Experimental studies of gas phase reaction kinetics and energy transfer at very low temperatures

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Chemistry at extremely low temperatures – and, in particular, the study of collisional processes in the gas phase – is a fascinating area of research. It provides a unique opportunity for a stringent comparison of experimental data with theoretical models of gas phase kinetics and energy transfer. It is also of direct application to the chemistry of such diverse environments as the atmospheres of Earth and other planets, and the synthesis of a wide range of molecular species within dense interstellar clouds (ISCs).

Over the last few years,[1] we have applied the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme, or Reaction Kinetics in Uniform Supersonic Flow) technique to the study of neutral-neutral reactions and energy transfer processes in the gas phase. This has enabled the rates of a wide range of reactions between electrically neutral species to be measured down to temperatures as low as ~10 K. These results have generated significant interest amongst theoretical chemists, and especially amongst astrochemists. Our measurements of low temperature rate coefficients have had a significant impact on the models used to simulate the chemistry of dense ISCs, as has been recognised by leading astrochemical modellers such as Millar[2] and Herbst.[3]

Apart from studies in the CRESU apparatuses in Rennes and Birmingham (now transferred to Rennes), there has been very little work on *reactive* collisions at extremely low temperatures. The free jet technique of M.A. Smith and co-workers,[4] which has permitted the study of certain aspects of ion-molecule reactions at ultralow temperatures, has not been found to be widely applicable to neutral-neutral reactions.

In this lecture I will review the experimental techniques available for studying gas phase reactive and inelastic processes at very low temperatures, and give a detailed description of the CRESU technique. I will then give an overview of the results obtained in Rennes and Birmingham, and attempt to highlight some general trends in reactivity at low temperatures. I will then focus on the results of some very recent (and as yet unpublished) studies, including rotational and spin-orbit energy transfer in collisions of CO and $C(^3P_J)$ with He and H_2, and the reaction $O + OH \rightarrow O_2 + H$.

1 See for example: I. R. Sims, J. L. Queffelec, A. Defrance, C. Rebrion-Rowe, D. Travers, P. Bocherel, B. R. Rowe, and I. W. M. Smith, J Chem Phys **100**, 4229 (1994); I. R. Sims and I. W. M. Smith, Annu. Rev. Phys. Chem. **46**, 109 (1995); I. R. Sims, in *Research in Chemical Kinetics*, edited by R. G. Compton and G. Hancock (Blackwell Science, Oxford, 1997), Vol. 4, pp. 121-148; I. W. M. Smith and B. R. Rowe, Accounts Chem. Res. **33**, 261 (2000); D. C. Clary, E. Buonomo, I. R. Sims, I. W. M. Smith, W. D. Geppert, C. Naulin, M. Costes, L. Cartechini, and P. Casavecchia, J Phys Chem A **106**, 5541 (2002); P. L. James, I. R. Sims, I. W. M. Smith, M. H. Alexander, and M. B. Yang, J Chem Phys **109**, 3882 (1998).

2 E. Herbst, H. H. Lee, D. A. Howe, and T. J. Millar, Monthly Notices of the Royal Astronomical Society **268**, 335 (1994).

3 E. Herbst, Annu. Rev. Phys. Chem. **46**, 27 (1995); E. Herbst, Chem. Soc. Rev. **30**, 168 (2001); R. Terzieva and E. Herbst, Astrophys. J. **501**, 207 (1998).

4 M. A. Smith, Int. Rev. Phys. Chem. **17**, 35-63 (1998).