ARTICLES

Slow Solvation Dynamics of Dimethylformamide in a Nanocavity. 4-Aminophthalimide in β-Cyclodextrin

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Solvation dynamics of a nonaqueous solvent, *N*,*N*-dimethylformamide (DMF) has been studied for the first time in a β-cyclodextrin (β-CD) cavity using picosecond time dependent fluorescence Stokes' shift and 4-aminophthalimide (4-AP) as a probe. Solvation dynamics of confined DMF molecules within the β-CD cavity is found to be described by a component of 400 ± 50 ps (25%) and a slow component of 8 ± 1 ns (75%). This is substantially slower than the solvation time (∼1 ps) in bulk DMF.

1. Introduction

Most biological systems involve water in a confined region, a few nm in size. Study of liquids in confined environments is of fundamental importance to understand how they influence the structure, dynamics, and reactivity in complex biological systems. As a result of this, the dynamics of liquids in confined environments is a subject of very active area of contemporary research.[1−20] Recently many groups have demonstrated that in confined environments water and other liquids behave very differently from the corresponding liquid in bulk.[1−20] Among all of the techniques used to study dynamics in liquids, ultrafast time dependent fluorescence Stokes' shift (TDFSS) or the more recent three photon echo peak shift (3PEPS) technique stand out because of their superior time resolution down to femtosecond time scale.[1,21] Perhaps the most important finding of the recent TDFSS studies in confined systems is the observation of a bimodal decay with one bulk liquid like fast component and another very slow component which is slower by 2−3 orders of magnitude.[8] The origin of the slow component has been the subject of intense debate,[8] and several interesting theoretical models have already been proposed to explain it.[2,11] The slow component of relaxation in confined systems is also detected in dielectric relaxation[18] and NMR studies.[19]

Among all of the confined systems, cyclodextrins is most well chracterized.[14] A cyclodextrin is a cyclic polymer of a sugar (α-amylose) containing six (α-CD), seven (β-CD), or eight (γ-CD) monomers, and hence, the size or shape of the cyclodextrin cavity is more or less fixed.[14] The structure of a supramolecule consisting of cyclodextrin as a host and an aromatic hydrocarbon along with several solvent molecules as guests is quite well defined.[14] Such a supramolecule is free from complications arising from the motion of individual surfactants in a surfactant assembly (e.g., in micelle, microemulsion, or lipid) or conformational motion of a macromolecule (e.g., protein or DNA). There are several reports on dynamics of molecules in cyclodextrin cavities. This includes study of kinetics of entry into and exit from the cavity,[15] orientational relaxation,[16] and isomerization dynamics.[17] Surprisingly, there is only one TDFSS study reported so far in CD.[1a] Fleming et al. studied solvation dynamics of water confined in γ-CD cavity using coumarin 480 as a probe.[1a] They observed that, while in bulk water solvation dynamics occurs in subpicosecond time scales (0.3 ps),[1a,22−24] inside the γ-CD cavity the solvation dynamics exhibits a very slow component. The slow dynamics in γ-CD is described by three components of 13, 109, and 1200 ps, respectively.[1a] Nandi and Bagchi attributed the slow component to almost complete suppression of the translational modes of the confined water molecules within the γ-CD cavity.[2a] Subsequently, similar slow dynamics of water has been reported in many other organized media, such as water surface,[4] protein,[1b,5] DNA,[6] microemulsion,[9,10] sol−gel matrix,[12] lipid,[13] micelles,[20] and so on. More recently, several groups have studied nonaqueous solvents in the confined solvent pool of microemulsions. Levinger et al.[10e] studied solvation dynamics of formamide, whereas Shirota and Horie studied acetonitrile[10f] and methanol[10f] in AOT microemulsions. In bulk, each of these three liquids exhibit solvation dynamics in ∼1 ps time scale. However, inside microemulsions, they exhibit very slow dynamics with solvation times of 250 ps for formamide[10e] and several 1000 ps for acetonitrile and methanol.[10f]

