MICROWAVE AND *AB INITIO* INVESTIGATION OF H_3N-HF-HF

S. W. HUNT, K. J. HIGGINS, M. CRADDOCK, C. S. BRAUER, K. R. LEOPOLD, *Department of Chemistry, University of Minnesota, Minneapolis, MN 55455*.

Rotational spectroscopy and *ab initio* calculations have been used to elucidate the gas phase structure and internal rotation dynamics of H_3N-HF-HF. The structure includes the formation of an HN-HF-HF ring, perturbing both the linear hydrogen bond in the H_3N-HF dimer and the angle of the HF-HF dimer. This indicates a weak secondary interaction between the fluorine of the outer HF and an ammonia hydrogen. Both the calculations and the observed spectrum indicate that a small, but significant, barrier exists for the internal rotation of the NH_3 unit. Transitions have been observed for 7 isotopic species, and for the parent isotopomer, observation of both a- and b-type transitions allows confirmation of the assignments via an internally consistent linking of the energy levels. While NH_3 and HF form an ionic solid ($NH_4{}^+F^-$) in the bulk, the isolated dimer is hydrogen bonded in the gas phase[a]. The addition of one HF represents the first step in the microsolvation of H_3N-HF and, as such, this complex is useful for understanding the role of local environment in promoting proton transfer. Additionally, energy calculations have been performed to explore the lowest frequency vibration of H_3N-HF-HF, a ring-opening motion that increases the NFF angle.

[a] A. C. Legon *Chem. Soc. Rev.* **22**,153 (1993).