

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

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The rotational spectra of 4-Fluoroacetophenone and Methyl 4-fluorobenzoate have been investigated by rotational spectroscopy, using a Fourier transform microwave spectrometer operated in the frequency ranges 2-20 GHz¹ and 2-26.5 GHz², 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 CH₃O- and CH₃- groups of 4-Fluoroacetophenone and Methyl 4-fluorobenzoate, the changes in the structure and the V_3 barrier of the methyl internal rotation were analyzed. Furthermore, the non-covalent interactions in 4-Fluoroacetophenone-H₂O and Methyl 4-fluorobenzoate-H₂O were visualized using Bader's quantum theory of atoms-in-molecules³ and Johnson's non-covalent interaction analysis⁴. The rotational spectrum of 4-Fluoroacetophenone-H₂O has already been analyzed. Interestingly, the same non-covalent interaction binding sites are also present in Methyl 4-fluorobenzoate-H₂O, but the preference in the binding sites for the global minimum reverses between the two most stable isomers of 4-Fluoroacetophenone-H₂O and Methyl 4-fluorobenzoate-H₂O at the MP2/6-311++G(d,p) level. The molecular electrostatic potential⁵ of 4-Fluoroacetophenone and Methyl 4-fluorobenzoate was mapped to visualize the different effect of the CH₃O- and CH₃- 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](https://doi.org/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](https://doi.org/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](https://doi.org/10.1021/cr00005a013), R. F. W. Bader, *Chem. Rev.*, **91**, 893-928, (1991).

⁴[doi:10.1021/ja100936w](https://doi.org/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](https://doi.org/10.1039/D1CP02805G), J. Zhang and T. Lu, *Phys. Chem. Chem. Phys.*, **23**, 20323-20328, (2021).