THE JOURNAL OF
PHYSICAL
CHEMISTRY A

VOLUME 104, NUMBER 7, FEBRUARY 24, 2000

ARTICLES

Solvent Influences on the Photophysics of Naphthalene: Fluorescence and Triplet State Properties in Aqueous Solutions and in Cyclodextrin Complexes

Gottfried Grabner,* Karl Rechthaler, Bernd Mayer, and Gottfried Köhler

*Institut für Theoretische Chemie und Molekulare Strukturbiologie, Universität Wien,
Althanstrasse 14, A-1090 Vienna, Austria*

Krystyna Rotkiewicz

Institute of Chemistry, Pedagogical University of Kielce, Chęcińska 5, PL-25020 Kielce, Poland, and Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44, PL-01224 Warsaw, Poland

Received: July 20, 1999; In Final Form: December 1, 1999

The photophysical properties of naphthalene were studied in aqueous solution (H_2O and D_2O), in some organic solvents (ethanol, hexane, and acetonitrile), and in complexes with the cyclodextrins (CDs) α-CD and β-CD, by means of absorption, steady-state and time-resolved fluorescence, circular dichroism, and triplet−triplet absorption spectroscopies. The structures of the CD inclusion complexes were computed using a dynamic Monte Carlo method. The main difference of the photophysics in the pure aqueous with respect to the organic media consists in a reduction of the fluorescence lifetime, τ_F, by a factor of about 2.5. Consideration of the triplet properties in aqueous and organic media led to the conclusion that this effect is most probably due to a corresponding increase of the intersystem crossing rate, induced by H_2O or D_2O. Inclusion of naphthalene in the CD hosts has the effect, at high CD concentration (>0.01 M), of increasing τ_F with respect to the aqueous medium, the value in α-CD being near to that in the organic media and the value in β-CD intermediate. The spectral and kinetic data are consistent with the predominant formation of 1:2 host:guest complexes with α-CD, and of 1:1 complexes with β-CD, although 2:2 complexes with β-CD are also formed and are identified by their excimer like fluorescence. Several experimental results, including the values of τ_F, and the temperature dependences of fluorescence and triplet−triplet absorption spectra on one hand and of triplet quenching and triplet−triplet annihilation kinetics on the other, point to a considerable structural flexibility of the 1:2 complex with α-CD.

Introduction

The torus-shaped cavities of the cyclic oligosaccharides known as cyclodextrins (CD) constitute interesting microenvironments for the study of the influence of solute−solvent interactions on the photophysics of encapsulated guest molecules. A recent review of the field[1] lists a broad range of photophysical properties and processes which are susceptible to be influenced by host−guest complexation.

Among the molecules used as guests in CD host−guest systems studied by photophysical techniques, unsubstituted polycyclic aromatics have received comparatively little attention, with the notable exception of pyrene which has been extensively studied on account of the effect of complexation on the vibronic structure of its fluorescence emission, and on formation of

---

* Corresponding author. E-mail: gottfried.grabner@univie.ac.at.

10.1021/jp992468y CCC: $19.00

excimers.[1] Complexation of naphthalene with β-CD in aqueous solution was investigated by Hamai[2] by means of fluorescence spectroscopy. Enhancement of the fluorescence intensity with increasing concentration of β-CD was interpreted by a model of consecutive formation of 1:1 and 2:2 complexes; fluorescence lifetimes of 40, 48, and 68 ns were assigned to the free molecule in water, to the 1:1 complex, and to the 2:2 complex, respectively. Formation of the latter was further evidenced by the appearance of a new emission band which was assigned to a naphthalene excimer.[2] A later study on complexes of naphthalene with dimethyl-β-CD prepared by sealed heating confirmed these results.[3]

A large number of studies of CD complexation were carried out using substituted naphthalenes as guest molecules. From the photophysical point of view, we may single out here Hamai's extension of his previous work on naphthalene,[2] showing that formation of 2:2 β-CD complexes with concomitant excimer emission is a common phenomenon among naphthalenes substituted with alkyl,[4] halogen,[5] or cyano[6] groups. On the other hand, complexes of 2-methylnaphthalene with α-CD were found to obey a different stoichiometry corresponding to stepwise formation of 1:1 and 1:2 (guest:host) complexes.[7] A further topic of interest in CD complexes of substituted naphthalenes, in particular those carrying a heavy atom substituent such as bromine, was the appearance of room-temperature phosphorescence, suggesting efficient shielding of the guest triplet state from quenching by molecular oxygen.[5a,8] Finally, it should be mentioned that the kinetic behavior of 1- or 2-naphthyl-1-ethanol triplet states included in β-CD has been used to determine the association and dissociation rate constants of the inclusion complexes formed in these systems.[9]

Our own approach to the study of CD host−guest complexes is based on a methodology combining structural model calculations with experimental spectroscopic techniques; guest molecules studied have included methyl-substituted phenols,[10] 2-naphthol,[11] dimethoxybenzenes,[12] and 4-hydroxybiphenyl.[13] In the present work, we have applied the same strategy to the study of the complexes of unsubstituted naphthalene with α-CD and β-CD. Previously, we found that 1,4-dimethoxybenzene forms strong 1:2 complexes with α-CD.[12] It was of interest to investigate whether naphthalene, which has similar molecular dimensions but is expected to interact differently with the CD cavity, behaves in a similar way, and to study the determinants of complex formation and the effect on the photophysical properties of the guest. This question has been addressed experimentally by means of absorption, circular dichroism, fluorescence, and time-resolved (triplet−triplet) absorption spectroscopies, and theoretically by applying a dynamic Monte Carlo technique. The photophysical data have been compared to those of naphthalene in neat solvents. The photophysics of naphthalene in aqueous solutions has not been studied previously; this part of the work revealed a hitherto unknown accelerating effect of an aqueous medium on the intersystem crossing rate of the molecule. A preliminary account of parts of the present work has been published earlier.[14]

Experimental Section

Chemicals. Water was distilled three times in a quartz apparatus. Naphthalene (scintillation grade, >99%), ethanol (absolute, p.a.), hexane (Uvasol), and deuterium oxide (Uvasol, >99.75% deuteration) were purchased from Merck, and the cyclodextrins (research grade) were from Serva.

Spectroscopic Methods. A saturated solution of naphthalene in water was obtained after 3 days of stirring; solutions were prepared without adding cosolvents to avoid complications caused by complexation of the latter with CDs. A saturated solution of naphthalene in water at 295 K was found to have a spectroscopically determined concentration of 2.18×10^{-4} M ($\lambda_{\max} = 276.2$ nm, $\epsilon_{\max} = 5230$ M^{-1} cm^{-1}), in excellent agreement with literature data.[15] In deuterium oxide, the solubility was somewhat lower (1.87×10^{-4} M). The stock solution of α-cyclodextrin (0.1 M) was slightly opalescent and was centrifuged at 4000*g* for 20 min to remove the opalescence; the amount of precipitate was negligibly small. Absorption spectra were obtained with a Hitachi U-3000 spectrophotometer, and spectra of induced circular dichroism with a Jasco spectropolarimeter (model J-715). Each circular dichroism spectrum was obtained from averaging over four scans. Fluorescence spectra with a spectral bandwidth of 2 nm and fluorescence decay time measurements were performed as described previously;[16] χ^2 tests and plots of weighted residuals were used to judge the goodness of fits. The fluorescence quantum yield of naphthalene in cyclohexane was used as a standard and taken to be 0.23.[17] Corrections for the refractive indices were performed using the values (298.0 K, D-line): cyclohexane 1.425, hexane 1.375, ethanol 1.361, acetonitrile 1.344, water 1.333, 0.01 M β-cyclodextrin solution 1.334, and 0.05 M α-cyclodextrin solution 1.346. Solutions were deoxygenated by thorough purging with argon for several minutes before measurements of stationary or time-resolved fluorescence. The absorptions of all solutions were checked before performing the measurements. If not stated otherwise, absorption, circular dichroism, and fluorescence measurements were carried out at room temperature.

Triplet states were studied by transient absorption spectroscopy in a setup described earlier.[18] The fourth harmonic ($\lambda = 266$ nm) of a Nd:YAG laser (Quanta-Ray DCR-1) was used for excitation. A thermostated cell holder was used for the present work. Measurements of triplet−triplet absorption spectra and O_2 quenching were carried out in air-equilibrated solutions. Transient spectra were measured at wavelength intervals ranging from 0.5 to 2.5 nm using monochromator band-passes between 0.2 and 0.7 nm. Pulse energies not exceeding 20 mJ·cm^{-2} were used in most experiments; transient absorbances increased linearly with pulse energy in this range. Measurements of triplet−triplet annihilation were carried out in the region of saturation of the triplet absorption. Deoxygenation by N_2 bubbling was applied for the annihilation experiments.

