Solvent Effects on the Fluorescence Depolarization Rates of Coumarins in Solution: The Likely Influence of Site-Selective Hydrogen Bonding

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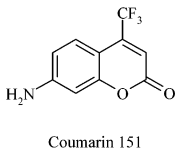
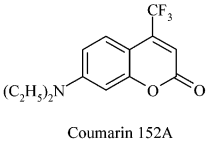
Fluorescence up-conversion gating experiments with resolution of ∼150 fs have compared the fluorescence anisotropy relaxation time profiles for coumarins (C's) 151, 152A, and 153 in different solvents. The selective occurrence of longer anisotropy relaxation times for C151 in the presence of long-chain normal alcohols provides evidence for a strong hydrogen-bonded interaction in fluid solution specifically involving the NH_2 group of C151. Experiments on coumarins in butanol/hexane binary solvents lead to similar conclusions, because C151 solutions show significantly longer anisotropy relaxation times than solutions of either C152A or C153. These results are consistent with measurements on jet-cooled molecular clusters, which showed that larger hydrogen-bonded aggregates selectively attach to the NH_2 group of C151 via an N−H···O type of hydrogen bond.

1. Introduction

Time-dependent fluorescence Stokes shifts are induced by changes in the electron distribution following the electronic excitation of molecules in a fluid solution.[1−3] In addition to the time-dependent shift of the emission spectrum, some reported Stokes shift studies also monitored relaxation of the fluorescence polarization anisotropy, which, in simple solutions, occurs on the same general time scale and can extend to the sub-10 ps regime. In particular, the nonexponential relaxation of the polarization anisotropy for coumarin 153 (C153) in *n*-alcohol solvents led to questions about the possible role of hydrogen-bonded interactions in solvent−solute relaxation dynamics.[3] These questions include the likely formation of hydrogen-bonded aggregates and the dependence of the types of aggregates on the structure of the solute molecules. A principal aim of the current work was to determine whether cluster-specific behavior could be revealed in solution through differences in the rotational diffusion dynamics of different coumarin solutes.



Coumarin 151
(C151)



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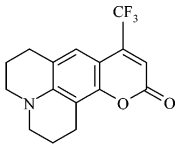
(C152A)



Coumarin 153
(C153)

Under supersonic jet conditions, low internal temperatures and low intermolecular collision rates can stabilize weak hydrogen bonds in molecular clusters. Among the most successful techniques to be applied to such studies has been mass-resolved infrared optical double-resonance spectroscopy.[4−10] This bond-specific technique provides much information about the types and number of hydrogen bonds in a given cluster, including different conformers, and can be applied to the study of differences induced by electronic excitation. The spectroscopic properties of gas-phase hydrogen-bonded clusters involving coumarins have been reported by this laboratory.[11−14] It was clear from that work that the molecule C151, which has a primary amino group, supports a much wider range of clusters having structured electronic spectra and assignable infrared transitions. Thus, all three of the molecules, C151, C152A, and C153, exhibit structured absorption spectra (i.e., $S_0 \rightarrow S_1$ excitation spectra for two-photon ionization followed by time-of-flight mass resolution) for clusters with one and two water molecules. On the other hand, only C151 exhibits well-resolved spectra for $n = 4$ and 5. C151 also showed structured spectra for clusters involving up to four methanol molecules,[12] whereas methanol clusters of any size involving C153 were more difficult to prepare and did not for the most part yield structured spectra. Infrared data show that the larger hydrogen-bonded clusters involving C151, which exhibit structured electronic spectra and large spectral red shifts (i.e., 3400−3700 cm^{-1}), are associated with a donor hydrogen bond from the NH_2 group. Some of these infrared spectra have been successfully compared with the results of simulations using density functional theory.[15]

Further to the above ground-state supersonic jet study, infrared optical double-resonance measurements involving electronically excited clusters showed a tendency for further stabilization of the NH_2 attachment site in C151. One particularly significant example was the case of the water dimer cluster attached to C151. In that example, time-resolved infrared studies show clearly that an initially excited cluster attached to the carbonyl group of C151 isomerized in the picosecond domain to a structure consistent with attachment to the NH_2 site.[13]

Stemming from work by Zewail and co-workers,[16−20] rotational coherence spectroscopy (RCS) has also been applied to conformational problems of jet-cooled single molecules and some hydrogen-bonded clusters involving aromatic molecules.[21−25] In a supersonic jet environment, the short-lived fluorescence polarization anisotropy appears as a periodic sequence of short pulses in the form of rotational quantum beats, which persist into the nanosecond domain.[26] This is because the rotational coherence persists for much longer than the time frame of molecular rotation, even for rotational temperatures near 5 K (i.e., $k_BT/h \approx 10^{11}$ s^{-1}). On the other hand, in fluid solution at

