Ultrafast Guest Dynamics in Cyclodextrin Nanocavities

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Contents

Abderrazzak Douhal, born in 1959, was educated in Beni Mellal, Morocco. He received his Ph.D. degree in chemistry from the Kadi Ayyad University (Marrakech) after working on solvation and photoinduced proton-transfer reactions at the same university and at the Institute of Physical Chemistry "Rocasolano" (CSIC, Madrid). From 1990 to 1992, he was a fellow of the Japanese Ministry of Education, Science and Culture and the JSPS for a two-year postdoctoral research position at the Institute of Molecular Science (Okazaki, Japan), working on ultrafast proton- and electron-transfer reactions dynamics in solution. In 1992, he joined the "Laboratoire de Photophysique Molecular" at Orsay (CNRS–University of Paris-Sud) to work on photoinduced proton transfer in molecular beam. In 1993, he moved to the University of Castilla-La Mancha (Toledo, Spain) as an associate professor, and in 1998 as a full professor of physical chemistry. He was a visiting researcher at California Institute of Technology during several periods of time (1995–2000), working with Professor A. H. Zewail in femtochemistry of H-bonds in gas, liquids, and in nanocavities. His current research focuses on proton- and charge-transfer ultrafast dynamics in nano-hosts.

1. Introduction

The invention and development of laser technology and other related ultrafast techniques has opened and established new areas in molecular science called femtochemistry and femtobiology.[1−13] Experiments in these fields have allowed us to witness how electrons are ejected, trapped, and solvated, and how atoms can collide, interact, and give birth to ions and molecules, and also to visualize in real time the dynamical and structural changes of matter at the electronic, atomic, and molecular levels as one bond breaks to give birth to another one. These studies in the gas phase, in the solid state, or in bulk solutions including clusters have brought a fundamental knowledge about the reactivity and stability of matter at the atomic and molecular levels. Therefore, fundamental knowledge has been acquired, providing new perspectives on a wide range of reactions playing a key role in many important fields ranging from atmospheric chemistry to semiconductors and biological molecules such as DNA or proteins.[1−13] In this special issue of *Chemical Reviews*, the reader will find extensive and precise information on the development and achievements in the field from the point of view of theory and experiments. In this review, we will survey the reports on fast and ultrafast dynamics (solvation, proton transfer, charge transfer, bond breaking and formation, twisting motion, hydrophobic interaction, etc.) in cyclodextrin cavities. Our aim is to provide a global but also a detailed picture of key events in the confined cyclodextrins systems. The collected information (up to August 2003) is relevant for a better understanding of many chemical and biological systems where the confinement effect is important for reactivity and function.

2. Concept of Femtochemistry in Nanocavities

Except for the area of atmospheric chemistry, where reactions happen in the gas phase (or clusters), most of the reactions in nature occur in the condensed phase (solid or liquid phase) and are influenced by the chemical and biological environment, such as polarity, dielectric friction, viscosity, acidity/basicity, H-bonding interactions, and caging. The first five effects are widely studied in several chemical and biological systems from the point of view of structural

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and dynamical (femtosecond time scale) changes. However, the femtochemistry of the caging effect due to a molecular pocket has been studied mainly for relatively small systems (like the iodine molecule), and recently the study has been extended to large molecules (aromatic systems) in chemical and biological hosts.[14−30] Caging a molecule into a molecular pocket (nanochamber) produces a confined system with interesting physical and chemical properties. It reduces the degrees of freedom available to the molecule to move along the reaction coordinates and confines the wave packet in a small area of propagation.[31] By reducing the space for relaxation, it makes the system robust and immune to transferring "damage" or heat over long distances.[4] Using femtosecond techniques and selecting the size and nature of the molecular chamber offered by the host to the guest, one will be able therefore to explore and control the spectroscopy (space domain) and dynamics (time domain) of chemical and physical changes in real time. Therefore, the reaction and product(s) can be controlled, as has been demonstrated in "shaping and sizing" the chemistry and physics of nanoparticles.[32−36]

Another class of confined systems having a strong interaction between the guest and the host was investigated.[37,38] The authors studied the spectroscopy and dynamics of low-lying Rydberg states of an impurity molecule (in their case NO) embedded in a low-temperature rare gas matrix cage.[37,38] The interest in this concept is that excitation of Rydberg states (6 eV) leads to electron orbitals of the same size as the first shell of the matrix. This induces a strong repulsive interaction between the Rydberg orbital and the closed-shell rare gas atoms, which leads to an expansion of the latter and the formation of a "bubble", with increases of the first shell radius by 10% (in Ar) to 30% (in D_2) compared to that of the ground state.[37,38] In matrices such as Ne and Ar, the authors could identify the inertial response of the medium upon impulsive femtosecond excitation and coherent oscillations due to the response of the bath to the impulsive perturbation.[38] The latter is quite remarkable, as it represents the first evidence for vibrational coherence in the modes of the bath (albeit a soft crystal in this case). In softer solids such as solid hydrogen, the medium response is characterized by a one-way expansion of the first shell of atoms and a very efficient dissipation of energy into the solids, probably in the form of a shock wave.[38]

Following an ultrafast electronic excitation of the embedded guest in a nanochamber, the nascent wave packet is trapped in a small area of the potential energy surface (caged wave packet), and its evolution along this surface and the subsequent relaxation dynamics to other states (or through chemical reactions) will funnel and will be controlled by the restricted confined geometry. Cooling (or vibrational relaxation) due to a fast (picosecond regime) exchange of heat with the environment (caging medium) might be also controlled by changing the nature or the size of the cage. It is very well known that the nature of the solvent plays a key role in a chemical reaction, in bulk solvent and in a cavity. Understanding the ultrafast dynamics for different cages may help us

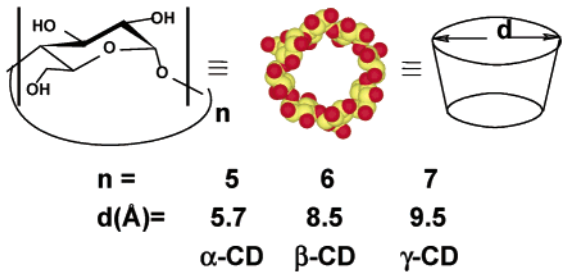

Figure 1. Structures of cyclodextrins (CDs) and approximate values of the largest diameter of their nanocage.

to better understand the catalytic mechanism in these cavities, like those involved in enzymes and zeolites. Water is a universal solvent and is known to have anomalous properties due to the nature of the H-bonds.[39−42] One of the interesting phenomena in studying nanocavity solvation is the slow solvation of water confined in a nanospace such as those offered by cyclodextrins. This special water is reminiscent of the water located at the surface of biological molecules, and it is under intensive studies from the point of view of theory and experiment.[43−63] Recently, a review on dielectric relaxation and solvation dynamics of water in chemical and biological systems has been published.[43] Here, we are mainly concerned with the reports on the dynamics of guests caged by cyclodextrin nanocavities in water solutions. Those involving longer time scales (i.e., longer than a 100 ps time constant) may include other processes like decomplexation of the nanostructure formed by the guest and the host, and self-motion of these entities will not examined here.

3. Cyclodextrin Nanocavities

The ability of cyclodextrins (CDs) (Figure 1), oligosaccharides of six, seven, or eight D-glucopyranose ($C_6H_{10}O_5$) units (the three popular and well-known ones are α-, β-, and γ-CD with diameters of ~5.7, 8.5, and 9.5 Å, respectively), to encapsulate organic and inorganic molecules has led to intensive studies of their inclusion complexes.[64−72] The relatively hydrophobic interior and hydrophilic exterior of their molecular pockets make them suitable and fascinating hosts for supramolecular chemistry and for studying the spectroscopy and dynamics of several molecular systems.[73−115] Therefore, the hydrophobic nanocavity of such hosts offers a unique opportunity for studying size-controlled nanoenvironment effects such as reduced degrees of freedom of the guest and modified coupling to the heat reservoir. On the other hand, the dynamics of water molecules found at both gates of CD (Figure 2) is reminiscent of that of biological water,[43,59,63] and their studies will shine some light on the anomalous behavior of biological water dynamics.

Several studies on CD complexes with aromatic molecules using steady-state and nanosecond spectroscopy have been reported. These studies aimed to understand and control the photophysical and photochemical behavior of organic guests such as fluorescence and phosphorescence enhancement, excimer/exciplex formation, photocleavage, charge and proton

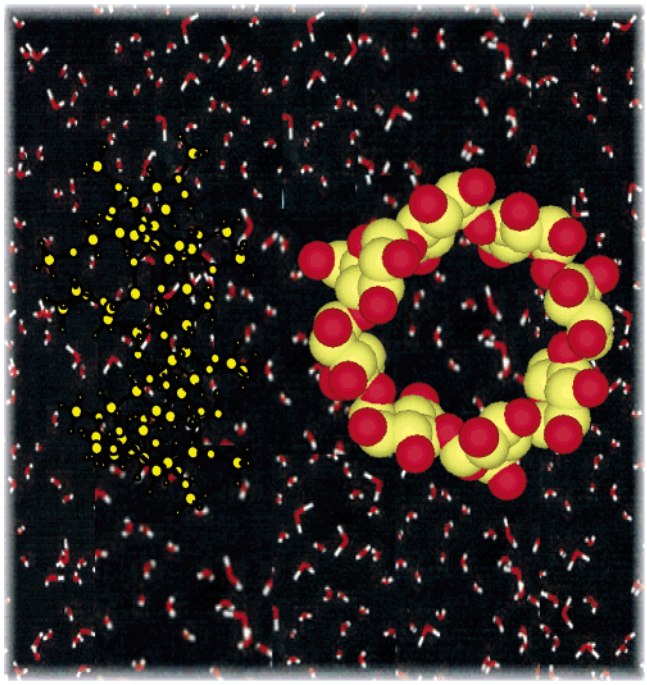

Figure 2. Schematic representation (not to scale) of β-CD nanocavity cage in a water environment.

transfer, energy hopping, and *cis*−*trans* photoisomerization. Most of these reports show the effects of molecular restriction, due to the cavity size of the host and protection of the guest (from quenchers such as oxygen molecules and H-bonding interaction with the medium, water) provided by CD cavity and its low polarity relative to that of water, on the photophysical and photochemical properties of the encapsulated guest. The presence of H-bonding, electron-accepting, and electron-donating groups and twisting groups influences the electronic properties of the encapsulated guest. The inclusion equilibrium constant depends on several parameters where H-bonding, polarity, and size of the guest relative to that of the cavity play important roles in the stability of the relative population of the confined system. Both enthalpic and entropic terms determine the energetic balance between the free and encapsulated guest. Some of the studies have shown the formation of higher stoichiometries (1:2, 2:1, and 2:2) or even the formation of nanotubes where a large number of CD capsules is involved.[71−73,100−108] A general rule to predict the effect of CD on the absorption and emission properties of dyes upon encapsulation cannot be determined, as the static and dynamic interactions are specific to the studied systems and might strongly change at the excited state.

Therefore, the chemistry of CDs is very rich, and many applications at the laboratory as well as at the industrial level have been proposed or done.[64−115] For example, CDs are being used as building blocks, nanoreactors, nanoprotectors, nanocapsules, and nanodelivering agents, fabric softeners, and antibacterial sheets, and for the removal of cholesterol in food production processes, recognition of amino acids, and innumerable uses in several fields—chemistry, cosmetics, foods, agriculture, pharmacy, and medicine to name a few. For example, recent reports suggested potential applications of the iodine molecule in the

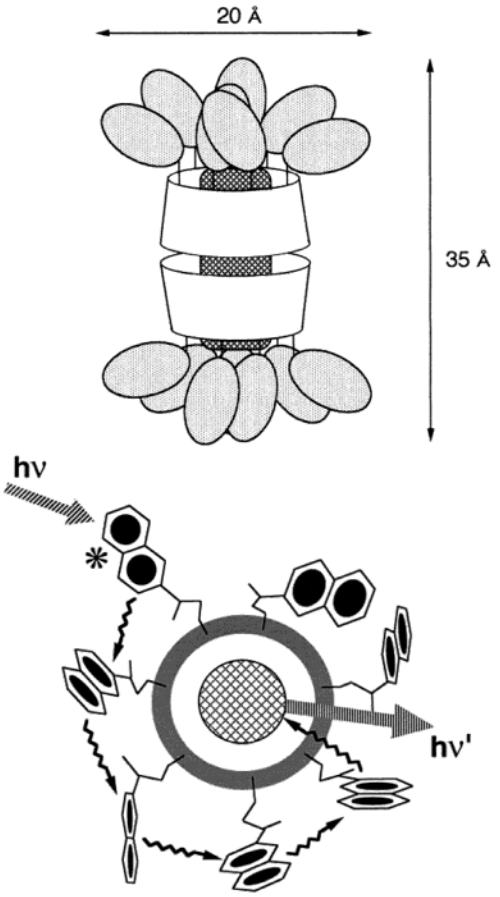

Figure 3. Schematic illustration of energy hopping and conversion in a complex formed between an encapsulated guest (the DCM-OH dye) and naphthalenic parts of a CD derivative. Adapted from ref 113.

