

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

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Introduction

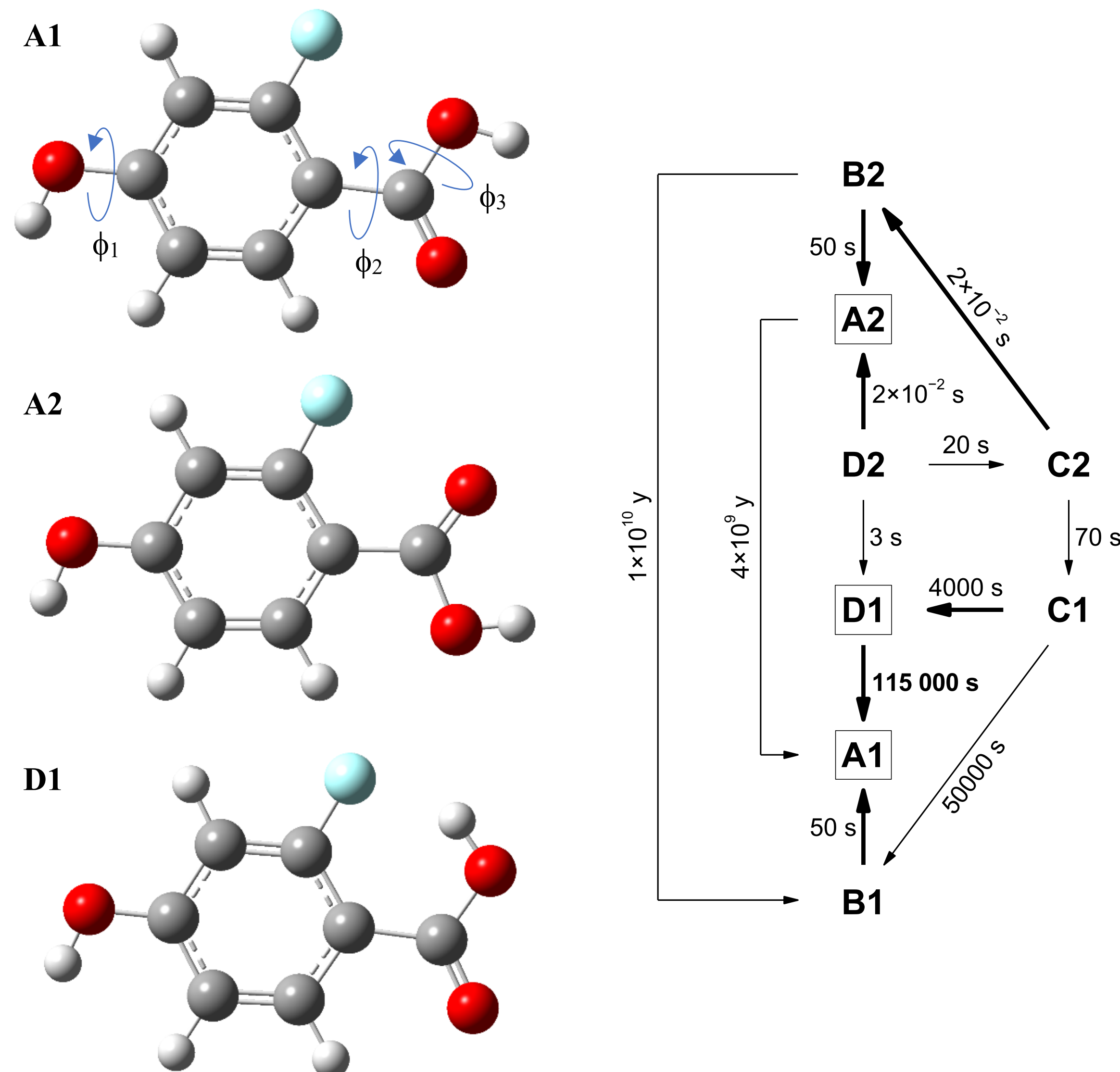
We aimed to investigate the selective conformational switching of a matrix-isolated 2-fluoro-4-hydroxy benzoic acid achieved by narrowband near-IR laser irradiation. This molecule serves as a great example, in which both ‘local’ and ‘remote’ switching can be done by exciting the same type of vibration (i.e., OH overtone) selectively, and their efficiencies can be directly compared with each other. [1]

Experimental Details

- $T_{\text{dep.}} \simeq 375 \pm 2$ K
- Codeposition with an excess of Ar on a CsI optical window at 13 K
- NIR- & MIR spectra of thiourea collected in Ar matrices
- Selective irradiation experiments with NIR laser light

Theoretical Results

- eight minima structures were found (B3LYP/cc-pVTZ)
- only three of them are expected to be experimentally observed
- anharmonic vibrational analysis was also carried out



