

Effect of fluorine substitution on non-covalent interactions in molecular complexes of aromatic compounds

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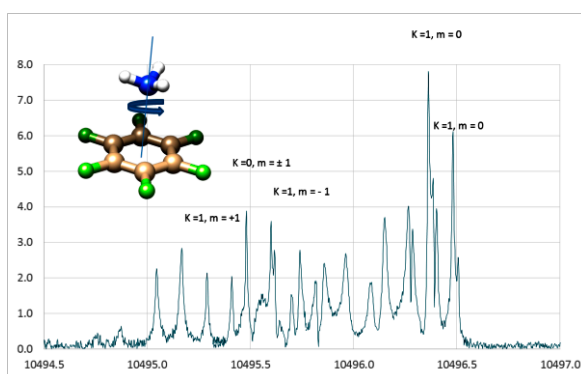
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The rotational spectra of pentafluoropyridine–water[1] and hexafluorobenzene–water[2] have shown unambiguously that substitution by fluorine atoms on the aromatic ring strongly influences its binding abilities causing both molecules to interact with water through a lone pair–p-hole interaction between the water oxygen and the ring.

A systematic study on the effects of fluorine substitution on the binding abilities of aromatic molecules was undertaken and we report rotational spectroscopy studies performed with a cavity based pulsed jet Fourier transform microwave spectrometer on a series of fluorine substituted pyridines, namely 2,4–fluoropyridine, 3,5–fluoropyridine and 2,4,6–fluoropyridine with water and more studies involving the complexes of pentafluoropyridine and hexafluorobenzene with different ligands such as NH₃ and CO.

In the complexes formed by the di-substituted pyridines, the water moiety forms an in-plane hydrogen bond with the heterocyclic nitrogen atom and this is by far the most stable conformation. In the tri-substituted pyridine–water complexes two isomers are possible, but the where the lone pair–p-hole form is present is the one observed in the rotational spectrum. The same interaction is present when pentafluoropyridine and hexafluorobenzene are used as substrate for the binding of CO and NH₃.

From the spectroscopic constants of various isotopic species the structures and the parameters related to the observed large amplitude motions have been determined, while theoretical calculations have allowed the unveiling and quantification of the different interactions present in the complexes.



[1] Calabrese, C.; Gou, Q.; Maris, A.; Caminati, W.; Melandri, S. *J. Phys. Chem. Lett.* 2016, **7**, 1513. <http://dx.doi.org/10.1021/acs.jpcclett.6b00473>

[2] Evangelisti, L.; Brendel, K.; Maeder, H.; Caminati, W.; Melandri, S.; *Angew. Chem. Int. Ed.* 2017, **56**, 13699. <https://doi.org/10.1002/anie.201707155>

Chalcogen bond formation: The non-covalent, intermolecular sulfur–sulfur interaction of dimethyl sulfide and sulfur dioxide

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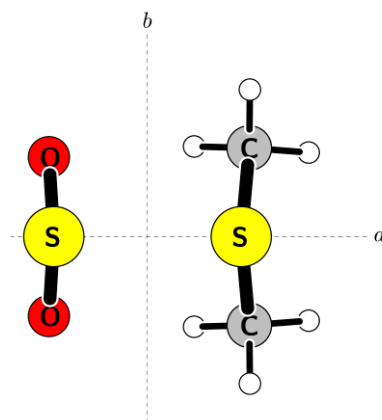
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An analog to the well-studied halogen–halogen bond, the chalcogen–chalcogen interaction occurs when one chalcogen atom acts as an electron donor to another chalcogen. This combined experimental and theoretical study presents a detailed analysis of the sulfur–sulfur interaction in the dimethyl sulfide and sulfur dioxide complex. The gas-phase chalcogen–chalcogen noncovalent interaction has been characterized by using state-of-the-art quantum-chemical computations combined with cavity type Fourier-transform microwave spectroscopy.

Rotational transitions belonging to seven different isotopologues, which are split by the motion of the two methyl tops of dimethyl sulfide, were fit using the XIAM program [1]. The abundance of isotopic information allows for a detailed determination of the structure of the complex. From the theoretical point of view, the accurate equilibrium structure was computed by exploiting the so-called “cheap” geometry scheme,[2] whose reliability also for molecular complexes has been demonstrated recently for the pyridine–ammonia complex [3]. From this, accurate equilibrium energetic and spectroscopic parameters have been computed, and corrected for zero-point energy and anharmonic vibrational effects obtained from density functional theory calculations.

The abundance of isotopic information allows for a detailed determination of the structure of the complex. Semi-experimental equilibrium and effective structures were determined using the Molecular Structure Refinement (MSR) software [4] taking into account anharmonic vibrational corrections at the B2PL-YP-D3/mau-cc-pVTZ-dH level [3]. The sulfur–sulfur interaction was further characterized by means of the nuclear quadrupole coupling in single ³³S substituted species of the complex and isolated molecules. The results of the “Natural Orbital for Chemical Valence/Charge-Displacement” (NOCV/CD) scheme [5] are also presented. Finally, chemical interaction energies were derived using the well-known pseudo-diatom model [6] and compared with that were obtained theoretically from the “cheap” composite scheme.



