STRUCTURE OF THE FLUOROBENZENE-HCl VAN DER WAALS COMPLEX BY MICROWAVE SPECTROSCOPY AND AB INITIO CALCULATION

SEAN A. PEEBLES, REBECCA A. PEEBLES, *(Present address: Department of Chemistry, Eastern Illinois University, Charleston, IL 61920), Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055*; ROBERT L. KUCZKOWSKI and FAITH C. BOMAN, *Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055*; MARIA EUGENIA SANZ, SONIA ANTOLÍNEZ, JOSÉ L. ALONSO and JUAN C. LÓPEZ, *Departamento de Química Física, Facultad de Ciencias, Universidad de Valladolid, 47005, Valladolid, Spain*; ELFI KRAKA and DIETER CREMER, *Department of Theoretical Chemistry, Göteborg University, S-41320 Göteborg, Reutersgatan 2, Sweden*.

The structure of the fluorobenzene-HCl complex has been studied by Fourier-transform microwave spectroscopy and ab initio calculations. Rotational constants for three isotopomers ($C_6H_5F$-$H^{35}Cl$, $C_6H_5F$-$H^{37}Cl$ and $C_6D_5F$-$H^{35}Cl$) are consistent with a $\pi$-hydrogen bonded structure with the HCl located above the fluorobenzene ring, near the ring center, and the H atom of HCl pointing towards the $\pi$-cloud of the ring. Two structures are consistent with the inertial data, one with the HCl almost perpendicular to the ring and the other with the H pointing toward the fluorine end of the ring. Ab initio calculations at the MP2/6-311++G(2df,2pd) level (+ BSSE corrections) were carried out to obtain difference electron density plots and indicate that the HCl is tilted by about $14^\circ$ from perpendicular, with the H atom toward the para carbon atom (where the $\pi$-density is significantly higher). An internal semi-circular libration of the H atom is possible, leading to an average inclination angle of about $0.7^\circ$, in reasonable agreement with the first of the two possible experimental structures. The calculations indicate that the bonding in the fluorobenzene-HCl complex is primarily electrostatic in nature with about 5.5 melectron transferred from the benzene ring to the HCl. Calculation of the complex binding energy at the CCSD(T)/6-311++G(2df,2pd) + CP(BSSE) level gives a value of 2.8 kcal/mole.