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Molecular Dynamics of Auramine O in Low-Viscosity Solutions as Investigated by an Ultrafast Lensing Effect

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Ultrafast change in refractive index after excitation by a femtosecond laser pulse was observed for dilute Auramine O solutions in low-viscosity solvents by detecting the change as an ultrafast lensing effect (ULE). The decay of the ULE signals was found to consist of two components, and both their relaxation times depended on solvents. This is the first reported observation of the faster component by this technique. The slower component had a similar relaxation time to that of the fluorescence lifetime. Molecular orbital calculation results attributed the faster to relaxation in the lowest excited singlet state S_1 by way of internal rotation and the slower to the subsequent relaxation from S_1 to the ground state. Solvent dependence of the experimentally determined relaxation time was strongly correlated with the molecular weight of the solvents rather than their bulk viscosity. A simplified model explaining these results was proposed in which solute and solvent molecules interact only via hydrogen bonding, the strength of which is solvent independent.

1. Introduction

Ultrafast dynamics of molecules in solutions has recently attracted a great deal of interest in association with solvation structure and energy transfer between molecules. Energy transfer between solvent molecules and a solute molecule through which activation occurs is a fundamental process to understand chemical reactions in the liquid phase. Therefore, studying the interaction between solute and solvent will provide great insight into the initial process of chemical reactions. Fluorescence lifetime measurements[1−4] and transient absorption spectroscopy[5−10] have been exclusively performed to observe the interaction between solute and solvent. Measurements of ultrafast dynamic Stokes shift of fluorescence can reveal detailed information about solvation dynamics, and they have been performed for a wide variety of systems.[2−4] However, the fluorescence technique has a disadvantage that it is not applicable to nonluminescent samples. Transient absorption spectroscopy has been used to investigate intramolecular vibrational redistribution (IVR), which gives information about the energy exchange between solute and solvent. Studies of relaxation in excited electronic states of dye molecules show that IVR occurs in 200−500 fs.[8−10] This method, however, has limited capability owing to its low sensitivity, which makes application to dilute solutions difficult. Recently, picosecond IR or picosecond Raman spectroscopy has been applied to the measurement of ultrafast dynamics in solution. Hamm et al.[11] investigated the vibrational cooling of azobenzene after photoisomerization from transient IR spectra using a 300 fs IR probe pulse. Qian et al.[12] reported that *trans*-stilbene has the IVR time of 3−5 ps based on picosecond resonance Raman spectra.

Refractive index distribution induced by a pulsed light focused into a solution temporally works like a lens element. This phenomenon has been used in thermal lens spectroscopy, applications of which have provided ultrahighly sensitive detection of nonluminescent species. After a preliminary trial to combine the same optical configuration as that adopted in a thermal lens method with an ultrafast pump and probe technique,[13] our research group developed a femtosecond ultrafast lensing effect (ULE) technique which was used to investigate ultrafast nonradiative dynamics of β-carotene.[14] We demonstrated that this method can be applied to observe nonradiative processes of nonluminescent samples directly with high sensitivity and with a relatively simple experimental setup. The ULE technique might be the only way to observe ultrafast molecular dynamics of nonluminescent dilute solutions.

In this paper, we focus on ultrafast molecular dynamics of Auramine O in low-viscosity solutions. This dye molecule is known as one of the fluorescent species sensitive to environmental viscosity. It has been used to estimate microviscosity in micelles and membranes.[15−17] Oster and Nishijima[18] observed that the fluorescence quantum yield of Auramine O in glycerol was markedly dependent on temperature. This was explained in terms of internal rotation of the *N*,*N*-dimethylaniline groups,

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which contributes effectively to the nonradiative decay to the ground state. This indicates that the fluorescent quantum yield becomes smaller with decreasing viscosity of solvent. It is therefore difficult to observe the dynamics of Auramine O in low-viscosity solvents, and there are few such reports. The ULE technique seems to be a powerful means to investigate such samples.

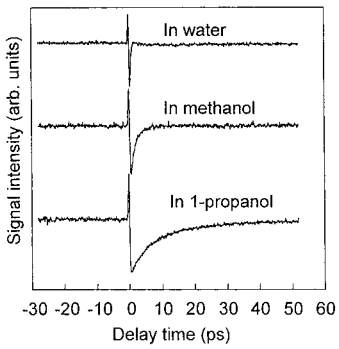
Here, we report the first measurement of nonradiative relaxation of Auramine O in low-viscosity solvents by ULE technique. We found a previously unknown ultrafast relaxation whose decay time depends on mean molecular weights for mixed hydrogen-bonding solvents, rather than their viscosity. We propose a simplified model to explain the experimental results based on observation of absorption and fluorescence emission spectra and MOPAC molecular orbital calculation.