Solvation dynamics of nonaqueous solvents inside a CD cavity has not been reported in any previous work. Vast majority of the works on CD is in aqueous solutions.[14] However, it was known for a long time that organic molecules bind to CD in many nonaqueous solvents, such as dimethyl sulfoxide, dimethylformamide, acetonitrile, and so on.[25] In this work, we report on the solvation dynamics of dimethylformamide (DMF) in β-CD cavity using 4-aminophthalimide (4-AP, Scheme 1) as a probe. It has been reported already that 4-AP binds to β-CD in aqueous solutions.[26a] Binding of 4-AP to β-CD in nonaqueous solutions has not been reported earlier. In bulk DMF solvation occurs in 1 ps time scale.[27] In this work, we will show that in

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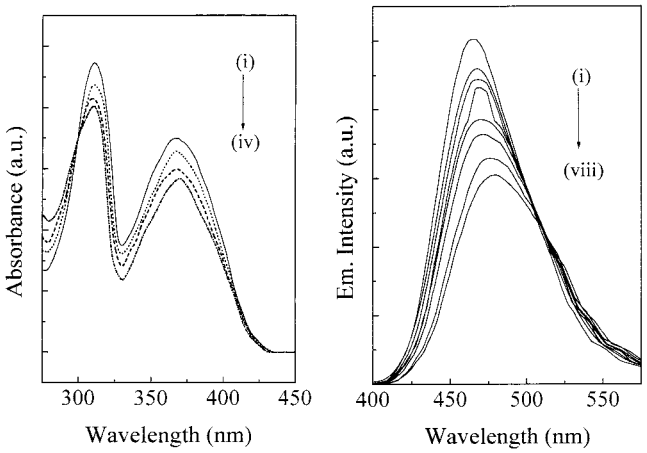
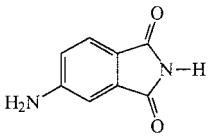


Figure 1. (a) Absorption spectra of 4.75×10^{-5} M 4-AP (i−iv) in neat DMF, and in the presence of 24, 72, and 155 mM β-CD in DMF, respectively. (b) Steady-state emission spectra of 4.75×10^{-5} M 4-AP (i−viii) in neat DMF, and in the presence of 12, 24, 36, 48, 72, 120, and 155 mM β-CD in DMF, respectively.

SCHEME 1: Structure of 4-Aminophthalimide (4-AP)



β-CD cavity solvation dynamics of DMF becomes slower by many orders of magnitude.

2. Experimental Section

4-AP (Eastman-Kodak) was purified by repeated crystallization from 1:1 aqueous ethanol. β-CD (Aldrich) and spectroscopic grade DMF were used as received. For lifetime measurements, the sample was excited at 300 nm by the second harmonic of a Rhodamine 6G dual jet dye laser with DODCI as saturable absorber (Coherent 702-1) synchronously pumped by a CW mode locked Nd:YAG laser (Coherent Antares 76s). The emission was collected at magic angle polarization using a Hamamatsu MCP photomultiplier (2809U). The typical fwhm of the system response is about 50 ps.

3. Results

3.1. Steady-State Absorption and Emission. 4-AP exhibits two absorption peaks at 310 and 375 nm in DMF (Figure 1a). On addition of β-CD, the absorption spectrum of 4-AP exhibits a slight red shift with a clear isosbestic point at 300 nm. Emision maximum of 4-AP is very sensitive to polarity and hydrogen-bonding ability of the solvent and shifts from 435 nm in dioxane to 550 nm in water.[9b,26] In DMF, 4-AP exhibits an emission maximum at 465 nm with emission quantum yield (ϕ_f) of 0.47. On addition of β-CD to DMF, the emission maximum of 4-AP shifts to the red (Figure 1b) and the intensity of the emission gradually decreases.

For determining the binding constant (K_b) of 4-AP to β-CD in DMF, emission spectra were recorded exciting the sample at 300 nm at various concentrations of β-CD. The binding constant, K_b corresponds to the following equilibrium:

$$\text{4-AP} + \beta\text{-CD} \rightleftharpoons [\text{4-AP:}\beta\text{-CD}] \qquad (1)$$

The value of K_b was determined from the double reciprocal plot of $\Delta\phi_f$ against concentration of β-CD, where $\Delta\phi_f$ is the difference in emission quantum yield of 4-AP in DMF in the absence of β-CD with that at various concentrations of β-CD. Such a plot is shown in Figure 2. K_b is determined from the ratio of intercept and slope of this curve.[28] From the data in Figure 2, the binding constant of 4-AP to β-CD in DMF is determined to be 12 ± 2 M^{-1}.