Theoretical Methods. Optimization of the structure of naphthalene complexes with cyclodextrins was based on computations applying Allinger's MM3-92 force field and a block diagonal matrix minimization method.[19] Low-energy geometries of complexes were obtained by means of a dynamic Monte Carlo (DMC) routine[20] implemented within the program package MultiMize.[21]

Results

Ground-State Absorption. The absorption spectra of naphthalene in ethanol, water, and aqueous solutions containing α-CD or β-CD are shown in Figure 1. Common organic solvents, such as alkanes or alcohols, exerted only little distinctive influence on the spectra, which were virtually identical in ethanol and hexane, to give an example. The vibronic substructure was somewhat less pronounced in a neat aqueous environment. Adding α-CD (0.05 M) to an aqueous solution of naphthalene resulted in a significant enhancement of the transition moment and of the vibronic substructure both for the forbidden $^1L_b \leftarrow {}^1A$ transition (located around 313 nm) and for

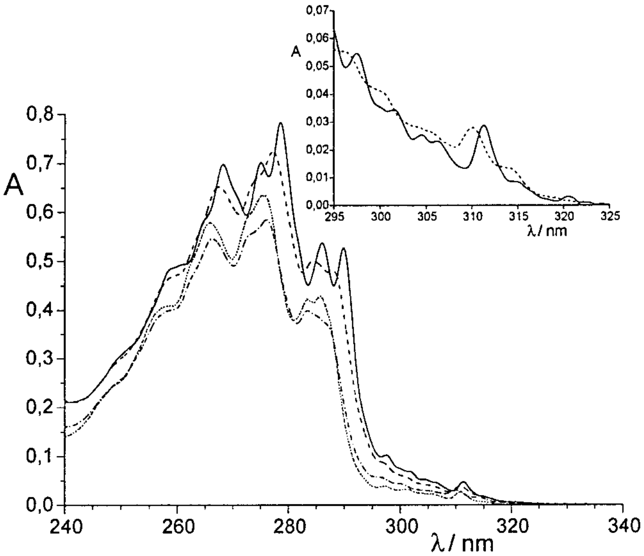

Figure 1. Absorption spectra of naphthalene (1.11 × 10^{-4} M) in pure water (dashed−dotted line), in the presence of 0.01 M β-CD (dashed line), in the presence of 0.05 M α-CD (full line), and in ethanol (dotted line).

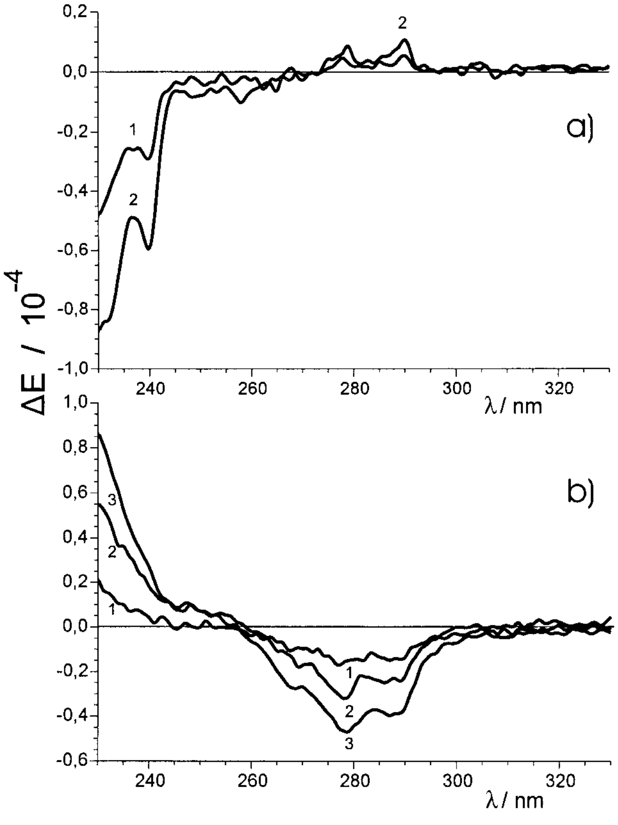

Figure 2. (a) Induced circular dichroism spectra of naphthalene (4.8 × 10^{-5} M) in the presence of 2.0 × 10^{-2} M (1) and 6.7 × 10^{-2} M (2) aqueous α-CD. (b) Induced circular dichroism spectra of naphthalene (4.8 × 10^{-5} M) in the presence of 8 × 10^{-4} M (1), 3 × 10^{-3} M (2), and 8 × 10^{-3} M (3) aqueous β-CD.

the ${}^1L_a \leftarrow {}^1A$ transition (located around 276 nm). The effect of β-CD was similar, but less distinct. The insert in Figure 1 shows that the effect of α-CD on the ${}^1L_b \leftarrow {}^1A$ transition is particularly strong. Values of the band maxima of the ${}^1L_a \leftarrow {}^1A$ transition are listed in Table 1; they show a progressive red shift in the sequence ethanol−water−β-CD−α-CD.

Induced Circular Dichroism. Circular dichroism is induced by complexation of achiral guests with the chiral CDs which themselves do not give a signal in the near-UV region.[22] The spectra recorded with naphthalene as a guest molecule are shown in Figure 2. With α-CD, a positive signal was recorded for the ${}^1L_a \leftarrow {}^1A$ transition and a negative one for the ${}^1B_b \leftarrow {}^1A$ transition. The position of the maxima was independent of the α-CD concentration for concentrations exceeding 0.02 M. As the complex with β-CD gave a negative signal (stronger in comparison to α-CD) for the ${}^1L_a \leftarrow {}^1A$ transition and a positive one for the ${}^1B_b \leftarrow {}^1A$ transition (see Figure 2), the geometry of this complex has to be different. It was interesting to note that the β-CD spectrum remained negative throughout the range of the ${}^1L_a \leftarrow {}^1A$ transition and showed no sign of the exciton splitting which would be expected to occur in a structure containing two chromophores.[23] A statement about the sign of the ${}^1L_b \leftarrow {}^1A$ transition is impossible both for the β-CD and the α-CD systems, as the signal was too weak.

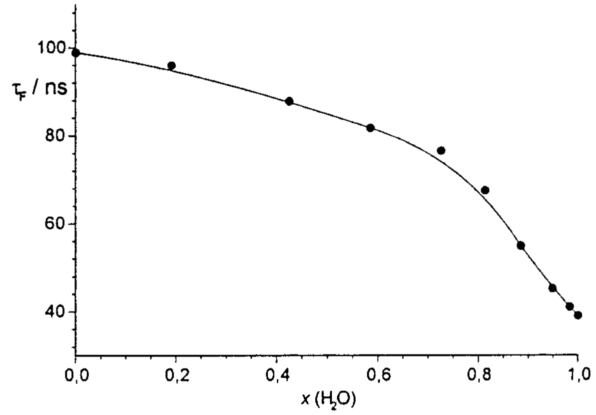

Figure 3. Fluorescence lifetimes of naphthalene in binary mixtures of ethanol with water.

Fluorescence in Neat Solvents and Binary Ethanol/Water Mixtures. The fluorescence spectra, quantum yields, and lifetimes of naphthalene were measured in solutions of H_2O and D_2O to allow an assessment of the effect of CD complexation in aqueous solution, and for comparison in some organic solvents (hexane, ethanol, and acetonitrile). The results are shown in Table 1. The most striking result was a marked reduction of the fluorescence lifetime in the aqueous solutions, as compared to the organic ones. Replacing H_2O by D_2O had no effect on the emission properties. The fluorescence data in the three organic solvents were very similar. The behavior in binary ethanol/water mixtures demonstrated that the addition of small amounts of ethanol (of the order of 10 mol %) already had a strong enhancing effect on fluorescence (Figure 3). Fluorescence quantum yield and lifetime increased in parallel when the ethanol content in the mixture was raised.

Fluorescence in Aqueous Solutions of Cyclodextrins. The fluorescence spectra in aqueous solution as well as in the presence of β-CD exhibited some little pronounced vibronic structure, which was strongly enhanced in a solution containing α-CD (Figure 4). The fluorescence quantum yield of naphthalene in water remained quite constant with increasing temperature (Figure 4a), whereas it decreased markedly upon addition of α-CD (Figure 4b). The vibronic structure became more diffuse at elevated temperatures. The fluorescence intensity of aqueous naphthalene was enhanced upon addition of both cyclodextrins, and a slight redshift was observed which, however, was much less pronounced than the one seen in the ground state or triplet−triplet absorption. In solutions containing both high naphthalene ($>5 \times 10^{-5}$ M) and β-CD ($>10^{-3}$ M) concentrations, the emission of the naphthalene dimer, similar to that of an excimer in liquid solution, became visible in the fluorescence spectrum,

TABLE 1: Photophysical Properties[a] of Naphthalene in Various Environments (25 °C)

solvent	additive	λ_{abs} (nm)	λ_F (nm)	Γ_F (cm^{-1})	Q_F	$\lambda_{max}(T_n \leftarrow T_1)$ (nm)	ϵQ_{ISC} (M^{-1} cm^{-1})	$\Delta\lambda_{1/2}$ (nm)	$\epsilon Q_{ISC}\Delta\lambda_{1/2}$ (M^{-1} cm^{-1} nm)	τ_F (ns)	k_{ISC}[b] (s^{-1})
hexane	none	275.1	322.6 336.7	3000	0.23	412	16500	8.1	1.34×10^5	103.9	7.2×10^6
ethanol	none	275.6	323.6 332.2	3000	0.23	412	14600	10.0	1.46×10^5	98.9	7.6×10^6
acetonitrile	none	275.9	321.5 334.5	2800	0.23	412	10900	11.6	1.26×10^5	98.2	7.6×10^6
H_2O	none	276.1	322.6 332.2	3100	0.11	412	7900	17.5	1.38×10^5	39.0	19.5×10^6
D_2O	none	275.8	322.6 331.1	3000	0.12	411	9040	14.6	1.32×10^5	39.3	19.1×10^6
H_2O	0.01 M β-CD	277.4	322.6 334.5	3000	0.15	415	8900	13.1	1.17×10^5	60.9[c] 90.7[d]	12.3×10^6
H_2O	0.05 M α-CD	278.8	322.6 335.6	2900	0.19	416	16800	6.6	1.11×10^5	86.2	8.7×10^6

[a] λ_{abs} denotes the wavelength of the most intense vibronic band of the $^1L_a \leftarrow {}^1A$ transition, λ_F the wavelengths of the fluorescence maxima, Γ_F the half-maximum bandwidth of the fluorescence band, Q_F the fluorescence quantum yield, Q_{ISC} the quantum yield of the intersystem crossing, $\Delta\lambda_{1/2}$ the half-maximum bandwidth of the triplet−triplet absorption band, $\lambda_{max}(T_n \leftarrow T_1)$ the maximum wavelength of the triplet−triplet absorption, ϵ the corresponding absorption coefficient, τ_F the fluorescence lifetime, and k_{ISC} the rate constant of intersystem crossing. [b] Calculated assuming $Q_{ISC} = 0.75$[25] independent of solvent. [C] Monitored at 340 nm. [d] Monitored at 420 nm.

