Photostability of hydrogen bonded system: Case study of imidazole and imidazole clusters

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Hydrogen bonds are of fundamental importance in chemistry and biology. Structure and functionality of hydrogen bonds in the ground state are quite well understood. However, their dynamics in the excited electronic states is still unclear. Photochemical processes taking part in the hydrogen bonded systems may be related to the photostability of biomolecular systems, i.e. their ability to sustain UV radiation. It has been proposed that electron-driven proton transfer processes along hydrogen bonds can play an important role for the ultrafast excited-state deactivation of biological molecules and supermolecular structures, such as DNA base pairs, peptides or UV-protecting pigments. [1, 2]

Here, we have picked imidazole as a system which is able to form strong hydrogen bonds in the ground state. We have investigated photochemistry of imidazole molecule both in gas phase and in form of a cluster by means of theoretical chemistry, both in time-independent approach (CASSCF and CASPT2 calculations) and *ab initio* quantum molecular dynamics methodology (Full Multiple Spawning approach [3]).

Main photochemical channel of the gas phase imidazole molecule consists of fast dissociation of the N-H bond. This channel is however suppressed by the other imidazole molecule for the imidazole dimer. In other words, it is shown that the complexation via hydrogen bonding brings photostability to the system. This conclusion is potentially important in a biophysical context, as similar bonding pattern as in imidazole clusters can be also find in DNA base pairs or peptides.

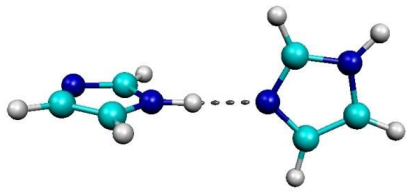

Fig. 1 – Ground state structure of imidazole dimer.

Our calculations provided a basis for interpretation of the photodissociation experiment performed in the group of Dr. Michal Fárník in J. Heyrovský Institute of Physical Chemistry. [4]

References

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