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Femtosecond fluorescence upconversion studies of barrierless bond twisting of auramine in solution

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Femtosecond fluorescence upconversion studies have been performed for auramine (a diphenylmethane dye), dissolved in ethanol, as a function of temperature. It is found that the (sub)picosecond decay components in the fluorescence slow down as the temperature is lowered from 293 K to 173 K. From the observation of a residual fluorescence, with a viscosity-dependent lifetime of about 30 ps (or longer at higher viscosity), and transient absorption results it is concluded that the two-state sink function model [B. Bagchi, G. R. Fleming, and D. W. Oxtoby, *J. Chem. Phys.* **78**, 7375 (1983)] does not apply in the case of auramine. Comparison of the auramine fluorescence kinetics in ethanol and decanol shows that diffusional twisting and not solvation is the main cause for the (sub)picosecond excited state relaxation. To explain the experimental results, adiabatic coupling between a locally excited emissive state (F) and a nonemissive excited state (D) is considered. Torsional diffusion motions of the phenyl groups in the auramine molecule are held responsible for the population relaxation along the adiabatic potential of the mixed state, S_1 (comprised of the F and D states). Simulation of the excited state dynamics is feasible assuming a barrierless-shaped potential energy for S_1 and applying the Smoluchowski diffusion equation. The temporal behavior of the auramine band emission was simulated for the temperature range $293\text{ K} > T > 173\text{ K}$, with the temperature, T , and the viscosity coefficient, η , being the only variable parameters. The simulated temporal behavior of the emission in the investigated temperature range is compatible with that obtained experimentally. The rotational diffusion coefficient for the auramine phenyl groups as extracted from the simulations is found to follow the Einstein–Stokes relation. From the numerical calculations the effective radius of the twisting phenyl groups is determined as $1.0\text{ \AA}$ which compares well with the actual value of $1.2\text{ \AA}$. © 2000 American Institute of Physics. [S0021-9606(00)51706-1]

I. INTRODUCTION

Ultrafast photoinduced intramolecular conformational changes are of great importance to many processes of chemical and biological interest.^{1,2} Especially when the excited state potential energy as a function of the reaction coordinate lacks an activation barrier, very high values for the reaction rate (often in excess of 10^{12} s^{-1}) can be expected. In the condensed phase, the dynamics of barrierless reactions in *fluorescent* excited states may be studied from time resolved Stokes shift (TRSS) measurements.^{3–5} In the experiment, an ultrashort laser pulse prepares the molecule in the photoreactive emissive state and, as the activationless reaction in this excited state develops, the red shift of the peak of the emission band (or its first moment) is probed with time. On a picosecond time scale, the motion of the excited-state population density distribution out of the Franck–Condon region may be considered as diffusive.⁶ Adopting some downhill shape for the excited state potential energy surface, the excited state population, $\rho_e(t)$, and thus the Stokes shift is obtained by solving a diffusion-type equation.^{6–11} Quite often, the lifetime of the fluorescent state is influenced by the solvent viscosity. The lifetime increases with increasing viscosity from picoseconds up to nanoseconds. The phenom-

enon has been observed for example for photoexcited di- and triphenylmethane dye molecules.^{12–40} Examples are malachite green,^{15,38–40} crystal violet^{12,13,16,17,24,26–28,33–35} and its julolidine analogue,^{23,28} ethyl violet,^{14,38} and parafuchsin.^{14,38} To simulate the temporal behavior of $\rho_e(t)$ in such excited state systems, Bagchi, Fleming, and Oxtoby⁷ (BFO) considered the incorporation of a reaction-coordinate dependent (nonlocal) sink function in the Smoluchowski diffusion equation. This sink function causes an enhanced *nonradiative* decay and its effect is more pronounced as the generalized reaction coordinate, $z(t)$, in the excited state approaches a value that corresponds to the excited product state. Especially, the population density of the reactive state is affected by the presence of this sink function; when the system has relaxed close to the potential energy minimum of the excited state, the population density has decreased appreciably and this is considered to be the cause for the fast drop in the fluorescence intensity.

In this paper, we study (sub)picosecond fluorescence transients of auramine (for a picture of the molecular structure, see Scheme 1), in liquid solution. Auramine has long been known for its highly viscosity dependent fluorescence quantum yield.⁴¹ The dye is weakly fluorescent in low-viscosity solvents, like water, and highly fluorescent in vis-

Auramine

Scheme 1

cous solvents, DNA and polymeric acids.^{42,43} Auramine has recently been applied as fluorescent probe in polymers,^{44,45} protein systems,⁴⁶ and in investigations of microviscosity and structure in micelles.^{47–49} Early investigations already suggested that rotational diffusion of the phenyl groups in the auramine molecule is responsible for the drastic influence of the solvent viscosity on the fluorescence quantum yield.^{41,50} In highly viscous solvents the torsional motions are impeded, thus radiationless decay is less efficient and the fluorescence is favored.⁵¹

