

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 may or may not yield products in an isolated cluster. Three types of systems will be discussed. First, we present a brief review of partially bound Lewis acid-base complexes and describe the role of crystallization in driving chemical bond formation. With that as an historical backdrop, we then describe the recent discovery of carboxylic sulfuric anhydrides. These species are shown to form via a nearly barrierless cycloaddition reaction between SO_3 and carboxylic acids within a putative $\text{SO}_3\text{-RCOOH}$ complex. Results of statistical thermodynamic calculations are presented and the potential atmospheric significance of these species will be discussed. Finally, we consider the role of microsolvation in promoting the spontaneous ionization of protic acids in their complexes with water. New work on the mono-, di-, and trihydrates of triflic acid demonstrates that only three water molecules are needed before the system is best regarded as a partially solvated hydronium triflate ion pair.