaching signal for probing times shorter than 10 ps (Figure 4a). This indicates that there is no ground-state repopulation while the fluorescent state is decaying, in agreement with the aforementioned idea of the motion of the excited-state population on the excited-state potential prior to the relaxation to the ground state. A delayed onset of the ground-state recovery was previously also observed for the 1,1′-diethyl-4,4′-cyanine dye and discussed in terms of a barrierless isomerization process in the excited state of the dye molecule.[28,29] For auramine, the ground-state repopulation is roughly 3 times slower than the average fluorescent-state decay (Figure 5). In ethanol, the ground-state repopulation kinetics was found to be about 10 times slower than the fluorescent-state decay.[19] The fluorescent state relaxes to a transient dark state, although it must be noted that in decanol a fluorescence decay component close to that of the ground-state repopulation (130 ps) is observed in the red tail of the emission band at 600 nm, suggesting that the red part of the emission in part might be due to the transient state. This is not observed in ethanol; in that case it is thus very likely that the transient state is totally nonemissive. The present experiments do not give any direct information on the geometrical change inferred above for the

probed reaction, but with respect to this one can gain insight from previous time-resolved anisotropy measurements with the TPM dye ethyl violet.[18] For the latter, a change in the direction of the $S_1 \rightarrow S_n$ transition moment direction of about 10° was deduced from time-resolved anisotropy measurements in transient absorption experiments, at a wavelength where both the locally fluorescent state and the transient dark state were probed, thus supporting a model that involves the formation of a transient state of different geometry.

For auramine in ethanol, the formation time of the dark twisted photoproduct was estimated[19] to be about 3 ps, which is in good agreement with the weighted average fluorescence lifetime found in the present study in this solvent. It is remarkable that the lifetime of the dark twisted transient state is less sensitive to the solvent viscosity than the formation time. In decanol, the dark-state lifetime is 4.3 times larger than in ethanol,[19] whereas the formation time is increased by a factor of 14. A similar viscosity effect on the formation and decay rates of the transient twisted dark state was also noted for the TPM dye ethyl violet[15] and for a bridged triphenylmethane dye (aminorhodamine).[32] Thus, also in the dark-state decay dynamics, the similarity between auramine and TPM derivative compounds is manifested.

It is of interest to recall that in the case of aminorhodamine, in the presence of hydrochloric acid, only a nanosecond monoexponential decay of the locally excited-state emission was observed,[32] showing that upon protonation the nonradiative excited-state deactivation channel is hampered. Since protonation of aminorhodamine occurs at the best electron donor site, that is the dimethylamino substituent attached to the phenyl group that is free to rotate in low-viscosity liquid, it was concluded that the nonradiative channel involves intramolecular charge transfer from the dimethylamino substituent to the central carbon atom. TPM dyes and analogues are organic cations, and the central carbon is generally assumed to carry the positive charge in the ground state. Scheme 1 shows one possible form of auramine; another possible form would be that the positive charge is on the central carbon, like in TPM dyes. Thus, based on the analogous properties between the TPM derivative compounds and auramine, an intramolecular charge shift from the dimethylamino substituents to the central carbon site is likely to contribute to the photoreaction observed here for auramine.

5. Conclusion

The locally excited-state relaxation dynamics for auramine in ethanol and decanol has been determined by fluorescence up-conversion and pump−probe transient absorption techniques. From the characteristics of the viscosity-dependent nonexponential fluorescence decays and the transient absorption data, it is concluded that the relaxation proceeds along a barrierless or low-energy activated potential energy surface by a diffusive twisting of the auramine phenyl groups. The results are discussed starting from the model of Bagchi et al.[11] for a barrierless photoreaction. However, a change in the radiative rate along the reaction path is proposed to explain the wavelength dependence of the fluorescence decays, i.e., a rapid decrease of the emission band intensity together with a small red shift, with no measurable rise time in the red wing of the band. A decrease in the transition electric dipole moment of auramine as the relaxation takes place supports the model of a photoreaction along an adiabatic potential resulting from the electronic coupling between the fluorescent locally excited state and a dark state. The dark state is considered to be characteristic of a twisted photoproduct with charge shift.

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