Photoreactivity and H-transfer in “classical” and “quantum” matrices

C. Crépin[1], *A. Gutiérrez-Quintanilla*[1,21], *M. Chevalier*[1], *J. Ceponkus*[3], *R. Platakyte*[1,3], *G. A. Rojas-Lorenzo*[2]

[1] Institut des Sciences Moléculaires d'Orsay (ISMO), CNRS, Université Paris-Saclay, Orsay, France
[2] Instituto Superior de Tecnologías y Ciencias Aplicadas (InSTEC), Universidad de La Habana, La Habana, Cuba
[3]Institute of Chemical Physics, Vilnius University, Vilnius, Lithuania
claudine.crepin-gilbert@universite-paris-saclay.fr

Cryogenic matrices of rare gas solids are well-known powerful tools for studying isolated molecular species, and especially unstable species, under experimental conditions close to the gas phase. Perturbations due to the rare gas environment are generally small. The quantum solid of parahydrogen (pH_2) is even more attractive for investigating molecular processes at play in guest species due to its softness. In particular, large amplitude motions of molecules trapped in pH_2 can be preserved. Part of our studies aims to probe the weak perturbations induced by pH_2 on this kind of molecular motions.

We use matrix isolation to investigate the properties of small molecules with an intra-molecular hydrogen bond (IHB) as well as their UV-induced photoisomerization. The UV irradiation leads to the formation of different conformers, depending on the molecule, the matrix and the UV wavelength. These conformers correspond to the IHB opening and are stabilized in the matrix. The infrared spectroscopy of the samples makes it possible to characterize the closed conformer (with IHB) and the photoproducts. We performed the experiments in rare gas and para-hydrogen matrices to highlight the possible specific role of the environment.

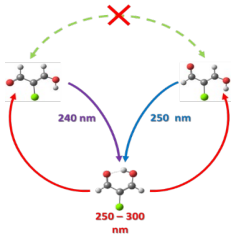

Figure 1: *The three most stable conformers of 2ClMA and UV irradiation favoring their production.*

The case of 2-chloromalonaldehyde (2ClMA) embedded in cryogenic matrices is especially interesting. This derivative of the simplest *β*-dialdehyde (malonaldehyde) exhibits a resonant assisted hydrogen bond (RAHB) in its enolic conformation of lowest energy [1] (Fig. 1, bottom). Three open conformers are characterized after UV irradiation of the matrix. By using specific sequences of UV irradiation at specific wavelengths, it was possible to obtain samples containing a single conformer [2] (Fig.1).

We also focus our attention on the process of H transfer (a large amplitude motion) occurring (or not) in chelated form with RAHB. The tunnelling splitting of the vibrational levels due to the H transfer in the IHB is detected by the observation of a few doublets in the IR spectrum of 2ClMA in pH_2. Of note, we have shown that orthohydrogen, as an impurity in pH_2, quenches the tunnelling process [3]. The tunnelling splitting does not exist in Ne. The sites where 2ClMA is trapped are explored by molecular dynamics calculations to document possible matrix specificities in order to explain the matrix effect on tunnelling [1]. The process of isomerization and tunnelling in matrices will be discussed.

Index Terms: hydrogen bond, tunnelling, cryogenic matrices, photoisomerisation, parahydrogen.

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1 Present address: IPREM, Université de Pau et des Pays de l’Adour, Pau, France