WEAK $CH\cdots F$ BRIDGES AND INTERNAL DYNAMICS IN THE CH_3F-CHF_3 MOLECULAR COMPLEX

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The few rotationally resolved investigations of molecular adducts with the monomers held together by $CH\cdots F$ or $CH\cdots O$ weak hydrogen bonds (WHB) have shown the specificity and directionality of these interactions. Among them, the dimer of difluoromethane is stabilized only by $CH\cdots F$ bridges[a]. Also the heterodimer fluoromethane-trifluoromethane is expected to contain only $CH\cdots F$ linkages. Its investigation is of particular interest to size the relative weights of WHB's and dipole-dipole interaction energies. Two plausible conformations of CH_3F-CHF_3 are considered: (I) three H s-orbitals of CH_3F overlap with three F p-orbitals of the opposing CHF_3; (II) two H s-orbitals and one F p-orbital of CH_3F overlap with two F p-orbitals and one H s-orbital of the opposing CHF_3. The orbitals in conformation (I) can probably better overlap but (II) does have a more favourable electrostatic potential energy from the dipole-dipole interaction, being the two dipole moments nearly anti-parallel to each other.

Studies on WHB have mainly been performed by X ray diffraction[b] and, to a lesser extent, by IR spectroscopy in rare gas solutions[c]. Information on WHB from solid state or solution investigations can be altered by other intermolecular interactions in condensed phases and thus affect the internal dynamics of the subunits. To elucidate the balance between the two stabilization mechanisms given above, we studied the pure rotational spectrum of CH_3F-CHF_3 and its two ^{13}C species isolated in the interaction-free matrix of a supersonic jet employing Fourier transform microwave (FT-MW) spectroscopy. The rotorsional analysis reveals the equilibrium conformation of fluoromethane-trifluoromethane and the internal dynamics of the two symmetric top subunits, almost freely rotating with respect to each other.

[a] W. Caminati, S. Melandri, P. Moreschini, and P. G. Favero, Angew. Chem. Int. Ed. 1999, 38, 2924.
[b] T. Steiner, Angew. Chem. Int. Ed. 2002, 41, 48).
[c] S. N. Delanoye, W. A. Herrebout, and B. J. Van der Veken, J. Am. Chem. Soc., 2002, 124, 11854.