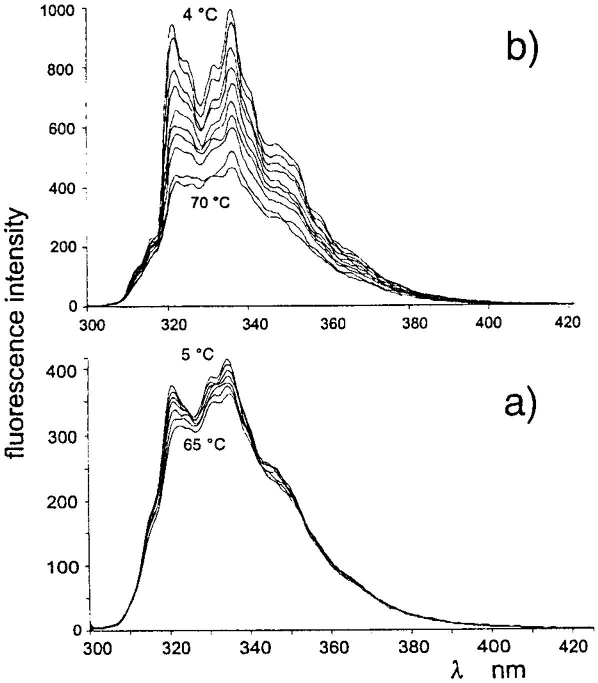

Figure 4. (a) Fluorescence spectra of naphthalene (2×10^{-5} M) in water as a function of temperature; (b) fluorescence spectra of naphthalene (2×10^{-5} M) in aqueous α-CD (0.01 M) as a function of temperature.

in agreement with previous results.[2] Figure 5 shows the emission spectra obtained in a saturated aqueous naphthalene solution in the presence of 0.01 M β-CD, i.e., in conditions designed to maximize the excimer emission. The broad, unstructured excimer band was clearly visible, but an emission similar to that of the naphthalene monomer remained present even at low temperature (8 °C). At 25 °C, the intensity of this band was higher in the presence of β-CD than in aqueous solution, in agreement with the enhancing effect of complex formation on the fluorescence.

Adding either α- or β-CD to an aqueous solution of naphthalene has a profound effect on the fluorescence lifetimes (Table 1). At sufficiently high host concentrations (0.05 M for α-CD and 0.01 M for β-CD), the decay curves were monoexponential, indicating the prevalence of one specific complex structure. Different lifetimes were obtained when the fluorescence of the β-CD complexes was monitored either within the monomer or within the excimer emission band. The fluorescence lifetimes of both the α-CD complex and the β-CD excimer are almost as long as in the organic solvents, whereas that of the short-wavelength emission of the β-CD complex is intermediate between those found in aqueous and organic solvents. It should be noted that all lifetimes were independent of naphthalene concentration.

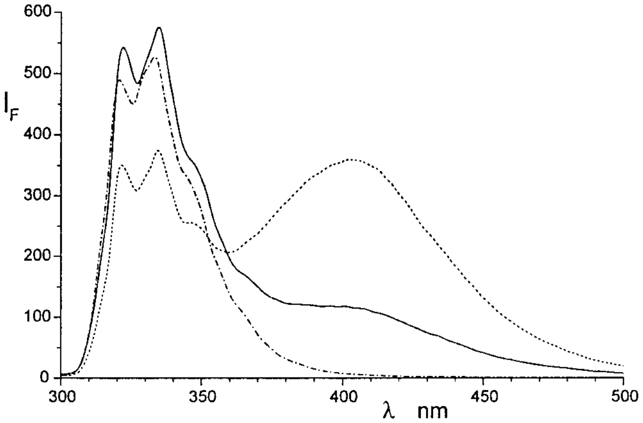

Figure 5. Fluorescence spectra of naphthalene (saturated solution, ≈2×10^{-4} M) in aqueous solution at 8 °C (dashed−dotted line), and in the presence of 0.01 M β-CD at 25 °C (full line) and at 8 °C (dashed line).

Intersystem Crossing and Triplet State Properties. *Triplet−Triplet Absorption Spectra.* In solutions at ambient temperature, naphthalene exhibits a well-known two-band T−T spectrum in the visible spectral region; the maximum of the stronger band has been located by various authors at wavelengths lying between 412 and 415 nm.[24] These bands are quite narrow; a half-width value for a hexane solution of 8 nm has been determined.[25] An extinction coefficient of 24 100 ± 2800 M^{-1} cm^{-1} at band maximum has been proposed based on a statistical analysis of published values obtained in various solvents except benzene.[26] Although the solvent effect on T−T absorption has to our knowledge not been systematically studied, it was considered to be statistically negligible by these authors[26] with the exception of benzene, which induces quite generally larger bandwidths and accordingly smaller extinction coefficients.[25]

Figure 6 shows the T−T spectra of naphthalene obtained at 25 °C in ethanol, in pure aqueous solution, as well as in aqueous

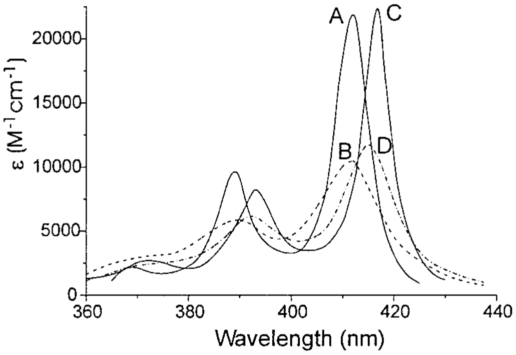

Figure 6. Triplet−triplet absorption spectra of naphthalene (10^{-4} M) in ethanol (A), in H_2O (B), in H_2O + 0.05 M α-CD (C), and in H_2O + 0.01 M β-CD (D). The experiments were performed at 25 °C and laser pulse energies between 8 and 10 mJ·cm^{-2}.

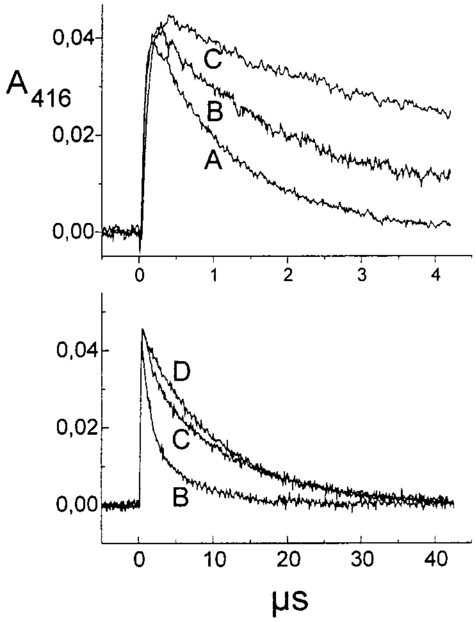

Figure 7. Oscilloscope traces showing the effect of α-CD concentration on the decay of naphthalene triplet−triplet absorption at two time scales (upper: 1 μs/division, lower: 10 μs/division): (A) without CD; (B) 0.015 M α-CD; (C) 0.025 M α-CD; (D) 0.05 M α-CD. The experiments were performed at 25 °C.

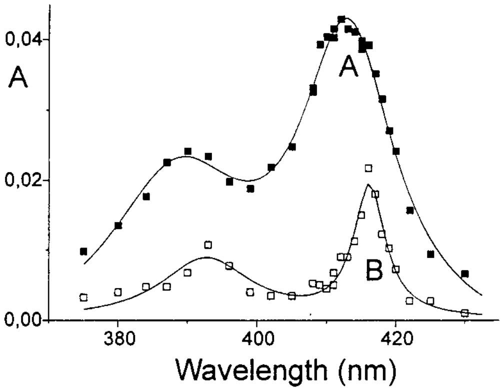

Figure 8. Spectra of fast and slow components of the naphthalene triplet−triplet absorption in a solution containing 0.01 M α-CD (25 °C): (A) difference of transient absorption at maximum and transient absorption 8 μs after pulse end; (B) transient absorption (multiplied by factor 4) 8 μs after pulse end.

solutions containing 0.01 M β-CD and 0.05 M α-CD, respectively. The extinction coefficients of the T−T absorption have been computed from the experimentally determined product of extinction coefficient and triplet quantum yield, ϵQ_{ISC}, assuming $Q_{ISC} = 0.75$;[25] as will be argued below, Q_{ISC} may be considered to be independent of the solvent. Figure 6 shows that the T−T band maximum is the same in ethanol and in water. A significant broadening is observed in aqueous solution. A marked effect of the addition of cyclodextrin is noted with respect to the spectrum in aqueous solution, consisting of (a) a red shift of the spectrum in both CD solutions and (b) a marked band narrowing observed in particular in the solution containing α-CD.