2. Experimental Section

Principle. When a solution is irradiated by light, a spatial distribution, typically a Gaussian type, of the light intensity generates a spatial distribution of the refractive index in the solution. This distribution gives rise to an optical effect similar to a lens. This effect has been termed a "thermal lens effect" since the distribution of the refractive index originates from heat, more specifically it is from a mass density distribution caused by thermal expansion after heat generation. In turn, an ultrafast laser pulse also generates a similar refractive index distribution just after irradiation, but its origin is not the mass density distribution since the mass density cannot change so fast. In some cases, the change in the refractive index can occur before the light energy is transformed into heat. We term this an "ultrafast lensing effect" (ULE). Many possible physical origins of ULEs have been reported.[19,20]

Apparatus. The experimental setup has been reported previously.[14] Only a brief outline follows here. A mode-locked Ti:sapphire laser (Coherent, Mira 900F) pumped by an Ar ion laser (Coherent, Innova 310) produced femtosecond optical pulses with a repetition rate of 76 MHz, centered at 780 nm. Each pulse had an energy of 1 nJ/pulse and 150 fs duration (fwhm) for the autocorrelation. The output beam was divided into two by a half mirror. One was used as a probe beam after passing it through a computer-controlled optical delay line. The other beam was frequency-doubled to generate a 390 nm pump beam after being intensity-modulated by an acousto-optic modulator at 1.4 MHz. The pump and probe beams were coupled with a dichroic mirror, focused by a convex lens ($f = 50$ mm) and collinearly incident into the sample solution of a 0.5 mm optical path length. On reaching the quartz sample cell, the pump beam was less than 10 mW in time-averaged intensity and 10 μm in diameter. Polarization planes of the pump and probe beams were set parallel to each other. Change in the divergence of the probe beam was detected as an intensity change at the center of the probe beam, which was measured with a small-area avalanche photodiode (0.1 mm diameter). A colored glass filter cut off the pump beam in front of the photodiode. The photodiode output was passed through a preamplifier and a homemade passive band-pass filter before being fed into a lock-in amplifier (EG&G Princeton Applied Research, model 5202) used for sensitive phase detection. We employed a flowing system consisting of a flow cell and a peristaltic tube pump as a sampling part. This successfully produced larger signal intensity because the usual thermal lens effect, which decreases the intensity of the ULE signal, was suppressed owing to the flow of sample solutions.

Absorption spectra were obtained with a UV−visible spectrometer (Jasco, V-570). Fluorescence emission spectra were obtained with F-3010 (Hitachi). The concentrations of solutions were 1×10^{-4} M for absorption measurements and 5×10^{-6} M for fluorescence measurements.



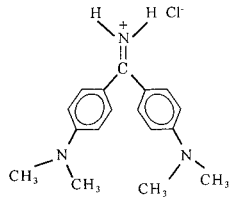


Figure 1. ULE signals for Auramine O solutions in water, methanol, and 1-propanol with the concentration of 5×10^{-4}M. Auramine O structural formula.

A molecular orbital calculation was also performed. We employed the AM1 method with MOPAC (MOPAC93, revision 2)[21] HITAC VOS3 in the Computer Center of University of Tokyo.

Auramine O (Schmid GmbH+Co., special grade) was used without further purification. Solvents used were ultrapure water purified by a Millipore system (18 MΩ/cm conductance), methanol, 1-propanol, ethylene glycol (EG), and acetonitrile (Kanto Chemical Co., Inc.; special grade). The concentration of the solutions for the ultrafast dynamics study was 5×10^{-4} M, except for the concentration dependence experiment. All the measurements were carried out at room temperature (22 °C).

3. Results and Discussion

ULE signals of Auramine O solutions in water, methanol, and 1-propanol are presented in Figure 1. Increase in the signal corresponds to the photoinduced increase in the refractive index of the solutions and vice versa. Around delay time zero, each signal shows an abrupt rise over the baseline followed by an abrupt fall beneath the baseline. After the initial sharp rise and fall, the signal increases gradually toward the baseline. These signal behaviors were observed for all the Auramine O solutions we measured. Speed of the signal recovery to the baseline depended on the solvents as shown in Figure 1.

