THE MICROWAVE SPECTRA OF FLUORINATED BENZENES ($C_6H_{6-n}F_n$) WITH WATER: STRUCTURES AND INTERNAL ROTATION DYNAMICS

KAI BRENDEL and HEINRICH MÄDER, *Institut für Physikalische Chemie, Universität Kiel, Olshausenstr. 40, D-24098 Kiel, Germany*.

The interaction of organic ring compounds with water is of special interest as it is the origin of solvation effects. A first step towards a better understanding of these effects is the investigation of the binary interaction. The technique of molecular beam Fourier transform microwave (MB-FTMW) spectroscopy has proven to be an excellent tool for such investigations. Over the last years we studied several dimers of fluorinated benzenes with water using MB-FTMW spectroscopy. An interesting feature of these dimers is the fact that *ab initio* calculations[a] predict two possible structures for fluorobenzene$\cdots$water and 1,4-difluorobenzene$\cdots$water dimer, respectively. In addition to a planar structure (σ-hydrogen bond) which corresponds to the global minimum, a local minimum corresponding to a position of the water molecule above the π-electron system of the ring (π-hydrogen bond) was found. Such a π-hydrogen bond has been reported for the benzene$\cdots$water dimer[b]. However, our investigations have shown that for the $C_6H_{6-n}F_n\cdots$water dimers (n=1,2 and 3) only the planar configurations were found to exist in the molecular beam. In the case of the dimer of hexafluorobenzene with water the complex can not be stabilized by the formation of an H$\cdots$O hydrogen bond. Instead, the electrostatic interaction favors a nonplanar structure. Since this interaction is rather weak it allows for large amplitude internal motions to occur. As a result, the dimer shows the rotational spectrum of a symmetric top although its equilibrium structure corresponds to that of an asymmetric top. The analyses of the rather complex spectra of hexafluorbenzene$\cdots$water and the structures of the different dimers will be presented.

---

[a] P. Tarakeshwar and Kwang S. Kim, B. Brutschy, JCP **110**, 17, 8501(1999)

[b] H.S. Gutowsky, T. Emilsson, and E. Arunan, JCP **99**, 7, 4883(1993)