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room temperature, the reverse situation is found. Thus, although the rotational coherence is rapidly dissipated through collisions, rotational motion is inhibited by the solvent. In fluid solvents at room temperature, therefore, the fluorescence anisotropy, $r(t)$-decays on a time scale on the order of 10s to 100s of

$$r(t) = \frac{I_{\mathrm{p}}(t) - I_{\perp}(t)}{I_{\mathrm{p}}(t) + 2I_{\perp}(t)} \tag{1}$$

picoseconds. Although the direct inertial information is lost, the rate of decay of the anisotropy in solution is determined by factors such as solvent viscosity and the effective dimensions of the solvated molecular chromophore. In their original work, carried out at ~30 ps resolution, Maroncelli and Fleming[1] reported the anisotropy decay rates of coumarin 153 in polar solvents ranging from ethanol to propylene carbonate, often varying the viscosity by temperature control. Among these measurements, they reported the anisotropy relaxation time for a solution of C153 in 1-butanol at 295 K to be 250 ps. Subsequently, Horng et al.[3] examined the rotational anisotropy dynamics of coumarin 153 in a wide range of polar and nonpolar solvents. Their experiments, which reported time resolution of ~120 fs, confirmed the earlier results. However, they also showed that, in *n*-alcohols, the anisotropy decay appears to be biphasic, having a faster component than could be resolved by the earlier study.[1] For example, in a 1-butanol solution of C153, they reported relaxation times of 19 and 210 ps, of which the shorter component amounted to ~30% of the zero-time signal. On the other hand, in nonpolar solvents such as alkanes of comparable viscosity to the *n*-alcohols, only a single relaxation time was detected, corresponding roughly to the longer of the two relaxation times observed in alcohol solutions.

Work by Moog et al.[27] was concerned with the effect of hydrogen-bonded cluster formation on the rotational diffusion dynamics of coumarin molecules in solution. Their sample was coumarin 102, which is structurally similar to coumarin 153, replacing the $-CF_3$ group by $-CH_3$. Their solutions had decalin as the major solvent, with an impurity (~2 mM) of the acidic material trifluoroethanol. That is, C102, like C153, is a tertiary amine and can only form hydrogen bonds with proton-donating solvents. The experiment was designed to provide a small concentration of 1:1 adducts between C102 and trifluoroethanol in a solvent medium having properties close to those of pure decalin. Comparisons were made between the anisotropy decay times of C102 in pure decalin and in the presence of trifluoroethanol, with the significant result that the anisotropy decay time nearly doubled from 125 to 220 ps between decalin and the aggregated case. Because the macroscopic viscosity did not change significantly, it was concluded that the increase in relaxation time was due to the larger 1:1 aggregate rotating in the slip limit in the nonpolar solvent.

The functional dependence of the rotational diffusion time has been expressed by[3]

$$\tau_{\mathrm{rot}} = \frac{V_{\mathrm{p}} f \eta}{k_{\mathrm{b}} T} C \tag{2}$$

Here, V_{p} is the effective spherical volume of rotation, f is a shape factor, η is the viscosity coefficient of the solvent, and C is a coupling factor between the chromophore and the surrounding molecules.

Work in a number of laboratories has shown correlations between the shape of a molecule in solution and the decay dynamics of the polarization anisotropy, $r(t)$.[3,28−31] Some workers have interpreted the often nonexponential anisotropy time profile in terms of double-exponential kinetics correlated with the diffusion of oblate and prolate molecular aggregates. In this model, the different components of a double-exponential fit to the anisotropy relaxation time profile have been attributed to two different diffusion coefficients correlating with inertial moments perpendicular to the transition moment direction (oblate model). This has been applied, for example, to solutions of C153 in *n*-alcohols.[3] On the other hand, observed single-exponential kinetic behavior was attributed to those cases having a single assignable coefficient perpendicular to the transition moment (prolate model).[29,30] Such has been reported to be the case for C153 in nonpolar solvents.[3] However, the actual dependence on molecular dimensions, and the possible presence of metastable molecular aggregates, is complex and very much open to interpretation for site-specific intermolecular interactions such as hydrogen bonding.

The study noted above by Moog et al.[27] addressed hydrogen-bonded clusters between the acidic molecule trifluoroethanol and the carbonyl group of coumarin 102 in decalin solvent. Also of significance to the present work is the work by Nibbering and co-workers,[32,33] who studied the ultrafast hydrogen-bonding dynamics of C102 complexes in solution with acidic molecules such as phenol and chloroform, again focusing on interactions of the carbonyl group. A significant feature of that work was the use of infrared pulses to probe the hydrogen-bonded carbonyl groups. In the present study, we focus on interactions of the amino group of the coumarin with more common solvents, principally alcohols. Specifically, we compare C151, which is a primary amine and can therefore function either as a proton donor or acceptor in solution, with C152A and C153, which are tertiary amines and can only function as proton acceptors. As will be shown, the absorption and emission spectra in binary solutions both indicate a clear difference in the properties of C151. The anisotropy measurements presented here reveal some of the dynamic consequences of those differences.