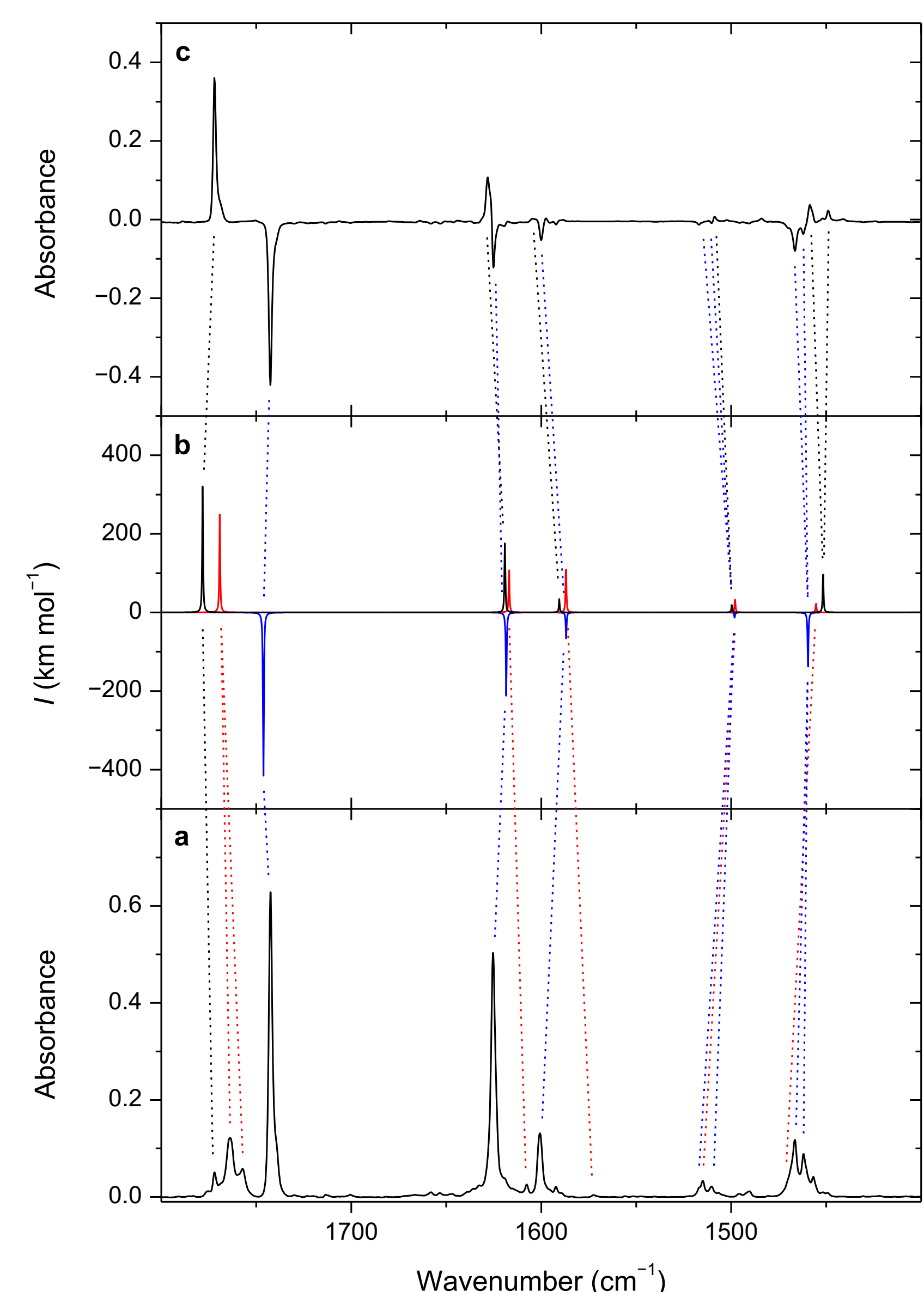
(left) Structures of the experimentally observed conformers. (right) Calculated tunneling half-lives. The values are scaled so that it matches that of the experimental $D1 \rightarrow A1$. The fastest processes for each conformers are highlighted in bold, whereas the labels of the conformers that can be experimentally observed are outlined.

Acknowledgements

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Experimental Results

- Selective excitation of the $2\nu(\text{OH})$ modes of the conformers
- ‘Local’ (OH of the COOH group) or ‘remote’ (4-OH) excitations
- Rotation of the H atom on the COOH group is induced in all cases
- **A1** converts to **D1** and vice versa
- Band response upon excitation confirms the vibrational assignment
- No similar effect could be observed for conformer **A2**
- Quantum efficiencies depend slightly on the excited group position
- Spontaneous conversion of the higher-energy **D1** to **A1** via tunneling
- Tunneling rate was found to be two orders of magnitude slower than that of the vibrationally induced one



(a) Mid-IR spectrum of the 2-F-4-OH benzoic acid in the 1800–1400 cm^{-1} range after deposition; (b) simulated spectrum of conformers **A1** (blue negative trace), **A2** (red), and **D1** (black) based on the anharmonic computations; (c) difference spectrum obtained by subtracting the spectrum taken after deposition from the one collected after ‘locally’ exciting **A1** at 6952 cm^{-1}

Future goals

- Repeat experiments in an other, exotic matrix: *para*-H₂
- *para*-H₂ is a soft quantum solid with unique properties
- The tunneling rate observed in *para*-H₂ is expected to be much closer to the theoretical value [2]

References

- [1] Góbi, S.; Balbisi, M.; and Tarczay, G., *Photochem*, **2022**, 2, 102–121.
- [2] Góbi, S.; Ragupathy, G.; Bzásó, G.; and Tarczay, G., *Photochem*, **2022**, submitted