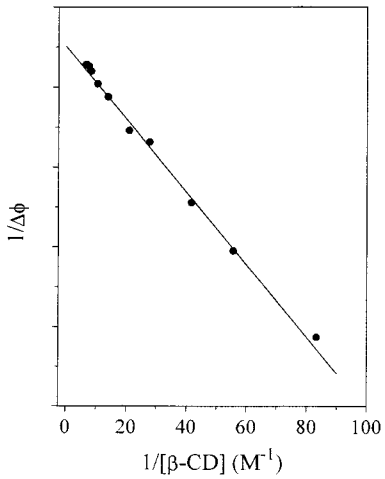


Figure 2. Plot of $1/\Delta\phi$ vs $1/[\beta\text{-CD}]$ for 4.75×10^{-5} M 4-AP in DMF.

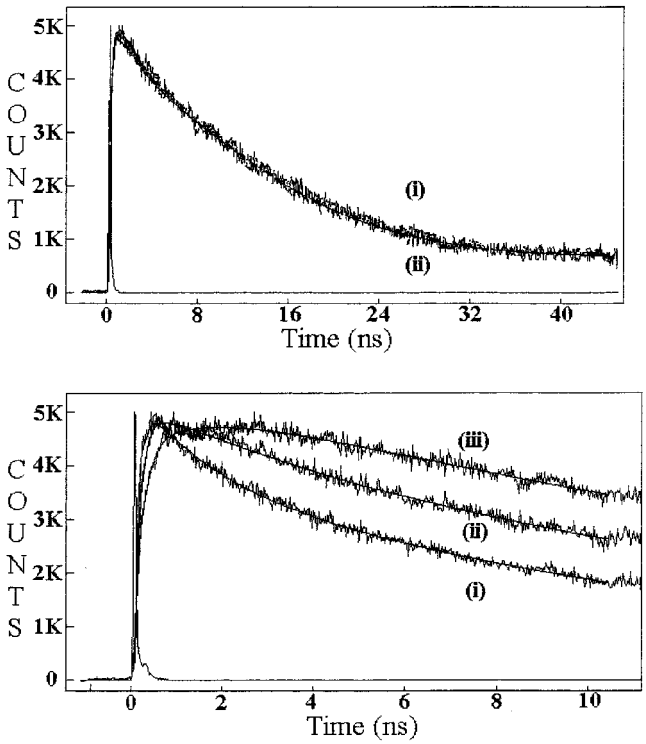


Figure 3. (a) Fluorescence decays of 4.75×10^{-5} M 4-AP in DMF at (i) 460 and (ii) 560 nm. (b) Fluorescence decays of 4.75×10^{-5} M 4-AP in 155 mM β-CD in DMF at (i) 445, (ii) 490, and (iii) 570 nm.

3.2. Time-Resolved Studies. Although the effect of β-CD on the steady-state emission properties of 4-AP is rather innocuous, there is a very dramatic change on the temporal decay of 4-AP on addition of β-CD. In neat DMF, 4-AP exhibits an emission decay with a lifetime of 13 ns, and the decay is independent of the wavelength of emission (Figure 3a). On addition of β-CD to DMF, the nature of the emission decays of 4-AP changes significantly. In the presence of 155 mM β-CD in DMF, fast decay is observed at the blue end, whereas at the red end, the decay is preceded by a growth. For example, the decay of emission of 4-AP at 570 nm (red end) is fitted to a triexponential function with rise times of 0.22 and 4.9 ns along