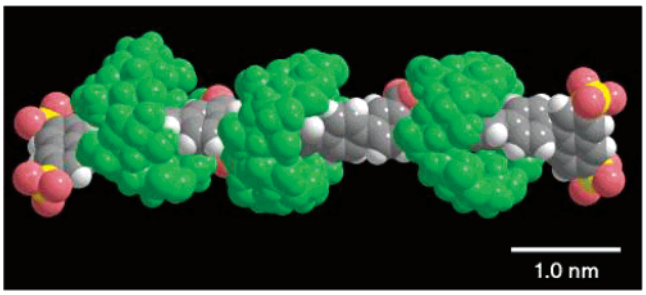

Figure 4. Fluorescent conjugated polymer chains entrapped by several CD cavities have been used to prepare blue and green-light-emitting diodes. Adapted from ref 114 with permission from the authors.

treatment of breast lesions.[109,110] The CD capsule forms a complex with iodine and serves as a carrier of these species that might be gradually released in the body. Modified CDs have been used for molecular switches,[111] energy conversion and storage (Figure 3),[112,113] and photonics (Figure 4),[114] and in making gold nanoparticles (size of ∼2−2.4 nm) by femtosecond laser ablation of a gold metal plate in an aqueous solution of CD.[115] So, besides the acquired fundamental knowledge, there are potential nanotechnological applications using light and involving CD. We will not review the nanosecond reports here, as we are concerned in this work with fast and ultrafast processes occurring on picosecond (ps) and femtosecond (fs) time scales inside and at the doors of the CD

nanocavities. In a few cases, we will compare the observed dynamics with that found using other cavities, such as micelles, proteins, sol−gel, and zeolites.

4. Picosecond Studies in CD Nanocavities

4.1. No Hydrogen-Bonding Guests

The effect of the charge and size of the guest on the behavior of the confined geometry offered by CD complexes has been examined using resorufin (anion), oxazine 118 (cation), and oxazine 725 (cation) in the presence of β-CD.[116] Time-resolved anisotropy experiments gave the rotational time of the guest inside the nanocage and the overall rotational time involving the CD host (Figure 5). The results show the relationship between the relative guest:host size and the character of intermolecular confined dynamics. For smaller guests (in size), i.e., resorufin and oxazine-118, a fast decay component (about 60 ps) was observed and assigned to the internal rotation of the guest inside the molecular box. In contrast, for the larger guest, oxazine-725, no fast component was observed which could be assigned to an internal rotation of the guest. The anisotropy decay using β-CD is monoexponential with a time constant of 405 ps, attributed to the overall complex (Figure 7). Clearly, the relationship between the size of the guest and that of the nanocavity is an important factor for the relaxation of CD complexes. The result of modeling of the guest:host confined structure is consistent with the observed size effect.[116] From the rotational relaxation data, a mean-square angle for the internal rotation of the guest was calculated, resulting in 18° and 20° for the resorufin and the oxazine, respectively. The similarity of these values indicates that, for averaged structures, the confined geometries are comparable.[116] While the intermolecular guest:host dynamics should be very fast, that responsible for molecular recognition and fitting (formation of the complex) should occur in the nanosecondto millilsecond regime. The robustness of the complex and resulting confinement should be determined by hydrophobic interactions which can be broken on a short time scale (picosecond to nanosecond regime), as was observed in guests which may undergo twisting motions, producing different structures.

Cis−trans isomerization along a carbon−carbon (C═C) double bond is one of the most studied photoreactions in chemistry, and stilbene (and its derivatives) constitutes the most popular prototype of molecular systems undergoing this kind of reactions.[117−127] It has been shown that the photochemistry of stilbene and its conversion to one of the isomers (cis or trans), and photocyclization of the cis isomer, can be affected by the presence of β-CD.[126,127] The trans-to-cis isomer photoreaction is inhibited in the cage, while that of the reverse process is not restricted. The molecular restriction to rotation, due to the confinement as discussed previously, was examined in a picosecond study of *trans*-stilbene photoisomerization in CD (Figure 6).[127] The fluorescence decay of *trans*-stilbene in α-CD gives a time constant, 137 ps, similar to that observed in viscous media, such as 1-octanol and 1-decanol. However, in

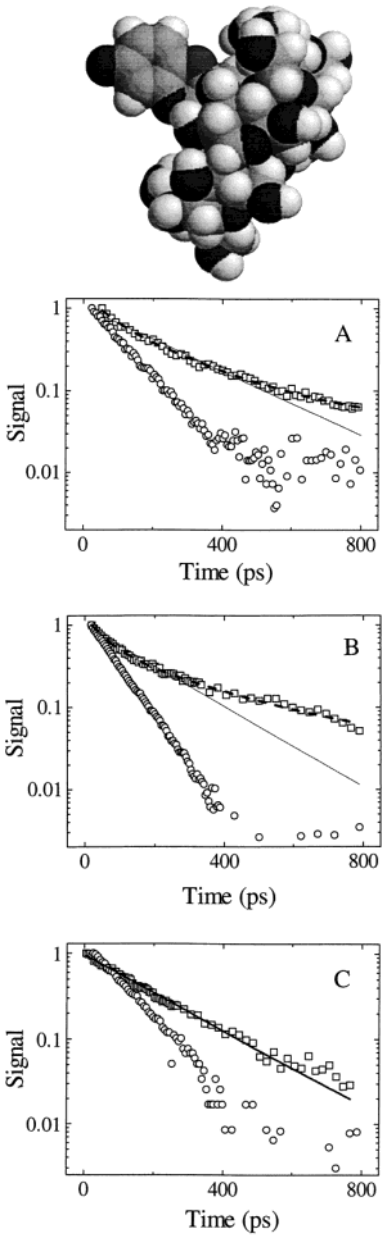

Figure 5. Relative host−guest confined geometry of the resorufin:β-CD complex, and anisotropy decays for resorufin (A), oxazine-118 (B), and oxazine-725 (C) in water (○) and in the presence of β-cyclodextrin (□). Single-exponential (solid line) and double-exponential (dashed line) fits are shown for the decay of chromophore in aqueous solution of CD. Adapted from ref 116 with permission from the authors.

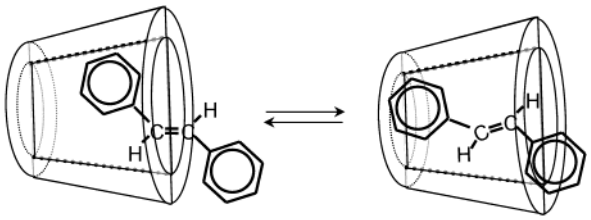

Figure 6. Schematic illustration of "loose" (left) and "tight" (right) 1:1 complexes of *trans*-stilbene and β-CD.

the presence of β-CD, the fluorescence decay was fitted using a biexponential function. The fastest component, with a time constant of 35 ps, was assigned to a "loose" 1:1 complex, while the longer

one (450 ps) was attributed to the tight 1:1 complex (Figure 6).[127] The larger degree of docking for the tightly confined geometry decreases the radiationless rate constant due to twisting motion, and thus increases the fluorescence lifetime of the caged trans isomer. Therefore, the rate of the trans−cis reaction inside β-CD is reduced. Both structures interconvert within the time scale of isomerization inside the cavity, and their populations depend on the temperature. The tightly confined structure is favored at low temperatures, while the loose one dominates at high temperatures.[128]

The fluorescence lifetime (τ_f) of *trans*-stilbene has been measured in zeolites NaY and ZSM-5 and in the presence of coadsorbed solvents.[128] These zeolites offer a wider cage to accommodate the stilbene molecules. In dehydrated NaY, τ_f is 52 ps, compared to 66 ps in hexane and 32 ps in methanol. Thus, in a NaY supercage, *trans*-stilbene undergoes a trans-to-cis photoreaction, and caging it in a dehydrated zeolite provokes only a small change in the fluorescence lifetime. The fluorescence lifetime (52 ps) is not very different from that assigned to a loose 1:1 complex with β-CD (35 ps),[127] but it is shorter than that of the tight 1:1 entity (450 ps). However, upon wetting the NaY sample in either water or cyclohexane, the value of τ_f increases by a factor of 4 or 5, respectively. This reflects the decreased mobility of *trans*-stilbene due to blocking effects of the now embedded solvent (water or cyclohexane) in the supercage. However, with small amounts of coadsorbed water equivalent to 13 H_2O per supercage, τ_f decreased by a factor of 2, showing then the increased mobility of *trans*-stilbene in this environment. Small amounts of coadsorbed cyclohexane, however, slightly increased τ_f, indicating that water molecules prefer to H-bond the hall of the zeolite. In the solvent-free zeolites, τ_f values are significantly smaller (higher degree of probe mobility) than those published earlier[129] and contradict the earlier conclusions regarding the mobility of *trans*-stilbene in zeolites. A possible reason for the observed difference in the fluorescence lifetime of embedded *trans*-stilbene resides in the subnanosecond time resolution used in the earlier work.[129]

Cyanine dyes have several potential applications, for example in photographic sensitizing materials,[130] mode-locking, and lasing media.[131] In addition to these applications, the cis−trans isomerization reaction which takes place in these molecules is studied as a model of many photochemical events in biological systems.[132] Thus, the photophysics and photochemistry of these molecules have received attention from several groups.[133−138] The obtained results show the influence of the environment properties (such as polarity and viscosity) on their spectral and dynamical behavior. The hydrophobic nanocavities provided by CDs were used to study the photodynamics of a caged 1-(2-naphthyl)-2-ethenyl-(2-benzothazolium) iodide (1,2-NEB, Figure 7).[140] 1,2-NEB in solution suffers a photoinduced twisting motion, as does stilbene, and a subsequent intramolecular charge-transfer reaction.[141] We term the full photoreaction reaction as a twisted intramolecular charge-transfer

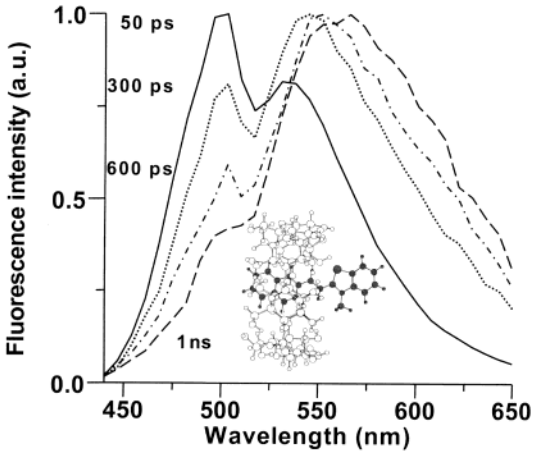

Figure 7. Time-resolved emission spectra (TRES) of *trans*-1,2-NEB in an aqueous solution of mM γ-CD at different gating times.[140] The inset shows the values of the gating time and the structure of a confined 1,2-NEN:γ-CD complex.

