Quantitative Distinction between Competing Intramolecular Bond Twisting and Solvent Relaxation Dynamics: An Ultrafast Study

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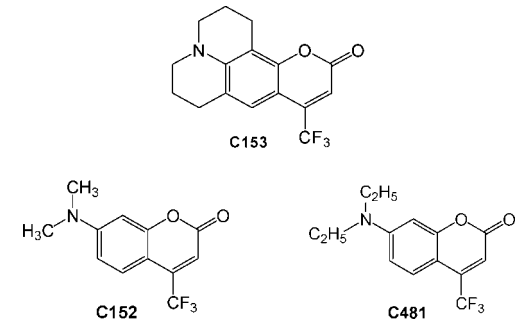
Often an intramolecular relaxation process takes place in a time scale similar to that of the solvent relaxation process. Under these circumstances the dynamic Stokes' shift of the probe can be modulated by the combined effect of these two relaxation processes. In the present article we have studied ultrafast solvent relaxation using three different coumarin dyes and proposed a methodology for the quantitative separation of the dynamics of two competing processes, namely, solvent relaxation and bond twisting, that take place simultaneously in the present systems.

Introduction

Dynamic Stokes' shift measurements for solvent relaxation study have been applied extensively to understand the structure and dynamics of different chemical and biological systems.[1–3] For example, this method has been used to understand the nature of water molecules in different microheterogeneous media, such as micelles[4,5] and vesicles,[6] as well as in biomolecules, such as DNA[7–9] and proteins.[10,11] Wide varieties of fluorescence probes have been used to understand the solvent relaxation dynamics and consequently the nature of the local environments. A judicious choice of a fluorescent probe for solvent relaxation studies largely depends on the nature of the microenvironment under investigation. A major bottleneck in studying solvent relaxation dynamics with large probe molecules is the interference of several intramolecular processes in the excited probe that takes place in the similar time scale of the solvent relaxation dynamics. The competing intramolecular processes that can significantly influence the solvent relaxation measurements are twisting of a functional group around a bond, cis−trans isomerization, and so forth. This poses a tremendous challenge to experimentalists in distinguishing various contributions of the different steps in relaxation process. In order to understand the actual dynamics of the solvent relaxation process, it is very essential to separate out the contribution of the interfering intramolecular processes from the solvent relaxation process.

The aim of the present study is to find out a methodology to quantitatively distinguish and separate out the effect of such competing intramolecular processes from the solvent relaxation process. To demonstrate this methodology, ultrafast fluorescence transient measurements have been carried out in acetonitrile solution with three different coumarin dyes, namely, C153, C481, and C152 (cf. Scheme 1 for molecular structures), as probes. Coumarin dyes have been extensively used as fluorescence probes for solvent relaxation studies, primarily because of the large Stokes' shifts and strong solvent polarity-dependent fluorescence properties of these molecules.[12] Among these dyes, C153 is the most popular probe for solvent relaxation studies,[13,14] because its rigid molecular structure ensures the absence of any interfering intramolecular relaxation process. It should be mentioned that slow S_1-S_0 internal conversion (IC) and S_1-T_1 intersystem crossing (ISC) processes (although negligible for coumarin dyes) are not expected to influence the solvent relaxation dynamics.

SCHEME 1



Unlike C153, however, the C481 and C152 dyes can participate in a fast twisting motion involving their free amino group, and it can compete with the solvent relaxation process. Detailed photophysical studies in different organic solvents indicate that, in polar solvents, the excited states of C481 and C152 molecules decay much faster as compared to C153.[15–18] This fast decay in C481 and C152 has been attributed to nonradiative transition due to twisting of the *N*,*N*-dialkyl groups around the carbon−nitrogen bond in the excited states. Unlike C481 and C152, no such bond twisting is possible for C153, because of the presence of a rigid julolidyl group in the latter molecule. This additional bond twisting process in the excited-state of C481 and C152 can modulate the measured solvent relaxation times from the dynamic Stokes' shift measurements. Acetonitrile has been selected as a solvent because its polarity is sufficient to induce the bond twisting process in the excited states of C481 and C152.[18] It has been shown that the solvent relaxation time measured with C152 is much faster as compared to C153.[19] However, the reason for this faster solvent relaxation with C152 has not been discussed explicitly. In the present study, time-resolved fluorescence transient measurements have been carried out to differentiate two competing processes, namely, the intramolecular bond twisting process and the solvent relaxation process. A method has been proposed for the first time to quantitatively extract the ultrafast time constant for an

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intramolecular process that is hidden or mingled up with the solvent relaxation process.

