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

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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 π-hydrogen bonded structure with the HCl located above the fluorobenzene ring, near the ring center, and the H atom of HCl pointing towards the π-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° from perpendicular, with the H atom toward the para carbon atom (where the π-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°, 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.