HALOGEN BOND AND INTERNAL MOTIONS: THE LOW-BARRIER CASE OF CF_3Cl-DIMETHYLETHER

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If halogen containing molecules form complexes and several non-convalent interactions are possible, subtle effects can determine the globally most stable conformation. While, intuitively, one might assume that hydrogen bonds are the dominating interactions, halogen haloge bonds can be competitive or even most important. Most investigations of halogen bonds come from X-ray diffraction in solid state or sometimes vibrational spectroscopy in (cryo)-solutions. However, the structural results obtained in condensed phase might be biased by lattice, matrix or solvent effects.

Perhalogenated hydrocarbons are found to prefer halogen rather then hydrogen bonds in complexes with other species, even when the partner molecule is water. In the case of F_3CCl-H_2O [a] the water molecule undergoes an almost free rotation with respect to the Cl...O connection, making the complex an effective symmetric top.

What will happen to the complex when water is substituted with a heavier, but still C_{2v} symmetric molecule? Formed in the supersonic-jet expansion we measured the Fourier transform microwave spectra of two isotopologs of the 1:1 adduct of CF_3Cl with dimethylether (DME) to determine its native global minimum shape and dynamics.

The structural and dynamical information encoded in the rotational spectra is consitent with a global minimum conformation that forms a F_3C-Cl...O halogen bond, and an almost free rotation of the -CF3 group. Besides the rotational constants and information on the internal dynamics, the quadrupole coupling constants of the chlorine atom have been determined.

[a] L. Evangelisti, G. Feng, P. cija, E. J. Cocinero, F. Castao, W. Caminati, Angew. Chem. Int. Ed. 50, 7807-7810 (2011).