Methods and Materials

Steady-state fluorescence measurements were made in a Hitachi fluorimeter (model F-4500). The emission spectra were corrected for the wavelength-dependent instrument responses. All measurements were made under magic angle conditions. All samples were excited with 400 nm light. The spectrum of standard quinine sulfate solution was recorded and compared with the standard spectrum,[20] given in units of photons per nanometer, to get the correction factors for the instrumental sensitivity. All the measured spectra for our sample have been multiplied by this correction term to get the corrected spectrum. The measured spectra, $I(\lambda)$, were in wavelength domain and have been converted to frequency domain $I(\nu)$ by using the following equation:[20]

$$I(\nu) = \lambda^2 I(\lambda) \tag{1}$$

The time-resolved measurements were carried out using femtosecond fluorescence upconversion technique. Briefly, this instrument is based on a mode-locked Ti-Sapphire laser pumped by a diode-pumped solid-state (DPSS) laser. The output of the oscillator is 50 fs laser pulses with an average power of 600 mW. The wavelength of the laser output was tuned at 800 nm. Second harmonic light was generated by passing the fundamental light through a type-I β-barium borate (BBO) crystal of 1 mm thickness. The visible second harmonic light was separated from the residual fundamental light using a dichroic mirror and was used for sample excitation. The residual fundamental light was used as the gate pulse for frequency mixing with the fluorescence light from the sample in a type-I BBO crystal of thickness 0.5 mm. The sum frequency signal from the upconverting crystal was focused on a double monochromator after passing through a filter to reject the fundamental and the exciting second harmonic light. The upconverted light was detected by Hamamatshu PMT (model 5000U-09) operating in photon counter mode. The data was collected using Lumex software from CDP, Inc., Russia. The sample thickness was 1 mm and taken in a rotating cell. The instrument response function (IRF) was measured as the cross-correlation function by upconverting the transmitted excitation light from the sample with the gate pulse. The IRF thus obtained had a width of 210 fs.

All coumarin dyes were from Exciton and used as received. The molecular structures of the three coumarins are given in Scheme 1. Spectroscopic grade acetonitrile from Spectrochem, India was used as received.

Results and Discussion

Fluorescence transient decays at different wavelength were measured using fluorescence upconversion technique for all three dyes. Representative fluorescence decays measured by the upconversion technique for C153 in acetonitrile solvent at the blue and red side of the emission spectrum are shown in Figure 1. It is evident from this figure that the transient fluorescence decay is strongly dependent on the wavelength at which it has been monitored. All the transient decays can be fitted to a multiexponential function convoluted to the IRF. At shorter wavelength, the transient decay has a very short time component, which increases with an increase in the monitoring wavelength. At red side of the fluorescence spectrum, the fast decay component is absent and it is replaced by a fast rise component. Thus, for the fluorescence transients, the decay components

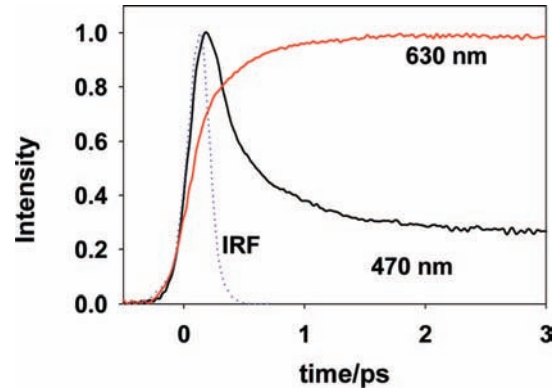

Figure 1. Transient fluorescence decay for C153 at 470 and 630 nm. The dotted line shows the instrument response function (IRF).

(both time constant and amplitude) are strongly wavelength dependent. It is already reported in the literature that this wavelength-dependent decay of the C153 in polar solvents, including acetonitrile, is due to the time-dependent motion of the solvent molecules around the photoexcited probe molecule.[21,22] Similar observations have also been made with the other two coumarin dyes, namely, C481 and C152.