Previous time-resolved fluorescence upconversion measurements of auramine have revealed a multiexponential fluorescence decay for which the kinetics is detection wavelength dependent.⁵² After spectral reconstruction, at room temperature two observations could be made; (a) a small dynamic Stokes shift of about 1000 cm^{-1} in a few picoseconds, and (b) the dynamic Stokes shift is accompanied by a drastic decrease of the fluorescence intensity to about 10% of its initial value. The longer-lived residual fluorescence has a weighted average lifetime of about 30 ps in ethanol (~ 130 ps in decanol). This lifetime is thus at least one order of magnitude longer than the typical Stokes shift kinetics. Yet, no (sub)picosecond fluorescence intensity rise (characteristic of a dynamic Stokes shift) could be observed when detection is at the red part of the emission band. The absence of such a rise component is a manifestation of the fact that, concomitant with the dynamic Stokes shift, fluorescence intensity is lost, and that this loss is on a time scale much faster than the 30 ps (or longer) residual lifetime. As discussed previously,⁵² the results cannot be reconciled within an approach that follows the BFO model, because according to this model the rapid fluorescence intensity loss in a few picoseconds would imply an excited state lifetime (shortened by the presence of the sink function) of also a few picoseconds and this is in contradiction with the observed residual lifetime of at least 30 ps.

In an alternative approach, we proposed⁵² that, concomitant with the torsional diffusive relaxation affecting $\rho_e(t)$, also the radiative decay rate constant, k_e^{rad} , may be z -dependent such that $k_e^{\text{rad}}(z)$ is reduced as the reaction takes place. The z -dependence of $k_e^{\text{rad}}(z)$ was discussed to originate from an adiabatic coupling of a locally excited emissive state and a nonemissive “phantom” state. Indeed, the existence of a short-living (30 ps–130 ps) dark excited state had been verified by means of transient absorption experiments.^{31,52} In these pump–probe experiments the fast decay of the gain signal above 470 nm for $\Delta t = 1\text{--}10$ ps (reflecting the fast decay of the fluorescent state) is accompanied by a simultaneous rise of a “new” transient absorption band around 465 nm, indicating the formation of a transient state from the fluorescent state. At longer delay times

($\Delta t = 10\text{--}50$ ps), the 465 nm transient absorption and the bleaching of the ground state absorption around 425 nm exhibit a simultaneous decay, thus giving rise to an isosbestic point around 450 nm. These results show that the time constants for the decay of the formed transient state and the ground state recovery are the same. The long lifetime of 30–130 ps (depending on the solvent viscosity) of the transient intermediate state is evidence for a transient dark electronic excited state, the population of which relaxes to the ground state.⁵² Twisting is accompanied by an energy relaxation along the adiabatic potential energy curve whereby the excited state radiative character is changed from radiative to nonradiative. The model could account in a natural way for the observation of short-living fluorescence components (with characteristic times of a few picoseconds) as well as the emission from the relaxed excited state with a lifetime of at least 30 ps.

In this paper, the proposed model of adiabatically coupled emissive and dark excited states of auramine is investigated in more detail, both experimentally and theoretically. We have undertaken a systematic (sub)picosecond study of the excited-state dynamics of auramine as a function of temperature and solvent viscosity. Femtosecond fluorescence upconversion and picosecond time-correlated single-photon-counting experiments were performed to determine the time-resolved emission spectra in the temperature range from 130 K $< T < 300$ K. The experiments were conducted for auramine dissolved in ethanol. We include results of simulations that start from a modified Smoluchowski equation. In this equation a potential energy function representative of the adiabatic coupling between the emissive locally excited state and the dark “phantom” state is incorporated. It is shown that upon application of the adiabatic coupling model a satisfactory agreement between the simulations and the experimental data is obtained.

II. EXPERIMENT

Auramine, 4,4'-(imidocarbonyl)-bis (*N,N*-dimethylaniline) monohydrochloride, was purchased from Aldrich (80%) and purified in several sublimation steps to eliminate fluorescent impurities. The solvent ethanol was UV spectroscopic grade and used as purchased (from Merck) without further purification. The sample concentration was chosen to be larger than $\sim 10^{-4}$ M in order to avoid deprotonation of auramine. In steady-state fluorescence measurements only auramine fluorescence could be detected showing that impurity emission is absent.