[1] Z. Naturforsch., 1996, 51a, 923

[2] Int. J. Quant. Chem., 2010, 29(2), 273

[3] Chem. Eur. J., 2017, 23, 4876

[4] J. Chem. Theory Comput., 2017, 13 (6), 3060

[5] J. Chem. Phys., 2015, 142, 084112

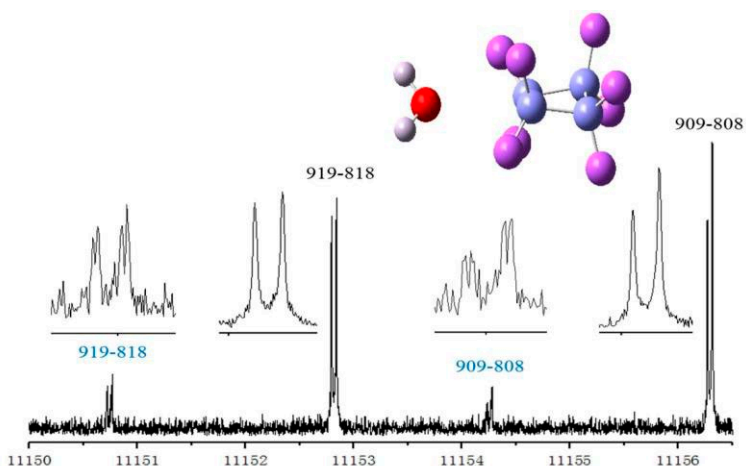
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Halogen bond and internal dynamics in Perfluorocyclobutane–water

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The rotational spectrum of the perfluorocyclobutane–water complex has been studied by Fourier transform microwave spectroscopy, which shows that the oxygen of water points toward the center of one of the C–C bond, forming a sort of halogen bond. Each rotational transition is split into three or four components, indicating that the internal rotation of water might be coupled with the ring puckering.



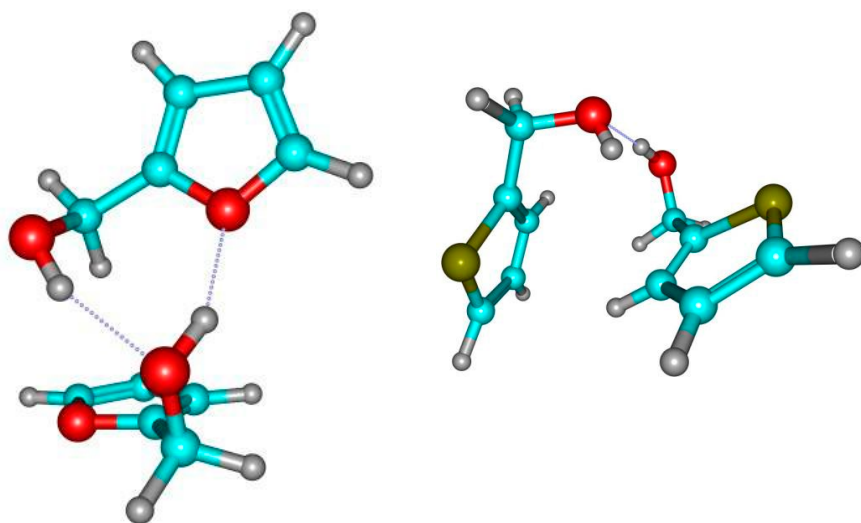
Rotational spectroscopy of the dimers and monohydrates of furfuryl alcohol and thenyl alcohol

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The dimers and the monohydrates of thenyl alcohol (TA₂, TA-H₂O) and furfuryl alcohol (FA₂, FA-H₂O) have been generated in a supersonic jet expansion and probed using both chirped-pulse and cavity Fourier transform microwave spectroscopy. The experimental results and supporting ab initio molecular orbital calculations allow comparing the conformational preferences and the role of the sulfur and oxygen atoms in the O-H...O/O-H...S/S-H...O hydrogen bonds (HBs) stabilizing the dimers. In the furfuryl monohydrates water behaves as a proton donor to the ring oxygen, in competition with a second HB to the alcohol or thiol side chain. Different behavior was observed when the ring oxygen is replaced by a sulfur atom in the thenyl monohydrates, as the water molecule is binding to the side chain and the *p* electronic cloud of the ring. Large-amplitude motions caused by water in both thenyl dimers are detected by tunneling splittings of the rotational transitions. Spectroscopic, structural and computational data will be reported.



Microwave spectroscopic characterization of the S...O/N chalcogen bond

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The intermolecular complexes formed between 2,2,4,4-Tetrafluoro-1,3-dithiethane ($C_2S_2F_4$) and water/ammonia were investigated by pulsed jet Fourier transform microwave spectroscopy and theoretical calculations. For these complexes, the most stable conformers predicted at MP2/6-311++G(d,p) level of theory were observed. Rotational assignments, ab initio calculations and quantum theory of atoms in molecules (QTAIM) analyses indicate that the observed complexes are stabilized through S...O or S...N Chalcogen Bond. The determination of the molecular structure, the tunneling splitting, and the bonding nature of S...O/N interaction will be discussed.