Time-resolved fluorescence spectra for all three dyes have been reconstructed from transient decays following the method proposed by Maroncelli.[21] However, the reconstructed spectral data points have been fitted with cubic spline[23] rather than by a log-normal equation, as proposed by Maroncelli.[21] It was shown by Berg and his group that cubic spline fitting of the reconstructed spectral data is superior to the log-normal fit.[23] The cubic spline fitting procedure does not rely on any prior assumption about the spectral shape other than smoothness. Thus, the cubic spline interpolation can reproduce an arbitrary spectral shape, but does not have the data averaging effect of a log-normal fit.

Reconstructed time-resolved spectra thus obtained for three dyes are shown in Figure 2. It is evident from this figure that, for all three dyes, the emission maxima shift to lower frequency with time along with a concomitant decrease in the emission intensity. To quantify the temporal changes of the emission frequency, the mean frequency or first moments (ω_1) of these transient spectra, as calculated by using eq 2, were correlated with time.

$$\omega_1 = \frac{1}{\omega_0}\int_0^\infty \nu I(\nu)\mathrm{d}\nu \tag{2}$$

where

$$\omega_1 = \int_0^\infty I(\nu)\mathrm{d}\nu \tag{3}$$

The mean frequency is a better measure of the spectral shift compared to another method, say peak frequency.[21,23,24] Mean frequency makes use of all the available data points, whereas the peak frequency measurement relies heavily on only a few data points around the peak position.

Figure 3 shows the variation of the mean frequency of the transient spectra with time for all three dyes. The changes in the mean frequency for C153, according to literature, are solely due to the solvent relaxation process.[21,22] Observed changes in the mean frequency with time for C153 were fitted with a biexponential function, and the two solvent relaxation time constants thus estimated are 0.39 (45%) and 1.1 (55%) ps. The average solvent relaxation time is accordingly calculated as ~0.78 ps, which is in good agreement with the reported value.[22]

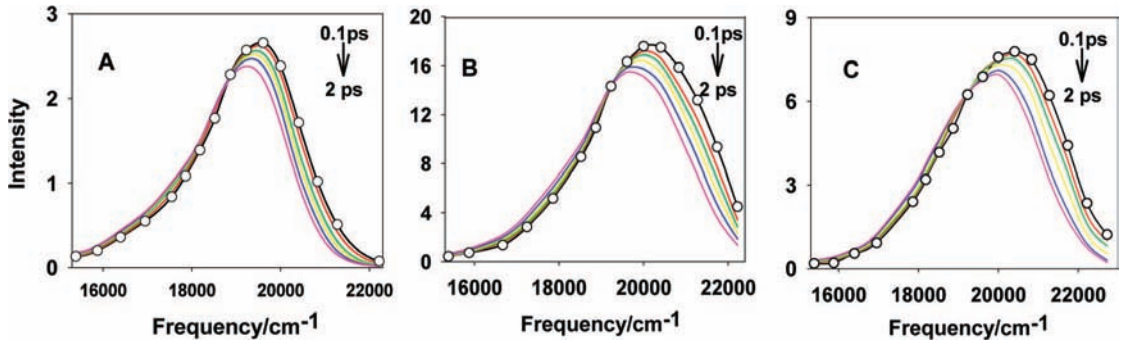

Figure 2. Reconstructed time-resolved fluorescence spectra for (A) C153, (B) C481, and (C) C152. Spectra shown are for time 0.1−2 ps. The points in each panel indicate the wavenumbers where the transient emissions are recorded.

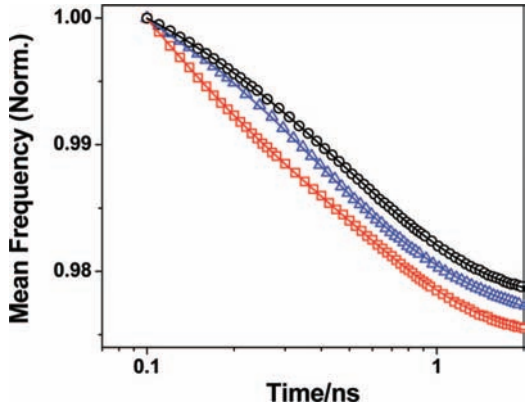

Figure 3. Changes in the mean frequency of the transient emissions with times for (○) C153, (□) C481, and (Δ) C152 in acetonitrile solution. Points are calculated from the reconstructed spectrum, and the solid lines are the multiexponential fitting to the data points (see text for details).