Subpicosecond fluorescence transients were measured using the femtosecond fluorescence upconversion equipment described previously.^{10,53} A diode-laser-pumped Millennia X laser was used to pump a Tsunami Ti: sapphire laser (~ 60 fs pulse width) with a repetition rate of 82 MHz. The pulses were led through a 1 mm thick BBO frequency doubling crystal after which the pulses were split by a dichroic beam-splitter into two beams, the first beam being the pump beam (at a wavelength of 420 nm) and the second beam being the gating beam (at 840 nm). Pulses with an energy of about 1 nJ/pulse were used to photoexcite the sample. The solution was contained in a cell of 1 mm thickness. The gating beam

passed a stepper motor-driven translational stage and was focused together with the fluorescence induced by the pump-beam onto a 1 mm thick BBO crystal (type I phase match). The upconversion signal was filtered by a UG11 filter and focused on the entrance slit of the monochromator (spectral resolution <5 nm) and detected by means of a photomultiplier connected to a photon counting system linked to a personal computer for data storage and analysis. To circumvent effects arising from reorientational motions of the probe molecules in the solution, the transients were measured under magic angle conditions. The instrumental response function, as deduced from the measured cross-correlation function of the excitation and the gating pulses (at 420 nm and 840 nm, respectively), was determined to be about 150 fs (FWHM).

For time windows longer than 60 ps, fluorescence transients of auramine solutions were measured using the picosecond laser system and the calibrated emission spectrometer described elsewhere.^{10,54} In this set-up, the laser pulses from a frequency-doubled picosecond dye laser (excitation was at 322 nm, pulse duration ~ 4 ps) synchronously pumped by a mode-locked Ar⁺-ion laser, served as the excitation pulses. In these experiments, time-correlated single-photon-counting detection was applied, with a time resolution of 16 ps. Steady-state emission spectra were measured using the calibrated emission spectrometer.

Temperature variation of the sample was realized by use of a homebuilt liquid nitrogen flow cryostat.⁵⁴ The temperature was varied by means of a Cryoson 17-90B/1 temperature regulator which is attached to the liquid nitrogen supply. The temperature of the sample was measured with a thermocouple attached to the copper cuvette holder. After thermal equilibration, the accuracy of the temperature control is ± 3 K.

III. RESULTS

A. Steady-state absorption and emission spectra

In Fig. 1(a) we show the steady-state absorption and emission spectra of auramine, dissolved in ethanol, at room temperature. Figure 1(b) shows the emission spectra of auramine, in ethanol, measured at a few temperatures. The latter figure illustrates that, at the lower temperatures, the emission band maximum is blue shifted by about 800 cm^{-1} . Also, the total band intensity rapidly increases as the temperature is lowered. This intensity increase is a characteristic feature of the auramine fluorescence and of course is a consequence of the well-known increase of the fluorescence quantum yield at the lower temperatures.^{41,50}

B. Femto- and picosecond fluorescence measurements

Fluorescence upconversion transients of auramine, dissolved in ethanol, were measured for a series of different detection wavelengths within the emission band. Typical upconversion transients at room temperature were already shown in a previous paper.⁵² For convenience, however, we reproduce these transients in Fig. 2, for $T=293$ K, and a time window of 13 ps. All transients show an instantaneous rise

FIG. 1. (a) Steady state absorption (solid line) and emission (dotted line) spectra of auramine in ethanol at room temperature. (b) Steady state emission spectra of auramine in ethanol at different temperatures as measured with photon counting ps fluorescence spectrometer. Experimental data points are indicated. Drawn lines show best fits to a log-normal function.

(within the system response of about 150 fs) followed by a fast decay with a typical time of a few picoseconds. The decay is dependent on the detection wavelength; as the wavelength is more to the red, the decay is slower. The experiments were repeated at a series of temperatures, in the range from 173 K up to 293 K, at intervals of 20 K. Figure 2 illustrates for the fluorescence upconversion transients, measured at 467 nm, 544 nm, and 600 nm, respectively, the

FIG. 2. Representative fluorescence upconversion transients of auramine in ethanol for various emission wavelengths and temperatures. Open circles are measured intensities, solid lines are best fits to multiexponential decay functions as detailed in text. Dashed line in top panel shows system response function.

TABLE I. Best-fit values of the time constants, τ_1 and τ_2 , characterizing the biexponential fit to the fluorescence transients, during first 15 ps, of auramine in ethanol, at several detection wavelengths and temperatures. τ_{av} is the weighted average decay time. Relative amplitudes of the two components are indicated between brackets.