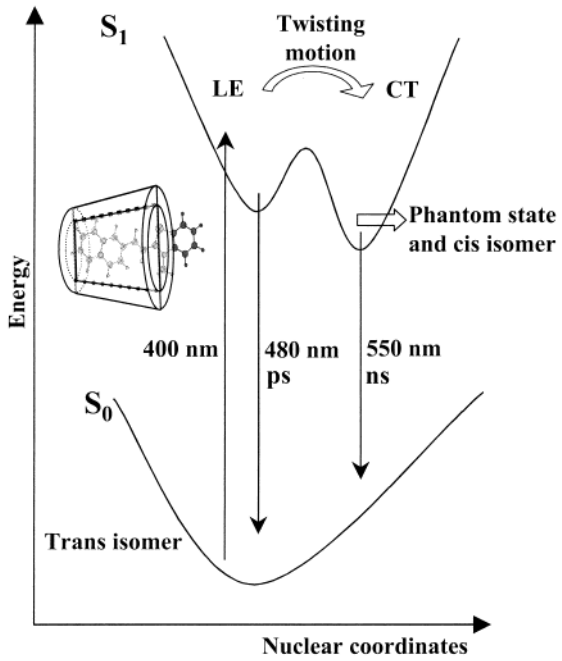

Figure 8. One-dimensional schematic energy profile for the photodynamical behavior of *trans*-1,2-NEB isomer in CD nanocavities. For simplicity, the potential wells of the phantom and cis isomers are not indicated. In media where the twisting motion is prevented (higher energy barrier), emission occurs from the local excited (LE) state. However, for media where the twisting is allowed (low energy barrier or barrierless potential energy surface), emission occurs from a charge-transfer (CT) state.[140]

(TICT) reaction. The study of 1,2-NEB in a nanocavity has provided information about the intramolecular charge-transfer reaction triggered by a fast twisting motion. The dye forms a 1:1 inclusion complex with β- and γ-CD[140] in which the naphthyl moiety is found in the cavity (Figure 7). The emission studies in aqueous solutions of CD show that the photoinduced twisting motion of 1,2-NEB along the middle C=C bond can be prevented by the size of the molecular box, controlling then the color of the emission and the dynamics of the TICT reaction in the guest. For a larger cavity (γ-CD) the emission

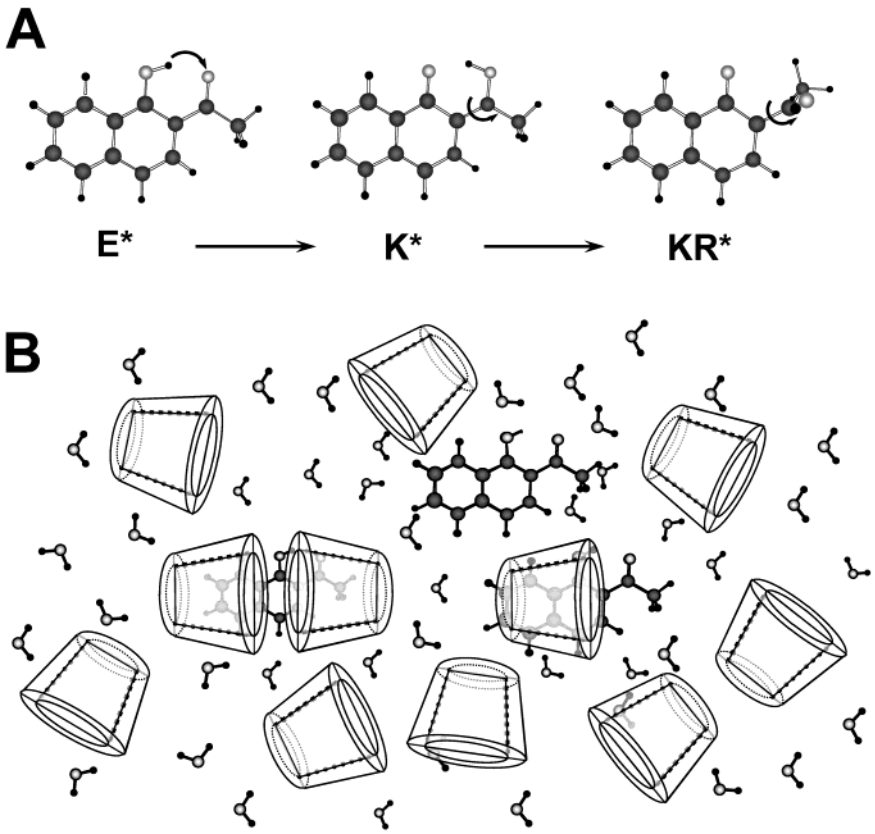

Figure 9. (A) Schematic representation of proton-transfer reaction in the enol form (E*) and twisting motion in the keto-type structure (K*) to generate the keto-rotamer (KR*) upon electronic excitation of 1′-hydroxy-2′-acenaphthone (HAN). (B) Illustration of free HAN in water and complexed with one or two CD molecules.

occurs at 550 nm, while for a small one (β-CD) the emission maximum is at 490 nm. The caged cis isomer resulting from a fast TICT reaction inside the host gives a yellow emission (550 nm) in the nanosecond regime.[140] It shows a dual emission in a larger cavity: emission from a nonrelaxed state (caged trans isomer) around 490 nm, and emission from a relaxed one (caged cis isomer). Therefore, depending on the size of CD, the *trans-cis* isomerization process of the caged cyanine dye can take place or not (Figure 8). The molecule can be used as a fluorescent probe for the size of chemical and biological nanocavities, as it has been shown for a system undergoing a fast proton-transfer reaction and twisting motion upon electronic excitation.[94−99,142] The emission behavior of 1,2-NEB:CD entity could be used for new potential applications of caged cyanine dyes in nanotechnology and for a better understanding of twisting motion in many chemical and biological systems.[143−145]

4.2. Hydrogen-Bonding Guests

While stilbene has a clear C═C bond at the ground state for which double-bond character is photoreduced upon electronic excitation, leading to a rich photochemistry and dynamics, 1′-hydroxy-2′-acetonaphthone (HAN) is an aromatic molecule with an internal H-bond and which is able to show double-bond character of the C−C bond between the acetyl group and the naphthalene moiety upon electronic excitation (Figure 9A). HAN has been studied in gas,[146−149] liquid,[150−152] polymers,[150] and in CD nanocavities.[152−154] The excited dye undergoes an ultrafast excited-state intramolecular proton-transfer (ESIPT) reaction, followed by a subsequent twisting motion along the C−C bond when the medium allows it (Figure 9A). The formed excited phototautmer, K*, called a keto-type structure and where the carbonyl group is on the aromatic ring, may experience an internal rotation, producing a twisted keto rotamer (KR*). The C−C bond linking the aromatic part to the protonated acetyl shows a double-bond character due the transfer of the proton and electronic charge rearrangement, as suggested by the ground- and excited-state ab initio calculations.[155,156] In the presence of CD, the stoichiometry of the formed inclusion complex depends on the nature and size of the cage. For β- and γ-CD, the complex has a 1:1 stoichiometry, while for α-CD, the stoichiometry is 1:2 HAN:$(\alpha\text{-CD})_2$ (Figure 9B). The spectroscopy and dynamics of the complexes have been also found to depend on the nature of the cage (Figure 10).[153,154] By comparison to the observations made using water or tetrahydrofuran (considered as a solvent with a polarity comparable to that of CD), the following picture has been provided. Due to the restriction offered by α- and β-CD cages, the rotation of the protonated acetyl group of the guest is restricted, giving rise to a stronger K* emission (460 nm). For γ-CD, a larger cage, the conversion of K* to KR* is allowed; the resulting emission is at 500 nm, and the phototautomers are more fluorescent due to the protection (from quenchers such as H-bond with water and O_2) provided by the cage. The lifetime of caged KR* is in the nanosecond regime, in contrast to that of free K*

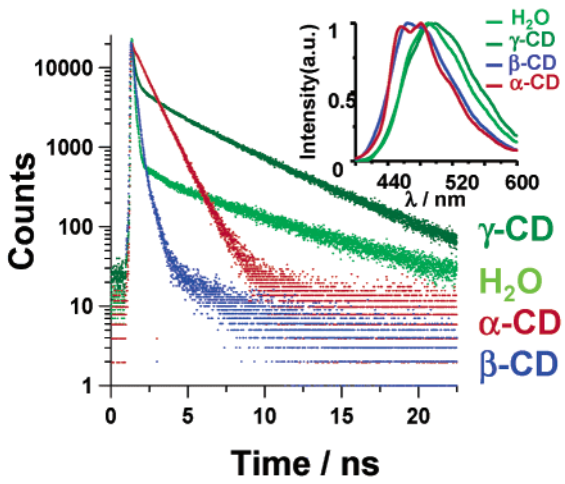

Figure 10. Emission decays of HAN in water and in the presence of millimolar concentrations of CDs. The inset shows the emission spectra of HAN in water and complexed to CDs.[152−154]

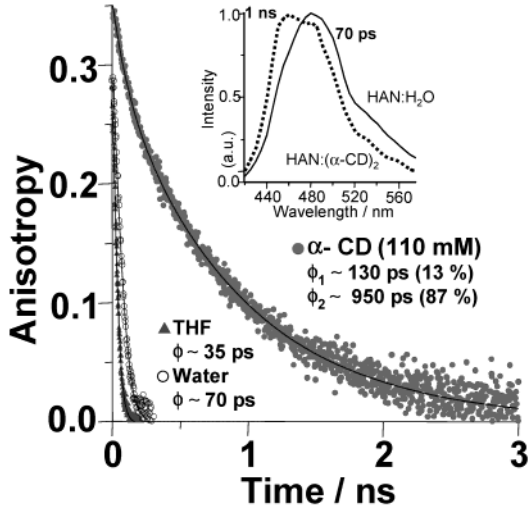

Figure 11. Anisotropy decays of HAN in water, tetrahydrofuran (THF), and in the presence of α-CD. The solid lines are the best fits using a single or a biexponential function giving the indicated rotational times. The inset also shows the gated emission spectra of the complexes at 70 ps and 1 ns.[154]

(about 90 ps). That of caged K* is on the subnanosecond or nanosecond time scale. Depending on the size of CD, the protonated acetyl group can be found inside or outside the cage. So, its twisting to produce KR* and connecting with nonradiative channels depend on the degree of confinement and the stoichiometry of the complex (Figure 10). The reorientation times of the guest and of the overall guest:host complexes have been examined using anisotropy experiments. For 1:1 complexes, this time is 70 and 47 ps for β-CD and γ-CD, respectively. Thus, for a small cage (β-CD), the internal molecular rotation in the trapped guest is restricted and its time is longer, while for a larger one, the internal rotation can occur, producing a caged KR* rotamer, in full agreement with the emission spectral position and fluorescence lifetime (Figure 10). As expected, the overall rotational time of the complex (HAN:CD) increases with the size of the caging entity: 745 ps and 1.1 ns for β- and γ-CD complexes, respectively.[153] For α-CD complexes the situation is different, as the complexes involve one or two H-bonded linked CD cavities (Figure 9).[154] Caged and photoproduced K* in 1:1 complexes has an emission lifetime, ∼90 ps, similar to that of free K* in water, while for the 1:2 complex the time is about 1 ns. For 1:1 complexes, the protonated acetyl group of K* is found outside the CD cavity, and it should not suffer any restriction for twisting to produce caged KR* (which was observed). For 1:2 complexes, restriction dictated by the cavity of two CDs does not allow the formation of KR* but enhances the nanosecond emission of caged K*, as it is now protected from quenchers and twisting nonradiative channels. The emission behavior of caged HAN in α-CD leads to a 40-nm blue shift (shortest wavelengths) in the time-resolved emission spectra when the gating time increases (Figure 11). The $COHCH_3$ rotation of K* to produce KR* involves an energy gain of about 16 kJ/mol, close to the energy gap (∼24 kJ/mol) between these structures in the gas phase obtained using theoretical calculations.[156] The rotational times of the complexes have been also measured (Figure 11). In pure solvents, such as water and tetrahydrofuran, the rotational times are 70 and 35 ps, respectively. These values show the role of H-bonding with the solvent (water) and the involvement of the solvation shell (water) in the friction dynamics of the dye. The rotational time of the caged phototautomers in α-CD cages depends on the emission wavelength, and it varies from 50 to 180 ps. The global rotational time of the 1:2 complex is almost constant, ∼950 ps. This value is in accord with that estimated for two linked CDs using the hydrodynamic theory under stick conditions.[157] The variation of the first time with the wavelength of emission indicates the existence of several rotamers (or conformers), and thus agrees with the involvement of 1:1 and 1:2 complexes. Clearly, the result indicates that the size (space domain) of the nanocavity of the host (one or two CDs) governs the photodynamics (time domain) from the picosecond to nanosecond regime and the emission spectroscopy (shift by about 40 nm) of the nanostructure.