The signal for pure solvent, e.g., water, showed a symmetric peak shape, which was fitted to a Gaussian shape of positive sign with less than 400 fs of full-width at half-maximum (fwhm). Such a signal with a smaller height was also observed for an empty cuvette. A negative signal was not observed for any of the pure solvents or the empty cuvette. The minimum of the signal intensity just after the sharp fall increased with increasing concentration of Auramine O, whereas the maximum value of the initial sharp peak remained constant. We concluded that the signal gradually increasing toward the baseline after the sharp fall was due to the solute, i.e., Auramine O, while the initial sharp peak was due to the solvent and the cell window. We found that the dynamics of the relaxation from the minimum

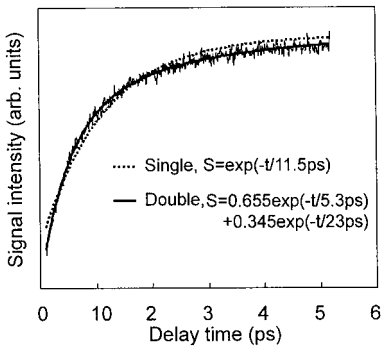


Figure 2. Fitting of the decay part of Auramine O in 1-propanol solution. The dotted line is the fitting curve by a single-exponential equation with a time constant of 11.5 ps, and the solid line is by a double exponential equation with time constants of 5.3 and 23 ps.

TABLE 1: Time Constants of the Relaxation Components of Auramine O Solutions Obtained by the ULE Technique

solvent	faster (ps)	slower (ps)
ethylene glycol	7.9	
methanol	1.5	8
1-propanol	5.3	23
acetonitrile	0.8	
water−ethylene glycol mixture		
93:7 (wt %)	0.5	
84:16 (wt %)	1.1	
70:30 (wt %)	2.4	
46:54 (wt %)	4.4	
water−methanol mixture		
80:20 (wt %)	0.6	
60:40 (wt %)	1.0	
40:60 (wt %)	1.3	
20:80 (wt %)	1.6	

value to the baseline depended on solvents; that is, the ULE of Auramine O was dependent on solvent molecules.

The initial sharp peak was attributed to the optical Kerr effect (OKE), a third-order nonlinear optical effect, of the solvent and the quartz cell wall.[22] The OKE for water and quartz increases the refractive index and the OKE temporal evolution follows cross-correlation between the pump and probe pulses because the OKE electronic response time dominating the sharp signal is much faster (∼1 fs) than the pulse width (∼100 fs). Thus, we regarded the peak center of the ULE signal for pure solvent as delay time zero. The component before the signal reached its minimum was neglected in the study on the dynamics of Auramine O. Since the signals of the pure solvent and the empty cuvette diminished within several hundred femtoseconds, they had no influence on the time constants we have determined for Auramine O solutions (Table 1).

We analyzed the observed ULE signals using a least-squares fitting method. It has been reported that fluorescence lifetimes of Auramine O in alcohols observed by time-correlated single photon counting measurement are well explained in terms of single-exponential decay.[23] However, our results for alcohols were not fitted with a single-exponential decay. As shown in Figure 2 for the ULE signal of the 1-propanol solution of Auramine O, it was necessary to assume at least a double-exponential decay. The curve representing a single-exponential decay showed obvious systematic displacement from the experimental data. The double-exponential fitting provided two relaxation time constants of 5.3 and 23 ps. The fluorescence lifetime from the first excited singlet state (S_1) to the ground state (S_0) has been reported to be 24 ps. Thus, the slower decay could be attributed to the relaxation process from S_1 to S_0.

With regard to the faster component, there are two possible interpretations. The first is reorientation dynamics of solvent molecules, i.e., the solvation process. However, the solvation time of Coumarine 153 in propanol has been reported as 18 ps from a dynamic Stokes shift measurement.[24] This is much slower than 5.3 ps, and thus we think that the faster component is not due to solvation dynamics. The second interpretation is a nonradiative relaxation process in the first excited state. It is probable that relaxation by way of internal rotation in the S_1 occurs more quickly than the relaxation from S_1 to S_0.

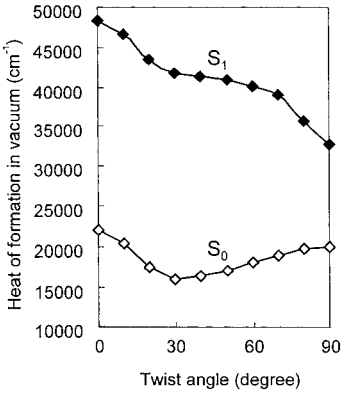


Figure 3. Electronic structure of Auramine O in a vacuum calculated by AM1 method with MOPAC93. The heat of formation represents the energy level. The twist angle means the rotational angle of *N*,*N*-dimethylaniline groups around C−C bond.