T (K)	λ_n (nm)	τ_1 (ps)(%)	τ_2 (ps)(%)	τ_{av} (ps)
293	467	0.7 (75)	2.7 (25)	1.2
	491	0.8 (65)	2.8 (35)	1.5
	544	1.9 (55)	3.3 (45)	2.5
	600	1.5 (55)	4.6 (45)	2.9
253	467	1.4 (77)	4.1 (23)	2.0
	491	1.3 (73)	3.9 (27)	2.0
	544	2.3 (82)	6.0 (18)	3.0
	600	3.6 (100)		3.6
233	467	1.6 (72)	5.2 (28)	2.6
	491	1.8 (69)	5.4 (31)	2.9
	544	2.7 (67)	6.5 (33)	3.9
	600	4.8 (100)		4.8
203	467	2.0 (63)	7.9 (37)	4.2
	491	2.3 (63)	8.9 (37)	4.7
	544	4.1 (61)	11.9 (39)	7.1
	600	6.8 (100)		6.8
173	467	2.9 (59)	15.6 (41)	8.0
	491	3.0 (59)	17.2 (41)	8.9
	544	5.3 (50)	22.4 (50)	13.8
	600	17.3 (100)		17.3

TABLE II. Best-fit values of the time constants, τ_1 , τ_2 , and τ_3 , characterizing the triexponential fit to the fluorescence transients of auramine in ethanol, at several detection wavelengths, at 133 K. τ_{av} is the weighted average decay time. Relative amplitudes of the components are indicated between brackets.

T (K)	λ_n (nm)	τ_1 (ps)(%)	τ_2 (ps)(%)	τ_3 (ps)(%)	τ_{av} (ps)
133	465	55 (32)	389 (37)	1428 (31)	463
	485	55 (17)	506 (31)	1689 (53)	907
	505	55 (18)	551 (31)	1655 (51)	863
	525	55 (3)	604 (34)	1762 (63)	1124
	545	55 (1)	822 (38)	2025 (62)	1258
	565	55 (-7) ^a	1177 (74)	2665 (33)	891
	585	55 (-14) ^a	1268 (86)	2826 (28)	810

^aThese are rise components; the sum of all relative amplitudes is chosen to be 100.

length, was normalized so that its time integrated value matched the steady-state emission intensity at the corresponding wavelength. In this way, for a set of detection wavelengths, the normalized fluorescence intensity is known at all times after the pulsed excitation. Point-to-point plots of the emission spectra at various (ps) delay times and for four different temperatures are presented in Fig. 3. The drawn lines represent the best fit of the point-to-point spectra to a log-normal line shape function. The figure clearly illustrates the salient features in the temporal dependence at the various temperatures. First, a small dynamic Stokes shift (i.e., the red shift of the first moment of the emission band) of approxi-

variation of the kinetics with temperature. In general, as the temperature is lowered, the decay slows down.

All upconversion transients in Fig. 2 could be fitted to a multiexponential decay function convoluted with the system response function. The zero-intensity level for the transients measured with the fs upconversion setup was determined by equalizing the intensities at the trailing edge of the transients, measured in the time interval $\Delta t > 30$ ps, with the intensity of the transients measured with the SPC setup in the same time interval. In this way the residual long-time components in the fs transients could be obtained. Table I collects, for a few wavelengths and temperatures, best fit values for the fastest two time constants, τ_1 and τ_2 (in ps), of the decay components, their relative amplitudes, as well as the weighted average decay time. The average decay time increases from 1.2 to 2.9 ps at room temperature to 8.0 to 17.3 ps at 173 K.

At temperatures lower than about 160 K ethanol forms a glass. In Table II, we present the time constants giving the best triexponential fit for the transients measured (not shown) with the time-correlated single-photon-counting fluorescence setup, at 133 K. For detection wavelengths below 550 nm, the fluorescence transients initially decay with a time constant of about 55 ps (cf. Table II). However, for fluorescence transients detected in the red part of the emission ($\lambda \geq 550$ nm) an initial rise component with a time constant of about 55 ps is measured for auramine in ethanol glass.

The time-dependent fluorescence spectra were reconstructed as reported previously.⁵² In brief, the deconvoluted multiexponential decay function, at each detection wave-

FIG. 3. Temporal dependence of auramine (dissolved in ethanol) emission spectra at various temperatures. The symbols represent the experimental data after spectral reconstruction. Solid lines represent best fits to log-normal shape functions.

FIG. 4. Time dependence of the first moment of the auramine emission band at the indicated temperatures.

mately 1000 cm^{-1} , within the first 10 ps, is observed at room temperature. At 173 K, this shift is approximately 700 cm^{-1} , within 50 ps. Second, the dynamic Stokes shift is accompanied by a drastic drop in the total fluorescence intensity. This intensity drop is also temperature dependent; it is more pronounced at room temperature (drop of about 90% of the initial value) and much less at 170 K (drop of about 20% of the initial value). The rate of this intensity decay is temperature dependent: as the temperature is decreased the decay rate becomes smaller. Third, at room temperature, the residual fluorescence for auramine in ethanol decays with a time constant of about 30 ps. When using the more viscous solvent decanol, the residual lifetime is about 130 ps.⁵² The lifetime becomes somewhat longer when the temperature is lowered to 173 K.