Solvent and Complexation Influence on Triplet State Properties. In order to further substantiate the effect of solvent environment on the naphthalene T−T spectrum, band maximum locations, half-widths, and band areas (proportional to oscillator strengths) have also been measured in D_2O, hexane, and acetonitrile. The results are shown in Table 1 along with those extracted from Figure 6. Table 1 demonstrates that the red shift observed in CD solutions is specific for these systems as λ_{max} is constant in pure solvents. In contrast, the band half-width is solvent-dependent and increases with solvent polarity. The product of ϵQ_{ISC} at band maximum multipied by the band half-width, taken as a measure of band area, is roughly the same for the systems studied; the somewhat lower values obtained in the CD-containing solutions are not significantly outside the probable error margin. Assuming that the oscillator strength of the T−T transition is solvent-independent, this result would indicate that the intersystem crossing yield is not markedly solvent-dependent.

Triplet Decay Kinetics. In aqueous solutions containing α-CD, the time dependence of triplet−triplet absorption consists of three components which are clearly separated in time: a fast one representing the growing-in of the signal due the intersystem crossing process, and two slower decay components, which in the presence of O_2, can both be fitted to a first-order rate law. Examples of decay traces are shown in Figure 7. Without α-CD, only the fast decay is seen, whereas only the slow decay is present when 0.05 M α-CD is added; both components contribute at intermediate concentrations. A similar behavior has been previously noted for triplet decays in other CD host−guest complexes, e.g., for 1,4-dimethoxybenzene/α-CD[12] and 6-bromo-2-naphthol/α-CD,[27] and attributed to different oxygen quenching rate constants for the uncomplexed and the complexed guest molecules. In the present case, we were able to test the validity of this interpretation by making use of the sensitivity of the T−T absorption to the presence of α-CD (Figure 6). In Figure 8, the spectra of both fast and slow component are shown for a solution containing a small concentration of α-CD (0.01 M). The slow component displays both the line narrowing and red shift that were noted above, whereas the fast component has the same spectrum as naphthalene in neat aqueous medium, in confirmation of the attribution of the fast and slow decay components to free and complexed naphthalene molecules. It will be shown below that the slow component can actually be assigned to 1:2 guest:host complexes, the equilibrium concentration of 1:1 complexes being negligible.

Triplet decay is somewhat slowed down in solutions containing β-CD, too, although much less than with α-CD. At 25 °C in the presence of air, the first-order decay was reduced from 8.6 × 10^5 s^{-1} in CD-free solution to 5.2 × 10^5 s^{-1} when 0.01 M β-CD was added. This effect indicated complex formation, but it was too small to be exploited for a determination of the stoichiometry and association constant. There was no hint of the presence of a significantly longer-lived component in the

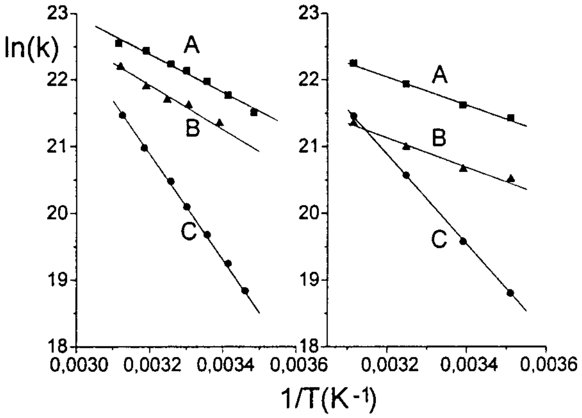

Figure 9. Arrhenius plots for reaction of naphthalene triplet with molecular oxygen (left) and for naphthalene triplet−triplet annihilation (right) in aqueous solutions: (A) in neat H_2O; (B) in the presence of 0.01 M β-CD; (C) in the presence 0.05 M α-CD.

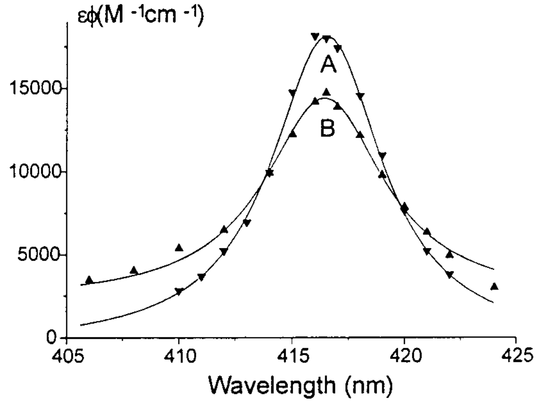

Figure 10. Temperature effect on the main band of the naphthalene triplet−triplet absorption in aqueous solutions containing 0.05 M α-CD: (A) 12 °C; (B) 40 °C.

decay, even in saturated naphthalene solutions at low temperature (5 °C). The excimer emission observed under this conditions (Figure 5) is thus not accompanied by a triplet−triplet absorption which could be assigned to the species responsible for this emission. Whether this is due to inefficient intersystem crossing in the singlet excimer, to rapid self-quenching of the triplet excimer, or to the fact that the extinction coefficient of the triplet excimer is too low for its detection cannot be decided from the data. An indirect effect of excimer formation was seen, however, in a decrease of the triplet−triplet absorption at 415 nm with decreasing temperature. In a solution containing 1.1×10^{-4} M naphthalene and 0.01 M β-CD, this decrease amounted to ≈30% when the temperature was lowered from 34 to 5 °C.

Temperature Dependence of Triplet Absorption and Decay. The temperature dependence of the rate constant for O_2 quenching of free and α-CD-bound as well as β-CD-bound naphthalene triplets is shown in Figure 9a. The behavior of the free form is characteristic of a diffusion-controlled reaction with an activation energy of the order of 16 kJ mol^{-1}. In contrast, both CD-bound forms show more pronounced temperature dependences, the Arrhenius plots yielding $E_A = 26$ kJ mol^{-1} for β-CD and 66.5 kJ mol^{-1} for α-CD complexes. The temperature dependence of the second-order rate constant for T−T annihilation, determined at high pulse energies, is similar to that of the O_2 quenching reaction (Figure 10b). Again, an unusually high activation energy is found for the 1:2 complex with α-CD.

TABLE 2: Total Potential Energy E_p, Complexation Energy ΔE_p Obtained from the Difference of E_p and the Sum of the Potential Energies for the Constituent Molecules, and Total Complexation Energy ΔE_t, Including the Free Energy of Solvation for the Main Minimum Complex Structures, for Complexes of Naphthalene with α-CD and β-CD

	energy (kJ mol^{-1})		
structure	E_p	ΔE_p	ΔE_t
1:1 α-CD	219.2	−54.5	−42.8
1:1 β-CD	250.6	−64.0	−54.9
1:2 α-CD	273.6	−257.3	−117.8
2:2 β-CD, A[a]	234.8	−393.9	−166.8
2:2 β-CD, B[a]	248.3	−380.4	−139.5

[a] See Figure 13, structures A and B.

A further remarkable temperature effect on naphthalene/α-CD complexes (at a concentration of 0.05 M α-CD) is shown in Figure 10. The main T−T absorption band is subject to marked broadening with increasing temperature; at the same time, the band maximum and symmetry are retained, which indicates that this effect is not due to a contribution of noncomplexed naphthalene triplets. At 12 °C, the half-width is only 5.7 nm and thus distinctly smaller than in hexane. This temperature effect was not encountered in neat solvents.

Model Calculations. Optimized reference structures of α-CD and β-CD were derived from a set of coordinates obtained from crystallographic data[28] and gave 257.3 and 298.3 kJ mol^{-1} as minimum potential energies, respectively. The potential energy of the guest molecule naphthalene was 16.3 kJ mol^{-1}. These reference structures were used in the calculations described below.

Both potential (calculated by the force field) and solvation energy (calculated by a continuum approximation assigning atomic solvation parameters σ_j to the solvent accessible molecular surface area A_j depending on the surface type) were considered in a modified Metropolis criterion. Details of the calculation were presented previously.[29] This method proved to be successful in calculations of mean structures of cyclodextrin complexes in an aqueous environment, as verified by the correctly predicted induced circular dichroism spectrum of the complexes.[12,29,30] It is an important prerequisite to include contributions arising from solvation effects and essentially from hydrophobic interactions in the calculations to obtain reasonable complex geometries.[29]

Every DMC run was started from a random relative orientation of host and guest molecules positioned within a distance of 0.5 nm. In each DMC step this relative position was stochastically changed by a maximum of 0.05 nm in the x, y, or z direction, the guest was rotated by a maximum of 5°, and each individual glucose unit of the host molecules was additionally tilted by maximally 5°. Each stochastically generated structure was minimized within the force field and accepted or discarded according to the modified Metropolis criterion including the free energy of solvation.[29] The simulation temperature was kept constant at 300 K and low-energy complex structures were obtained within 1000 DMC steps. The complexation energy, ΔE_p, was calculated from the difference between the sum of the potential energies of the isolated host and guest molecules and the calculated potential energies, E_p, of the complex. The total complexation energy, ΔE_t, includes the change in potential energy as well as the change of the free energy of solvation when the complex is formed. Computed energy values are listed in Table 2.