The appearance of the biexponential nature of the frequency shift with time has been noted earlier for different other solvents.[19,21,22,25] The nonsingle exponential nature of the frequency shifts is due to the differences in the responses of the solvent molecules that are directly in contact with the probe from those situated away from the probe. Because of the molecular nature of the solvent and the probe, the dielectric response is different for these two types of solvent molecules. For this reason, the Debye nature of the dielectric response of the solvent is not valid in real systems and they show the nonsingle exponential nature of the solvent responses.

The standard solvent relaxation theory predicts that the frequency of the emission spectra will shift with time without changing the shape of the spectra.[24,26–29] To check this prediction, all the time-resolved emission spectra of C153 have been plotted in Figure 4A after removing the frequency shift with time and normalizing the area under each of the emission spectra. It is evident from Figure 4A that the spectral shapes do not change with time for C153 dye, which is in accordance with the standard solvent relaxation theory. From these results we can infer that the observed change in the mean frequency for C153 in acetonitrile is solely associated with the solvent relaxation process.

Following the procedure mentioned above for C153, when the variation of mean frequency with time for C481 and C152 are analyzed, it results in average solvent relaxation times of about 0.47 and 0.62 ps, respectively, which are significantly shorter compared to that obtained with C153. These apparently rapid changes in the mean frequency with time for C481 and C152 cannot be explained on the basis of the solvent relaxation process alone. According to continuum dielectric theory,[30–33] the motion of solvent molecules around a probe is independent of the nature of the probe used and solely depends on the nature of the solvent molecules involved. Chapman et al.[27] measured the solvent relaxation times with 16 different probes in 1-propanol solution and observed that the solvent relaxation times measured with 11 out of 16 probes (including C153 and C152) are similar, as expected from continuum dielectric theory. For the remaining five probes, however, the solvent relaxation times are found to be shorter by a factor of about 2, which was explained by the specific H-bonding interaction of these probes with the solvent molecules. Since a similar specific interaction is not expected in the present systems, the differences observed in the changes of the mean frequencies for the three dyes studied must be related to some other factors than the specific solute−solvent interaction.

As mentioned earlier, the presence of a fast bond twisting process in the excited-state of a probe can interfere with the solvent relaxation process and result in an apparent rapidity in the dynamics of the fluorescence Stokes' shifts. Accordingly, the apparently faster solvent relaxation rate with C481 and C152 is attributed to the interference of the fast intramolecular relaxation to the solvent relaxation process. To check how this fast intramolecular bond twisting process can affect the observed changes in the emission mean frequency, we have compared the shape of the emission spectra for C152 and C481 at different times. Figure 4B shows such a plot for C152, where the emission spectrum has been plotted after removing the frequency shift with time and normalizing the area under the emission curve at each time. It is clearly evident from Figure 4B that, in contrast to the standard solvent relaxation theory, the shapes of the emission spectra do change with time for C152. Similar observation has been made for C481. To check how the spectral shape for these two dyes changes with time, we have also plotted the width (full width at half-maximum (fwhm)) of the emission spectrum for these two dyes at different times in Figure 5. It is clearly evident from Figure 5 that the shape of the spectrum becomes narrower with time for C152 and C481. The spectral shape changes up to ~0.4 and 0.8 ps for C481 and C152, respectively, and, after that, the shape of the spectrum remains almost unchanged with time, as predicted by the standard solvent relaxation theory. This clearly indicates that besides the solvent relaxation process, there is an additional process that takes place in these two dyes causing the observed changes in the shape of the spectra in the initial times. The change in the spectral shape due to the twisting of a chemical bond and subsequent formation of a rotamer have been reported in the literature.[34]

Another interesting point to be noted from Figure 4B is that the change in the spectral shape mostly occurs at the blue side

