

## Prof Dwayne Heard

[d.e.heard@leeds.ac.uk](mailto:d.e.heard@leeds.ac.uk)

phone: 0113 343 6471

For more details of active research projects and publications please visit our webpages at:

<http://www.chem.leeds.ac.uk/People/Heard.html>

<http://www.chem.leeds.ac.uk/fage>



### The kinetics of astrochemical and planetary reactions studied at very low temperatures

Neutral – neutral reactions are important in low temperature environments such as the interstellar medium (ISM), dense molecular clouds of star forming regions and planetary atmospheres, for example Titan, which is considered as an analogue of the primeval atmosphere of Earth. However, the chemical databases used to model such environments contain a relatively small number of this class of reaction and the low-temperature chemistry is poorly understood. We have recently shown [1-4] that despite the presence of an energy barrier, the reaction between the OH radical and ketones, alcohols and ethers can proceed to products rapidly at very low temperatures, which we interpret via a mechanism involving the formation of a weak hydrogen bonded association adduct, and quantum mechanical tunnelling, as shown schematically in Figure 1 below. These two features are present in many reactions involving hydrogen atom transfer and we propose that this behaviour (shown in Figure 2) may be widespread under the low temperature conditions found in space. Recently our data were included in an astrochemical model [5].

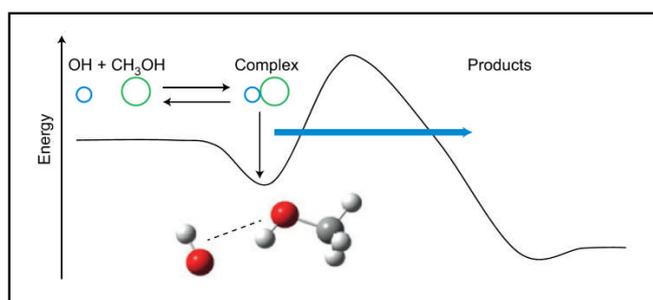
In this project you will measure rate constants and product branching ratios at very low temperatures using laser flash-photolysis combined with a variety of laser-based spectroscopic detection methods. You will use a pulsed Laval nozzle apparatus [1-6] to study the kinetics of reactions between ~40 and 150 K representative of the atmospheres of other planets and moons, for example Titan, as well as in star-forming regions, stellar outflows and the interstellar medium. [1-5]. Large molecular clouds of acetone, methanol and ethanol have been observed in space, and the large rate constants can be rationalised by the formation of a hydrogen-bonded complex, which can either be stabilised or undergo quantum mechanical tunnelling through the activation barrier to form products (Figure 1). For the OH-methanol reaction we observed the CH<sub>3</sub>O radical product, which was recently observed in space by astronomers [1, 5]. We have also studied the kinetics of singlet methylene, <sup>1</sup>CH<sub>2</sub>, which is a metastable radical, and which is implicated in the formation of benzene and hazes on Titan. There are two competing paths for <sup>1</sup>CH<sub>2</sub>, collisional quenching to the ground-state <sup>3</sup>CH<sub>2</sub>, or reaction to form products.

You will interpret the laboratory measurements using theoretical methods, making use of *ab initio* potential energy surfaces and master equation calculations (using the MESMER program [7], developed in Leeds) to calculate rate constants as a function of temperature and pressure. These experiments use laser flash-photolysis combined with laser-induced fluorescence (LIF) spectroscopy, will be extended to study further reactions of OH, <sup>1</sup>CH<sub>2</sub> and other radicals, and will monitor both reactants and products, using LIF.

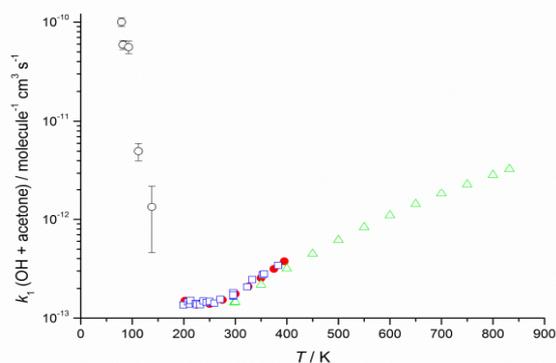
The PhD will provide a broad spectrum of training in the use of high power lasers, vacuum systems, optics, computer controlled data acquisition systems and numerical calculations. You will work in a well equipped laboratory and be part of the active, thriving and well-funded *Atmospheric and Planetary Chemistry* group within the School of Chemistry. You will be supported to attend both national and international conferences, and will receive a wide range of training, for example in communication skills and other technical aspects.

### References

1. R. J. Shannon, M. A. Blitz, A. Goddard and D. E. Heard, *Nature Chemistry*, 5, 745-749, 2013.
2. R. J. Shannon, S. Taylor, A. Goddard, M. A. Blitz and D. E. Heard, *Phys. Chem. Chem. Phys.*, 2010, 12, 13511–13514.
3. R.J. Shannon, R. L. Caravan, M.A. Blitz and D.E. Heard, *Phys. Chem. Chem. Phys.*, 16, 3466, 2014.
4. R.L. Caravan, R. J. Shannon, T. Lewis, M. A. Blitz and D. E. Heard, *J. Phys. Chem.*, DOI: 10.1021/jp505790m, 2014.
5. K. Acharyya, E. Herbst, R.L. Caravan, R.J. Shannon, M.A. Blitz & D.E. Heard, *Mol. Phys.*, 113, 2243-2254, 2015.
6. S. E. Taylor, A. Goddard, M. A. Blitz, P. A. Cleary and D. E. Heard, *Phys Chem Chem Phys*, 2008, 10, 422-437.
7. D. R. Glowacki, C.-H. Liang, C. Morley, M. J. Pilling and S. H. Robertson, *J Phys Chem A*, 116, 9545-9560, 2012.



**Figure 1.** Schematic potential energy surface for the reaction between OH and methanol showing the formation of a hydrogen bonded pre-reactive complex, from which quantum mechanical tunnelling occurs through the barrier to form products. From [1].



**Figure 2.** Dramatic increase in the rate constant for the reaction of OH with acetone below 200 K studied using the pulsed Laval nozzle technique. Data taken from reference [4].