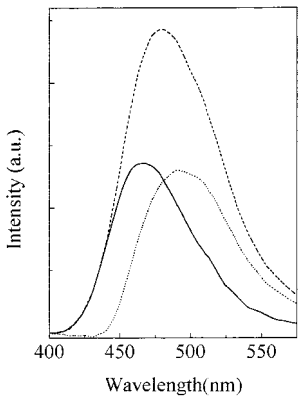


Figure 4. (—) 35% emission of 4.75×10^{-5} M 4-AP in DMF, (- - -) emission of 4.75×10^{-5} M 4-AP in 155 mM β-CD in DMF, and (•••) emission spectrum corresponding to 4-AP bound to β-CD in DMF.

with a decay of 13 ns (Figure 3b). However, for the same solution, at 445 nm (blue end), there is a triexponential decay with three decay components of 0.98, 2.84, and 13 ns. Such a wavelength dependence of emission decays indicate that, in the β-CD cavity, 4-AP exhibits solvation dynamics in a time scale much slower than the solvation dynamics observed in neat DMF (1 ps).[27]

4. Discussion

The most spectacular observation of this work is the detection of slow rise time in the red end of the emission spectrum of 4-AP in β-CD cavity in DMF. It should be emphasized that in 155 mM β-CD in DMF a significant amount of 4-AP remains in the unbound, free form. Thus, to extract the solvation dynamics of 4-AP bound to β-CD, it is necessary to subtract the contribution of the free 4-AP in DMF both from the steady state and the time-resolved emission data. According to the value of K_b determined in this work, at a concentration of 155 mM β-CD and 4.75×10^{-5} M 4-AP in DMF, $65 \pm 4\%$ 4-AP remain in the bound from. Thus, contribution of free 4-AP to the total steady-state emission spectrum in 155 mM β-CD is 0.35 times the emission intensity of 4-AP in DMF in the absence of β-CD. The emission spectrum due to 4-AP molecules bound to β-CD is obtained by subtracting the contribution of free 4-AP ($35 \pm 4\%$) from the total emission spectrum in 155 mM β-CD in DMF. This is shown in Figure 4. The emission maximum of 4-AP bound to β-CD is observed to be at 490 nm which is red shifted by 25 nm from that of 4-AP in DMF.

At all wavelengths, the decay of emission of 4-AP in 155 mM β-CD were found to be triexponential function with a very long bulk like component of 13 ns (τ_3) along with two other faster components. Although the two fast components were invariably due to 4-AP bound to β-CD, the long component contains contribution from both bound and free 4-AP. At any wavelength λ, the decay of the emission of 4-AP bound to β-CD is given by

$$I^{b}(\lambda,t) = \frac{I^{b}_{ss}(\lambda)}{\sum_i b_i\tau_i}[b_1 e^{-t/\tau_1} + b_2 e^{-t/\tau_2} + b_3 e^{-t/\tau_3}] \qquad (2)$$

where $I^{b}_{SS}(\lambda)$ denotes the steady-state intensity due to bound 4-AP and $b_1 + b_2 + b_3 = 1$. In 155 mM β-CD when 35% of 4-AP molecules exist in the free form and displays a single-exponential decay of lifetime 13 ns and the rest (65%) of 4-AP

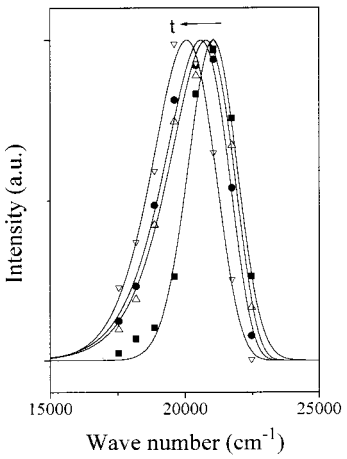


Figure 5. Time-resolved emission spectra of 4-AP bound to β-CD in DMF at 25 (■), 1000 (△), 3000 (●), and 30 000 ps (▽).