In minimum structures of 1:1 complexes with α-CD the naphthalene is merely attached to the secondary hydroxylic rim

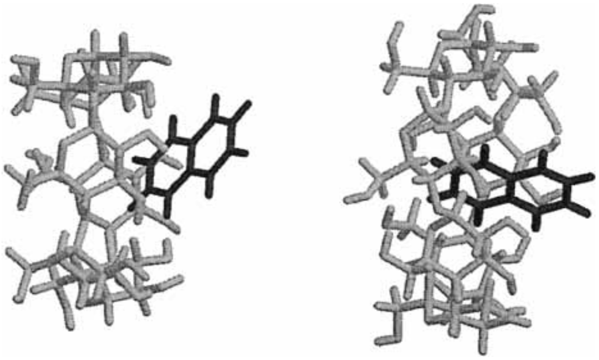

Figure 11. Minimum potential energy structures for 1:1 complexes of naphthalene with α-CD (left) and *β*-CD (right).

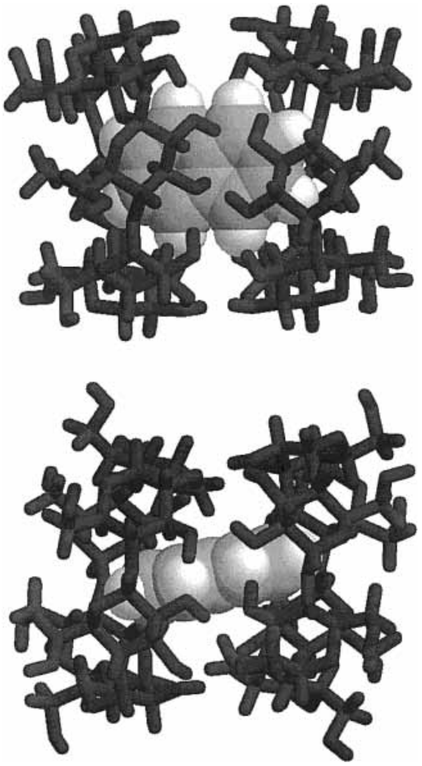

Figure 12. Minimum potential energy structure for a complex of naphthalene with two α-CD molecules. In the lower part of the figure, the structure is rotated by 90° about the long axis (view from the bottom).

of the macrocycle (see Figure 11). An energy barrier prevents a deeper penetration of the guest into the CD cavity[11,31] because of the rigidity of the α-CD conformation.[32] In complexes with *β*-CD, naphthalene is well embedded within the cavity and the energy varies only slowly when the guest is shifted along the axis through the cavity. This shows that the 1:1 complexes of this aromatic molecule with *β*-CD are much more stable than those with α-CD.

An α-CD complex with the aromatic molecule protruding into the aqueous medium favors complexation with a second α-CD. This results in stable 1:2 guest:host complexes where naphthalene is tightly encapsulated. Figure 12 shows that in the most stable complexes the secondary hydroxylic rims are facing each other and the complex is stabilized by hydrogen bonding between hydroxylic groups. A complex where the primary rim of one CD is facing the secondary rim of the second one has a much higher energy; a value of 337.5 kJ mol^{-1} is obtained for a relevant minimum structure, which is approximately 84 kJ mol^{-1} above the energy of the optimum structure (see Table 2). This is in good agreement with recent studies of threading of cyclodextrins on polymers where tubes in which corresponding rims are facing each other; i.e., a secondary rim facing a secondary one and a primary rim facing a primary one were found to be the most stable structures.[33] For 2:2 host:guest complexes between *β*-CDs and 4-hydroxybiphenyl, a similar structure was recently deduced from model calculations and circular dichroism data.[13]

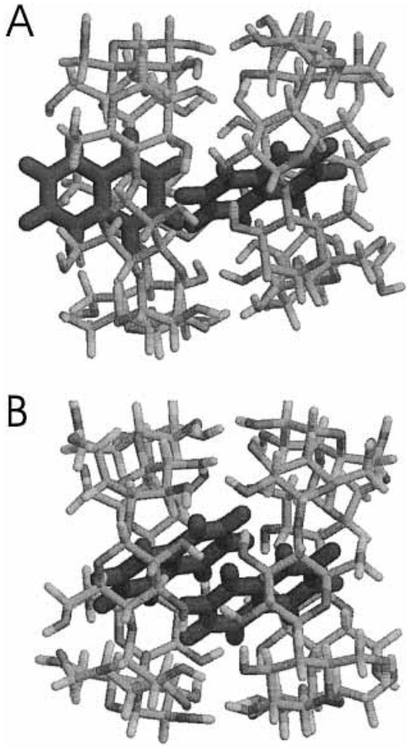

Figure 13. Structures for complexes of two naphthalenes with two *β*-CD molecules: (A) depicts an example for the most stable structure (see Table 2 for energies) whereas in (B) a local minimum structure in which the chromophores form a sandwich like dimer is shown.

The structure shown in Figure 12 clearly indicates the stabilization of the complex by hydrogen bonding and the induced fit of the two rather rigid cyclodextrin caps to the molecular shape of the aromatic guest. The latter is due to optimization of van der Waals interactions between the host molecules and the easily polarizable guest. It is also indicated that the encapsulation of the guest is not completely tight, as the complex is slightly open (see the upper view in Figure 12). Naphthalene is slightly too large to fit completely into an optimum double cavity. Wobbling of the caps is the main dynamic mobility observed in the dynamic Monte Carlo simulations.

Models for 2:2 complexes of naphthalene with *β*-CD (see Figure 13) show the important contribution of intramolecular hydrogen bonding between the secondary hydroxylic groups to the stabilization of the cavity consisting of two hosts. This is also indicated by the large decrease of the potential energy upon binding (see Table 2). The two chromophores can move rather freely within the cavity between sites of similar energy and structures analogous to that plotted in Figure 13, structure A, are found as the most stable ones. They appear just as an association of two 1:1 complexes, and the chromophores are oriented nearly orthogonal to each other with small orbital overlap. A local minimum structure where the chromophores form a sandwich-like dimer which could be responsible for excimer fluorescence is also found (Figure 13, structure B), but with more than 20 kJ mol^{-1} higher complexation energy (see Table 2).

Discussion

Photophysics in Neat Solvents. The comprehensive overview of the photophysical properties of naphthalene in various solvent environments, presented in Table 1, first underlines the fact that the fluorescence yield and lifetime are very similar for the organic solvents considered, i.e., hexane, ethanol, and acetonitrile. The obtained quantities are in good agreement with literature data.[34] A significant reduction in fluorescence quantum yield and lifetime is observed when naphthalene is dissolved in either H_2O or D_2O; there is no effect of deuteration on emission characteristics. The band maximum of the triplet−triplet absorption is not solvent-dependent. The band shape, in contrast, shows a trend in the neat solvents which implies a bandwidth that increases with increasing solvent polarity. The band areas, when calculated with the assumption of a solvent-independent transition oscillator strength, are, however, constant within error limits; as a consequence, the intersystem crossing yields are constant too. This is a well-known result for organic solvents,[35] implying that the intersystem crossing rate is not significantly solvent-dependent in organic media. The unexpected conclusion is that an aqueous environment significantly enhances the intersystem crossing rate.

In order to assess the validity of this conclusion, it is necessary to summarize and discuss the assumptions which have led to it. These included, on one hand, the assumption of the solvent independence of the oscillator strength of the triplet−triplet absorption, from which the constancy of the absorption band area was derived. This seems reasonable since the idea of the enhancement of the oscillator strength of an allowed $\pi^* \leftarrow \pi$ transition by a factor of nearly 3, induced by H_2O or D_2O, appears rather exotic.

On the other hand, the special situation observed in the aqueous environment rests on the observation of the reduced fluorescence lifetime. From an experimental point of view, the measurement of rather long lifetimes poses a problem due to possible quenching by residual O_2, despite the greatest care applied in carrying out the measurements. We can exclude this cause of error as a possible explanation of the observed effect on the grounds of the reduced solubility of O_2 in water as compared to organic media. A further reason for concern is the possibility of formation of ground-state complexes or even aggregates of naphthalene molecules in aqueous medium, induced by the hydrophobicity of the molecule. There is, however, no experimental evidence for this process. All spectra (absorption, fluorescence, and T−T absorption) were found to be independent of naphthalene concentration over a wide range (in the case of T−T absorption, between 5×10^{-6} M and the saturation concentration of about 2×10^{-4} M at 25 °C). There was no evidence of excimer emission in the fluorescence spectra even at saturation, whereas excimers are readily observable in 2:2 complexes with β-CD (see Figure 5); it is known that naphthalene concentrations at least 2 orders of magnitude higher than those used in the present work are needed to induce excimer emission in organic solvents.[36] Moreover, a decrease of fluorescence lifetime and quantum yield is also observed in the presence of a high concentration (0.01 M) of β-CD, i.e., in a situation when the majority of naphthalene molecules form 1:1 complexes with the host and, therefore, are unavailable for other complexes.

A solvent-influenced intramolecular process, competing with radiative decay, must therefore account for the reductions of fluorescence quantum yields and lifetimes observed in H_2O as well as in D_2O, and to a lesser degree in the presence of β-CD. This might be internal conversion to the ground state, but the insensitivity of the photophysics with respect to replacement of H_2O by D_2O and the lack of a solvent influence in organic media both argue against this possibility. Furthermore, in order to account for the data the water-induced increase of the internal conversion rate would have to be dramatic (from $<5 \times 10^5$ s^{-1} in hexane to 1.4×10^7 s^{-1} in H_2O and D_2O, assuming a constant intersystem crossing rate); at the same time, the intersystem crossing yield would drop to about 0.33. This, in turn, leads back to the triplet−triplet oscillator strength argument which has already been discussed above.

