Local and Remote Conformational Switching in 2-Fluoro-4-Hydroxy Benzoic Acid

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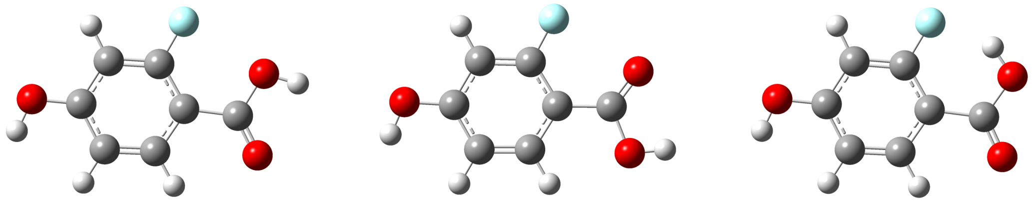
In this work, 2-fluoro-4-hydroxy (2-F-4-OH) benzoic acid was isolated in Ar matrices and selective conformational changes were induced by near-IR irradiating the sample. Upon deposition, three conformers could be observed in the matrix, denoted as **A1** (left), **A2** (middle), and **D1** (right), respectively.[1]



The first two of them (**A1** and **A2**) are *trans* carboxylic acids as they contain an intramolecular hydrogen bond between the H and the carbonyl (C=O) O atoms in the carboxylic (COOH) group, whereas **D1** is a *cis* carboxylic acid with an intramolecular hydrogen bond between the F atom and the H atom in the COOH group, which otherwise has the same structure as **A1**. The difference between **A1** and **A2** lies in the orientation of the O atom in the C=O moiety with regard to the F atom, *i.e.*, whether they are on the opposite or on the same side of the molecule, respectively. All three conformers have their H atom in their 4-OH group facing the opposite direction with regard to the F atom.

The stretching overtones of the 4-OH and the OH groups of the COOH moiety were selectively excited in the case of each conformer. Unlike **A2**, which did not show any response to irradiation, **A1** could be successfully converted to the higher-energy form **D1**, which latter spontaneously converts back to **A1** via tunneling. However, the conversion rate could be significantly increased by selectively exciting the OH vibrational overtones of **D1**. Besides, quantum efficiencies have been determined for the 'local' or 'remote' excitations, *i.e.*, when the OH stretching vibrational overtone in the COOH or in the 4-OH group is excited in order to induce the OH rotamerization in the COOH group. Both 'local' and 'remote' conformational switching are induced by the same type of vibration, which allows for a direct comparison of how much energy is lost by energy dissipation during the two processes. The experimental findings indicate that the 'local' excitation is only marginally more efficient than the 'remote' one.

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[1] Góbi, S.; Balbisi, M.; Tarczay, G. Local and Remote Conformational Switching in 2-Fluoro-4-Hydroxy Benzoic Acid. *Photochem.* **2022**, 2, 102–121.