2. Experimental Techniques

The primary experimental technique employed here involved fluorescence up-conversion gating spectroscopy at ~150-fs time resolution, using harmonics of a Ti:sapphire laser for excitation and gating pulses. An amplified laser delivered 200-μJ pulses at a ~1-kHz repetition rate, from which second-harmonic pulses (~400 nm), generated by type I mixing in a 1-mm BBO (β-BaB_2O_4) crystal, were used for excitation. The polarization of the exciting pulses was controlled by a $\lambda/2$ plate before focusing into a flowing sample cell with a thickness of 1 mm. The temperature was ~22 °C. Forward-emitted fluorescence from the sample was collected, filtered, and focused into a 0.2-mm BBO gating crystal via a pair of off-axis elliptical reflectors. Precise imaging compensated for temporal dispersion and polarization anisotropy of the reflectors. The residual 800-nm fundamental beam was passed through a variable optical delay and concentrated into the gating crystal via a 30-cm focal-length gold mirror. The type I phase-matched gating crystal also served as a detection polarizer. Up-converted radiation, generated by combining fluorescence and fundamental pulses in the BBO crystal, was detected by a photomultiplier tube mounted on a double monochromator. The output was fed to a lock-in amplifier and computer.

Complementary experiments employed a time-correlated single-photon counting (TCSPC) apparatus with a resolution of ~100 ps. Here, a Glan−Taylor prism placed before the entrance slit of the monochromator served as the detection

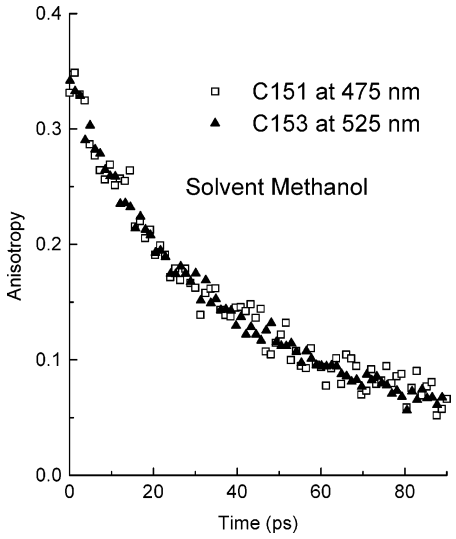

Figure 1. Time dependence of the anisotropy, $r(t)$, of C151 and C153 in methanol solution. Excitation wavelength was ~400 nm in Figures 1−3 and 7, from the second harmonic of an ultrashort-pulsed Ti:sapphire laser. The emission profiles for C151 and C153 were monitored at 475 and 525 nm, respectively.

polarizer. Calculation of the anisotropy time profiles from the TCSPC experiment required deconvolution of the instrument response function and tail-matching to compensate for the intrinsic polarization response of the detection monochromator.[3] This approach provided a useful extension of the experiment for longer-chain alcohols, where a measurable polarization anisotropy persisted for several nanoseconds. Direct comparison between the two approaches was made for the 1-propanol solution of C151, with satisfactory agreement.

3. Results

3.1. Coumarins in Pure Solvents. We have carried out experiments on solutions of coumarins in different alcohols, with some other solvents used as controls. The experimental conditions for experiments on C153 were similar to those used by Horng et al.[3] First, we investigated some polar, but non-hydroxylic, solvents. The anisotropy time profiles for the solvents acetonitrile and acetone were found to exhibit almost identical decay kinetics for both C151 and C153. A first-order fit yielded a time constant of 22−25 ps for all of these cases. The C153 results were in reasonable agreement with literature values (22 and 19 ps, respectively),[3] whereas the C151 data are reported here for the first time.

Now, considering a hydroxylic case, Figure 1 shows a scatter plot corresponding to the anisotropy time profiles for both C153 and C151 in the solvent methanol. Each trace was monitored at a wavelength close to the fluorescence maximum (475 nm for C151; 525 nm for C153). Although each fluorescence time profile depends critically on the monitoring wavelength, because of the rapid Stokes shift, we observed that the anisotropy time profiles, $r(t)$, were insensitive to wavelength in the range we explored. Moreover, consistent with the data reported in ref 3 for C153, a first-order fit did not appear valid, and the results are presented instead from a double-exponential fit. On the other hand, given the signal-to-noise ratio of the experiments, we did not wish to overestimate the significance of a double-exponential fit, as opposed to some other functional form, and so, we have also calculated average relaxation times, τ_{avg}'s, on the basis of measured double-exponential parameters. This approach is also consistent with the usage in ref 3. Table 1 contains both the parameters for the double-exponential fit and those for τ_{avg}, computed according to

$$\tau_{avg} = a \times \tau_{short} + (1 - a) \times \tau_{long} \quad (3)$$

Although we have not measured the short components of the decay for all solvents used, we did find for methanol, ethanol, and 1-propanol that the short-term components remained in the range 10−15 ps. In contrast, both the average and longer-term components measured for the same set of solvents ranged over an approximate factor of 2 for C153 and a factor of 3 for C151. Variations in the assigned coefficient a were subject to signal-to-noise limitations, but generally, they tended to be in the same range (20−40%) as reported in ref 3. Our results for C153, including the peak anisotropy values, were generally close to those reported in ref 3, although our interpolated lifetimes tended to be slightly longer.

