STRUCTURE AND PHOTODYNAMICS OF ACETYLACETONE ISOLATED IN PARA-HYDROGEN

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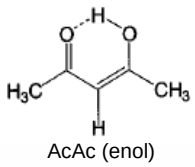
Introduction

Acetylacetone

- One of the smallest molecules exhibiting proton transfer between two O atoms in gas phase.



AcAc (enol)

Open questions:

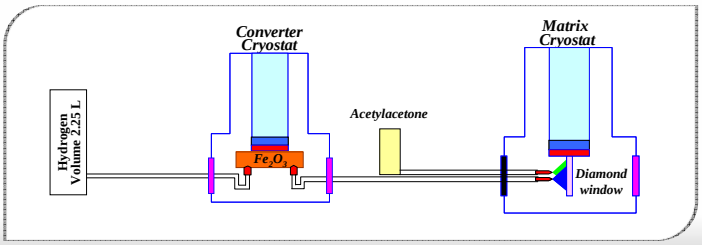
- CH_3 Rotamers or spin conversion?
- Tautomeric enol– keto equilibrium?
- Isomerization vs. fragmentation upon UV irradiation?

Para-hydrogen matrices

- Solid molecular hydrogen with all molecules in the J=0 rotational state → a very attractive medium for matrix isolation experiments [1,2].
- Very weak interaction and "softness" of pH_2 crystal result in very small perturbation on the molecules.

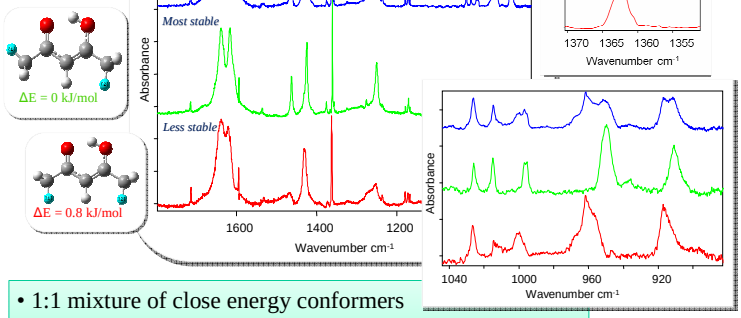
Experimental

- pH_2 prepared in a copper converter (Ø 1 cm, l = 5 cm) filled with Fe_2O_3 inside a closed-cycle helium cryostat
- pH_2 directly deposited from the converter held at ~ 18 K
- Acetylacetone deposited through separate inlet
- Flow rate of Acetylacetone and pH_2 regulated by adjusting needle valves
- Diamond window stabilized at 4.1 K



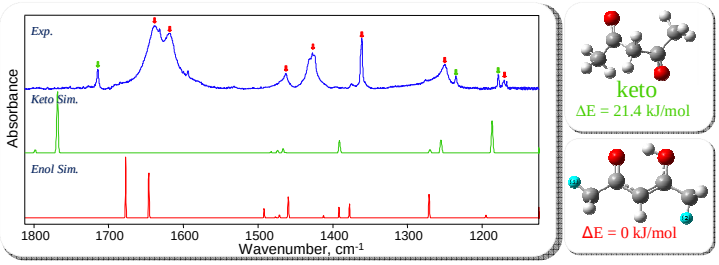
Acetylacetone in pH_2

CH_3-conformers



- 1:1 mixture of close energy conformers
- 295 K thermal equilibrium frozen in the p-H_2 matrix
- Relaxation to the most stable conformer at 4.1 K.

Enol-keto tautomers

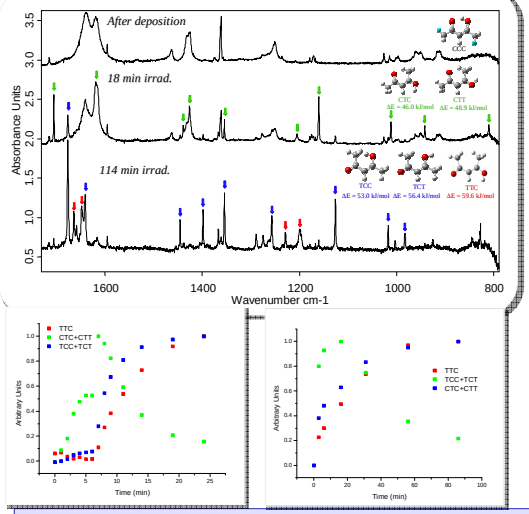


Estimations: enol/keto = 93/7 compared to 78/22 in GP[3], 82/18 in LP[4]

Geom. Opt. MP2/6-311++G(2df, 2pd) . / Freq. B3LYP/6-311++G(3df, 3pd)
Nonscaled frequencies

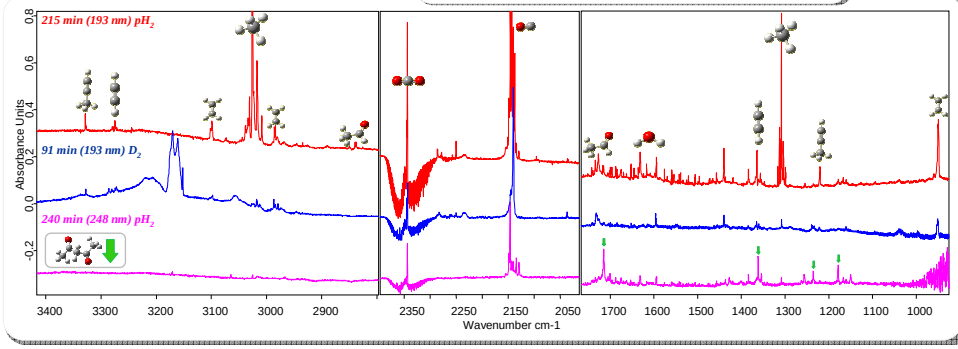
UV irradiation

Laser irradiation at 266 nm



Five additional isomers in pH_2 matrices after UV (266 nm) irradiation, compared to four in Neon [5]

Laser irradiation at 193 and 248 nm



- Fragmentation of the acetylacetone takes place after long time of UV irradiation.
- Breaking of pH_2 molecules under UV (193 nm) irradiation explains all products.
- Enol – Keto tautomerization is favored under UV (248 nm) irradiation

Perspectives

-To assign and explain the new and unassigned bands in pH_2 and D_2 matrices.
-Make the simulation of the system in the ground state to understand the CH_3 issue.
-Make the simulation in order to understand the isomerization and fragmentation pathways.

References :

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Acknowledgements

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