Soutenance de thèse

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Dynamics and Photodynamics of Acetylacetone in para-Hydrogen matrices

Acetylacetone (AcAc) exists as a mixture of enol and keto tautomers. Besides providing a good example for the study of tautomerization, it is a model system for investigating intramolecular hydrogen bonds in its enol form. Trapping AcAc in the soft parahydrogen (pH_2) environment brings out new opportunities to investigate its properties. Infrared spectra of the samples give a good characterization of the two stable enol and keto tautomers. The keto/enol ratio in solid pH_2 is found to be higher than in other matrices. While vibrational bands of keto are narrow, those of enol are broad, reflecting the intrinsic properties of the enol which exhibits three entangled large amplitude motions (two methyl torsions and the intramolecular hydrogen transfer). Surprisingly, narrowing of some of these bands is observed in a slow time evolution. This effect is interpreted as a consequence of nuclear spin conversion in the hydrogen atoms of the methyl groups, giving access to AcAc species differing by their nuclear spin symmetry. This offers new pertinent investigations on the large amplitude motions, especially on the intramolecular hydrogen transfer.

AcAc/pH_2 samples have been irradiated by UV laser beams. Irradiation at 266 nm induces isomerization from the stable chelated enol form to non chelated conformers, similarly to the case of other matrices. A clear IR signature of the conformers is obtained thanks to the parahydrogen host. Irradiation at 248 nm induces the enol/keto tautomerization. The kinetics of this interconversion highlights a non-direct process. Fragmentation is clearly observed under irradiation at 193 nm, followed by chemical reaction with the hydrogen host.

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Thèse en co-tutelle soutenue à Cuba

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