molecules remain in the bound form, the emission intensity is given by

$$I_{tot}(\lambda,t) = 0.65I^{b}_{ss}(\lambda,t) + 0.35I^{f}_{ss}(\lambda,t) \qquad (3)$$

where $I^{f}_{ss}(\lambda,t)$ is the contribution of free 4-AP. Thus

$$I_{tot}(\lambda,t) = 0.65\frac{I^{b}_{ss}(\lambda)}{\sum_i b_i\tau_i} b_1 e^{-t/\tau_1} + 0.65\frac{I^{b}_{ss}(\lambda)}{\sum_i b_i\tau_i} b_2 e^{-t/\tau_2} + \left[0.35\frac{I^{f}_{ss}(\lambda)}{\tau_3} + 0.65\frac{I^{b}_{ss}(\lambda)}{\sum_i b_i\tau_i} b_3\right] e^{-t/\tau_3} \qquad (4)$$

From the ratio of steady-state emission intensities of bound and free form (I^{b}_{SS}/I^{f}_{SS}) from Figure 4 and from the amplitudes of the triexponential decay components in Figure 3, one can obtain the amplitudes of the decay components (b_i) for the bound form. Then the time-resolved emission spectra (TRES, Figure 5) is constructed following the method of Maroncelli and Fleming.[21a] The solvation dynamics are described by the decay of the solvent response function $C(t)$, defined by

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \qquad (5)$$

where $\nu(0)$, $\nu(t)$, and $\nu(\infty)$ are the emission frequencies at time zero, t, and infinity. The decay of $C(t)$ for 4-AP in 155 mM β-CD in DMF is shown in Figure 6. It is readily seen that the decay of $C(t)$ is biexponential with one component of 400 ±50 ps (25%) and a long component of 8 ±1 ns (75%; Table 1).

It is obvious that we are missing a part of the solvation dynamics which occurs in a time scale faster than the time resolution (50 ps) of the set up used in the present work. The amount of solvation missed may in principle be estimated using the procedure formulated by Fee and Maroncelli.[21d] The procedure is rather simple when one excites the sample at the lowest energy absorption maximum. However, using our dye laser, we excited 4-AP at 300 nm which is far from its lowest energy absorption maximum at 375 nm. When we are so far away from the absorption maximum, the several stages of curve fitting suggested by Fee and Maroncelli[21d] are not likely to provide reliable numbers. However, following Fee and

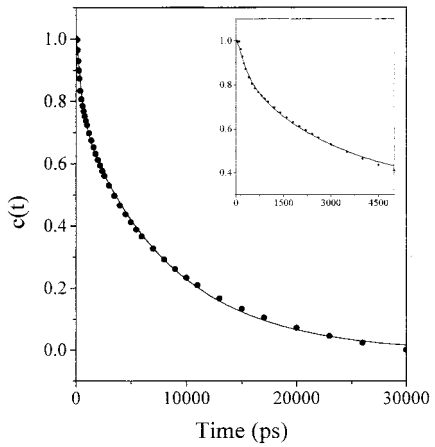


Figure 6. Decay of response function, $C(t)$, of 4-AP bound to β-CD in DMF. The points denote the actual values of $C(t)$, and the solid line denotes the best fit to a biexponential decay. The decay of the initial portion is given in the inset.

TABLE 1: Decay Parameters of $C(t)$ of 4-AP Bound to β-CD in Dimethylformamide

$\Delta\nu$ (cm^{-1})	a_1	τ_1 (ps)	a_2	τ_2 (ns)
980 ± 20	0.25	400 ± 50	0.75	8.0 ± 1.0

Maroncelli[21d] it is estimated that if the sample is excited at 375 nm, about 26% of the solvation occurs in the ultrafast time scale and is not detected in a picosecond set up.

The slow solvation components (400 ps and 8 ns) of dimethylformamide in β-CD are significantly slower than the solvation dynamics in 1 ps time scale reported earlier in bulk DMF.[27] This observation is qualitatively consistent with the previous studies of slow solvation dynamics of water in many confined environments and the retardation of other nonaqueous solvents in microemulsion.[1a,2a,8,10c−f] It is interesting to note that the components of solvation dynamics of DMF in β-CD are very similar to the components of solvation dynamics of water in protein (600 ps and 10 ns)[5b] and in DNA (300 ps and 13 ns).[6]

As noted earlier, Nandi and Bagchi[2a] ascribed the slow components of solvation dynamics of water in the γ-CD cavity to the freezing of the translational modes of the solvent inside the nanocavity of cyclodextrin. It is obvious similar mechanism may be operating in the case of DMF confined in β-CD cavity. One should note that a β-CD (radius $\approx$ 6.5 Å) cavity is smaller in size than a γ-CD cavity (radius $\approx$ 8 Å). Again the DMF solvent molecules are bigger in size compared to the water molecules. This is probably responsible for the slower components of solvation dynamics for DMF in β-CD compared to those for water in γ-CD.