Significantly, our data for methanol, shown in Figure 1, reveal little difference between C153 and C151, echoing the result for acetone and acetonitrile solutions. The difference between the solvents is the significantly higher viscosity of methanol (0.55 cP vs 0.30 and 0.34 cP[3]), which extended the average lifetimes to appoximately double those in the other two solvents. Although the double-exponential fits indicated, within the available signal-to-nose ratio, a possibly longer decay time for the C151 case, the value of τ_{avg} was in fact effectively the same at ~50 ps for both solutes. This similarity can be seen from the overlaid plots.

Differences between the different coumarin molecules begin to emerge for longer-chain alcoholic solvents. Figure 2 shows the case for ethanol solutions, where the anisotropy time profiles for C151 and C153 are clearly different. Either by the measure of the longer-duration components of the decay (C151, 110 ps; C153, 90 ps) or the average decay time, τ_{avg}, as defined by eq 3 (C151, 100 ps; C153, 72 ps), C151 begins to show a significantly slower relaxation of the anisotropy.

The difference between the C151 and C153 is more pronounced for 1-propanol solutions, as shown in Figure 3. Again, our optically gated data for C153 in a propanol solution were similar to values reported in ref 3, but the new data on C151 show that the ratio of relaxation times between the two solutes has increased to ~1.7. To justify this result, we first note that the time scale (90 ps) of the scan at ultrafast resolution, shown in Figure 3, was insufficient for precise calculation of longer relaxation times, although we note that the value we obtained for C153 was close to that reported in ref 3. Therefore, we also measured the anisotropy decay of the propanol solution via TCSPC. Although that experiment could not resolve the shorter-duration component, it was an important complement to the ultrafast experiments for the longer-duration component of the anisotropy decay. In this case, we found very good agreement for the C151 solution with the value of 220 ps estimated from the ultrafast work. This value is ~70% longer than that observed for C153 in the same solvent.

TCSPC experiments were also applied to the longer-chain normal alcohols butanol, pentanol, and hexanol, finding in all cases a clear difference between the anisotropy decay times of C151 and C153. Data from the combined techniques are presented in Table 1 and Figure 4. The maximum ratio of the anisotropy decay times (~1.7) was observed for 1-propanol, 1-butanol, and 1-pentanol.

3.2. Binary Solvents. For pure solvents, molecular rotational diffusion is limited by the viscosity of the bulk solvent, and the boundary between the rotating entity and the bulk solvent is not well defined. This phenomenon greatly complicates attempts to model such phenomena on a molecular scale.[3] For

TABLE 1: Anisotropy Relaxation Times of coumarins 151 and 153 in Different Solvents

		anisotropy relaxation time (ps)				
solvent	viscosity (cP)	C151[a]	C151 av	C153[a]	C153 av	lit. for C153[b]
acetone	0.30[b]	25[c]	25	22[c]	22	19
acetonitrile	0.34[b]	24[c]	24	24[c]	24	22
methanol	0.55[b]	15 (44%), 80[c]	50	12 (29%), 63[c]	49	6, 44
ethanol	1.08[b]	11 (15%), 110[c]	100	10 (23%), 90[c]	72	10, 89
1-propanol	1.94[b]	10 (17%), 220;[c] 225[d]	184	9 (19%), 130[c]	110	15, 146
1-butanol	2.57[b]	375[d]	n/a[e]	225[d]	n/a	19, 211
1-pentanol	3.51[b]	485[d]	n/a	280[d]	n/a	32, [405]
1-hexanol	[5.4]	550[d]	n/a	390[d]	n/a	n/m[f]

[a] For C151, measured at 475 nm; for C153, measured at 525 nm. [b] See ref 3. [c] At ~150 fs resolution via up-conversion gating: range ~90 ps. [d] At ~100 ps resolution via TCSPC. [e] n/a = not applicable. [f] n/m = not measured.

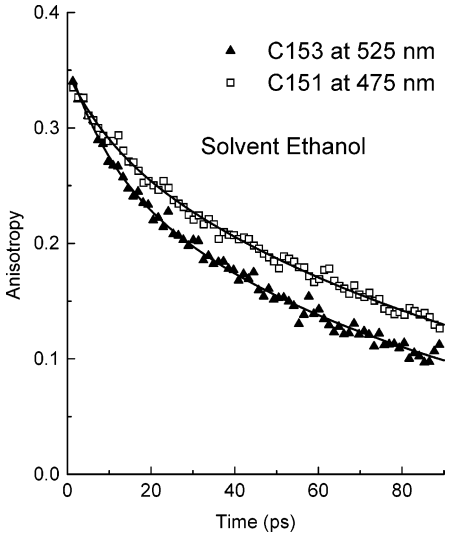

Figure 2. Time dependence of the anisotropy, $r(t)$, of C151 and C153 in ethanol solution.