A significant acceleration of intersystem crossing induced by the aqueous medium therefore remains as the only possible explanation. If we assume that internal conversion is negligible, it follows that the quantum yield of intersystem crossing in aqueous medium should be higher than that in organic solvents; the increase can, however, amount to 20% at most over its value in organic solvents, and this is not easily demonstrable by transient absorption in view of the spectral broadening of the T−T transition in aqueous environment.

The mechanistic explanation of the aqueous solvent-induced acceleration of intersystem crossing necessarily involves a great deal of speculation, since related observations are scarce. It must first be noted that it will probably not be easy to detect this effect in other polycyclic aromatic systems. Naphthalene, on account of its high symmetry, exhibits small photophysical rate constants (in effect leading to a high probability for intersystem crossing in spite of a long fluorescence lifetime); in addition, it is exceptional among polycyclic aromatic hydrocarbons in being comparatively water-soluble. From the basics of intersystem crossing, there seem to be two possible factors able to account for the observed effect. First, a solvent-induced shift of relevant energy levels might lead to a situation where singlet donor and triplet acceptor levels are tuned toward resonance. Such an effect, although opposite in direction, has been demonstrated for 1-cyanonaphthalene and its complexes with acetonitrile or water in molecular beams;[37] in this system, intersystem crossing is more efficient in the bare molecule than in the complexes. Second, there might be specific solute−solvent interactions able to enhance intersystem crossing by reducing the symmetry of the system in an interaction complex, e.g. by switching on the symmetry-forbidden $\pi\pi$ spin−orbit coupling pathway.[38] An influence of the solvent on the vibronic $\pi\sigma$ coupling mechanism prevailing in the isolated molecule[38] seems less likely on account of the lack of a solvent deuteration effect. Specific interaction has to the best of our knowledge not been demonstrated for the naphthalene/water system, but it does take place between benzene and water,[39] where 1:1 and 1:2 complexes involving a water−π-electron interaction have been described. Electronic excitation of the aromatic molecule may well change the nature and strength of this interaction; the observation that the $S_2 \leftarrow S_0$ transition of naphthalene is red-shifted in water with respect to ethanol, whereas the $S_1 \rightarrow S_0$ and the $T_n \leftarrow T_1$ transitions are not influenced (see Table 1), indeed provides an indication that the excited states are more stabilized than the ground state. This red shift of the ground-state absorption is also known for benzene[40] and has been theoretically interpreted by a model based on hydrophobic hydration.[41] Further work is required for an elucidation of this problem.

Cyclodextrin Complex Stoichiometry. Although it was not the primary goal of the present work to provide a quantitative picture of the association equilibria of the naphthalene−CD complexes, some discussion of this point is nevertheless useful in view of the assignment of the spectroscopic and photophysical data to the computed complex structures.

The complexes of naphthalene with α-CD are characterized by a circular dichroism spectrum featuring a positive signal for the $^1L_a \leftarrow {}^1A$ transition and a negative one for the $^1B_b \leftarrow {}^1A$ transition (Figure 2). This pattern is similar to that reported in earlier work on the 2-methylnaphthalene/α-CD system, and assigned to the formation of 1:2 guest−host complexes.[7a] This type of complex was also shown to be prevalent in the 1,4-dimethoxybenzene/α-CD system, and characterized by significantly longer excited singlet and triplet lifetimes with respect to those in aqueous solution,[12] a trend analogous to that found in the present work. In view of these similarities, it seemed reasonable to base the discussion of the interaction between naphthalene (N) and α-CD (C) on a model of consecutive formation of 1:1 and 1:2 guest−host complexes:

$$\mathrm{N} + \mathrm{C} \leftrightarrows \mathrm{NC} \tag{1}$$

$$\mathrm{NC} + \mathrm{C} \leftrightarrows \mathrm{N(C)_2} \tag{2}$$

Assuming that the total concentration of naphthalene, $[\mathrm{N}]_0$, is negligibly small compared to the concentration of α-CD, [C], a condition which was always fulfilled in our work, the concentration of 1:2 complexes, $[\mathrm{N(C)_2}]$, can be expressed as

$$[\mathrm{N(C)_2}] = \frac{[\mathrm{N}]_0 K_1 K_2 [\mathrm{C}]^2}{1 + K_1[\mathrm{C}] + K_1 K_2 [\mathrm{C}]^2} \tag{3}$$

where K_1 and K_2 are the association constants of the complexation steps 1 and 2.

A convenient approach to an analysis of the formation of the 1:2 complexes can be based on the large effect of α-CD addition on the decay kinetics of triplet naphthalene (see Figure 7).[12] It was assumed that the contributions of the free and 1:1 complexed triplets are both contained in the fast decay component, F; the slow component, S, was assigned to the 1:2 complex. The following equation then holds:[12]

$$\frac{[\mathrm{F}][\mathrm{C}]}{[\mathrm{S}]} = \frac{1}{K_2} + \frac{1}{K_1 K_2 [\mathrm{C}]} \tag{4}$$

Triplet data recorded at two wavelengths have been used, namely (a) at the isosbestic point of the spectra of both forms (413.2 nm at 25 °C), and (b) at the absorption maximum of the bound form (416.5 nm), thus allowing measurements over a wide range of host concentrations. The result of this treatment is shown in Figure 14 for three different temperatures (5, 12, and 25 °C). A fairly good linear correlation is obtained for each of the data sets; the slope increases with increasing temperature, and the y-axis intercept is too small to be determined. This result shows that the 1:2 complexes are predominant in the concentration range studied; the value of K_2 exceeds that of K_1 by 3 orders of magnitude or more. As for 1,4-dimethoxybenzene,[12] the product K_1K_2 (given by the inverse of the slope) increases with decreasing temperature, from 4000 M^{-2} at 25 °C to 6300 M^{-2} at 12 °C and 9600 M^{-2} at 5 °C. Contrary to the 1,4-dimethoxybenzene case,[12] the two association constants could not be determined separately; therefore, a thermodynamic analysis of complex formation in terms of association enthalpies and entropies for each complexation step could not be performed in the naphthalene/α-CD system.

The validity of these results was further tested by applying a Benesi−Hildebrand type analysis to the ground-state absorption data (22 °C) at $\lambda = 290$ nm, corresponding to the first vibrational subband of the $^1L_b \leftarrow {}^1A$ transition that is strongly enhanced by α-CD complexation (see Figure 1). Assuming that the complexation equilibrium can be approximated by the simultaneous addition of two host molecules to one guest molecule, the following equation should hold:

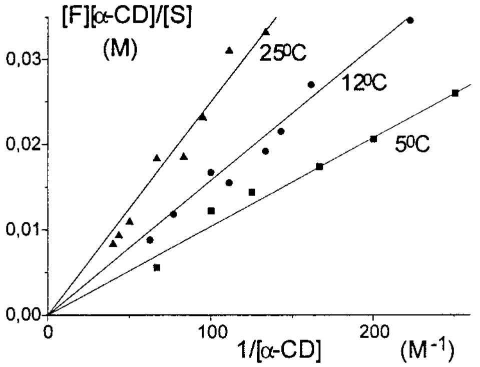

Figure 14. Plots according to the model of consecutive 1:1 and 1:2 complexation (eq 4) for the system naphthalene/α-CD at three different temperatures: 5, 12, and 25 °C, as determined from triplet−triplet absorption data.

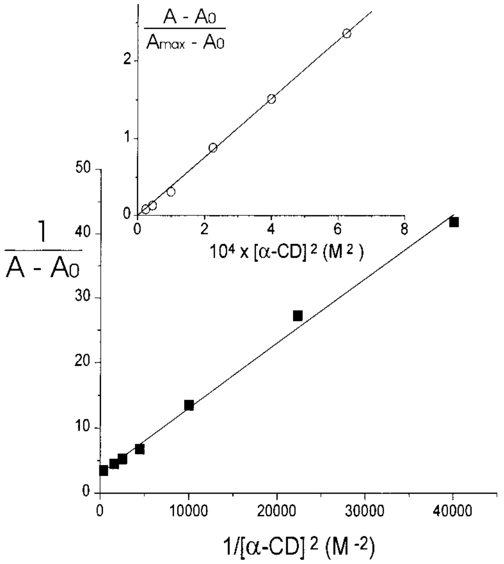

Figure 15. Benesi−Hildebrand type plots for complexation between naphthalene (1.1 × 10^{-4} M) and two α-CD molecules at 22 °C, determined from ground-state absorbance data at $\lambda = 290$ nm. Treatments were based on eq 5 (main plot) and eq 6 (insert).

$$\frac{1}{A - A_0} = \frac{\epsilon_{\mathrm{N}}}{\epsilon_{\mathrm{N(C)_2}} - \epsilon_{\mathrm{N}}}\left(1 + \frac{1}{K[\mathrm{C}]^2}\right) \tag{5}$$

Here, A is the absorbance measured as a function of α-CD concentration, A_0 is the absorbance in the absence of α-CD, and $K \approx K_1K_2$. The extinction coefficient at $\lambda = 290$ nm for naphthalene in neat aqueous solution was determined as $\epsilon_{\mathrm{N}} = 2060\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$. The corresponding plot generated from absorbance data with [α-CD] ranging from 0.005 to 0.05 M is shown in Figure 15. The good linearity of the plot confirms the validity of the model. The extinction coefficient of the 1:2 complex at $\lambda = 290$ nm results as $\epsilon_{\mathrm{N(C)_2}} = 4900\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$, and the association constant for 1:2 complex formation as $K = 3200\ \mathrm{M}^{-2}$, in satisfactory agreement with the treatment based on the triplet data.