5. Conclusions

The present work demonstrates that inside the β-CD cavity motion of the confined DMF molecules is highly constrained and as a result, DMF molecules exhibit markedly slow solvation dynamics. While in bulk, DMF exhibits solvation dynamics in 1 ps time scale, but inside a β-CD cavity, the solvation dynamics of DMF is described by two components of 400 ps (25%) and 8 ns (75%). The dramatic retardation of the solvation dynamics inside the β-CD cavity is attributed to the loss of translational modes in analogy to a similar model proposed for slow solvation dynamics of water in γ-CD.[2a,8] The time constants of the slow components observed for DMF in β-CD is found to be slower than those for water in γ-CD. This is attributed to the fact that the β-CD cavity is smaller than the γ-CD cavity, whereas a DMF molecule is larger than a water molecule.

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References and Notes

(1) (a) Vajda, S.; Jimenez, R.; Rosenthal, S. J.; Fidler, V.; Fleming, G. R.; Castner, E. W., Jr. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 867. (b) Jordandies, X. J.; Lang, M. J.; Song, X.; Fleming, G. R. *J. Phys. Chem. B* **1999**, *103*, 7995.

(2) (a) Nandi, N.; Bagchi, B. *J. Phys. Chem.* **1996**, *100*, 13914. (b) Nandi, N.; Bagchi, B. *J. Phys. Chem. A* **1998**, *102*, 8217.

(3) (a) Zhong, D.; Douhal, A.; Zewail, A. H. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 14056. (b) Chachisvilis, M.; Fiebig, T.; Zewail, A. H. *J. Phys. Chem. A* **1998**, *102*, 1657.

(4) Zimdars, D.; Eisenthal, K. B. *J. Phys. Chem. A* **1999**, *102*, 10567.

(5) (a) Changenet-Barret, P.; Gooding, E. F.; Degrado, W. P.; Hochstrasser, R. M. *J. Phys. Chem. B* **2000**, *104*, 9322. (b) Pal, S. K.; Mandal, D.; Sukul, D.; Sen, S.; Bhattacharyya, K. *J. Phys. Chem. B* **2001**, *105*, 1438.

(6) Brauns, E. B.; Madaras, M. L.; Coleman, R. S.; Murphy, C. J.; Berg, M. A. *J. Am. Chem. Soc.* **1999**, *121*, 11644.

(7) (a) Cho, C. H.; Singh, S.; Robinson, G. W. *Faraday Discuss.* **1996**, *103*, 19. (b) Eisenthal, K. B. *Chem. Rev.* **1996**, *96*, 1343. (c) Benjamin, I. *Annu. Rev. Phys. Chem.* **1997**, *48*, 401. (d) Gelbart, W. M.; Ben-Shaul, A. *J. Phys. Chem.* **1996**, *100*, 13169.

(8) (a) Nandi, N.; Bhattacharyya, K.; Bagchi, B. *Chem. Rev.* **2000**, *100*, 2013. (b) Bhattacharyya, K.; Bagchi, B. *J. Phys. Chem. A* **2000**, *104*, 10603.

(9) (a) Sarkar, N.; Datta, A.; Das, S.; Bhattacharyya, K. *J. Phys. Chem.* **1996**, *100*, 10523. (b) Das, S.; Datta, A.; Bhattacharyya, K. *J. Phys. Chem. A* **1997**, *101*, 3299. (c) Pal, S. K.; Mandal, D.; Sukul, D.; Bhattacharyya, K. *Chem. Phys. Lett.* **1999**, *312*, 178. (d) Mandal, D.; Datta, A.; Pal, S. K.; Bhattacharyya, K. *J. Phys. Chem. B* **1998**, *102*, 9070. (e) Lundgren, I. S.; Heitz, M. P.; Bright, F. V. *Anal. Chem.* **1995**, *67*, 3775.