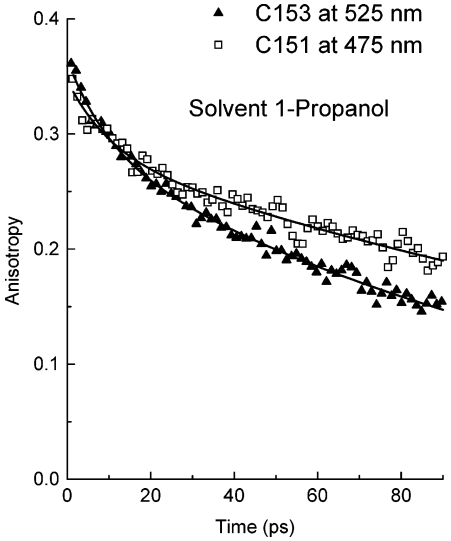

Figure 3. Time dependence of the anisotropy, $r(t)$, C151 and C153 in 1-propanol solution.

this reason, we have attempted to separate the rotating entity from the hydrogen-bonding solvent by using selective hydrogen bonding to form small clusters. Thus, in a binary solvent such as *n*-hexane containing a small amount of an alcohol, selective solvation can create a situation where hydrogen-bonded clusters are diffusing in a predominantly nonpolar medium.

First, a comment is needed about the spectroscopic properties of the binary solvents. Recent TCSPC work in this laboratory studied the fluorescence time profiles of C151 in binary solvents

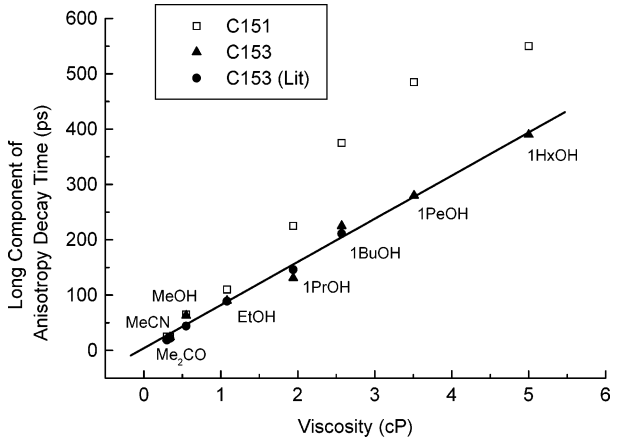

Figure 4. Correlation of the long component of the anisotropy decay time with solvent viscosity.

involving *n*-hexane as the major component, with added methanol quantities from 0.006% to 0.4% (v/v).[34] Those data showed a range of fluorescence decay times from 0.9 to 5 ns, depending in the middle range on both excitation wavelength and solvent composition. These lifetimes represent the known extremes of behavior of C151 between nonpolar and polar environments.[35,36] At methanol concentrations <0.1% (v/v) in *n*-hexane, we found that the fluorescence time profile was a function of concentration and that the red edge of the excitation spectrum converged toward the pure hexane case of ~375 nm. In this domain, although the absorption and emission spectra varied with concentration, the time-resolved fluorescence spectrum showed little evidence of a Stokes shift. This is very unlike the case of a pure polar solvent, where the anisotropy relaxation time and the time scale for the Stokes shift are similar. Above 0.1% methanol, we found the onset of a diffusion-limited Stokes shift on a nanosecond time scale, which is attributed to a shift in the solvation equilibrium induced by stronger solute−solvent hydrogen bonds in the excited state. At a methanol concentration of ~1%, we found that the red edge of the excitation spectrum for C151 red-shifted to >400 nm. It is noteworthy that jet-cooled water and methanol clusters formed with C151 under supersonic jet conditions exhibit red shifts up to 3700 cm^{-1} for up to five hydrogen-bonded molecules,[12,15] so that such a shift in solution is consistent with the existence of hydrogen-bonded interactions involving only a few molecules.