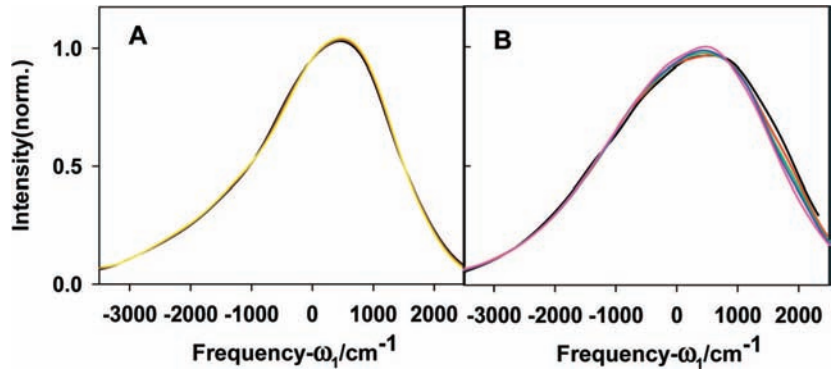

Figure 4. Reconstructed transient fluorescence spectrum for (A) C153 and (B) C152 at different times (0.1−2 ps). Each spectrum has been moved along the frequency axis to remove the time-dependent spectral shift, and the area under all spectra has been normalized for comparison.

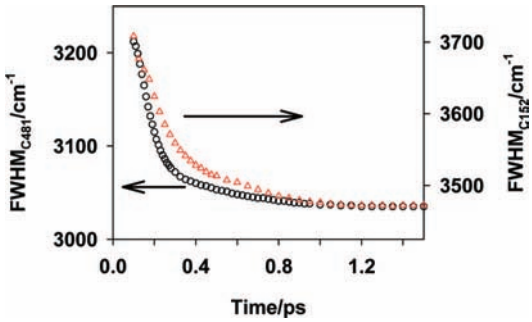

Figure 5. Changes in the width (fwhm) of the emission spectrum at different times for (○) C481 and (△) C152. Two different scales have been shown for the two dyes for comparison.

of the emission spectra. As the intensity at the blue side of the spectra decreases, the mean frequency of the spectra moves faster to the red side of the spectra. Because of this we have observed an increase in the rate of mean frequency shift for C481 and C152. It is also evident from Figure 5 that the change in the spectral width for C481 is much faster than that for C152. As a result, the change in the mean frequency is also found to be faster for C481 than C152, and hence an apparently faster solvent relaxation occurs.

In the present circumstances with C481 and C152 dyes, since the effect of intramolecular bond twisting and solvent relaxation processes are mingled up with the dynamic Stokes' shift, resolving the dynamics of these two relaxation processes is not straightforward. In fact, in the literature, so far no clear methodology has been suggested to resolve the dynamics of such two interfering processes. In the present study, to extract the rate constant for the bond twisting process in C481 and C152, the total fluorescence intensity was plotted against time as shown in Figure 6. The total fluorescence intensity, $I(t)$, was calculated by measuring the area under the fluorescence spectra at different times. It is seen that $I(t)$ does not decay exponentially with time. Such nonexponential decay of the florescence intensity along with the change in the mean frequency for C153 in 1-propanol at lower temperature has been explained by Agmon on the basis of the inhomogeneous solvent distribution around the excited dye.[35] Their results are supported by the fact that the width of the transient emission spectra decreases with time as a rseult of the distribution of the lifetimes resulting from the inhomogeneity in the system. However, in the present case it is seen that the shape of the transient emission spectra of C153 does not change with time (cf. Figure 4A). This eliminates the possibility of inhomogeneity in the present systems. The appearance of the nonexponential decay in $I(t)$, for the present systems, can be easily explained on the basis of the time-dependent shift in the emission frequency. One of the consequences of Einstein's equation for radiative transition is that the rate of this process depends on the emission frequency. Because of the nonequilibrium solvent relaxation in the excited state, the emission frequency is a function of time. This makes the radiative decay rate, k_r, also time dependent, and it should follow a relation such as[36]

$$k_r(t) \propto \langle \nu^3(t) \rangle \tag{4}$$

where

$$\langle \nu^3(t) \rangle = \frac{\int I(\nu, t) d\nu}{\int I(\nu, t) d\nu / \nu^3(t)} \tag{5}$$