In Fig. 4, the temporal behavior of the first moment of the emission band is given for different temperatures. The magnitude and the rate of the shift in the first moment of the emission band are temperature dependent. The shift of the first moment (dynamic Stokes shift) is larger and faster at higher temperatures.

In Fig. 5, plots for the temporal dependence of the width of the emission band, at a few temperatures, are given. Note that the auramine emission band broadens in time, but for lower temperatures the broadening is much smaller and at a smaller rate.

IV. DISCUSSION

A. Existing models

The dynamic behavior of diphenylmethane (DPM) and triphenylmethane (TPM) dyes has been extensively studied in the past.^{22–37} Generally, torsional motions of the phenyl groups are held responsible for the relaxation processes observed for the molecules in the excited state. In the case of auramine, the excited state dynamics has been studied by varying the solvent viscosity.^{31,52} Upon changing the solvent viscosity, but keeping the polarity almost the same, the kinetics of the fluorescence transients was affected appreciably. These observations are strong evidence that torsional

FIG. 5. Time dependence of the width of the auramine emission band in ethanol at the indicated temperatures.

motions of the auramine phenyl groups (and not solvation dynamics involving dielectric relaxation) determine the excited state dynamics of auramine. For auramine, several models have been considered previously. Oster and Nishijima (ON) (Ref. 41) have measured the viscosity (η) dependence of the fluorescence quantum yield (ϕ) and found that, $1/\phi \sim T/\eta$. To interpret their results, Oster *et al.* assumed that the excited-state potential energy is independent of the torsional angle of the auramine phenyl groups. Twisting was considered to contribute to the broadening of the excited-state population by diffusion over a flat potential [Fig. 6(a)].

FIG. 6. Sketch of potential energy curves and dynamics of the excited state population according to Oster and Nishijima (Ref. 41) (a), Förster and Hoffmann (Ref. 50) (b), Bagchi, Fleming, and Oxtoby (Ref. 7) (c).

Through the introduction of two local sink functions, the population leaks away thus affecting the excited-state lifetime. The leakage is diffusion controlled and the ON model is compatible with the experimental behavior of $1/\phi \sim T/\eta$.⁴¹ As regards the applicability of the ON model to laser-pulse excitation experiments, we remark that the model predicts a broadening of the emission band as twisting of the phenyl groups proceeds, but a drift of the population density maximum, or equivalently, a diffusion-controlled dynamic Stokes shift is not expected. Although our experiments show, on the one hand, that a dynamic broadening of the auramine emission band is present indeed (see Fig. 5), the observed dynamic Stokes shift (see Figs. 3 and 4), on the other hand, is incompatible with the ON model. In conclusion, like in the case of the results of Förster and Hoffmann,⁵⁰ our results are not in agreement with the ON model.

Förster and Hoffmann (FH) reported a $\phi \sim \eta^{2/3}$ dependence of the auramine fluorescence quantum yield, ϕ , as a function of the solvent viscosity, η , in a series of different solvents.⁵⁰ To explain this behavior, FH considered relaxation along a parabolically shaped excited-state potential [see Fig. 6(b)]. In the FH model, the viscosity of the solvent exerts a high enough friction so that the motion along the potential energy surface is overdamped. Furthermore, a sink function at the potential energy minimum [cf. Fig. 6(b)] is introduced to warrant that the rate for radiationless decay to the ground state becomes dependent on the torsional coordinate. Förster and Hoffmann derived a $\phi \sim \eta^{2/3}$ viscosity dependence of the fluorescence quantum yield after time-integration of the derived expression for the time-dependent decay rate constant. In an analogous approach, Bagchi, Fleming and Oxtoby (BFO) have considered the *dynamics* of the twisting processes in TPM molecules.⁷ The parabolically shaped potential energy function as well as the nonlocal sink function [see Fig. 6(c)] were now used as input functions for solving the population density in the excited state from the Smoluchowski diffusion equation. Phenomenologically, both approaches, FH and BFO, lead to a dynamic Stokes shift after ultrashort laser excitation of the photoactive molecules. The main difference would be that FH gives rise merely to a dynamic Stokes shift without emission band broadening, whereas according to BFO both a Stokes shift and a band broadening are expected. Both models have in common that there is one radiative excited state for which the eventual lifetime is determined by the decay rate imposed by the sink function. It is to be expected that if these models would be applicable for the auramine results discussed in this paper, the shortening of the excited state lifetime predicted by the models (due to the twisting dependent radiationless decay) should be responsible for the observed drop in the total fluorescence intensity with time (cf. Fig. 3).

Recent transient absorption^{31,52} and femtosecond fluorescence upconversion⁵² experiments for auramine in liquid solution have shown, however, that the picosecond decay of the initially excited state is into a dark (nonemissive) “phantom” state with a lifetime of about 30 ps (in ethanol, at room temperature). The observations cannot be explained by considering rotational diffusion alone, without additional effects.