Time-resolved anisotropy measurements on the binary solvents in the present study in all cases used fluorescence up-conversion methods, because of the much faster relaxation times than those recorded in pure alcoholic solvents. Rather than doping the hexane solution with methanol, we used *n*-butanol, anticipating a greater effect on the rotational dynamics of a dissolved solute. We carried out measurements for C151,

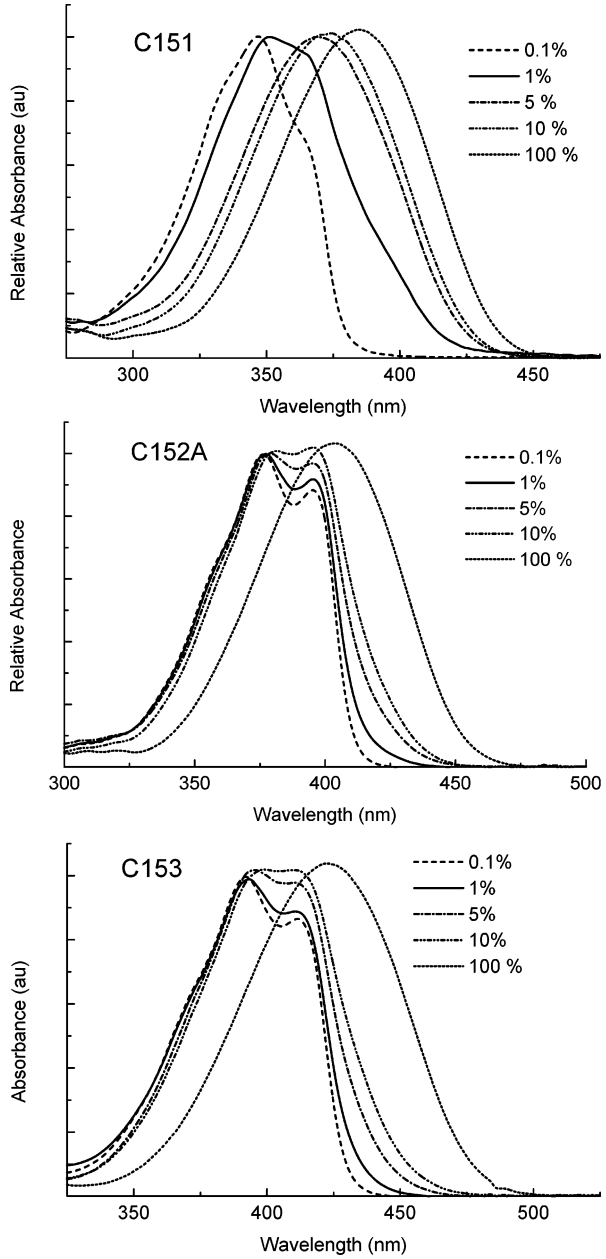

Figure 5. Sequence of absorption spectra for C151, C152A, and C153 in binary solvents involving different amounts of 1-butanol in *n*-hexane.

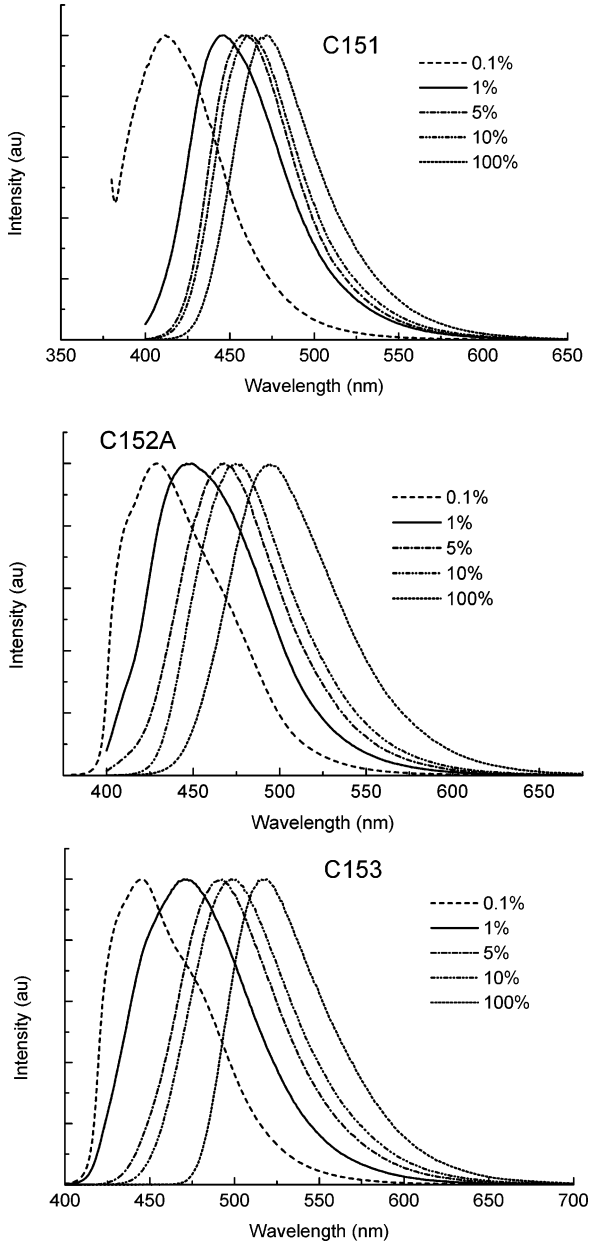

Figure 6. Sequence of fluorescence spectra for C151, C152A, and C153 in binary solvents involving different amounts of 1-butanol in *n*-hexane. All samples were excited at 380 nm.