A related approach consists of assigning the absorbance measured at high α-CD concentration ([C] > 0.05 M), $A_{\max}$, to the 1:2 complexes. The complexation process is then described by

$$\frac{A - A_0}{A_{\max} - A} = K[\mathrm{C}]^2 \tag{6}$$

The corresponding plot, generated from the same absorption measurement ($\lambda = 290$ nm), is shown in the insert of Figure 15. Again, the linearity of the plot is excellent. The association constant now results as $K = 3800$ M^{-2}.

The performed analysis of complex stoichiometry in the naphthalene/α-CD system demonstrates beyond doubt that 1:2 guest:host complexes are by far predominant over a wide range of host concentrations. The second association step (reaction 2) is so much more efficient than the first one (reaction 1) that, kinetically speaking, the formation of the 1:2 complexes may well be described as a concerted process. Moreover, the good agreement between the treatments based on eq 5 on one hand and eq 6 on the other indicates that the absorbance data are consistent with 1:2 complex formation even at the highest concentrations of α-CD; there is no indication of a contribution from higher-order complexes.

A comparably thorough analysis of complexation stoichiometry in the naphthalene/β-CD system could not be performed on account of the much weaker influence of complexation on the spectroscopic data, in particular on ground-state absorption and triplet decay kinetics. Attempts to use these measurements in the same way as described above for the α-CD system did not allow an unequivocal decision in favor of a specific complexation model. The only conspicuous data on which to base a discussion are the fluorescence spectra (Figure 5) and lifetimes (Table 1). The appearance of an excimer-type emission band at high concentrations of both host and guest (Figure 5) is a strong indication of the formation of 2:2 complexes. As previously shown by Hamai,[2,4–6] this behavior is common in the association between β-CD and naphthalene or substituted naphthalenes, and can be exploited to yield the equilibrium properties of successively formed 1:1 and 2:2 complexes. Using Hamai's data,[2] 2:2 complexation should be nearly quantitative at [β-CD] = 0.01 M provided the naphthalene concentration exceeds $\approx 10^{-5}$ M. This conclusion is at variance, however, with the observation of a major nonexcimer component around 340 nm in the emission spectrum under these conditions, as shown in Figure 5; this band is undistinguishable from that of the naphthalene monomer emission. The quantitative contribution of excimers cannot be deduced from these data, but it should be noted that the naphthalene monomer (^{1}L$_b \rightarrow {}^1$A) emission is symmetry-forbidden and thus has low intensity. The excimer may therefore well have a higher transition moment than the monomer; this is in agreement with the observation that reducing the temperature enhances the emission of the 420 nm band more than it reduces that of the 340 nm band (Figure 5). It can be inferred from these considerations that the species responsible for the excimer emission in the presence of β-CD is not in the majority in the conditions used for the larger part of the measurements discussed in the present work. This conclusion is supported by the comparatively small decrease of the monomer triplet–triplet absorption with decreasing temperature, and by the absence of an exciton splitting in the induced circular dichroism; this signature of interchromophore interaction in the 2:2 complex is clearly observed in the 4-hydroxybiphenyl/α-CD system, to give an example.[13] Furthermore, the clear difference in fluorescence decay times observed for the two mentioned emission bands (see Table 1), both of which were extracted from monoexponential decays, underlines that they originate from distinct species. At [β-CD] = 0.01 M, a major contribution of free aqueous naphthalene to the 340 nm band is unlikely because the corresponding decay component was absent. This band is therefore assigned to the 1:1 complexes between naphthalene and β-CD, although a contribution from 2:2 complexes that do not give exciplex emission cannot be ruled out, as will be discussed below.

Structures and Photophysics of Cyclodextrin Complexes. Formation of the CD inclusion complexes has the effect of increasing both fluorescence quantum yield and lifetime with respect to those in neat aqueous solution. The values listed in Table 1 show that the fluorescence properties of the 1:2 complex with α-CD are near to those in the organic solvents. The same is true for the β-CD complexes that give excimer emission, whereas the properties of the nonexcimer emitting β-CD complexes are intermediate between the organic and the aqueous media.

The triplet–triplet absorption properties are characterized by a spectral red shift in both cyclodextrins with respect to the neat solvents (see Figure 6). This shift parallels that seen in the ground-state absorption; it can be interpreted as reflecting a polarizability-induced stabilization of the Franck–Condon state in the inclusion complex. The bandwidths in the CD complexes are significantly different from those in the neat solvents: that in the β-CD complex is intermediate between those in acetonitrile and water, whereas that in the α-CD 1:2 complex is narrower even than that in hexane.

The sensitivity of the spectroscopic properties of naphthalene to the presence of an aqueous environment can be exploited to get information about the nature of the host–guest interaction prevalent in the CD complexes. The experimental observations are consistent with the complex structures determined by means of the model calculations (Figures 11, 12, and 13), which show that in the α-CD 1:2 and the β-CD 2:2 complex the naphthalene guests are well shielded from the aqueous environment. The environment provided by the cyclodextrin host can be compared to that of an alcohol solvent.[10] Taking the value of the fluorescence lifetime as a gauge for water accessibility, a comparison with the results obtained in the water/ethanol mixed solvent system (Figure 3) likens the β-CD 1:1 complex to a mixture with $x(\mathrm{H_2O}) = 0.85$, and the α-CD 1:2 complex as well as the β-CD exciplex-forming 2:2 complex to a mixture with $x(\mathrm{H_2O}) = 0.47$.

Accessibility to water is a dynamic process and will depend on the flexibility of the complex. In this respect, the model calculations point to significant differences between the α-CD 1:2 complexes and the β-CD 2:2 complexes. In the latter, the two guests have an unusally high flexibility within a rather stable cavity defined by two β-CD hosts. Structures with a sandwich-type naphthalene dimer structure are, however, less favorable than conformations with orbitally decoupled chromophores. These latter structures might not be spectroscopically discernible from 1:1 complexes; they might contribute to the fluorescence behavior observed at high β-CD concentrations, as mentioned above. If we assume, however, that the fluorescence lifetime is mainly determined by the accessibility of the chromophore to the aqueous environment, all 2:2 structures should show similar τ_F values. The fact that τ_F is significantly shorter for the short-wavelength emission (60.9 ns) than for the excimer emission (90.7 ns) can therefore be taken as an indication that 1:1 complexes are majority. This conclusion is supported by the triplet decay kinetics in the β-CD complexes, which show that shielding of the included guest toward interaction with O_2 is inefficient.

The inherently greater rigidity of α-CD compared to β-CD, and the tightness of the guest inclusion in the α-CD 1:2 complex result in a somewhat less favorable interaction between the two host molecules. The calculations indicate the possibility of a wobbling motion of the two α-CD moieties, which could allow temporary exposure of the guest to the bulk. Some spectroscopic and kinetic consequences of this dynamics can be seen in the temperature dependences of the naphthalene fluorescence and triplet properties. The loss of the vibronic substructure in fluorescence emission (Figure 4) as well as the broadening of the main triplet−triplet absorption band (Figure 10) indicates that the environment of the molecule becomes more “water-like” when the temperature is increased. This observation is consistent with the fact that the differences of the rate constants for O_2 quenching and triplet−triplet annihilation between the α-CD and β-CD complexes become small at temperatures exceeding 50 °C (Figure 9). The activation energies measured for these reactions are different for each system, but do not depend on the type of reaction. The values found in neat aqueous solution and in β-CD are both within the range expected for diffusion-controlled reactions in an aqueous environment,[42] in agreement with the diffusion-controlled character of both reactions.[43] In α-CD, however, a distinctly higher activation energy is observed. The similarity of the temperature dependences for O_2 quenching on one hand and for triplet−triplet annihilation on the other indicates that a second activated process is seen in the 1:2 complex, besides reactant diffusion, which quite likely is related to its conformational flexibility.

It seems unlikely that triplet molecules which are tightly included in a 1:2 complex should be able to decay by triplet−triplet annihilation, since this process requires orbital overlap between the reaction partners. This reaction might become possible due to a rapid dissociation−reassociation equilibrium of triplet naphthalene with the host, as has been observed for the related systems of the naphthyl-1-ethanols with β-CD;[9] the fact that the spectral shift of the triplet−triplet absorption, which is the signature of the complex, prevails at higher temperatures indicates, however, that this is not the case in the naphthalene/α-CD system. Triplet−triplet annihilation as well as O_2 quenching may, therefore, take place on account of structural motions of the complex, without the need for dissociation.

It is instructive to compare the results for the naphthalene/α-CD system with those obtained earlier on the 1,4-dimethoxybenzene/α-CD system.[12] In the latter, 1:2 complexes are prevalent at suitably high α-CD concentrations, just as in the naphthalene case. There is a marked difference, however, in the temperature dependence of the triplet reactions; the slope of the Arrhenius diagram for O_2 quenching determined for the 1,4-dimethoxybenzene/α-CD 1:2 complex is not significantly higher than that found in aqueous solution, although the rate constants are smaller by more than 1 order of magnitude over the whole temperature interval.[12] In the spirit of the discussion outlined above, this can be interpreted as showing that the 1,4-dimethoxybenzene complex is conformationally too inflexible to allow a contact between the included triplet and the quencher by way of a transient opening of the complex. The computed complex energies (Table 2 and ref 12) are very similar, but a closer look at the structural details shows that both the host carbohydrate moieties and the guest aromatic frame are distorted as a consequence of the tight inclusion of naphthalene, whereas 1,4-dimethoxybenzene fits into the cavity without inducing a distortion. We may conclude that very small structural alterations are able to induce quite substantial differences in the dynamic behavior of cyclodextrin host−guest complexes.