FIG. 7. Integrated fluorescence intensity of auramine dissolved in ethanol at room temperature as a function of the first moment of the emission spectrum. Open circles represent the experimental data and the dotted line is the best fit of the data points to a function of the form, $f(\nu) = \alpha\nu^3$.

This is seen as follows. If only rotational diffusion would take place, this would cause relaxation along the excited state potential energy curve, but during this process the electronic part of the wave function would not change. Consequently, the optical transition moment would not be influenced by the twisting process and the total integrated emission intensity at all times would follow a ν^3 -dependence, in accordance with Einstein's expression for spontaneous emission. As illustrated in Fig. 7, this clearly is not the case. While rotational diffusion occurs in the excited state, the ν^3 -law does not apply in the case of auramine, and in fact the total integrated intensity decays much faster than predicted by this law.

If this enhanced decay were due to “sink function effects,” the auramine results show then that the characteristic time associated with this additional sink function decay would be only a few picoseconds. Since in the BFO model the sink function represents a radiationless decay to the ground state, this would, of course, also mean that the total excited state lifetime would be of the order of a few picoseconds. The latter is not corroborated by the experimental results: for auramine a residual excited state lifetime of at least 30 ps is measured, both in transient absorption^{31,52} and emission.⁵² We conclude that the BFO and FH models are not applicable for auramine.

Alternatively, a decrease in k_e^{rad} , as the phenyl group twisting takes place, may be considered as a possible explanation for the initial ps fluorescence decay. In the next section we consider a three-state model, in which the three states refer to the electronic ground state and two electronically excited states, the upper of which is emissive, the lower being nonemissive. Adiabatic coupling between the two excited states is assumed. Due to the two-state coupling, the radiative decay constant and the lifetime of the resulting lower excited state become dependent on the phenyl-bond twisting angle. The dynamics of a barrierless decay along the lower excited-state potential is considered starting from a Smoluchowski equation. The simulations yield the temporal dependence of the auramine fluorescence. The results are in reasonable agreement with the experimental data.

FIG. 8. (a) Potential energies of mixed excited state (S_1) and the zero order emissive excited (F) and nonemissive excited (D) states. (b) Simulated time dependence of the population distribution in the excited S_1 state at room temperature.

B. Adiabatic coupling model

Figure 8(a) shows a sketch of the functional dependence on some relative twisting coordinate, z , for the energies of the three-state system we are considering. The relative twisting coordinate, z , is defined in terms of the time-dependent twisting angle, $\varphi(t)$, as,

$$z = \frac{\varphi(t) - \varphi(0)}{\varphi(\infty) - \varphi(0)}. \quad (1)$$

The energies of the ground state (G) and the fluorescent state (F) and the dark state (D) as a function of the twisting coordinate z are, in zero order, taken as,

$$G(z) = \frac{1}{2}kz^2, \quad (2)$$

$$F(z) = F_{\text{eq}} + \frac{1}{2}kz^2, \quad (3)$$

$$D(z) = D_{\text{eq}} + \frac{1}{2}k(1-z)^2. \quad (4)$$

The parameter k is the rotation force constant and has the dimension of energy. For simplicity the harmonicity in ground and excited states is taken to be the same. F_{eq} and D_{eq} correspond to the zero-order minimum energies of the fluorescent and dark state, respectively. The zero order energies for $F(z)$ and $D(z)$ are sketched in Fig. 8(a) as dashed and dotted curves, respectively. We now consider an adiabatic coupling of the two excited states, so that the energy of the lowest of the two mixed states becomes

$$S_1(z) = \frac{1}{2}(F(z) + D(z)) - \frac{1}{2}\sqrt{(F(z) - D(z))^2 + 4C^2}, \quad (5)$$

where C is the coupling strength parameter. The energy of the resulting excited state, S_1 , is given as a drawn curve in Fig. 8(a). Since the S_1 state is a z -dependent mixture of fluorescent and a non-fluorescent zero order states, the transition

FIG. 9. Moment for radiative transition as a function of the normalized twisting coordinate, z .

moment for the optical transition to the ground state is also z -dependent. Normalizing the optical transition moment for $F(z)$ to a value of 1 and that for $D(z)$ to a value of 0, one readily obtains for the transition moment, $M(z)$, for the optical $G \leftarrow S_1$ transition,

$$M(z) = \cos^2 \left(\frac{1}{2} \arctan \left(\frac{2C}{F(z) - D(z)} \right) \right). \quad (6)$$

The variation of $M(z)$ with z is plotted in Fig. 9.