C152A, and C153 in solutions ranging from 0.1% to 10% (v/v) of 1-butanol in *n*-hexane. The exception was that data were not obtained for C151 for a solution containing 0.1% butanol because of the low absorption cross section at the fixed laser wavelength of 400 nm. That is, only those C151 molecules that were partially solvated in the ground state by alcohol molecules could be excited.

To illustrate briefly the trends in the absorption spectra, we compare the cases of C151, C152A, and C153 for different 1-butanol/*n*-hexane mixtures (see Figure 5). For all three solutes, the solution at 0.1% in butanol has an absorption spectrum that is nearly indistinguishable from the pure hexane case. The emission spectra for these dilute solutions, following excitation at the absorption maxima, are also similar to those in pure hexane.

For a 1% butanol solution, the behavior of C151 is conspicuously different from that of the other two, because the absorption red edge at 30% of maximum cross section shifts to ∼400 nm from 375 nm in pure hexane, equivalent to a red shift of ∼1700 cm^{-1}. On the other hand, the shift in C152A for the same solution is from ∼406 to ∼409 nm and, for C153, from ∼425 to ∼427 nm, which is <200 cm^{-1} in each case. This is good evidence that the interaction between C151 and the butanol component of the solvent is selectively strong.[12]

For a 5% solution, all three solutes show a significant increase in the absorption red shift. Thus, the shift of C151 increases to 2300 cm^{-1}, and C152A and C153 both shift to ∼500 cm^{-1}. While there is some convergence, the shift in C151 is still clearly much larger than for the other two. For 100% butanol, C151 shifts >3000 cm^{-1}, whereas C152A and C150 shift by about 2000 cm^{-1}. Therefore, we observe that C151 shows a greater red shift than either of the other two molecules between hexane and butanol solutions. Possibly more significantly, ∼75% of the shift in the C151 case is achieved for a binary solvent having only 5% butanol, at which concentration both C152A and C153 show that the shift is only 25% complete.

We now consider the emission spectra, which are shown in Figure 6. In all three solvents, there is a significant change upon

TABLE 2: Anisotropy Relaxation Times of coumarins 151, 152A, and 153 in Different Mixtures of 1-Butanol and *n*-Hexane

solution	anisotropy relaxation time(s), ps					
% butanol	C151	τ_{avg}	C152A	τ_{avg}	C153	τ_{avg}
0.1	n/m		3.5 (12%), 18	16.3	3.7 (18%), 20	17.1
1	4.2 (19%), 26	21.9	n/m		6.2 (27%), 23	18.5
5	3.5 (23%), 51	40.1	4.7 (17%), 27	23.2	14 (67%), 37	21.6
10	20 (41%), 102	68.4	14 (50%), 56	35	13 (52%), 53	32.2
100	375[a]	[375]	n/m		225[a]	[225]

[a] The pure butanol data were measured by TCSPC at 100 ps resolution, yielding only the long-duration component.

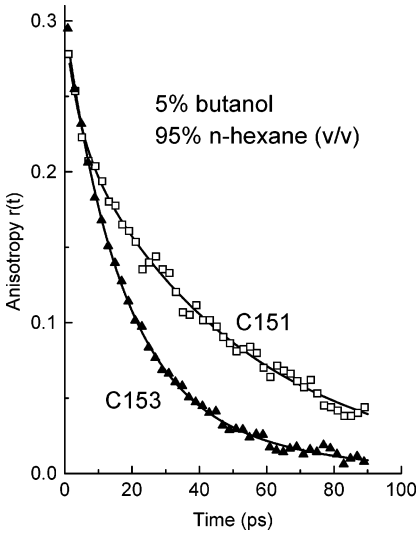

Figure 7. Time dependence of the anisotropy, $r(t)$, of C151 and C153 in a binary solvent containing 5% of 1-butanol in *n*-hexane.

addition of the 1% butanol to a hexane solution. Thus, the maximum in C151 shifts from 412 to 445 nm (1800 cm^{-1}), in C152A from 429 to 449 nm (1000 cm^{-1}), and in C153 from 445 to 471 nm (1200 cm^{-1}). This more comparable shift in the (time-integrated) emission spectrum is readily attributed to the existence of a diffusive Stokes shift, which occurs with a time constant on the order of 1 ns. This effect contributes to an enrichment of the polar environment in the vicinity of the solute molecule. However, this relatively slow process should have little impact on the relaxation of the fluorescence anisotropy, which we find to be complete on the time scale of ~100 ps. (see Figure 5).