To verify this interpretation, we performed a molecular orbital (MO) calculation using MOPAC93. We calculated energy levels of S_0 and S_1 states at each twist angle every 10° for a rotation of an *N*,*N*-dimethylaniline group round the C−C bond of the Auramine O molecule. At the twist angle of 0°, the Auramine O molecule has planar geometry. For simplicity, the Auramine O molecule was assumed to be in a vacuum. Each point on the excited state was calculated by freezing the other degrees of freedom. As shown in Figure 3, the energy levels of S_0 and S_1 exhibit different dependence on the twist angle, reflecting the difference of the electronic structure of each state. The stable twist angle in S_0 is at 30° and that in S_1 is at 90°. This suggests the following process. The geometry of the initial ground state is at twist angle 30°. After excitation and vibrational relaxation from the Franck−Condon state occurs at 30° in the excited state, the relaxation by way of internal rotation from twist angle 30° to 90° in S_1 occurs as a fast process, followed by the slower process of the relaxation from S_1 to S_0. We attribute the faster process (5.3 ps) to relaxation by way of internal rotation in the S_1 state. We might say that the detailed relaxation process of Auramine O after photoexcitation was first observed by using the ULE technique.

In this study, we focus on the fast process of vibrational relaxation within the first excited singlet state, since the latter process of relaxation from S(1) to S(2) has been reported previously. This temporal difference is very significant because the IVR within S(1) might be expected to occur before breakage of a hydrogen bond formed with the solvent, whereas deactivation of S(1) to S(0) is probably slower than dissociation of a hydrogen-bonded solvate.

In previous studies, it has been reported that the relaxation time of Auramine O in solutions depends on only viscosity of the solvents. The observed relaxation times of ULE signals in methanol, 1-propanol, and water−ethylene glycol (EG) mixtures were plotted as a function of solvent viscosity in Figure 4. In the water−EG mixtures, the slower component was not observed, which seemed to correspond to the fluorescence process. Although both plots for monohydric alcohols and water−EG mixtures showed a good linear correlation, the linear

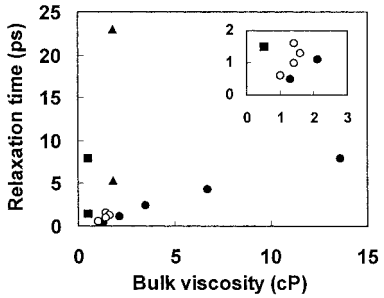


Figure 4. Plot of the relaxation time vs solvent bulk viscosity. The water−ethylene glycol system is depicted by (●), the water−methanol system by (○), methanol by (■), and 1-propanol by (▲). The inset is an expanded view.

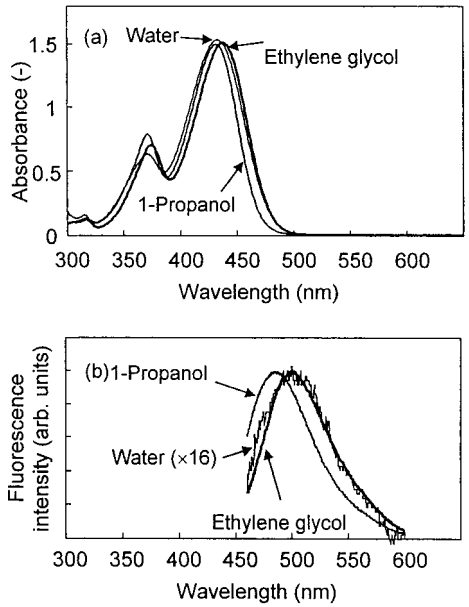


Figure 5. Absorption (a) and fluorescence emission (b) spectra in water, 1-propanol, and ethylene glycol. The fluorescence emission spectra were intensity normalized, in which Raman peaks by solvents were eliminated.

correlations themselves were not consistent with each other. For example, a similar relaxation time was observed between 1-propanol and EG despite the great difference of viscosity between them. Gautam and Harriman[23] have proposed the concept of "microviscosity"[25,26] instead of bulk viscosity, and they reported a good correlation between the relaxation time and viscosity in monohydric alcohols. In this study, however, a plot of the relaxation time vs microviscosity did not improve linearity. This suggests that solvent viscosity cannot well explain the dependence of the decay time on solvents. This fact has not been noticed before because ultrafast dynamics of Auramine O in various low-viscosity solvents has not been investigated until now.

