INTERNAL ROTATION IN 4-FLUOROACETOPHENONE AND METHYL 4-FLUOROBENZOATE AND THEIR MONO-HYDRATES

X. WANG, J.-U. GRABOW, *Institut für Physikalische Chemie und Elektrochemie, Leibniz Universität Hannover, 30167 Hannover, Germany* ; **J. LI, Y. ZHENG, Q. GOU**, *School of Chemistry and Chemical Engineering, Chongqing University, Daxuecheng South Rd. 55, 401331, Chongqing*

The rotational spectra of 4-Fluoroactophenone and Methyl 4-fluorbenzoate have been investigated by rotational spectroscopy, using a Fourier transform microwave spectrometer operated in the frequency ranges 2-20 GHz[1] and 2-26.5 GHz[2], respectively. Quantum chemical calculations were employed to perform conformational analyses, obtaining only one stable conformer at the MP2/6-311+G(d,p) level for both molecules. Arising from the different CH_3O- and CH_3- groups of 4-Fluoroactophenone and Methyl 4-fluorbenzoate, the changes in the structure and the V_3 barrier of the methyl internal rotation were analyzed. Furthermore, the non-covalent interactions in 4-Fluoroactophenone-H_2O and Methyl 4-fluorbenzoate-H_2O were visualized using Bader's quantum theory of atoms-in-molecules[3] and Johnson's non-covalent interaction analysis[4]. The rotational spectrum of 4-Fluoroactophenone-H_2O has already been analyzed. Interestingly, the same non-covalent interaction binding sites are also present in Methyl 4-fluorbenzoate-H_2O, but the preference in the binding sites for the global minimum reverses between the two most stable isomers of 4-Fluoroactophenone-H_2O and Methyl 4-fluorbenzoate-H_2O at the MP2/6-311++G(d,p) level. The molecular electrostatic potential[5] of 4-Fluoroactophenone and Methyl 4-fluorbenzoate was mapped to visualize the different effect of the CH_3O- and CH_3-groups on the electron densities, which explains why the preference for the global minimum is predicted to be opposite.

[1] doi:10.1063/1.4994865, J. Chen, Y. Zheng, J. Wang, G, Feng, Z. Xia and Q. Gou, *J. Chem. Phys.*, **147**, 094301, (2017).

[2] doi:10.1016/j.jms.2012.07.006, M. K. Jahn, D. A. Dewald, D. Wachsmuth, J.-U. Grabow and S. C. Mehrotra, *J. Mol. Spectrosc.*, **280**, 54-60, (2012).

[3] doi:10.1021/cr00005a013, R. F. W. Bader, *Chem. Rev.*, **91**, 893-928, (1991).

[4] doi:10.1021/ja100936w, E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen and W. Yang, *J. Am. Chem. Soc.*, **132**, 6498-6506, (2010).

[5] doi:10.1039/D1CP02805G, J. Zhang and T. Lu, *Phys. Chem. Chem. Phys.*, **23**, 20323-20328, (2021).