(10) (a) Levinger, N. E. *Curr. Opin. Colloid Interface Sci.* **2000**, *5*, 118. (b) Willard, D. M.; Levinger, N. E. *J. Phys. Chem. B* **2000**, *104*, 11075. (c) Willard, D. M.; Riter, R. E.; Levinger, N. E. *J. Am. Chem. Soc.* **1998**, *120*, 4151. (d) Riter, R. E.; Undiks, E. P.; Levinger, N. E. *J. Am. Chem. Soc.* **1998**, *120*, 6062. (e) Riter, R. E.; Undiks, E. P.; Kimmel, J. R.; Pant, D. D.; Levinger, N. E. *J. Phys. Chem. B* **1998**, *102*, 7931. (f) Shirota, H.; Horie, K. *J. Phys. Chem. B* **1999**, *103*, 1437.

(11) (a) Faeder, J.; Ladanyi, B. M. *J. Phys. Chem. B* **2000**, *104*, 1033. (b) Senapathy, S.; Chandra, A. *J. Chem. Phys.* **1999**, *111*, 207.

(12) (a) Loughnane, B. J.; Farrer, R. A.; Scodinu, A.; Reilly, T.; Fourkas, J. T. *J. Phys. Chem. B* **2000**, *104*, 5421. (b) Pal, S. K.; Sukul, D.; Mandal, D.; Sen, S.; Bhattacharyya, K. *J. Phys. Chem. B* **2000**, *104*, 2613. (c) Jordan, J. D.; Dunbar, R. A.; Bright, F. V. *Anal. Chem.* **1995**, *67*, 2436. (d) Pant, D.; Levinger, N. E. *J. Phys. Chem. B* **1999**, *103*, 7846.

(13) (a) Datta, A.; Pal, S. K.; Mandal, D.; Bhattacharyya, K. *J. Phys. Chem. B* **1998**, *102*, 6114. (b) Pal, S. K.; Sukul, D.; Mandal, D.; Bhattacharyya, K. *J. Phys. Chem. B* **2000**, *104*, 4529.

(14) (a) Luzhkov, V.; Aqvist, J. *Chem. Phys. Lett.* **1999**, *302*, 267. (b) Special issue; D'Souza, V. T., Lipkowitz, K. B., Eds.; *Chem. Rev.* **1998**, *98*, 1741−2076. (c) Bortulos, P.; Monti, S. *Adv. Photochem.* **1995**, *21*, 1. (d) Bhattacharyya, K.; Chowdhury, M. *Chem. Rev.* **1993**, *93*, 507.

(15) (a) Rohrbach, R. P.; Rodriguez, L. J.; Eyring, E. H.; Wojcik, J. F. *J. Phys. Chem.* **1977**, *81*, 944. (b) Ugawa, T.; Nishikawa, S. *J. Phys. Chem. A* **2001**, *105*, 4248. (c) Okano, L. T.; Barros, T. C.; Chou, D. T. M.; Bennet, A. J.; Bohne, C. *J. Phys. Chem. B* **2001**, *105*, 2122.

(16) Balabai, N.; Linton, B.; Nappaer, A.; Priyadarshi, S.; Sukharevsky, A. P.; Waldeck, D. H. *J. Phys. Chem. B* **1998**, *102*, 9617.

(17) Duvenek, G. L.; Sitzmann, E. V.; Eisenthal, K. B.; Turro, N. J. *J. Phys. Chem.* **1989**, *93*, 7166.

(18) (a) Mashimo, S; Kuwabara, S.; Yagihara, S.; Higasi, K. *J. Phys. Chem.* **1987**, *91*, 6337. (b) Fukuzaki, M.; Miura, N.; Sinyashiki, N.; Kunita, D.; Shiyoya, S.; Haida, M.; Mashimo, S. *J. Phys. Chem.* **1995**, *99*, 431. (c) Belton, P. S. *J. Phys. Chem.* **1995**, *99*, 17061.