While HAN shows an ESIPT reaction between two groups, both located on the molecular frame of the dye, and does not need solvation for the occurrence of internal proton motion, 1- and 2-naphthol, which are among the most studied aromatic systems, show an excited-state intermolecular proton transfer to the medium (water, alcohols).[158−166] The produced anionic structure emits at the blue side of the normal form. The effects of CD on the intermolecular proton-transfer reaction from 1-naphthol (1-NP)[167,168] to water and from water to 1-aminopyrene (1-AP)[168] have been studied by emission spectroscopy. For 1-NP in pure water, the decay of the 360-nm emission band (that of the neutral reactive species leading to the anionic one emitting at the blue side, 460 nm) was fitted with a 36 ps exponential component.[168] In presence of β-CD, the decay at 370 nm needed two exponential functions with time constants of 700 (75%) and 1600 ps (25%).[168] The average time constant for deprotonation of 1-NP in the presence of β-CD (1:1 stoichiometry) is 930 ps. The difference in the deprotonation times for free (36 ps) and caged

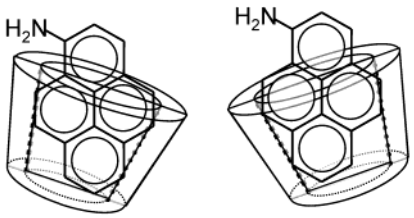

Figure 12. Proposed confined geometries of 1-aminopyre: β-CD complexes.[168]

(930 ps) guest was interpreted as a signature of different mechanisms for proton-transfer reactions from 1-NP to water.[168] The time for deprotonation of the caged 1-NP in other media, such as micelles (600, 1900 ps)[148] and polymer−surfactant aggregates (1600, 5300 ps),[169,170] was much slower (or almost blocked) than that of uncomplexed dye.[169]

For 1-AP, the rate of the proton-transfer reaction from water to the dye was found to increase upon formation of 1:1 complexes involving β-CD.[168] To explain this observation, the authors suggest using geometrical factors for the confined structures (Figure 12) which influence the dynamics of proton-transfer reaction. For geometries where the amino group is found near the hydroxyl rims of β-CD, the rate of proton transfer is affected by the microenvironment due to the cage: it is enhanced by a factor of 2.[168] This rate is similar to that observed in mixtures of water and simple alcohols with comparable molar ratios to water. For geometries where the amino group is farther away from the hydroxyl rims, the amino group is then surrounded by water molecules. The rate constant of the proton-transfer reaction is not affected by complexation, and it is similar to that of uncomplexed 1-AP. Under the experimental conditions used (dye:CD ratio, pH, and picosecond time resolution), the authors suggest that the former confinement is favored by a ratio of 1.5:1.[168] By comparison to the behavior they observed when using ethanol−water mixtures, the authors proposed modeling CD's effect on the proton-transfer rate constant of 1-NP and of 1-AP by using suitable homogeneous mixtures of water and organic solvents. However, such a molecular model cannot be realistic, as it does not take into account several microscopic differences, such as those of hydrophobic interactions, solvation of the transition state, proton jump mechanism once the atom was ejected, diffusion and geminate recombination of the anion and cation, different H-bond networks with different cooperativities, and the different friction factors of the two media, to cite few. It has been found that the lifetime of the H-bond of a water molecule to an organized medium (the polar headgroup of a micelle) is about 13 times longer than that of a water−water H-bond, and 3.5 kcal/mol is needed to "liberate" the bound water molecule from the polar head of the micelle.[171] Further more, careful analysis of the emission decay of 1-NP in water leads to nonexponential behavior,[165] and changes in the dielectric constant,[172] solvation time, and diffusion should be taken into account, even in organized media.[164] Thus, to understand the origin of the slow component of deprotonation of 1-NP in CD or in organized media, and most probably of other

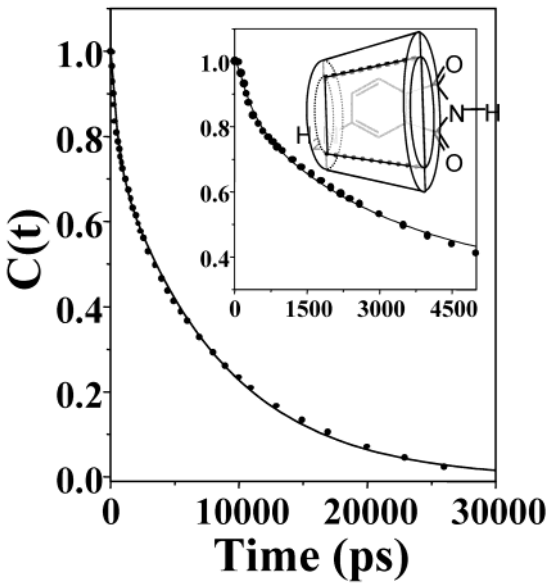

Figure 13. Decay of response function $C(t)$ of 4-aminophthalimide (4-AP) bound to β-CD in *N*,*N*-dimethylformamide. The experimental values of $C(t)$ and the solid line denote the best fit to a biexponential function. The decay of the initial portion is given in the inset. The inset shows also the structure of 4-AP:β-CD complex.[173]

dyes showing slow solvation dynamics (time constant longer than 300 ps or so), one has to take into account several factors influencing the microscopic and heterogeneous solvation, the self-motions of the guest and host for an efficient encounter (subnanosecond to microsecond regime), and related H-bond networks dynamics.[63] Therefore, the slowest time constant (more than 100 ps) assigned to solvation dynamics might contain strong contributions from the above factors which should not be included in solvation processes in a classical restricted terminology. We will consider this in the femtosecond dynamics part.

4-Aminophthalimide complexed to β-CD aqueous solutions has been used for studying the picosecond solvation dynamics of dimethyl formamide (DMF) in a nanocavity (Figure 13).[173] The response function $C(t)$ has been found to be described by a component of 400 ps (25%) and a slow one, 8 ns (75%) (Figure 13).[173] However, solvation dynamics in pure bulk DMF occurs in less than 1 ps.[174] The dramatic retardation of solvation dynamics inside the molecular box was assigned to the loss of translational modes of DMF, as has been suggested for the slow solvation dynamics of water in the presence of γ-CD.[175] Compared to water, the time constant of the slow component for DMF in the presence of CD is slower than that observed for water molecules in γ-CD (vide infra). To explain this, one has to take into consideration, among other factors, the relative size of the solvating molecule (DMF or water), the nature of the guest (polarity, ability to form H-bond) and of the host (β- or γ-CD), the number of solvent molecules inside the cavity, and the kind of interactions between these molecules themselves and with the nanocavity. To reach a more comprehensive conclusion, one should use the same molecular probe for both solvations inside the same nanocavity. Further more, self-diffusion of both entities for

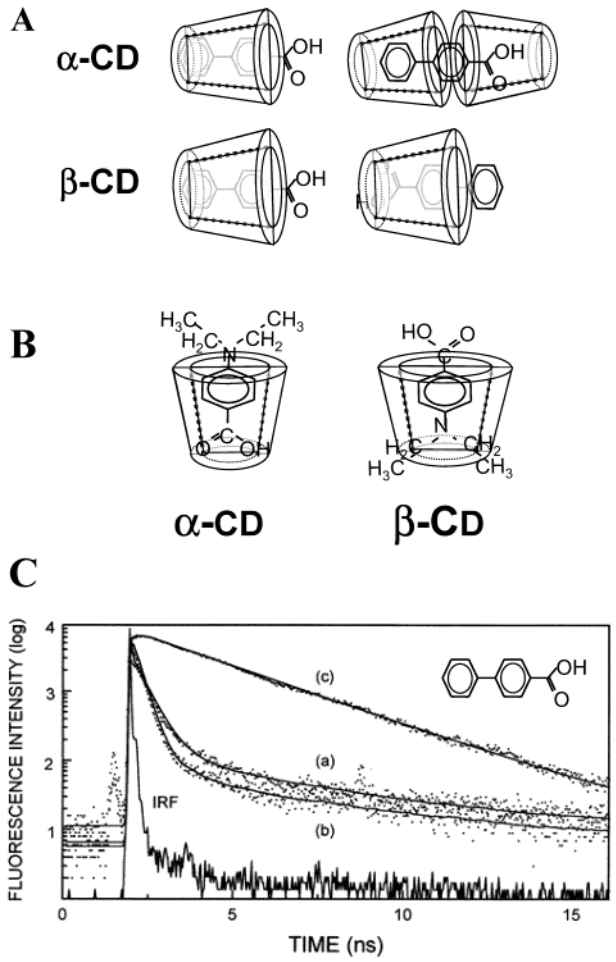

Figure 14. Proposed structures for (A) 4-biphenylcarboxylic acid and (B) (*N*,*N*-diethylamino)benzoic acid (DEABA) with CDs. (C) Emission decays of DEABA (a) in water and in the presence of (b) β-CD and (c) β-CD. The instrument response function (IRF) is also indicated. The solid lines are obtained from the best-fitting exponential functions.[176,177]

complex formation should affect the observed dynamics when it is gated in a longer time scale (subnanosecond regime). Such long-time dynamical events should be detected in the width of ^{1}H (^{13}C) NMR signals (ground-state equilibrium) or in that of time-resolved emission spectra (excited-state equilibrium) of the complexes.

The effect of CD complexation on rotational or twisting motion has been examined using the so-called twisted intramolecular charge-transfer (TICT) process which some dyes may undergo upon electronic excitation. Polarity, restriction, degree of complexation, and different stoichiometry have been used to account for the abnormal CD effect on the emission of several dyes undergoing this kind of reaction.[73−85] For example, the emission of the structure resulting from a fast TICT reaction in 4-biphenylcarboxylic acid (BPCA) in solution is blue-shifted upon encapsulation by CD, indicating that the excited-state TICT reaction is partially inhibited when a 1:1 inclusion complex is formed (Figure 14A).[176] The interaction of the carboxylic group with the water molecules located at the gate of CD through H-bonds and the relatively lower polarity of CD do not help to reach a molecular conformation with coplanarity favorable to produce a TICT reaction in the guest. For α-CD, where two isoemissive points and dual fluorescence decays were observed, a 1:2 entity is also formed involving two molecules of α-CD in the formation of the nanostructure, as in the case of HAN.[176] The emission study for 1:2 complexes suggested that the excited-state geometry change toward coplanarity of the biphenyl moiety becomes slightly more possible with suppression of the intramolecular charge transfer in the 1:2 complex. The internal rotation barrier energy is about 6 kJ/mol. *p*-(*N*,*N*-diethylamino)benzoic acid (DEABA) is another system that has been studied in aqueous solutions of CD by the same group (Figure 14B).[177] The dye suffers a TICT process in solution and in the cage. The ratio of the emission intensity which results from a TICT reaction to that of the normal emission of DEABA increases with β-CD concentration, while it decreases differently upon addition of α-CD.[177] The emission decay of the TICT reaction in the presence of α-CD and the decay of the normal emission are different from that in the presence of β-CD (Figure 14C). The observed rise time for emission resulting from the TICT reaction increases with β-CD concentrations, whereas no rise time was observed in the case of α-CD. The results were explained on the basis of different geometries of the complexes. The entrapment of the amino group in the β-CD cavity seems to inhibit the reverse TICT process by restricted back-torsion from nonplanar to planar conformation of the diethyl amino group. While for α-CD complexes the carboxyl group of the guest is encapsulated inside the cavity, for β-CD complexes this group is exposed to the water molecules found at the gate of the cage (Figure 14B). The dependence of the TICT state emission on the size of CD cavity demonstrates the key role played by the H-bonds of the special water molecules found at the gate with the embedded guest. It demonstrates also that robustness is important to the dynamics of the guest, as has been shown previously. Femtosecond studies of small and large guests involving hosts that are different in nature and size have provided a microscopic picture of solvation and confinement. This is reviewed in the following section.

5. Femtosecond Studies

5.1. A Simple Molecule: Iodine

Several decades ago, Franck and Rabinowitch proposed that solvent can trap the geminate pair of atoms that are products of photodissociation in a molecule.[178−180] Because of its conceptual simplicity (two bonded identical atoms) and accessibility to optical techniques, the iodine molecule (I−I) is then one of the most studied prototype systems for understanding dissociation−recombination and non-adiabatic dynamics in gas and liquid phases.[181−190] With femtosecond resolution, the dynamics of dissociation, caging, and vibrational relaxation was studied in clusters,[186] dense fluids,[182] liquids,[187,188] and solid matrices (for an overview on the iodine molecule and ionic iodine atom, see refs 185 and 189−191). Recently, the results of ultrafast rotational anisotropy

Figure 15. Illustration of the iodine molecule (I_2) encapsulated by heptakis(2,6-di-*O*-methyl)-β-CD (I_2:DMβ-CD).[193]

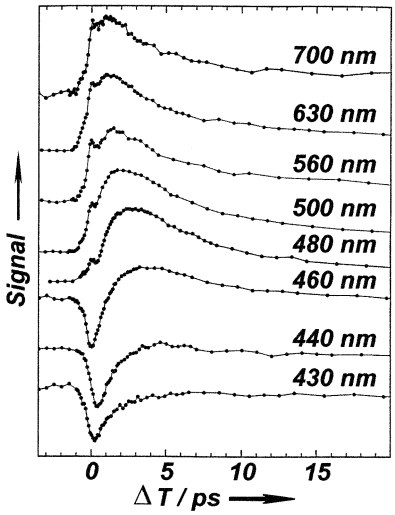

Figure 16. Femtosecond transient absorption signal of I_2 in water containing DMβ-CD, observed after femtosecond excitation at 400 nm. The probe (signal) wavelengths are indicated. The solid lines represent results of multiexponential fit.[193]

experiments have shown the effects of strong-field nonlinear saturation on the reactive pathways of iodine at room temperature.[192] The simple concept of two atoms which can separate, recombine, and cool in a small molecular box, such as that provided by CD, was used to interrogate the dynamics of an I−I molecule trapped in a CD cavity (Figure 15).[193]

Steady-state absorption studies of iodine:CD complexes in aqueous solutions have been reported.[193,194] The results show the formation of a trapped iodine molecule within one CD cavity, in agreement with the X-ray study of I_2/dimethyl-α-CD inclusion complexes.[194] In aqueous solution of dimethyl-β-CD (DMβ-CD) and I_2, the inclusion equilibrium constant is high, $K_c = 7800 \pm 800\ M^{-1}$ at 296 K, leading to an intense UV−visible absorption broad spectrum with maxima at 293 and 385 nm.[193] Both bands may contain a contribution from a transition due to a charge-transfer interaction between the guest (I_2) and the oxygen atom of the di-*O*-methylglucose units of the host (CD), as was observed for I_2 in dioxane, where the I_2- - -dioxane interatomic distance was estimated to be 2.81 Å.[195]

