MOLECULAR COMPLEXES ON THE BRINK OF CHEMICAL CHANGE

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The study of weakly bound complexes has been a multidimensional endeavor for over forty years. In this talk, we focus on microwave spectroscopic studies of reactive complexes, i.e., those formed from molecules that would ordinarily react under bulk conditions but which may or may not yield products in a cold, isolated cluster. The work will be put in context with a brief review of partially bound Lewis acid-base complexes, highlighting the role of near-neighbor interactions in driving chemical bond formation. With that as an historical backdrop, we then describe the recent discovery of carboxylic sulfuric anhydrides, $RCOOSO_2OH$. These species are shown to form via a barrierless or nearly barrierless cycloaddition reaction between SO_3 and carboxylic acids within a putative SO_3-RCOOH complex. Results of statistical thermodynamic calculations are presented and the potential atmospheric significance of these species will be discussed. Finally, we consider the subject of spontaneous proton transfer in cold molecular complexes and the role of microsolvation in promoting chemical change. New work on the mono-, di-, and trihydrates of the superacid "triflic acid" (CF_3SO_2OH) demonstrates that only three water molecules are needed before acid ionization takes place. In contrast, with trimethylamine, no microsolvent is necessary for proton transfer and the 1:1 complex is best regarded as a trimethylammonium triflate ion pair. Simple energetic arguments rationalize these results.