It is evident from eq 4 that, if the solvent relaxation process causes an observable shift in the emission spectra, one would expect that k_r should also be time-dependent accordingly. On the basis of this model, the variation of the total fluorescence intensity can be expressed by the following equation:[37]

$$I(t) = A k_r(t) \exp\left[-k_{nr} t - \int_0^t k_r(\tau) d\tau\right] \tag{6}$$

where, A is the proportionality constant, and k_{nr} is the nonradiative decay rate constant. In eq 6, k_{nr} denotes the nonradiative intramolecular conversion from the S_1 to the S_0 state of the dye. Detail photophysical studies show that this S_1-S_0 nonradiative process is very slow ($\sim 1 \times 10^8$ s^{-1})[15] for all three dyes used in the present study as compared to our experimental time window. Thus we may neglect the effect of k_{nr} on the fluorescence intensity decay for the dyes in the present time scales of measurements. Maroncelli et al. have also shown that eq 6 can be fitted suitably for some coumarin dyes in *i*-propanol after neglecting the contribution of k_{nr}.[37]

Our experimental data was fitted using eq 6 (without the k_{nr} term) by a least-squares fitting method, and the fitted curves are shown in Figure 6. It is seen that the decay of $I(t)$ for C153 can be fitted quite satisfactorily with eq 6. This result reinforces that the observed nonexponential decay of $I(t)$ for C153 is solely due to the solvent relaxation induced shift in the emission frequency. However, it is evident from Figure 6 that the experimental data for C481 and C152 do not fit well with eq 6.

As mentioned earlier, the twisting of the amino groups in the excited states of C481 and C152 results in the formation of dark twisted intramolecular charge transfer (TICT) states.[17,18] The formation of these dark states indicates that the twisting of the amino group results in the decrease of the transition dipole

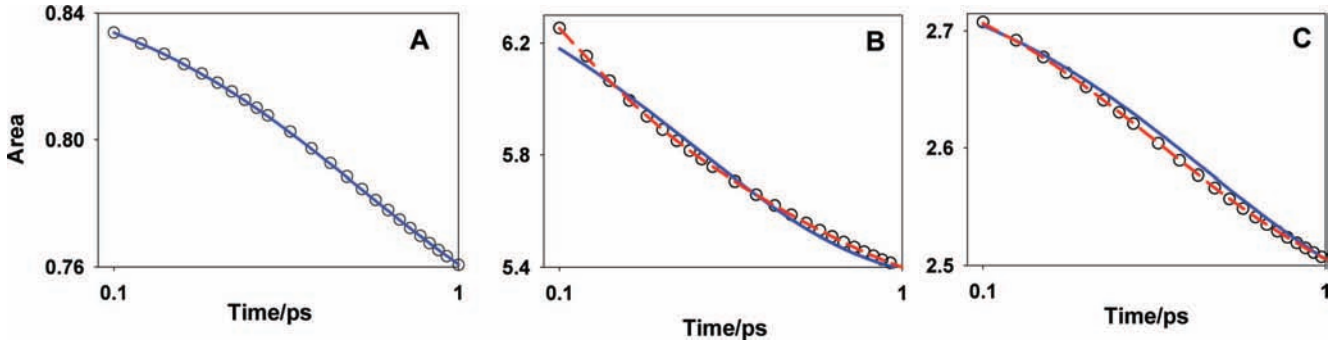

Figure 6. Changes in the integrated intensity of (A) C153, (B) C481, and (C) C152 as a function of time. The solid lines are the fitted data according to eq 6. The dashed lines for C481 and C152 are fitted data according to eq 7.

moment and hence a decrease in the observed emission intensity. To incorporate this effect, eq 6 has to be modified to eq 7:

$$I(t) = Ak_r(t)\exp\left[-\int_0^t k_r(\tau)d\tau\right] + B\exp(-kt) \qquad (7)$$

where B is a pre-exponential term, and k is the rate constant for the additional decay process, i.e., the bond twisting process.