Prior to the photoexcitation of the auramine molecule, the system is in the electronic ground state in thermal equilibrium with the bath of solvent molecules. Immediately after the assumed impulsive excitation to the excited state S_1 , the population distribution will no longer be in equilibrium with the bath. Excitation is at least 2100 cm^{-1} above the 0–0 transition and the effects of fast vibrational relaxation within the pulse duration time have to be considered also. The simulations appear to give relatively poor fittings with the experimental data when the initial population distribution in the excited S_1 state, $\rho(z,0)$, is Gaussian. Good agreement (see later) is obtained assuming that the initial population distribution is no longer a symmetric function of z . We take a distribution according to an asymmetric log-normal shape function, represented as,

$$\rho(z,0) = \begin{cases} \exp \left(-\ln(2) \left(\frac{\ln \left(1 + 2bz / (2\sqrt{k_B T/k}) \right)}{b} \right)^2 \right) & \text{if } 2bz / (2\sqrt{k_B T/k}) > -1 \\ 0 & \text{else } 0, \end{cases} \quad (7)$$

k_B is the Boltzmann constant, T is temperature, and b is the asymmetry factor. We consider that the time evolution of $\rho(z,0)$ follows the Smoluchowski equation,⁷

$$\frac{\partial \rho(z,t)}{\partial t} = D_r \frac{\partial^2 \rho(z,t)}{\partial z^2} + \frac{D_r}{k_B T} \frac{\partial}{\partial z} \left\{ \frac{\partial}{\partial z} S_1(z) \rho(z,t) \right\}, \quad (8)$$

with D_r being the diffusion coefficient characteristic of the rotation diffusion motions of the auramine phenyl groups. The first term on the right-hand side (rhs) is the diffusion term that gives rise to a spreading of the population distribution function in the excited state. The second term on the rhs of Eq. (8) is representative of the density flow as determined by the frictional parameter $D_r / (k_B T)$. Finally, the temporal

FIG. 10. Simulated (solid line) and measured (dotted line) absorption spectrum of auramine in ethanol at room temperature.

dependence of $\rho(z,t)$, as calculated from Eq. (8), gives rise to a time-dependent fluorescence spectrum for which the intensity as a function of the emission frequency, ν , and time, t , is proportional to^{9,11}

$$I_{\text{fl}}(\nu, t) \propto \int dz g(\nu_0(z), \nu - \nu_0(z)) |M(z)|^2 \rho(z, t) \nu^3. \quad (9)$$

In this expression, $g(\nu_0(z), \nu - \nu_0(z))$ is a line shape function characteristic of the Franck–Condon factor, and $\nu_0(z)$ is the torsional-angle-dependent energy gap between the excited state and the ground state. Equation (9) reflects that the simulated spectrum results from the convolution of the inhomogeneously broadened emission band with the homogeneous line shape of the emission. Here, inhomogeneous broadening is due to the dispersion of the population density distribution $\rho(z,t)$ with z and homogeneous broadening is due to the Franck–Condon factor.

In the numerical calculations of the emission spectra according to Eq. (9), some of the parameters were determined from the experimental steady-state absorption and emission spectra. The energy for the 0–0 transition to the excited state S_1 is then found as $21\,700\text{ cm}^{-1}$. The best-fit calculation for the broad absorption band was obtained for k equal to 3500 cm^{-1} and a width (FWHM) of the Lorentzian shaped function, $g(\nu_0(z), \nu - \nu_0(z))$, of 3500 cm^{-1} . The auramine absorption spectrum, at room temperature, simulated with these parameter values, is given in Fig. 10 (drawn curve). The values for the remaining parameters, F_{eq} , D_{eq} , C , and D_r , were obtained from the best-fit results for the time-resolved emission data. Optimized simulation results were obtained for the following values: $F_{\text{eq}} = 22\,600\text{ cm}^{-1}$, $C = 800\text{ cm}^{-1}$, $D_{\text{eq}} = 21\,700\text{ cm}^{-1}$, and $b = 0.6$, whereas, at a temperature of 273 K , the best-fit value for D_r was found to be 0.045 ps^{-1} . With these parameter values, we have simulated the fluorescence spectrum at various times assuming impulsive photoexcitation of the auramine solute. Fig. 11(a) shows the results of the simulated fluorescence spectra for auramine at 273 K . For comparison we have included the experimental spectra of Fig. 3(a). The development with time of the population distribution in the excited state corresponding to the simulated fluorescence spectra of Fig. 11(a)

FIG. 11. Solid lines, simulated time-resolved emission spectra at 273 K (a), 233 K (b), 213 K (c), and 173 K (d). Dotted lines, log-normal shaped time-resolved emission spectra obtained after spectral reconstruction from the fluorescence transients.

is shown in Fig. 8(b). It is noted that on account of the (quasi-) barrierless shape of the excited-state potential, the population dynamics, and thus the dynamic Stokes shift, is on the (sub)picosecond time scale, in agreement with the experimental results.

