A MICROWAVE AND AB INITIO STUDY OF THE NITRIC ACID - TRIMETHYLAMINE COMPLEX

GALEN SEDO, *Department of Chemistry, The University of Manitoba, Winnipeg, MB Canada R3T 2N2*;
KENNETH R. LEOPOLD, *Department of Chemistry, The University of Minnesota, Minneapolis, MN 55455*.

The microwave spectrum of the gas phase nitric acid - trimethylamine complex has been observed using Fourier transform microwave spectroscopy. The experimental rotational constants and $(CH_3)_3{}^{15}N\text{-}HNO_3$ isotope shifts are consistent with a complex in which the nitric acid proton forms a hydrogen bond to the nitrogen of the amine, similar to the experimentally determined structure of $H_3N\text{-}HNO_3$[a]. Analysis of the hyperfine structure in both the parent and $(CH_3)_3{}^{15}N\text{-}HNO_3$ spectra made it possible to determine, unambiguously, the quadrupole coupling constants of the ^{15}N nuclei in both the nitric acid and trimethylamine moieties. Ab initio calculations, using the MP2/6-311++G(2df,2pd) level of theory and basis set, have been performed and are in quantitative agreement with the available experimental data. Both the experimentally determined quadrupole coupling constants and the ab initio structure have been used to assess the degree of proton transfer occurring in the nitric acid - trimethylamine complex. These results will be compared to those obtained for the $H_3N\text{-}HNO_3$ and $HNO_3\text{-}(H_2O)_n$ [n = 0 - 3] complexes and discussed in terms of how binding partner basicity and the number of solvent molecules influence the incipient ionization of nitric acid moiety.

[a]M. E. Ott, and K. R. Leopold, *J. Phys. Chem. A* **1999**, 103,1322-1328