The fluorescence time profiles obtained by up-conversion spectroscopy show, for the 1% solution, that the anisotropy relaxation dynamics of C151 and C153 are on the same time scale, and not much longer than the pure hexane case (see Table 2). We conclude that the viscosity of the bulk solvent is not greatly affected by the addition of small quantities of butanol. Also, at this level of hydrogen-bonded cluster formation, the behavior of the two solutes is not readily distinguished. However, in the 5% solution, whereas the C153 relaxation time increased only slightly, that of the C151 solution had increased by more than a factor of 2 (see Table 2 and Figure 7).

4. Discussion

The aim of this work was to establish differences in the behavior of three coumarin molecules, which could be correlated with hydrogen-bonding effects in a fluid solution. As an illustration, the longer-duration components of the anisotropy decay times for C151 and C153 solutes in simple solutions are plotted against viscosity in Figure 4. Linear plots were used, as suggested by eq 2, because they illustrate the trend, although the appropriate functional relationship is not clear at this stage. Quite clearly, the case of C151 departs significantly from the linear trend indicated by C153. Although the relaxation dynamics of C151 and C153 varied according to the solvent viscosity, each solute showed the same relaxation dynamics in acetone, acetonitrile, and methanol. This argues that the model for anisotropy decay holds in the non-hydroxylic solvents, and even for methanol. That is, the two solute molecules of comparable dimensions exhibit similar decay dynamics.

In considering the dimensions of these two molecules, it is important to consider the relevance of the dimensional measurement. Thus, just as in the case of rotational coherence analysis in the gas phase,[20,26] the most sensitive dimensions involve the inertial moments (or rotational diffusion coefficients) about axes perpendicular to the transition dipole moment. Taken as a whole, molecules C151 and C153 have distinctly different three-dimensional molecular volumes of rotation, because the latter is effectively derivatized from the former through the formation of the julolidine ring system. However, the dimensions along the transition-moment axis, which contribute the greatest component to the inertial moments perpendicular to the axis, are similar (9.4 ± 0.8 Å). Thus, it is not surprising to find similar relaxation dynamics for all three coumarin molecules (see Table 2) in nonaggregating solvents. However, longer-chain pure alcohols, starting with ethanol, clearly show differences, indicating that aggregation effects are causing differences in effective molecular size that affect the rotational diffusion coefficients and hence the anisotropy relaxation dynamics. This would be consistent with the nucleation of hydrogen-bonded clusters around the NH_2 group of C151, because neither C153 nor C152A shows this effect, and both are blocked to such an interaction. Because all three molecules possess a similarly unrestricted C═O group, the differences do not appear to be associated with that site. Also, excitation-induced changes in charge distribution at the carbonyl site are calculated to be of similar magnitude.

A comment is also needed concerning the difference between the 1% and 5% binary solvent cases. We report here that in the 1% case the anisotropy dynamics are similar between C151 and C153, which indicates the following: First, the effective solvent viscosity is unchanged from the pure hexane case. Second, although the C151 spectrum is clearly much more red-shifted by the presence of small amounts of butanol, those hydrogen-bonded clusters that do form are not evidently of sufficient size to change the anisotropy relaxation time. We compare this with the 5% case, where both solutes show a significant shift in the absorption spectrum, but now, the C151 case shows a significant increase in the rotational diffusion time. This may imply that the average cluster size for C151 is now sufficiently large to increase the effective rotational volume, or we may be observing an emergent microscopic component of the viscosity. Clearly, however, the increased rotational diffusion time reflects the selective solvation of the C151 molecules, as compared with C153, but the effect is not manifested in the same concentration

range as the more obvious shift in the red edge of the absorption spectrum (i.e., the 1% range).

5. Conclusion

We have established a correlation between the dynamic behavior of coumarin molecules in a fluid solution and the results of earlier reported studies of jet-cooled, hydrogen-bonded clusters using infrared double-resonance spectroscopy. Specifically, C151 shows evidence in the gas phase for an organized sequence of hydrogen-bonded molecular cluster structures, which are largely associated with the presence of the proton-donating primary amine group. coumarin 153, which contains a tertiary amino group, does not show such organization. The important conclusion from the present work is that this difference in behavior appears to be echoed in a fluid solution, because C151, in the presence of alcohol molecules, shows conspicuously slower anisotropy relaxation dynamics than C153. This supports the idea that organized hydrogen-bonded clusters are present in C151, and, because of the differences in structure of the two molecules, favor association with the primary amino group.

This work is significant because it shows evidence for the influence of a site-selective interaction on the picosecond dynamics of a hydrogen-bonded molecule in solution. In addition, we have shown that this effect can be observed in binary solvents, where the range of hydrogen-bonded interactions can be controlled. In that case, although it is well-known from past work that such polar molecules exhibit a selective affinity for polar components of a solvent, in the present case, C151 shows an even further level of selectivity than the other coumarins.

Considering the success under gas-phase conditions, future condensed-phase work also needs to probe the key vibrational-mode transitions of these hydrogen-bonded cases, so that the nature of the solvent−solute associations can be probed more deeply.

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