Project MNiSW: Influence of environment on photochromism. Investigation of intramolecular proton transfer and photoinduced structural changes in some aromatic Schiff bases; 2007-2010

The project concerns the influence of the homogenous and heterogeneous environment on the photochromic cycle of the selected molecules belonging to aromatic Schiff bases with intramolecular hydrogen bond. The measurements of the spectra and the lifetime dynamics has been performed for each forms (tautomers) of Schiff bases taking part in the photochromic cycle in a number of differently interacting solvents (as well as in the function of temperature), in micelle systems and micro- and mesoporous molecular sieves (zeolites, MCM-41). The photobehavior of the chosen compounds from salicylideneaniline and hydroquinone family of Schiff bases has been compared.

It has been observed that the excited state of the primary enol tautomer decays due to the two ultrafast competing processes: proton transfer (ESIPT) and internal conversion. The first one takes place in most cases within 100 fs, with the exception of strongly protic alcohols in which it is increased up to 400 fs due to the participation of the intramolecular hydrogen bond in the proton transfer. The second process decreases the efficiency of the creation of the photochromic form (absorbing in the visible part of the spectrum) and leads to the occurrence of very long-lived form absorbing in the ultraviolet region.

The lifetime of the keto form, which is a direct precursor of the photochromic form, changes in a large range from single ps to ns, and shows the influence of the two factors: the structural changes with rate constant decreasing with lowering temperature, and the internal conversion which dominates below 200 K. The lifetime of the keto tautomer increases in the solvents with stronger specific interactions (hydrogen bonds) and with increasing viscosity of the solvent but decreases with increasing polarity of the solvent. W micelle systems and in molecular sieves the lifetime is considerable longer and decays in a multiexponential way due to the heterogeneity and the existence of different conformers.

The lifetime of the photochromic form is longest in polar environment (ms). It is decreased when the concentration of the photochrome is increased or in specifically interacting solvents, which is explained in terms of the role of intermolecular hydrogen bonds in the mechanism of the decay of the photochrome. Due to the presence of the water, the photochromic form has a vary short lifetime in micelles, whereas the lifetime in molecular sieves increases up to several days. An additional problem has been found due to the hydrolysis which cause the degradation of the system. Moreover, in molecular sieves and the solvents with hydrogen bonds ability the enol tautomer is not the only present in the ground state but the equilibrium shifts towards the keto tautomer.