Femtosecond transient absorption pump−probe spectroscopy has been used to study the ultrafast dynamics of I_2:DMβ-CD in aqueous solutions.[193] The complex was excited at 400 nm, and its dynamics was interrogated by a femtosecond laser probe at several wavelengths. The wavelength of the probe is critical for locating the window in which femtosecond internuclear separation between the iodine atoms occurs (Figure 16). In general, longer wavelengths probe longer I···I internuclear distances.[182,185,187,188] On the basis of the results of studies of the dissociation and recombination dynamics of the iodine molecule in the gas phase[182,186,190] and in solution and solids,[185,187−189] the authors proposed the following picture for I_2:DMβ-CD ultrafast caged dynamics.[193] The femtosecond excitation pulse (400 nm) puts the confined geometry in a region (B state) where the wave packet moves the caged iodine molecule to longer I−I internuclear distances in ∼200 fs. Due to the small and restricted molecular cage provided by CD, the two atoms of iodine recombine and suffer vibrational relaxation, and cross to the ground-state potential (or A state) in ∼1 ps. In normal solvent cage, the recombination time is ultrashort, ∼0.6 ps.[186] After the molecule crosses to the ground state, the vibrational cooling of iodine in the confined entity occurs in ∼30 ps. For I_2:THF solutions, comparable times for the initial dissociation and recombination have been found. However, the ∼30 ps subsequent relaxation observed in the molecular pocket is slower in THF, ∼46 ps. Vibrational relaxation times up to ∼150 ps were found for I_2 in CCl_4 and in chlorinated methanes, which were explained as due to vibrational-to-rotational energy transfer.[196] Because of charge-transfer coupling between the guest and the host (the distance between the guest and the oxygen atoms of the host is small, ∼2.8 Å)[194] and the large number of vibrational modes of the molecular chamber, the rates of vibrational cooling of caged I_2 are enhanced in the CD cavity. In addition to that, the nanosecond background component observed in the I_2:THF transients, and due to geminate recombination,[182] is absent in the transients of the confined geometry, indicating a significant effect of the confinement on the rate of remaking of this bond. Thus, for the iodine molecule, the confinement offered by the molecular nanocavity enhances the rates of vibrational cooling and geminate recombination processes, demonstrating the concept of a trapped wave packet in a nanocavity. Part of the femtodynamics of the iodine molecule can be then controlled by simply caging it in a selected molecular chamber.[83,194] The iodine molecule has also been studied in a large and rigid molecular cage.[197−201]

Femtosecond studies of I_2 molecules embedded in well-defined cages of the crystalline microporous SiO_2-modified decadodecasil 3 R (DDR) (Figure 17)

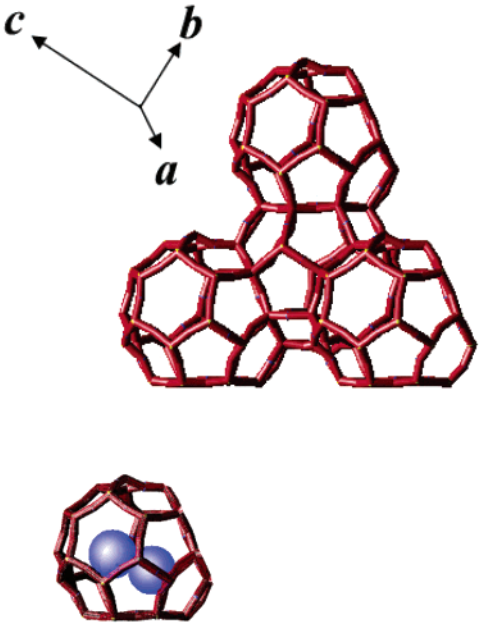

Figure 17. Ciew of the $[4^3 5^{12} 6^1 8^3]$ cages of the crystalline microporous SiO_2 modified decadodecasil 3R (DDR), and I_2 molecule encapsulated in a large cage of DDR. Note that each cage of the zeolite adjoins the three neighboring cages in an angle of 120°, and has a volume of ~350 Å^3.[199,200]

using pump−probe transient absorption spectroscopy have been reported.[199] Each cage of the zeolite-like microporous crystal used is occupied by one guest I_2 molecule, leading to a high density of iodine molecules. Raman, UV, and X-ray spectroscopies indicate no evidence of interactions between the trapped iodine molecules.[197−201] Upon femtosecond excitation of the caged guest to its B state (535 nm) and probing with different wavelengths, the results show a collision-induced predissociation (time constant ~3 ps) and a subsequent recombination onto A and A′ states, where the guest undergoes vibrational relaxation (~45 ps).[199−201] The predissociation time constant in the cage (volume ~350 Å^3) is not very different from those observed in argon at 200 and 400 bar, respectively. However, it is ~15 times longer than that observed in DMβ-CD (~200 fs).[193] The authors used a kinetics model to simulate the experimental observation.[200] Within the zeolite cage, geminate primary recombination has a time constant (~8 ps) very similar to that observed for I_2 in argon at high pressures (200−400 bar). Therefore, the confinement offered by the zeolite induces coupling between the B state and several repulsive states which cross the B state. These are responsible for the predissociation of I_2 via different channels. In addition to that, no geminate secondary recombination was detected. Nearly 10% of the recombination is supposed to be nongeminate, having a time constant (~20 ps) which corresponds to the movement of iodine atoms to the neighboring cages, therefore allowing reaction with another caged iodine atom. Comparison with the results obtained in liquid-like media[182] and those obtained at low pressures[202] indicates that in the zeolite, binary collisions also induce the predissociation of the iodine molecule. The time required for vibrational cooling for the CD complex is about 30 ps, while that for the zeolite one is longer (~45 ps), similar to that observed in THF (~46 ps). However, for the DDR:iodine complexes, a nongeminate recombination involving other iodine molecules found at the neighboring cage was observed, in contrast to the situation with the CD entity. The DMβ-CD:I_2 complex has only one trapped iodine molecule (Figure 15), while the zeolite supercage ($V \approx 350$ Å^3)[199] may have many iodine guests trapped in the neighboring cages (Figure 17). Molecular dynamics simulation of the iodine−zeolite femtosecond experiment, which takes into account the non-adiabatic transitions in the guest and the adsorbate−framework interactions between I_2 and DDR zeolite, has been carried out.[200] The results show that the observed transient signal contains contributions from four transitions which are influenced by the dynamics of predissociation and vibrational relaxations. In addition to that, the observed transients strongly depend on the probe wavelength. The simulation reproduces well the long-time behavior of the transients, so processes such as nongeminate recombination are not needed for a simplified understanding of the femtodynamics of I_2 in the zeolite-like structure. In a recent work, the same group carried out further experiments and theory (Brownian dynamics simulations) for a better understanding of the photodissociation and recombination of I_2 with the same system.[201] They showed that, by switching the polarization of the laser relative to the axis of the crystal of DRR containing the iodine molecule (Figure 18), the predissociation photodynamics of the excited B state can be influenced.[201]

5.2. Coumarins 460 and 480

Coumarins have been the subject of many steady-state and ultrafast studies.[203−213] They have also been studied in CD cavities for different purposes.[66,213−222] For coumarin 480 (C480) and coumarin 460 (C460) in aqueous solutions, the blue shift in the emission spectrum and the increase of the fluorescence lifetimes in the presence of γ-CD have been assigned to the formation of an inclusion complex with CD.[220−222] Molecular mechanics calculations for the C460:γ-CD complex suggest that the most stable inclusion complex has the carbonyl end of the guest near the narrower, primary OH end of the host and the amino end group of C460 near the secondary OH side of the cavity.[222] The calculations also suggest the formation of a H-bond between the carbonyl group of the guest and two hydroxyl groups of the host. The time-dependent Stokes shift of the emission of γ-CD:coumarin complexes has been studied.[222] The solvation time of the excited complex ranges from <50 fs to 1.2 ns, and most of the solvation takes place within 1 ps. The fast component of the solvation decay for both complexes (C480:γ-CD and C460:γ-CD) is similar to that in bulk water, suggesting that the first solvation shell does not dominate the solvent response and is mainly due to a collective response of water molecules found near the guest and outside the cavity. However, at longer times, the solvation dynamics in γ-CD is at least 3 orders of magnitude slower when compared to that observed in water.[222]

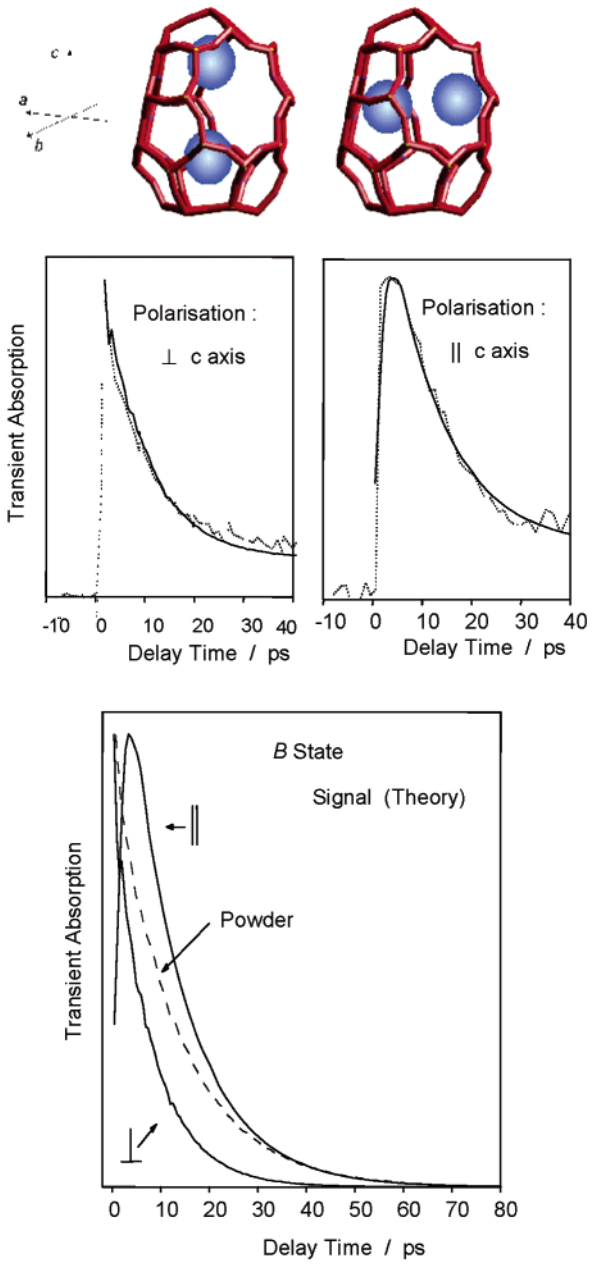

Figure 18. Perpendicular and parallel orientations of iodine molecule relative to the *c* axis of the DDR single crystal, and experimental/simulated polarization-dependent transient pump−probe signals of I_2 in the DDR zeolite. Adapted from ref 201 with permission from the authors.