The experimental data for C481 and C152 have been fitted with eq 7, and the results are shown in Figure 6. It is very evident from this figure that the introduction of the additional exponential decay term in eq 7 satisfactorily fits the experimental data for C481 and C152. These results confirm that the change in the total intensity for C481 and C152 is a consequence of the combined effect of two processes, i.e., the intramolecular twisting process and the solvent relaxation process. The decay times ($1/k$) for the twisting processes thus estimated are 70 and 230 fs for C481 and C152, respectively.

The rate constant for the twisting process thus measured can be used to estimate the solvent relaxation time from the experimental frequency shift data obtained with C481 and C152. As it is mentioned earlier, because of the presence of the bond twisting process, the apparent solvent relaxation time becomes faster for these dyes. The variation of the mean frequency with time for these two dyes was fitted with a triexponential function, where one of the decay times was fixed to that obtained for the twisting process. After using this methodology, the other two time constants for solvent relaxation process are obtained as 0.45 ps (49%)/1.35 ps (39%) and 0.33 ps (26%)/1.1 ps (65%) for C481 and C152, respectively. The average solvent relaxation times thus calculated are 0.75 and 0.80 ps, respectively. These estimated solvent relaxation times are in good agreement with that obtained with C153 and also with those reported in the literature in acetonitrile solvent.[22] Thus, using this methodology, as discussed in this article, it is possible to distinguish two competing ultrafast processes that mutually interfere with each other to affect the observed spectral or kinetic measurements. It is also possible to quantitatively extract the rate constant for the individual processes by adopting this methodology.

From the present results, it is indicated that the bond twisting process for C481 is much faster than that of C152. This is in fact expected from the structural point of view of the dyes. In the case of C481, the 7-amino group has two ethyl substituents, which have a stronger electron donating nature than the methyl substituents in C152. This makes the twisted charge transfer state energetically more stable for C481 than for C152. Moreover, the formation of the twisted state releases more steric hindrance in C481 than in C152, because of the bulkier *N*-ethyl substituents in the former dye compared to the *N*-methyl substituents in the latter. It is thus realized that the better stabilization of the twisted state in C481 drives the bond twisting process to occur faster compared to C152. This is also in accordance with the results obtained from photophysical studies of the two dyes in different solvents.[18] The fluorescence quantum yield for C481 and C152 in acetonitrile solution are reported to be 0.08 and 0.22, respectively.[18] These fluorescence quantum yields are much lower compared to those of the other coumarin dyes. This lowering of the quantum yield for C481 and C152 is attributed to the twisted-state-mediated nonradiative de-excitation channel. These fluorescence quantum yield results also indicate that the formation of the twisted state is more favorable for C481 as compared to C152, an inference similar to that made from the present study.

In brief, the present results indicate that the intramolecular bond twisting process largely interferes with the dynamic Stokes' shift for C481 and C152, causing the observed solvent relaxation dynamics to apparently become faster. Following the procedure of time-dependent changes in the integrated intensity of the time-resolved emission spectra and using Einstein's theory of radiative decay rate, we are able to separate out the dynamics of the bond twisting process from the solvent relaxation process. This procedure can be applied to differentiate and quantitatively estimate the rate of an intramolecular process that is otherwise hidden or mingled up with the solvent relaxation process.

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References and Notes

(1) Nandi, N.; Bhattacharyya, K.; Bagchi, B. *Chem. Rev.* **2000**, *100*, 2013.

(2) Raguraman, H.; Kelkar, D. A.; Chattopadhyay, A. Novel insights into protein structure and dynamics utilizing the red edge excitation shift approach. In *Reviews in Fluorescence*; Geddes, C. D., Lakowicz, J. R., Eds.; Springer: New York, 2005; p 199.

(3) Chudoba, C.; Nibbering, E. T. J.; Elsaesser, T. *Phys. Rev. Lett.* **1998**, *81*, 3010.

(4) Shirota, H.; Tamoto, Y.; Segawa, H. *J. Phys. Chem. A* **2004**, *108*, 3244.

(5) Kumbhakar, M.; Nath, S.; Pal, H.; Sapre, A. V.; Mukherjee, T. *J. Chem. Phys.* **2003**, *119*, 388.

(6) Dutta Choudhury, S.; Kumbhakar, M.; Nath, S.; Pal, H. *J. Chem. Phys.* **2007**, *127*, 194901.

