

INTERROGATING ONE AND SEVERAL MOLECULES WITHIN NANOTUBES, NANOCAPSULES AND NANOPOOLS

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Studies by our group on the excited state dynamics of guest molecules encapsulated in various nanohosts have contributed to the characterization of the confinement effect. It is of great importance to gather knowledge regarding the behavior of chromophores encapsulated in tubes, capsules and pools, at both single molecule and ensemble levels. In this Lecture, we report on three classes of observations.

Single molecule within nanotubes (Figure 1): We discuss results of the first observation of a single molecule photodynamics within a mesoporous structured silicate (MCM-41) and bonded to silicate. A representative image, the photobleach fluorescence trace and the derived monoexponential decay of such complex is presented in Figure 1. We gated its picosecond time-resolved emission using single molecule microscopy. We were able to isolate single lifetime distribution arising from single molecule-nanotube complexes prepared by the ship-in-a-bottle technique whereas the system prepared by free diffusion and interaction with the zeolite framework has three individual lifetime distributions. These we assign to three separate single molecule-zeolite complexes. This assignment is confirmed by additional studies on the single molecule behavior of the proton transfer chromophore covalently bound to silica. We further report on the effect of chemical modification to the framework on the excited state behavior of a single encapsulated chromophore. We also compare the result with that of the ensemble.

Femtosecond dynamics with nanotubes (Figure 2): In this part of the lecture, I will focus on femtosecond dynamics of conformational change of Sudan I within MX (M = Na⁺, Li⁺, Mg²⁺), NaY zeolites and MCM-41 mesoporous silica in presence of solvents. The results show that the rate constant of the initial excited state intramolecular proton transfer (ESIPT) reaction in the trans-azoenol (trans-AZO) structure to give trans-ketohydrazone (trans-HYZ) form of Sudan I remains ultrafast ($\tau < 50$ fs) as in pure solution. However, within these nanocavities/nanopores the time necessary for a trans-cis isomerization in the formed trans-HYZ tautomer to yield the cis-HYZ structure increases. The largest effect was obtained when the pores contain polar and H-bonding solvents (water, methanol). The result is explained in terms of a stronger solvation of the metal cation enhancing its shielding and therefore lowering its interaction with the included dye. The use of different metal cations of MX zeolite shows that nanosolvation of cations increases the measured times for isomerization and relaxation of the involved structures. Furthermore, the observation of similar times for NaX, NaY and MCM-41 (hosts different in polarity and diameter of the pore/cavity) suggests that the trans-cis isomerization occurs by an inversion mechanism.

Motion of confined water within a nanopool (Figure 3): The last part of the talk will focus on the picosecond and femtosecond dynamics of water confined in a nanocapsule. Using ultrafast spectroscopy and a H-bonded probe to interrogate the dynamics of water network, we were able to get microscopic information on the translational and rotational motion of confined water molecules. We observed and for the first time a new and early domain in the nanostructure of confined water, characterized by a strong transition of water compactness at low water density. The fs-dynamics gives ultrashort time scale for H-bond breaking and making in confined water.

The results show that the behavior of a confined single molecule is far from that of the ensemble where the heterogeneity plays a key role in the observed signal. Within the nanopores, the dynamics is slow, due to a slow nanosolvation guided by the nature of the framework of the tube. For confined water, it is clear that the nanospace provokes a compactness not allowing a free motion of water molecules. The results obtained here is important for a better understanding of several confined phenomena happening chemistry, physics and biology.