(19) (a) Halle, B. In *Hydration Processes in Biology: Theoretical and Experimental Approaches*; Bellissent-Funnel, M.-C., Ed.; IOS press: Amsterdam, 1999; pp 233−249. (b) Denisov, V. P.; Halle, B. *Faraday Discuss.* **1996**, *103*, 227. (c) Otting, G.; Liepinsh, E. *Acc. Chem. Res.* **1995**, *28*, 171.

(20) (a) Sarkar, N.; Datta, A.; Das, S.; Bhattacharyya, K. *J. Phys. Chem.* **1996**, *100*, 15483. (b) Pal, S. K.; Sukul, D.; Mandal, D.; Sen, S.; Bhattacharyya, K. *Chem. Phys. Lett.* **2000**, *327*, 91.

(21) (a) Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1987**, *86*, 6221. (b) Castner, E. W., Jr.; Maroncelli, M. *J. Mol. Liq.* **1998**, *77*, 1. (c) Stratt,

R. M.; Maroncelli, M. *J. Phys. Chem.* **1996**, *100*, 12981. (d) Fee, R. S.; Maroncelli, M. *Chem. Phys.* **1994**, *183*, 235. (e) Maroncelli, M. *J. Mol. Liq.* **1993**, *57*, 1.

(22) (a) Jarzeba, W.; Walker, G. C.; Johnson, A. E.; Kahlow, M. A.; Barbara, P. F. *J. Phys. Chem.* **1988**, *92*, 7039. (b) Jimenez, R.; Fleming, G. R.; Kumar, P. V.; Maroncelli, M. *Nature* **1994**, *369*, 471. (c) Silva, C.; Walhout, P. K.; Yokoyama, K.; Barbara, P. F. *Phys. Rev. Lett.* **1998**, *80*, 1086. (d) Jarzeba, W.; Barbara, P. F. *Adv. Photochem.* **1990**, *15*, 1.

(23) (a) Nandi, N.; Roy, S.; Bagchi, B. *J. Chem. Phys.* **1995**, *102*, 1390. (b) Schwartz, B. J.; Rossky, P. J *J. Chem. Phys.* **1996**, *105*, 6997.

(24) (a) Ohmine, I.; Saito, S. *Acc. Chem. Res.* **1999**, *32*, 741. (b) Ohmine, I.; Tanaka, H. *Chem. Rev.* **1993**, *93*, 2545.

(25) (a) Siegel, B.; Breslow, R. *J. Am. Chem. Soc.* **1975**, *97*, 6869. (b) Kobyashi, N. *J. Chem. Soc. Chem. Commun.* **1989**, 1126. (c) de Namor, A. F. D.; Traboulssi, R.; Lewis, D. F. V. *J. Am. Chem. Soc.* **1990**, *112*, 8442. (d) Feliciano, C. E.; Quinones, E. *J. Photochem. Photobiol. A* **1999**, *120*, 23. (e) Panja, S.; Bangal, P. R.; Chakravorty, S. *Chem. Phys. Lett.* **2000**, *329*, 377.

(26) (a) Soujanya, T.; Krishna, T. S. R.; Samanta, A. *J. Phys. Chem.* **1992**, *96*, 8544. (b) Soujanya, T.; Fessenden, R. W.; Samanta, A. *J. Phys. Chem.* **1996**, *100*, 3507. Andrews, P. M.; Beyer, M. B.; Troxler, T.; Topp, M. R. *Chem. Phys. Lett.* **1997**, *271*, 19. (c) Harju, T. O.; Huizer, A. H.; Varma, C. A. G. O. *Chem. Phys.* **1995**, *200*, 215.

(27) (a) Horng, M.-L.; Gardecki, J. A.; Papazyan, A.; Maroncelli, M. *J. Phys. Chem.* **1995**, *99*, 17311. (b) Jarzeba, W.; Walker, G. C.; Johnson, A. E.; Barbara, P. F. *Chem. Phys.* **1991**, *152*, 57.

(28) Hoshino, M.; Imamura, M.; Ikehara, H.; Hamai, Y. *J. Phys. Chem.* **1981**, *85*, 1820.