For C480:γ-CD, three components of the slow relaxation were observed: 13, 109, and 1200 ps. For C480:γ-CD and C460:γ-CD entities, molecular dynamics simulations suggest 13 and 16 water molecules, respectively, inside the cavity.[222] These numbers of water molecules are symmetrically distributed around the guest, with one molecule of water near the oxygen of the carbonyl group of the guest. A comparable number of water molecules in the first solvation shell of atomic solutes in pure water have been calculated.[223] The authors suggested that the slower relaxation components may be due to motion of the guest in to and out of the restrictive host, fluctuations of the CD ring, or the orientation of highly constrained water molecules.[222]

5.3. Bound and Free Water Molecules

A multishell continuum model and molecular hydrodynamic theory have been used to get a better insight into the solvation dynamics of coumarin within CD.[175] The theory can explain solvation dynamics having time constants of less than ~100 ps or so, where the contribution of self-motion of the (large) probe (and of a large host) is still not important in the solvation dynamics of the probe. The theoretical results found that the contribution of the translational component is small, while the orientational component governs the polarization relaxation. For a short time scale (1 ps), inclusion of the intermolecular vibrational mode in the dielectric model leads to a good agreement between the calculated and experimental solvation time correlation function.[175] For a longer time scale (more than 100 ps or so), although the theory does not reproduce well the experimental observation, it suggests that the slower component is controlled by the rotational motion, which is affected by the freezing of translational modes of water inside the restricting nanocavity. The models used for simulations cannot describe properly the effects of the CD rings on the solvent dynamical modes.[175] Note also that at least two kinds of water molecules can be found within CD or at the gate and in proximity of cyclodextrins: water molecules bound to the hall of the cage, where two types of intermolecular H-bonds may occur due to the H-bond-donating and -accepting nature of water and CD, and structurally different networks of water molecules in the vicinity of the host. To some extent, this prevents them for playing a more important role in the ultrafast solvation dynamics. Comparable situations have been suggested for water at the interface of micelles.[43,54−56,61−63,224] Two geometrical relaxations are key elements for the H-bonds' cooperativity and related solvation: the H-bond coordination of water molecules (the number of water molecules involved in process) and the O···O distance shrinkage.[40−42] The number of water molecules trapped inside CD (up to seven molecules for crystalline hydrated β-CD)[225] or bound to the gates is limited, and the energy to cooperate is increased when compared to the situation in bulk water. Neutron scattering experiments on β-CD at room temperature[226] showed that the disorder of water molecules inside the cavity is dynamic in nature and involves jump time constants of about 10−100 ps. The conformational flexibility of the glycopyranoside units and the dynamics of disorder of water can influence the solvation dynamics of CD. Molecular dynamics simulations of water diffusion both in CD with different degrees of hydration and in water have been performed.[227] The calculations show that water molecules found outside the cavity have access to the main diffusion pathway. The results also suggest that the diffusion constant for transport of water molecules along the main diffusion pathway (0.007 Å^2/ps), parallel to the crystallographic axis *b*, is about 1/30 of the value in bulk water at room temperature, and 1/53 at 320 K.[227] The water molecules outside of the main diffusion pathway have an easy and fast (picosecond time scale) access to this channel. Inter-

estingly, no significant change in the diffusion constants and pathways with the relative humidity of crystalline β-CD was found. For the coumarin 480 trapped in CD, the water molecule H-bonded to the carbonyl group of the coumarin, as suggested by calculations,[222] can be involved in a H-bond network formed by water molecules at the gate of the host and may cause an intramolecular charge-transfer dynamics, leading to a slower solvation dynamics. Furthermore, the slow motion of water molecules at both gates of cyclodextrins has been observed for guests able to undergo excited-state proton-transfer reactions.[228] For 2-naphthol and 7-hydroxyquinoline,[228] the change of the proton-transfer rate constant upon encapsulation by CD is clear evidence that the H-bond network at the gates of CD is special and plays a crucial role in the reaction and solvation dynamics of the trapped guest. Furthermore, molecular dynamics simulations have shown a nearly 50% decrease of the dielectric constant of water confined in a nanocavity.[229] Such a decrease will influence the electrostatic field around the guest and therefore may cause large changes in its dynamics, especially when the probe suffers significant changes in its dipole moment upon electronic excitation, as in the case of coumarins. Indeed, several studies of water involving micelles, biological systems, and channels have shown a significant decrease of polarity[230−235] and a slowing down of the rate constant of water molecules' relaxation inside these media.[236−251] Water molecules confined in such environments exhibit a larger degree of spatial and orientational order than in bulk phase, with the formation of well-defined molecular layers in the vicinity of the cavity or channel surface.[236−251] The water at this special layer (comparable to biological water) plays a crucial role in the activity of many biological molecules such as enzymes, proteins, and DNA. The current view of protein−water interactions is associated with a variety of functional roles, some of which are specific to a given system, whereas others are general to all proteins. The water molecules associated with the proteins surface are in constant exchange with the bulk solvent, and the related nonlinear dynamics plays a key factor in the function and stability: water is a rate-limiting partner in biological and biochemical processes. Reference 47 is a review on the protein−water interaction in a slow dynamic world, and ref 61 is a recent review article on femtosecond dynamics of macromolecular hydration, where biological water is critical to the stability of the structure and function of the biological system.

Using femtosecond time resolution, two residence times of water at the surface of two proteins (Sublitisin Carlsberg and Molenin) have been found (Figure 19).[61] The natural probe tryptophan amino acid was used to follow the dynamics of water at the protein surface. For comparison, the behavior in bulk water was also studied. The experimental result, together with the theoretical simulation of dynamical equilibrium in the hydration shell, shows the direct relationship between the residence time of water molecules at the surface of proteins and the observed slow component in solvation dynamics. For the two

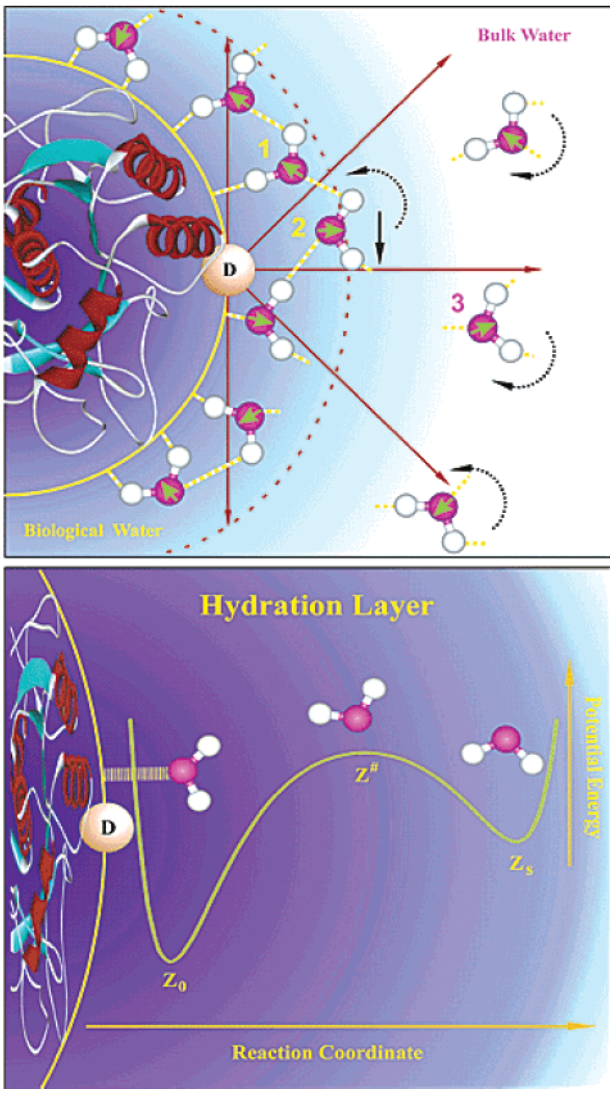

Figure 19. Illustration of the dynamic equilibrium of water molecules at the hydration layer of a protein, with bound (1), *quasi-free* (2), and free water molecules (3). The potential energy for the exchange is shown in the lower part.[61]

biological studied systems, a "bimodal decay" was observed for the hydration correlation function, with two primary relaxation times: an ultrafast time, typically 1 ps or less, and a longer one, typically 15−40 ps (Figure 20).[61] Both times are related to the residence period of water at the protein surface, and their values depend on the binding energy. Measurement of the OH librational band corresponding to intermolecular motion in nanoscopic pools of water and methanol confined in reverse micelles has been reported.[252] The result shows that the librational band, which has its maximum at 670 cm^{-1} in the bulk liquids, shifts to lower frequencies and its shape changes considerably as the size of the reverse micelle decreases. A two-state model based on bound and free water fractions of water (or methanol) was used to fit the shape of the librational band.[252] Using large-scale atomistic molecular dynamics simulation, the Bagchi group proposed, for an aqueous micelle solution of cesium perfluorooctane, that water molecules at the interface fall into two categories, bound and free, with a ratio of 9:1.[62] The water molecules

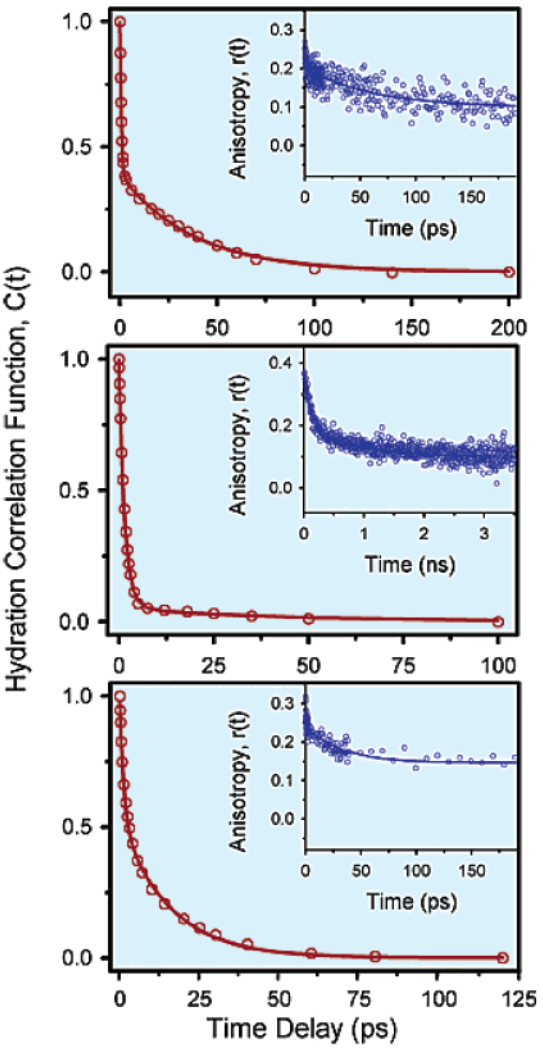

Figure 20. Observations of the hydration for the proteins Sublitisin Carlsberg (SC) and Monellin (Mn). The time evolution of the constructed correlation function is shown for the protein SC (top), the Dansyl dye-bonded SC (middle), and the protein Mn (bottom). The corresponding time-resolved anisotropy $r(t)$ decay is given in the inset of each part.[61]

bound to the hall can be further classified on the basis of the number of H-bonds linking them to the polar headgroups of the micelle. Entropy contribution is found to be critical in determining the relative populations of the free and bound water molecules. It has also been shown that the H-bond dynamics of two tagged water molecules bound to the polar heads of a micellar surface is almost 13 times slower than that found in bulk solution. Water molecules can remain bound to the micellar surface for more than 100 ps.[62] In general, interfacial water is energetically more stable than bulk water, and this will affect its ability to translate, and possibly to reorient. This finding may help to explain the origin of the universal slow relaxation at complex aqueous interfaces of several systems where water resides at their surface or interfaces.

Using ultrafast optical Kerr effects spectroscopy, the orientational dynamics of liquids (including water) in nanoporous sol−gel glasses has been studied.[56] In the pore, a ~3 ps time constant was observed and assigned to orientational relaxation of water in a

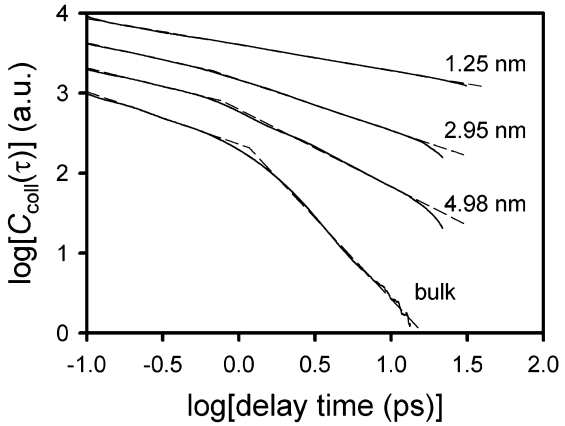

Figure 21. Experimental log−log plot (solid lines) of the collective orientational correlation functions C_{coll} for water confined in pores of different diameters (inserted number) and power-law fits (dashed lines). In each pair, the lower trace is for hydrophilic pores and the upper one is for hydrophobic pores.[56]

hydrophobic pore, in agreement with a previous report.[57] At the pore surface, the orientational relaxation time of water was found to be much slower (15−35 ps) and to depend on the size of the pore (Figure 21). However, for all pore sizes, the water relaxation at the surfaces is faster for hydrophobic sites than for hydrophilic ones. Thus, the nature of the surface (involving hydrophilic or hydrophobic sites) is a key factor in the dynamics of confined water molecules, as it will influence the number of H-bonds involved in the networks. As noted,[56] the rate of relaxation at the surfaces depends on the pore diameter, suggesting that water relaxation at these sites is highly cooperative, and it may extend out to zones significantly larger than that defined by a single water molecule. An average solvation time of 220 ps for C-480 in a sol−gel glass of pore size 10−20 Å has been reported.[253] Taking into account the size of the probe and that of the pores, the rotational mobility of the guest should be restricted. Furthermore, the presence of the polar guest inducing an electric field within the pores, and enhancing the local polarization field, should slow the trapped water molecules' motion, thus causing a slowing in the solvation dynamics of C-480 in the sol−gel matrix. For ethanol in sol−gel glass, the average nonexponential behavior of the solvation time of Nile Blue A is about 19 and 36 ps within 75 and 50 Å average pores, respectively.[254] Within a polyacrylamide hydrogel having larger pores, a solvation time shorter than 50 ps has been reported.[255] However, because of the limited time resolution of the picosecond technique used, the fast component of solvation dynamics of the above system is missing, and comparison of the results with those based on ultrafast techniques should be done with precautions. For CD, the water molecules of interest will H-bond with the hydrophilic gate of CD, leading to a decrease of the number of water−water H-bonds, and then to a slower dynamics. Inside the CD capsule, the surface is hydrophobic, but the small number (seven molecules for crystalline β-CDs) of water molecules which might be trapped there does not help to accelerate the caged dynamics, and then a slow solvation is observed. In addition to that, a

