

Large amplitude motions of molecules in solid *para*-hydrogen

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Solid parahydrogen (*p*H₂) offers unique conditions for the study of molecular properties by matrix isolation. In particular, this quantum solid is a very low-disturbing environment and large amplitude motions can be preserved. The spectroscopic analysis of these motions is a powerful probe of the weak perturbations induced by *p*H₂. Our group studies two kinds of large amplitude motions: (i) H-transfer in molecules involving internal hydrogen bond (IHB), and (ii) methyl torsion/rotation in methylated linear molecules.

(i) β -dicarbonyls – molecular family of malonaldehyde (MA) and acetylacetone - are prototype molecules with an IHB reinforced by a conjugated π -electron system (resonance assisted H bond: RAHB) in their chelated enol forms. The H-transfer in MA is revealed in the isolated molecule by the tunneling splitting of vibrational levels.¹ A similar signature is observed for the first time in *p*H₂ with the chlorine derivative (see Figure). This work highlights the weakness of the perturbation due to the quantum solid.² The spectroscopic results on the halogenated derivatives of acetylacetone also show a good similarity between the gas phase and solid *p*H₂. The matrix experiments provide new data to exploit in order to understand some of the puzzling patterns observed in the spectra.

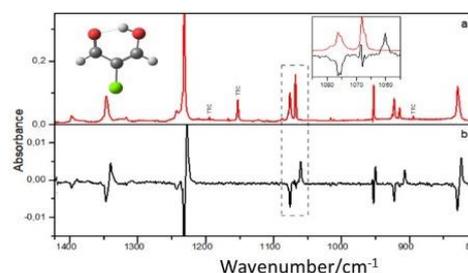
(ii) Methyl rotation was found to be weakly perturbed in *p*H₂ in the case of small molecules such as CH₃F.³ The spectroscopic structure in the case of propyne (study in collaboration with *D.T. Anderson* - Wyoming University), reveals a greater perturbation of methyl motion.⁴ In addition, unexpected spectral lines and structures are detected, which could signify isolation of the molecule in more than one trapping site, with site-dependent specificities. Other methylated linear molecules are under study.

Figure: IR spectra of chloromalonaldehyde in *p*H₂

Top: spectrum at 3K

Bottom: difference spectrum at 5K minus at 3K.

All vibrational bands of the chelated form show a structure due to the tunneling effect (see the insert). The populations of the doublet components in the ground state depend on the temperature.



¹ Lüttchwager, N. O. B.; Wassermann, T. N.; Coussan, S.; Suhm M. A. Vibrational tuning of the Hydrogen transfer in malonaldehyde – a combined FTIR and Raman jet study *Mol. Phys.*, **2013**, *111*, 2211 and refs therein.

² Gutiérrez-Quintanilla, A.; Chevalier, M.; Platakyte, R.; Ceponkus, J.; Crépin C. Intramolecular hydrogen tunneling in 2-chloromalonaldehyde trapped in solid *para*-hydrogen, *Phys.Chem.Chem.Phys.*, **2020**, *20*, 28658.

³ Lee, Y.-P.; Wu, Y.-J.; Hougén, J. T. Direct spectral evidence of single-axis rotation and ortho-hydrogen-assisted nuclear spin conversion of in solid parahydrogen. *J. Chem. Phys.* **2008**, *129*, 104502.

⁴ Strom, A. I.; Gutiérrez-Quintanilla, A.; Chevalier, M.; Ceponkus, J.; Crépin, C.; Anderson, D. T. Matrix Isolation Spectroscopy and Nuclear Spin Conversion of Propyne Suspended in Solid Parahydrogen *J. Phys. Chem. A*, **2020**, *124*, 22, 4471.