The time-resolved emission spectra at lower temperatures were simulated keeping the values for all of the parameters used in the simulations of the room temperature results the same, with the exception of the values for D_r and $D_r/(k_B T)$. The latter two parameters were varied to obtain the best fit with the temporal fluorescence behavior as reconstructed from the experimental transients. The results obtained in this way at $T = 233\text{ K}$, 213 K , and 173 K are given in Figs. 11(b)–11(d). As illustrated by these figures, at these temperatures, the time dependence of the emission spectrum can be simulated reasonably well until the fluorescence intensity maximum has decayed to about 20% of its initial value. At later times, additional factors like lifetime decay (which during the initial few picoseconds could be disregarded) and changes in Franck–Condon factor, when emission shifts to the red, might become important. However, in view of the approximations of the simulations (twisting represented by just one generalized reaction coordinate, relaxation along adiabatic potential of mixed state, validity of diffusion approximation, no change of Franck–Condon factor during relaxation, no loss of excited-state population) the simulated spectra show reasonable agreement with the spec-

FIG. 12. Diffusion coefficient (D_r), as numerically evaluated from the simulations, as a function of T/η . The solid line represents the best linear fit.

tra reconstructed from the experimental data. We conclude that the excited-state adiabatic coupling model provides a satisfactory simple framework to account for the observed dynamic Stokes shift, the strong drop in the fluorescence intensity within a few picoseconds and the existence of a longer-lived excited state with a lifetime of about 30 ps or longer.

The applied fitting procedure provides us with best-fit values for the diffusion coefficient parameter, D_r , as a function of temperature. In Fig. 12 we plot these best-fit values for D_r as a function of T/η , where the values for η were taken from Ref. 55. The plot displayed in Fig. 12 illustrates that the diffusion coefficient parameter, D_r , extracted from the simulations, shows an almost linear T/η dependence. This indicates that the Einstein–Stokes relation for a sphere, subject to a rotational diffusion motion, $D_r = k_B T / \zeta$, where ζ is the total friction coefficient, is found to hold here on a molecular level. If we take into account the twisting of both phenyl groups, then $\zeta = 2\zeta_r$ and $\zeta_r = 6V\eta$, where V is the volume of the diffusing sphere.⁵⁶ From the slope of the best-fit linear dependence of D_r on T/η in Fig. 12, the friction coefficient, ζ , and thus also V , can be determined. The radius of the twisting sphere is then estimated as 1.0 Å which should be compared with the effective radius of 1.2 Å of each of the auramine phenyl groups. This result further validates that torsional motions of the auramine phenyl groups determine the excited-state dynamics of auramine.

As mentioned in Sec. III, the fluorescence transients, for auramine in the ethanol glass ($T < 170$ K), display a 55 ps rise component when detection is in the red part of the emission. Such a rise is typical of a dynamic Stokes shift. Note that for auramine in liquid solution the fluorescence transients showed an *instantaneous* rise at all detection wavelengths; a “slow” rise in the red emission region, as in the glass, was not observed. Yet, in liquid solution a dynamic Stokes shift could be inferred, but this was possible only after spectral reconstruction. For auramine in the glass environment, however, a dynamic Stokes shift can immediately be concluded from the ps decay in the blue and a concomi-

tant ps rise component in the red regions of the emission. The difference with the liquid solution results may reflect that the initial excitation population distribution for auramine in a glass, as a function of z , is not broad but relatively narrow and therefore the red part of the emission is not observed instantaneously upon short-pulse excitation. Furthermore, as rotational diffusion takes place in the highly “viscous” glass, the trajectory traversed by z is not as long and therefore the quenching of the fluorescence intensity is less pronounced. Consequently, the dynamic Stokes shift is not accompanied by a drastic drop in fluorescence intensity. Thus, for auramine in a glass, the characteristics normally observed for a dynamic Stokes shift,^{10,53,57} are observed. A relatively narrow initial population distribution in the excited state, immediately after impulsive excitation from the ground state, is indicative that k [cf. Eqs. (1)–(3)] for auramine in the glass attains larger values than in liquid solution. A larger k value illustrates that “caging” in the glass is more pronounced than in liquid solution. On the other hand, the size of the cavity available for the auramine molecules in the glass is still large enough for the molecule to be still flexible and to undergo twisting motions in its excited state.

In summary, the measurements of the temporal behavior of the fluorescence, in the temperature range from 293 K to 173 K, show that the initial picosecond decay kinetics slows down appreciably. The time dependence of the reconstructed fluorescence spectra could be simulated on the basis of a model that assumes the adiabatic coupling of two excited states, the locally excited emissive state, F , and the lower lying nonemissive state, D . It has been discussed that good agreement with the experimental data can be obtained starting from a barrierless potential shape, as a function of the twisting angle of the phenyl groups, and adopting the validity of the application of the Smoluchowski equation.

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