A further interesting difference between the naphthalene/α-CD and 1,4-dimethoxybenzene/α-CD systems is revealed by the observation that for the latter system the intermediate formation of a 1:1 complex could be evidenced,[12] whereas for naphthalene the association constant of the second step is at least 3 orders of magnitude higher than that of the first step. This raises the interesting question of the role of the guest in the dynamics of the formation of the 1:2 complex. A comparison of the structures computed for the 1:1 complexes shows that 1,4-dimethoxybenzene is considerably better included in the α-CD cavity than naphthalene. This appears to confer a stability to the 1:1 complex which is less favorable for the addition of the second CD moiety in comparison to the naphthalene case.

Conclusions

The application of different spectroscopic methods (absorption, steady-state, and time-resolved fluorescence, induced circular dichroism, and triplet−triplet absorption) has provided a comprehensive picture of the photophysics of naphthalene in aqueous solutions (H_2O and D_2O) and in CD inclusion complexes. The reduction of the fluorescence lifetime in aqueous media with respect to that in organic media finds a probable explanation in an enhancement of the intersystem crossing rate, which may be due to a specific interaction between naphthalene and H_2O or D_2O. The possibility to observe this previously undetected effect is linked to the slow excited-state deactivation rates of the unperturbed molecule; for the same reason, the fluorescence of naphthalene is a sensitive probe for the assessment of effects of CD inclusion complexation. Of equal sensitivity are the naphthalene triplet properties on account of the narrow bandwidth of the triplet−triplet absorption and the large impact of complexation on triplet quenching and annihilation reactions.

As in previous studies,[10−13] the confrontation of experimental data with model calculations of complex structures has been invaluable in strengthening stoichiometric assignments and in allowing structural interpretations. In the cases of the 1:2 and 2:2 complexes of naphthalene with α-CD and β-CD, respectively, this approach opens a window on the structural flexibility of the complex and its possible causes.

Acknowledgment. K.R. is indebted to S. Monti (Istituto FRAE-CNR, Bologna, Italy) for the possibility to use the spectropolarimeter. K.R. and G.K. thank the Fonds zur Förderung der wissenschaftlichen Forschung (projects P09750-CHE and P11880-CHE) for financial support. The Polish Committee of Scientific Research and the Austrian Ministry for Research are acknowledged for financial support (projects 01-03 and 06/R98/R99) in the framework of the Austrian−Polish Convention of Scientific and Technological Cooperation. B.M. thanks the Austrian Academy of Sciences for financial support within the APART program.

References and Notes

(1) Bortolus, P.; Monti, S. *Adv. Photochem.* **1996**, *21*, 1.

(2) Hamai, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2721.

(3) Yamamoto, K.; Nakao, T.; Yonemochi, E.; Oguchi, T. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1996**, *25*, 121.

(4) (a) Hamai, S. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 543. (b) Hamai, S.; Hatamiya, A. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2469.

(5) (a) Hamai, S.; Monobe, N. *J. Photochem. Photobiol., A*: *Chem*. **1995**, *91*, 217. (b) Hamai, S. *J. Phys. Chem. B* **1999**, *103*, 293.

(6) Hamai, S. *J. Phys. Chem*. **1990**, *94*, 2595.

(7) (a) Hamai, S. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1997**, *27*, 57. (b) Hamai, S.; Ikeda, H.; Ueno, A. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1998**, *31*, 265.

(8) (a) Du, X. Z.; Zhang, Y.; Huang, X. Z.; Li, Y. Q.; Jiang, Y. B.; Chen, G. Z. *Spectrochim. Acta, Part A* **1996**, *52*, 1541. (b) Du, X. Z.; Zhang, Y.; Huang, X. Z.; Jiang, Y. B.; Li, Y. Q.; Chen, G. Z. *Appl. Spectrosc.* **1996**, *50*, 1273. (c) Du, X. Z.; Zhang, Y.; Jiang, Y. B.; Lin, L. R.; Huang, X. Z.; Chen, G. Z. *J. Photochem. Photobiol., A*: *Chem*. **1998**, *112*, 53. (d) Hamai, S. *Bull. Chem. Soc. Jpn*. **1998**, *71*, 1549.

(9) Barros, T. C.; Stefaniak, K.; Holzwarth, J. F.; Bohne, C. *J. Phys. Chem. A* **1998**, *102*, 5639.

(10) Monti, S.; Köhler, G.; Grabner, G. *J. Phys. Chem*. **1993**, *97*, 13011.

(11) Park, H.-R.; Mayer, B.; Wolschann, P.; Köhler, G. *J. Phys. Chem*. **1994**, *98*, 6158.

(12) Grabner, G.; Monti, S.; Marconi, G.; Mayer, B.; Klein, Ch. Th.; Köhler, G. *J. Phys. Chem.* **1996**, *100*, 20069.

(13) Bortolus, P.; Marconi, G.; Monti, S.; Mayer, B.; Köhler, G.; Grabner, G. *Chem. Eur. J.*, in press.

(14) Köhler, G.; Grabner, G.; Klein, Ch. Th.; Marconi, G.; Mayer, B.; Monti, S.; Rechthaler, K.; Rotkiewicz, K.; Viernstein, H.; Wolschann, P. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1996**, *25*, 103.

(15) Davis, W. W.; Krahl, M. E.; Clowes, G. H. A. *J. Am. Chem. Soc.* **1942**, *64*, 108.

(16) (a) Köhler, G.; Rotkiewicz, K. *Spectrochim. Acta A* **1986**, *42*, 1127. (b) Köhler, G.; Wolschann, P.*J. Chem. Soc., Faraday Trans. 2* **1987**, *83*, 513.

(17) Berlman, I. B. *Fluorescence Spectra of Aromatic Molecules*; Academic Press: New York, 1971.

(18) Grabner, G.; Getoff, N.; Gantchev, T.; Angelov, D.; Shopova, M. *Photochem. Photobiol*. **1991**, *54*, 673.

(19) Allinger, N. L.; Yuh, Y. H.; Lee; J. H. *J. Am. Chem. Soc.* **1989**, *111*, 8551.

(20) (a) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. B.; Teller, A. H. *J. Chem. Phys. 1953*, *21*, 1087. (b) Kirkpatrick, S.; Gelatt, C. D.; Vecchi, M. P. *Science* **1983**, *220*, 671.

(21) Mayer, B. Program Package MultiMize, 1997.

(22) Kodaka, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 3702.

(23) Nakanishi, K.; Berova, N. In *Circular Dichroism, Principles and Applications*;VCH: Darmstadt, Germany, 1994; Chapter 13.

(24) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.

(25) Bensasson, R.; Land, E. J. *Photochem. Photobiol. Rev*. **1978**, *3*, 163.

(26) Carmichael, I.; Helman, W. P.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1987**, *16*, 239.

(27) Hamai, S. *J. Phys. Chem.* **1995**, *99*, 12109.

(28) Betzel, C.; Saenger, W.; Hingerty, B. E.; Brown, G. M. *J. Am. Chem. Soc.* **1984**, *106*, 7545.

(29) Mayer, B.; Klein, Ch. Th.; Marconi, G.; Köhler, G. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1997**, *29*, 79.

(30) Marconi, G.; Mayer, B.; Klein, Ch. Th.; Köhler, G. *Chem. Phys. Lett*. **1996**, *260*, 589.

(31) Marconi, G.; Monti, S.; Mayer, B.; Köhler, G. *J. Phys. Chem*. **1995**, *99*, 3943.

(32) Mayer, B.; Köhler, G. *THEOCHEM* **1996**, *363*, 217.

(33) (a) Harada, A.; Li, J.; Kamachi, M. *Nature* **1994**, *370*, 126. (b) Mayer, B.; Klein, Ch. Th.; Topchieva, I. N.; Köhler, G. *J. Comput.-Aided Mol. Des.* **1999**, *13*, 373.

(34) *Handbook of Photochemistry*, 2nd ed.; Murov, S. L., Carmichael, I., Hug, G. L., Eds.; Marcel Dekker: New York, 1993.

(35) Amand, B.; Bensasson, R. *Chem. Phys. Lett*. **1975**, *34*, 44.

(36) (a) Mataga, N.; Tomura, M.; Nishimura, H. *Mol. Phys*. **1965**, *9*, 367. (b) Li, F.; Lee, J.; Bernstein, E. R. *J. Phys. Chem*. **1983**, *87*, 1175.

(37) Lahmani, F.; Zehnacker-Rentien, A.; Breheret, E.; Ebata, T. *J. Chem Soc., Faraday Trans*. **1993**, *89*, 623.

(38) Henry, B. R.; Siebrand, W. *J. Chem. Phys*. **1971**, *54*, 1072.

(39) (a) Engdahl, A.; Nelander, B. *J. Phys. Chem.* **1985**, *89*, 2860. (b) Suzuki, S.; Green, P. G.; Bumgarner, R. E.; Dasgupta, S.; Goddard III, W. A.; Blake, G. A. *Science* **1992**, *257*, 942. (c) Gotch, A. J.; Zwier, T. S. *J. Chem. Phys*. **1992**, *96*, 3388.

(40) Bayliss, N. S.; Hulme, L. *Aust. J. Chem.* **1953**, *6*, 257.

(41) Urahata, S.; Coutinho, K.; Canuto, S. *Chem. Phys. Lett*. **1997**, *274*, 269.

(42) Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; Clarendon Press: Oxford, UK, 1969; p 205.

(43) Saltiel, S.; Atwater, B. W. *Adv. Photochem*. **1988**, *14*, 1.