(7) Brauns, E. B.; Madaras, M. L.; Coleman, R. S.; Murphy, C. J.; Berg, M. A. *Phys. Rev. Lett.* **2002**, *88*, 158101.

(8) Andreatta, D.; Lustres, J. L. P.; Kovalenko, S. A.; Ernsting, N. P.; Murphy, C. J.; Coleman, R. S.; Berg, M. A. *J. Am. Chem. Soc.* **2005**, *127*, 7270.

(9) Andreatta, D.; Sen, S.; Lustres, J. L. P.; Kovalenko, S. A.; Ernsting, N. P.; Murphy, C. J.; Coleman, R. S.; Berg, M. A. *J. Am. Chem. Soc.* **2006**, *128*, 6885.

(10) Pierce, D. W.; Boxer, S. G. *J. Phys. Chem. B* **1992**, *96*, 5560.

(11) Pal, S. K.; Peon, J.; Zewail, A. H. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 1763.

(12) Jones, G., II; Jackson, W. R.; Konaktanaporn, S. *Opt. Commun.* **1980**, *33*, 315.
(13) Jimenez, R.; Fleming, G. R.; Kumar, P. V.; Maroncelli, M. *Nature* **1994**, *369*, 471.
(14) Maroncelli, M.; Macinnis, J.; Fleming, G. R. *Science* **1989**, *243*, 1674.
(15) Jones, G., II; Jackson, W. R.; Helpern, A. M. *Chem. Phys. Lett.* **1980**, *72*, 391.
(16) Jones, G., II; Jackson, W. R.; Choi, C.; Bergmark, W. R. *J. Phys. Chem.* **1985**, *89*, 294.
(17) Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971.
(18) Nad, S.; Kumbhakar, M.; Pal, H. *J. Phys. Chem. A* **2003**, *107*, 4808.
(19) Jarzeba, W.; Walker, G. C.; Johnson, A. E.; Barbara, P. F. *Chem. Phys.* **1991**, *152*, 57.
(20) Velapoldi, R. A.; Mielenz, K. D. *Natl. Bur. Stand. (U.S.) Spec. Publ.* **1980**, 260.
(21) Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1987**, *86*, 6221.
(22) Kahlow, M. A.; Kang, T. J.; Barbara, P. F. *J. Chem. Phys.* **1988**, *88*, 2372.
(23) Somoza, M. M.; Andreatta, D.; Murphy, C. J.; Coleman, R. S.; Berg, M. A. *Nucleic Acids Res.* **2004**, *32*, 2494.
(24) Gearheart, L. A.; Somoza, M. M.; Rivers, W. E.; Murphy, C. J.; Coleman, R. S.; Berg, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 11812.
(25) Maroncelli, M. *J. Mol. Liq.* **1993**, *57*, 1.
(26) Lakowicz, J. R. *Principle of Fluorescence Spectroscopy*, 3rd ed.; Springer: New York, 2006.
(27) Chapman, C. F.; Fee, R. S.; Maroncelli, M. *J. Phys. Chem.* **1995**, *99*, 4811.
(28) Spry, D. B.; Goun, A.; Fayer, M. D. *J. Phys. Chem. A* **2007**, *111*, 230.
(29) Smith, N. A.; Meech, S. R.; Rubtsov, I. V.; Yoshihara, K. *Chem. Phys. Lett.* **1999**, *303*, 209.
(30) Wyman, J. J. *J. Am. Chem. Soc.* **1936**, *58*, 1485.
(31) Bakshiev, N. G. *Opt. Spectrosc.* **1964**, *16*, 446.
(32) Barbara, P. F.; Jarzeba, W. *Adv. Photochem.* **1990**, *15*, 1.
(33) Bagchi, B.; Oxtoby, D. W.; Fleming, G. R. *Chem. Phys.* **1984**, *86*, 257.
(34) Röcker, C.; Heilemann, A.; Fromherz, P. *J. Phys. Chem.* **1996**, *100*, 12172.
(35) Agmon, N. *J. Phys. Chem.* **1990**, *94*, 2959.
(36) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970.
(37) Maroncelli, M.; Fee, R. S.; Chapman, C. F.; Fleming, G. R. *J. Phys. Chem.* **1991**, *95*, 1012.

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