THE EFFECT OF MICROSOLVENT POLARITY ON A PARTIALLY BONDED SYSTEM: A MICROWAVE AND *AB INITIO* STUDY OF HCN-SO_3···AR AND HCN-SO_3···CO

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

Rotational spectra of HCN-SO_3···Ar and HCN-SO_3···CO, as well as several of their isotopically substituted derivatives, have been observed by Fourier transform microwave spectroscopy. Both complexes are symmetric tops with the Ar and CO moieties weakly bound to the sulfur atom on the side opposite the HCN. These systems represent the first step in microsolvation of partially bound HCN-SO_3 by non- or weakly polar species and, combined with previous results on HCN···HCN-SO_3, test the effect of microsolvent polarity on a partially bonded system. *Ab initio* results for both complexes also are reported. We find that HCN-SO_3···CO displays a marked *increase* in the N-S and S-C distances relative to those observed in bare HCN-SO_3 and SO_3-CO, respectively. In particular, for HCN-SO_3···CO, the *ab initio* results indicate a 0.076 $\AA$ expansion of the N-S partial bond, and a 0.166 $\AA$ elongation of the S-C van der Waals bond. For the argon complex, the changes are less dramatic, with increases of the N-S and S-Ar distances of only about 0.01 $\AA$ each. Preliminary analysis of the measured rotational constants is in agreement with these results. Further refinements of the experimental structures, as well as measurements of the dipole moments of both species are in progress. The structural results are in sharp contrast to previous work on HCN···HCN-SO_3, in which the addition of a polar HCN microsolvent molecule caused a large contraction of the partially formed N-S bond. We attribute this difference to the inability of the SO_3 to simultaneously optimize interactions on both sides of its plane.