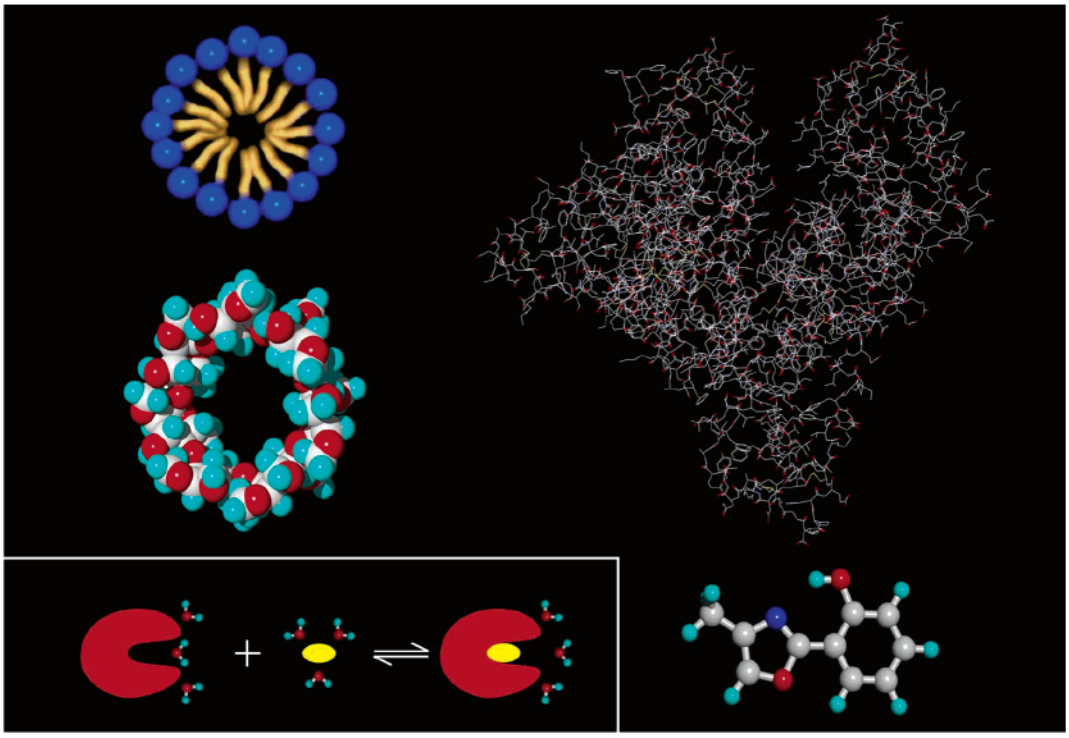

Figure 22. (Right) X-ray structure of the Human serum albumin (HSA) protein and molecular structure of the ligand HPMO. (Left) Schematic representation of a normal micelle structure (top), X-ray structure of β-cyclodextrin (middle), and a protein−ligand recognition process (bottom).[98]

(polar) guest with strong local electric field may induce important local polarization of the trapped water molecules, which decreases their orientational and translational motions, resulting in longer solvation times for confined structures when compared to bulk solutions.

5.4. 2-(2′-Hydroxyphenyl)-4-methyloxazole

Noncovalent interactions which govern the ligand-binding process during guest:host complexation have been studied using 2-(2′-hydroxyphenyl)-4-methyloxazole (HPMO) as a probe (guest) and CD, micelles, and human serum albumin (HSA) proteins as hosts (Figure 22).[96−99] The interest in HSA protein caging effect resides in the important biological function of this protein in body carriers and in the discovery of new drugs and development of phototherapy.[256−258]

The first report on a femtosecond dynamics study of HMPO in aqueous solutions of CD showed the confinement effect on the ultrafast dynamics of HPOM caged into a β-CD nanocavity (Figure 23).[96] After an ultrafast intramolecular proton-transfer reaction in the guest, a subsequent twisting motion can take place, which is restricted in the nanocavity. The produced keto-type phototautomer emits a large Stokes-shifted band (~10 000 cm^{-1}), and the wavelength of the maximum emission depends on the caging medium.[97] The blue transient behavior of HPMO in β-CD (430 nm) is different from that observed in 3-methylpentane (3MP) (420 nm).[96] After the femtosecond excitation, the excited enol structure suffers a loss of aromaticity in the six-membered ring and the charge rapidly redistributes. This constitutes the driving force for the femtosecond proton transfer from N···H−O to N−H···O configuration.[97,259] The

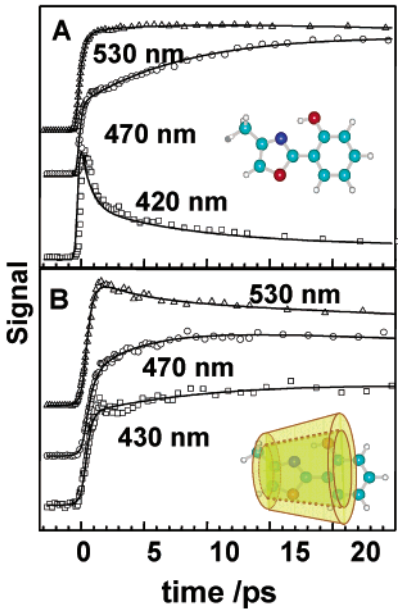

Figure 23. Femtosecond fluorescence transients gated at different wavelengths for HPMO (A) in 3-methylpentane and (B) in water solution containing β-CD. The structures of HPMO and the 1:1 complex with β-CD are indicated. The observation wavelengths are inserted.[96]

charge redistribution barely changes the direction of transition moment, as suggested by the observed initial anisotropy (0.34), which is close to the ideal one (0.4) involving a parallel transition. A more detailed study of HPMO in dioxane and in different cavities has been reported.[98] Although the observed patterns of the femtosecond transients are similar, they have been divided into two groups of time-resolved fluorescence emission transients overlapping at 430 nm. For wavelengths shorter than 430 nm,

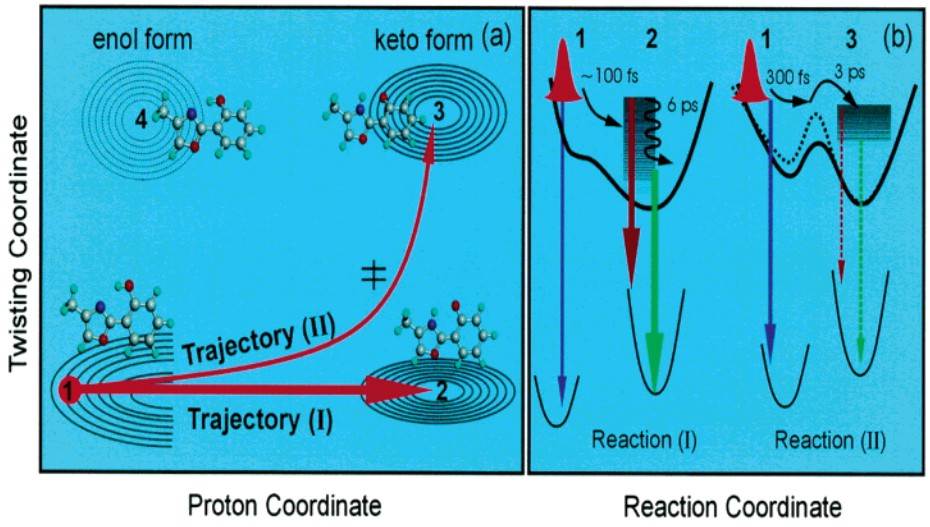

Figure 24. (a) Schematic illustration for two trajectories of the direct proton-transfer reaction I and the one involving twisting motion (II). (b) Potential energy curves along the reaction coordinate for trajectories I and II with the observed emission indicated schematically. The dashed line represents the potential energy in the protein environment. Note that rotamers of nonplanar enol ground state can undergo proton transfer on the upper surface following an initial twist toward planarity.[98]

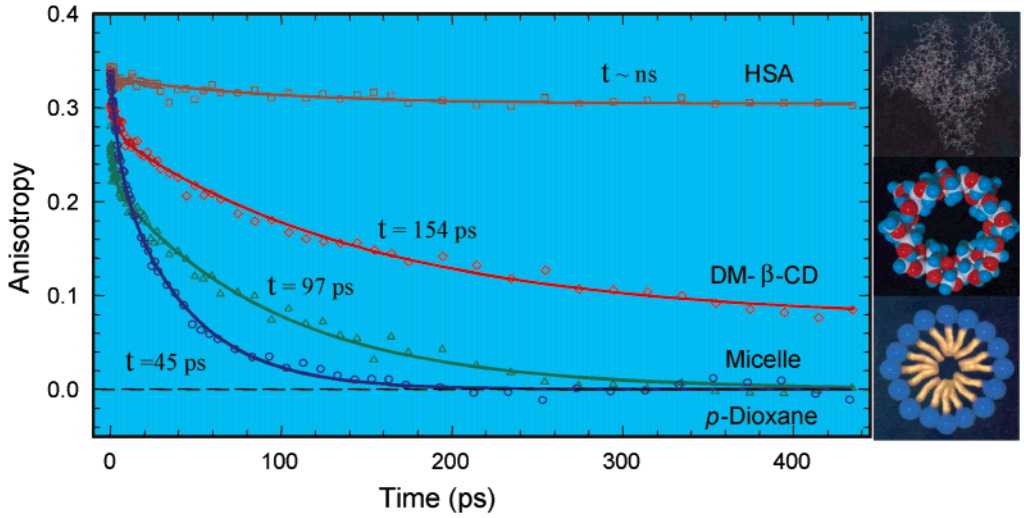

Figure 25. Femtosecond-resolved fluorescence anisotropy decays of HPMO in four typical environments of HPMO. Left: illustration of the nanocavities used (HAS protein, DM-β-CD, and normal micelle).[98]

all the transients show fast decays, while at wavelengths longer than 430 nm, the transient shows rise and decay. To explain the observed behavior, two trajectories of femtosecond dynamics of the guest have been proposed (Figure 24),[98] a direct one (I) in which the wave packet moves quickly along the proton coordinate without any barrier, and a second one (II) where the system evolves along the repulsive potential toward the keto-type structure involving two types of motions: the proton motion at earlier times and the twisting motion of the heterocyclic moieties at a later time. This last motion involves an energy barrier, as also predicted by calculations,[259] which will increase upon confinement by CD or by HSA protein, making the time for barrier crossing longer in these cavities. The times for both motions along trajectory II become significantly longer in the cavity of HSA protein. While the barrier crossing in dioxane occurs in 3 ps, in HSA it depends on the interrogated wavelength: 8, 20, and 37 ps at 415, 420, and 430 nm, respectively.[98,99]

To get more insight into the effect of confinement on the binding between HPMO and the host, a time-resolved anisotropy measurement has been carried out.[98] The result (Figure 25) shows a remarkable difference in the anisotropy decays, especially for the HSA protein case. While in dioxane the rotational time constant (45 ps) is close to that expected on the basis of hydrodynamic theory,[98] this time increases with the rigidity of the host (97 ps for micelle, 154 ps for β-CD, and ~nanoseconds for HSA), indicating the increase of confinement. While the orientation relaxation of the guest is almost complete in the micelle after 500 ps, it persists for longer times in CD and HSA protein, indicating the slowing down (CD) or absence (HSA) of diffusive orientational motion in these cavities. Proton NMR studies of HPOM in CDs solutions suggested that the oxazole ring of the guest is fully inserted into the cavity of the host.[98] Using initial and final anisotropy values, the calculated average change in direction of the transition moment of the guest inside CD is about

30°. For HSA, the high value of the initial anisotropy and the lack of any initial ultrafast decay indicate a strong hydrophobic interaction between the guest and the probe, the hindrance of molecular structure relaxation, and the rigidity of the local nanoenvironment where the guest is trapped. The observed result is consistent with X-ray structural studies showing a strong hydrophobic interaction between the ligand's aromatic ring and the residues located at site I of the HSA protein.[260]

