**MAKING HYDROGEN BONDS: Reaction kinetics of heterodimer formation**

Alberto Macario, *a,b* Myriam Drissi, *a* Chinmai Sai Jureddy, *a* Omar Abdelkader Khedaoui,*a* Theo Guillaume,*a* Brian M. Hays,*a* Ahren W. Jasper,*c* Stephen J. Klippensteinc and Ian R. Sims*a*

*a Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251, F-35000 Rennes, France*

*b Current address: Univ Sorbonne Paris Nord, CNRS, LPL (Laboratoire de Physique des Lasers) - UMR 7538, 93430 Villetaneuse, France*

*c Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, 60439, USA*

The determination of the structures of hydrogen bonded complexes has been a major field of research in gas-phase chemistry. By contrast, the characterization of the process of complex formation has barely been addressed, despite its importance in a wide range of applications. Complex formation is a key step in homogeneous nucleation and new particle formation, for example in cloud formation in planetary atmospheres and dust particle inception in circumstellar shells. What is more, under the appropriate conditions, low temperatures and/or high degrees of supersaturation, the formation of the first complex, the dimer, is the-rate limiting step of nucleation, which can become a barrierless process.

A few previous studies have been performed on the kinetics of formation of homodimers. These studies used the CRESU (reaction kinetics in uniform supersonic flow) technique mainly coupled with mass spectrometric detection and high-level quantum calculations and models. Here we have employed a completely new detection scheme, chirped-pulse FTMW spectroscopy, to study for the first time the kinetics of formation of heterodimers. This innovative technique combines the ability to generate continuous cold uniform supersonic flows with the high selectivity and general applicability of rotational spectroscopy, allowing us to follow both reactant and product concentrations simultaneously. Furthermore, the high sensitivity achieved has allowed us to employ pseudo-first-order conditions to obtain absolute rate constants. Complementary quantum chemistry calculations have been performed in order to model and better understand the reaction paths of the complexation process. We will report the measurements of rate constants for the formation of formic acid-CO2 heterodimer in a range of different pressures and temperatures. We will also address the impact that the buffer gas may cause on the complexation process. All of these results characterize for the first time the kinetics of heterodimer formation, opening a new branch in this research field.