Since water and EG are highly polar solvents, solvent polarity may influence the electronic energy of a molecular orbital, the change of which affects the relaxation time. To examine the influence of solvent polarity on the energy gap, UV−visible absorption and fluorescence emission spectra of several solutions were measured (Figure 5). The peak position in the spectra represents the value of the energy gap between electronic states. Figure 5 shows that there is only a slight change among solvents both in absorption spectra and in fluorescence emission spectra. The peak shift is as small as 10 nm, which is reduced to approximately 600 cm^{-1} as a wavenumber, while the peak position is approximately 400 nm, which means the value of

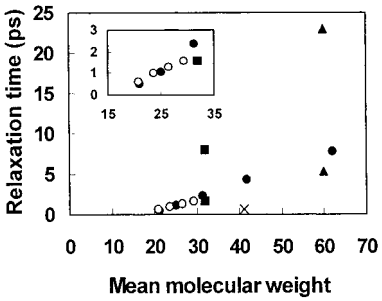


Figure 6. Plot of the relaxation time vs mean molecular weight of solvents. The water−ethylene glycol system is depicted by (●), the water−methanol system by (○), methanol by (■), 1-propabol by (▲), and acetonitrile by (×). The inset is an expanded view.

the energy gap between S_1 and S_0 is 25 000cm^{-1}. The peak shift seems too small to cause a significant change in decay time. It is unlikely that the solvent polarity affects the decay time substantially by way of the change of the energy gap. This result is consistent with the general description that the kinetics of Auramine O is not influenced by solvent polarity.[23]

We attempted to plot the relaxation time vs molecular weight of solvents instead of bulk viscosity based on the model that blocking by a solvent molecule affects the relaxation time. When the internal rotation is taken into account, this model seems reasonable from a microscopic viewpoint. We define mean molecular weight (MW_{mean}) of mixed solvents by the next equation,

$$MW_{mean} = \sum_i n_i w_i \qquad (1)$$

where i is denotes the solvent and n_i is the mole fraction and w_i is the molecular weight of solvent i. The results are shown in Figure 6 (see experimental data in Table 1). We obtained the interesting result that the plots of the decay time vs MW_{mean} for hydrogen-bonding solvents showed a linear correlation. Moreover, the relaxation time in acetonitrile, a non-hydrogen-bonding solvent, was shorter than that in the hydrogen-bonding solvents. On the basis of our experimental results, we propose a simple model describing solvent−solute interaction.

In solutions, a hydrogen-bonding solvent molecule is connected with an Auramine O molecule as well as other solvent molecules by way of hydrogen bonding. We assume that force of hydrogen bonding between the solute and a hydroxyl group of a solvent molecule has almost the same strength regardless of the kind of the molecule. This assumption seems much too simple, but it is reasonable because the structures of hydrogen-bonding solvents studied in this paper are very similar to each other. On the basis of this assumption, the rotational mobility of *N*,*N*-dimethylaniline groups will be influenced by the mass of the solvent molecule (molecular weight) in terms of an inertial effect. Therefore, larger solvent molecules hinder rotation around the C−C bond in Auramine O more effectively, which results in the increase of the relaxation time. On the other hand, the interaction between solute and a non-hydrogen-bonding solvent such as acetonitrile is very weak, and such solvent molecules influence the internal rotation less effectively. This is because the relaxation time for non-hydrogen-bonding solvent becomes shorter. Thus, this model explains the good correlation in Figure 6 for hydrogen-bonding solvents and the deviation for non-hydrogen-bonding ones. We think these behaviors of solvent molecules are limited to molecules in the first or second solvation shells around the solute molecule so that ultrafast observation of nonradiative relaxation processes is essential to

investigate them. We believe we can provide details by quantitative discussion using the moment of inertia of the hindered rotor from the measurements of various solvents with different hydrogen-bonding strength at various temperatures.

In conclusion, we investigated the dynamics of Auramine O in dilute solutions using the ULE technique and found that the relaxation by way of intramolecular rotation was affected by molecular weight of solvents and hydrogen bonding. We demonstrated that the ULE technique could be a useful tool to investigate interactions between solute and solvent molecules. We can expect that this technique will be applied to the chemical systems which are difficult to measure by other techniques.

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