5.5. Methyl Orange, Orange II, and Thiacyanine

Azobenzene derivatives are well known to exhibit excited-state cis−trans isomerization, and they have been proposed for potential technological applications such as ultrafast photoswitching and information storage devices.[261−265] Mainly two mechanisms for trans−cis isomerization have been proposed: n−π* inversion when the excitation brings the system to the S_1 state, and $\pi-\pi$* rotation when the excitation reaches the S_2 state.[266−269] In *trans*-azobenzene derivatives without any restriction, trans−cis conversion depends on the nature of the excitation, and it is always smaller for $\pi-\pi$* excitation. However, for restricted azobenzenes,[270] the quantum yield of isomerization is almost independent of the nature of the transition. Recently, the femtosecond dynamics of azobenzene derivatives as photochromic systems has been reviewed.[265] In the presence of CD, azobenzene derivatives form inclusion complexes.[271−277] The ultrafast transient lens (UTL) method and transient absorption spectroscopy have been used to study the ultrafast relaxation of methyl orange (MO) trapped inside the cavities of α-, β-, and γ-CD in water solutions (Figure 26).[278] In pure water, the transient signal was fitted using two exponential functions with two time constants: ≤1 ps and ∼10 ps (Figure 26). These times were assigned to the decays of the first-formed trans S_2 state to the vibrationally excited S_0 state, and the vibrational relaxation of the S_0 state, respectively.[278] In the UTL experiment, the formation of the cis isomer and cis−trans thermal isomerization are indicated by the recovery of the negative signal state (Figure 26). Depending on the used MO:CD concentration ratio, the inclusion complex of MO with CD has different stoichiometries,[271−277] and therefore the complexes show different femtosecond behavior.[278] The transient signal of the 1:1 complex is similar to that of free (in water) MO (Figure 26). This is because the active part (−N=N−) of the dye in the isomerization process is still located outside of the CD cavity. However, for a 1:2 MO:(α-CD)$_2$ complex, where the dye is found completely inside the macrocapsule provided by the two α-CD capsules, a slower relaxation time (1.5 ps, about 2 times longer than that of free MO in water) and considerably lower trans−cis isomerization yield (30%) were observed. The result clearly indicated that the confinement of MO by two CD cavities affects its dynamics and the photoisomerization is controlled by the restriction imposed by the cavity. For the case of the γ-CD cavity, it was found to host two molecules of MO, forming a trapped dimer, 2(MO):γ-CD, and changes in the relaxation dynamics and isomerization yield

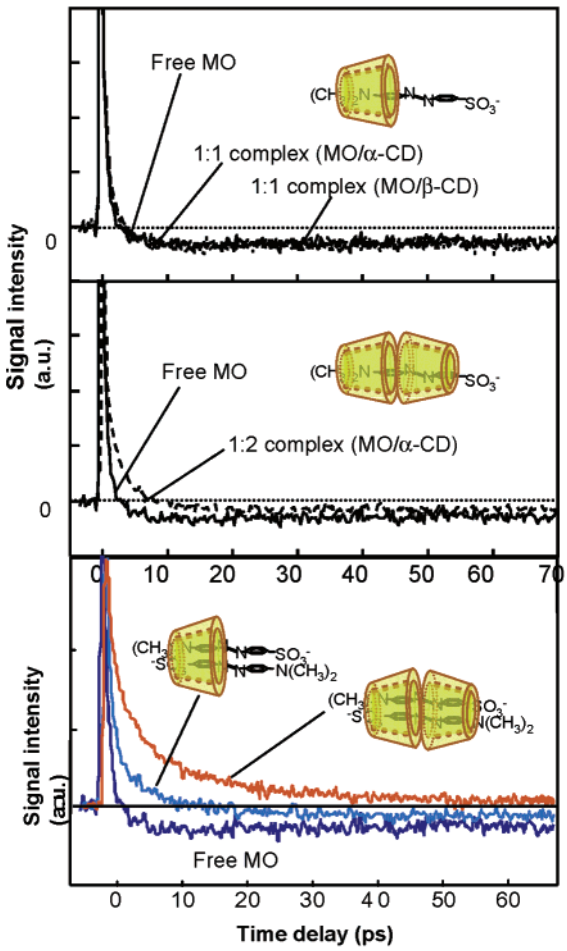

Figure 26. Decays of ultrafast transient lens (UTL) signal of methyl orange (MO) in water and in the presence of CD. Note the dependence of the signal on the stoichiometry of the complexes shown as insets.[278]

were also observed. The result was explained on the basis of a strong molecular interaction between the encapsulated stacked monomers of the guest inside the cavity. Upon addition of another molecule of γ-CD to close the nanospace, leading to there being two MO molecules trapped within the cage formed by two CD molecules, ((MO)$_2$:(γ-CD)$_2$, the relaxation dynamics becomes significantly slower (∼1.5 and ∼15 ps), and remarkably no cis isomer was formed. Most probably, the intermolecular interaction between the two sequestered MO molecule is enhanced in the 2:2 confined structure. The formation of an aggregate-like intermediate was proposed on the basis of transient absorption spectra of free, 2:1, and 2:2 complexes, where a blue transient band appears only for the case of the 2:2 complex.[278]

Femtosecond dynamics of Orange II (OII) encapsulated by CD, which is similar to MO, was also studied by the same group using the UTL technique.[279] OII in the presence of CD only shows the formation of a 1:1 inclusion complex, in which the confined structure (mode of penetration of the dye inside the cavity) depends on the nature of host (Figure 27). For OII:β-CD, the benzenesulfonate moiety is not included in the cavity, while for OII:γ-CD this part is protected by the molecular cage.[280,281] The transient made from the UTL measurements carried out in the absence and in the presence of β-

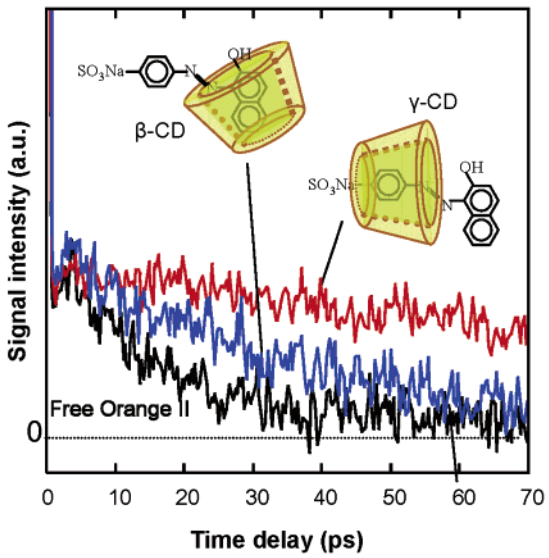

Figure 27. Decays of UTL signal of Orange II in water and in the presence of β- and γ-CD.[279]

and γ-CD showed a remarkable slowing down of the long component in comparison with the dynamics of water solution (Figure 27).[279] This component changes from 13 ps in water to 28 and 140 ps in β- and γ-CD, respectively. The difference was interpreted as a result of the formation of H-bonds between the OH groups of the guest and those of the cyclodextrin glucopyranose unit, hindering the free motion of the guest inside the nanocavity, extending the time needed for the intermediate state to isomerize, and slowing down the cooling process. Comparison of the behaviors of MO and OII in the presence of CD suggests that these hosts can also interact with the guest by H-bonding interactions rather than only by hydrophobic ones.

The ultrafast isomerization dynamics of cyanine dyes along the methine chain (barrier reaction coordinate) connecting the aromatic rings has been extensively studied in solution.[132,137] Several studies have been done in different solvents having different viscosity and under different experimental conditions.[282−286] The theory of Bagchi, Fleming, and Oxtoby (BFO)[287] was used to explain the potential energy surface with no barrier along the reaction coordinate, and at least for the cyanine dye used, the shear viscosity can indeed be taken as a reasonable parameter of the solvent friction in the barrier isomerization process.[286] The fluorescence dynamics of a cyanine dye, 3,3′-di(3-sulfopropyl)thiacyanine triethylamonium salt (STTS), encapsulated by β-CD (Figure 28) was investigated by the femtosecond fluorescence time-resolved technique.[288] The observed ultrafast dynamics of the 1:1 inclusion complex was compared to that in water solution. At short wavelengths, the decay components are 1−2 and 10 ps. At longer wavelengths, the fast decay time component increased and its contribution decreased, while the slow component increased only a little. The behavior was explained on the basis of a barrierless isomerization reaction according to a previous work where an enhancement of the fluorescence intensity was observed upon blocking the isomerization of the dye in the excited state.[289,290] Using BFO theory, the

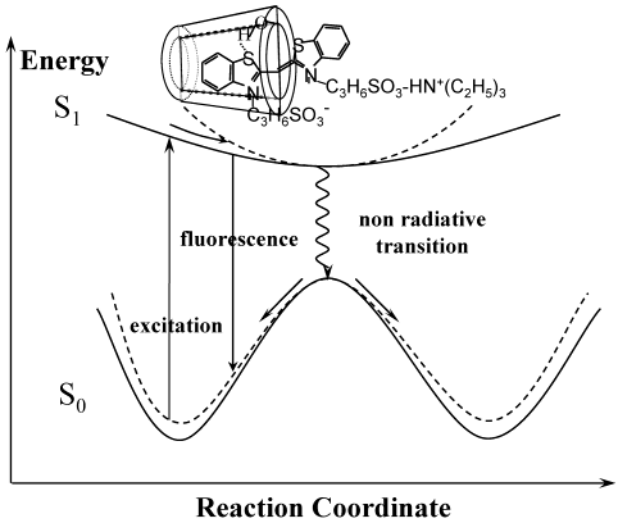

Figure 28. Structure of the inclusion complex between the STTS cyanine dye and β-CD, and one-dimensional representation of the potential energy surface at the electronic ground (S_0) and first excited (S_1) states of free (solid lines) STTS and embedded in CD (dashed lines). The reaction coordinate involves the reactive twisting motion and the nonreactive vibration. Adapted from ref 288.

fast component was assigned to the relaxation of the molecular population on the excited-state potential energy surface along the reaction coordinate, governed by the downhill potential surface and the dominant radiationless relaxation to the ground state at the minimal energy gap between the excited state and the ground state (Figure 28). The slow component was attributed to a direct radiative relaxation. Encapsulation by CD affects the short time constant, while it does not affect the dynamics of the radiative transition. On the basis of previous reports on the same dye,[289,290] the authors suggest a quickening up of the decay of excited guest along the potential energy surface upon encapsulation, where one dimension was supposed to represent the twisting process as a reactive mode, and a second dimension was supposed to represent nonreactive modes, a high-frequency vibrational mode of the excited electronic state coupled to the fast initial excitation (Figure 28).[288] The vibrational energy excess in the reactive mode could dissipate quickly, bringing the system down to the zeroth vibrational level of this mode. The included dye has more coupled atoms providing many degrees of freedom, including CD, for internal vibration in comparison with the free molecule. This affects the noradiative processes resulting from vibrations.

6. Concluding Remarks

In this review, we have examined the effect of the CD nanocavity on the fast and ultrafast events undergone by a trapped guest simple in concept, like the iodine molecule, and complex in dynamics, like the HPMO and MO molecules. It appears that the degree of confinement, which is reflected by the structure, the orientation of the guest, docking and rigidity of the complex, as well as the polarity of the cage, is the main player in defining a created wave packet in the cage and the special nature of confined

water. The system has open only a few channels to move along the reduced potential energy surface, and the neighboring water molecules may direct its evolution. A similar situation occurs in semiconductors, where the conduction electrons are not only particles but also waves. So, trapped in a confined area, electrons can have only the energies dictated by the present wave patterns that will fit in this small region. Therefore, in a similar but easy way, a free electron can then be possibly trapped by a molecule−chamber entity, such as cyclodextrins, calixarenes, Cram boxes, and zeolites, as has been realized in solution and in finite clusters. A complementary and challenging experiment in this direction will be the study of an electron:molecular chamber complex (an electron caged into a unique molecular entity), comparing the result with the available understanding of electrons dynamics in bulk and in cluster solutions. Interestingly, the surrounding of the confined geometry (external reservoir) might be changed, allowing a tuning of the (electrical field) properties of the outer-sphere solvation shell. Water molecules located inside and at both gates of CD have special properties reminiscent of the biological water. Their dynamics, restricted in rotation and translation, is slower than that found in bulk water. This abnormal behavior plays a key role in molecular recognition, protein solvation and transport, and enzyme catalysis. Taking advantage of this relatively slow response might open new directions for research and potential applications in nano- and biotechnology. Finally, besides the fast and ultrafast reports on CDs reviewed here, several studies have been carried out using other nanospaces offered by membranes, normal or reverse micelles, polymers, lipid vesicles, liquid crystals, sol−gels, dendrimers, proteins, DNA, zeolites, and nanotubes.[14−30] Remarkable findings have been reported on the primary events of solvation that play key roles in the function and stability of these chemical and biological nanostructures. Potential technological applications in nano- and biotechnology due to chemical and biological confinements have already been suggested or appeared. Combining femtosecond techniques with a nanoscopic tool (using, for example, single-molecule spectroscopy) will allow one to study the femtosecond behavior of a single instead of an ensemble of wave packets. Both fields are growing up, and the future seems bright for the use of ultrafast laser techniques.[291]

7. Acknowledgment

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