Institution: University of Birmingham

Unit of Assessment: UoA 8 - Chemistry

Title of case study: Astrochemistry: a network of gas-phase reactions used in low-temperature interstellar chemistry by the world's leading space agencies

1. Summary of the impact

The spectroscopic observation in the interstellar medium (ISM) of an increasing number of molecules has demonstrated the presence of a rich chemistry, especially in the low temperature (*ca*. 10 K) environment of dense interstellar clouds. Understanding this chemistry requires the combined efforts of modellers and laboratory scientists. In the 1990's, research at the University of Birmingham pioneered a series of unique measurements in which rate coefficients for reactions were measured at temperatures down to as low as 13 K. These results have made a significant impact on the world leading space agencies (NASA and ESA), who have benefited from this research through gaining a better understanding of interstellar chemistry. Mission priorities and instrument design have been influenced by this improved understanding with three (out of a total of 21) instruments carried by NASA's Rosetta comet-rendezvous mission designed to carry out activities that draw significantly on the Birmingham findings. This demonstrates the impact on the allocation of budgets by these agencies and their scientific aims. The detection of molecules and the study of their formation are now viewed as top priorities, which ultimately impacts on the search for bio-signatures and life elsewhere in the Solar System.

2. Underpinning research

Between 1990-2002, Ian Smith (FRS, Mason Professor of Chemistry, University of Birmingham (UoB), up until his retirement in 2002) and Ian Sims (EPSRC Advanced Fellowship and then Senior Lecturer, School of Chemistry, UoB, up until his move to Rennes as an EU Marie-Curie Chair in 2003) developed a technique for the study of bimolecular reactions between neutral species at much lower temperatures than hitherto studied. This technique had originally been developed to study reactions between cations and stable molecules. Since they show zero or even negative dependence of the rate constant with temperature (Langevin 1905), they proceed at the same or higher rate at very low temperatures as they do at room temperature. Such reactions had always been assumed to be the primary building blocks for molecules in the ISM, where the temperature can be as low as 5 K. The primary (and surprising) finding of the Smith/Sims research was that there are a significant number of neutral-neutral reactions that also proceed rapidly at these very low temperatures, with the result that all the old models for the chemistry of the ISM have had to be re-assessed and re-written. Whereas it was not unexpected that reactions between two open-shell free radicals (*e.g.* N + OH → NO + H) are rapid at low temperatures, a remarkable and unexpected finding was that these rapid neutral-neutral reactions include an atom or a molecular free radical reacting with a 'stable' molecule (*e.g.* $CN + C_2H_2 \rightarrow HC_3N + H$). [Refs 3 and 4] Some of this research was carried out in collaboration with Dr Bertrand Rowe, Université de Rennes / CNRS Rennes, France.

This research has deep and rather far-reaching implications. For example the European Space Agency's (ESA) GIOTTO space mission performed the first comet encounter with Halley's Comet in 1986 and discovered a large number of complex carbon-based molecules (CHON or Carbon Hydrogen Oxygen and Nitrogen particles). Only after the work of Smith/Sims did astrochemists understand how these molecules might be synthesised. There is a particular interest in these species because they may have contributed to the start of life on Earth - and, possibly other planets such as Mars and the Jovian moons such as Europa. ESA, supported with some instrumentation from NASA, quickly developed the Rosetta mission to rendezvous with and land on a comet to study, in part, these CHON particles and the complex chemistry underway at low temperatures – the goal being nothing less than to determine the content and nature of the molecules present in comets.

It is clear that our understanding of how these CHON molecules form, both in comets and in molecular clouds, is of fundamental importance to modelling the evolution of the universe and in particular our solar system and its associated biological evolution. ESA Solar System exploration missions are built around four axioms: science objectives, design, development and operations, all of which are underpinned by the work of Smith, Sims and co-workers. Indeed specific past papers (see below) from the UoB School of Chemistry dealing with reaction rates at these very low temperatures have been particularly useful in shaping the Rosetta and JUICE missions in this area of science. In addition two of ESA's astrophysical missions, Infrared Space Observatory (ISO) & Herschel, have also benefited from this work (for scientific publications arising from ISO, see: http://iso.esac.esa.int/science/publications.html).

To the present day, the UoB, including the Physical and Theoretical Chemistry Research Unit, continues with experimental physical chemistry research, including gas phase work (e.g. Tuckett, School of Chemistry and Mayhew, School of Physics).

3. References to the research (indicative maximum of six references)

Professors Smith and Sims have published 39 joint papers, working together since ~1990 to develop the CRESU (Cinetique de Reaction en Ecoulement Supersonique Uniforme) apparatus to study the kinetics of reactions between neutral species at temperatures down to 10 K in the gas phase. For example:

[1] I. W. M. Smith, E. Herbst and Q. Chang, "*Rapid neutral–neutral reactions at low temperatures: a new network and first results for TMC-1*", *Mon. Not. R. Astronom. Soc.,* **2004**, 350, 323.
(118 citations)

[2] D. Chastaing, P. L. James, I. R. Sims and I. W. M. Smith, "*Neutral–neutral reactions at the temperatures of interstellar clouds: Rate coefficients for reactions of atomic carbon, C(^{3}P), with O_2, C_2H_2, C_2H_4 and C_3H_6 down to 15 K*", *Phys. Chem. Chem. Phys*., **1999**, *1*, 2247. (68 citations)

[3] I. R. Sims, J. L. Queffelec, D. Travers, B. R. Rowe, L. B. Herbert, J. Karthauser, and I. W. M. Smith, 'Rate constants for the reactions of CN with hydrocarbons at low and ultra-low temperatures', *Chem. Phys. Lett.* **1993**, *211*, 461-468. (176 citations)

[4] I. R. Sims, J. L. Queffelec, A. Defrance, C. Rebrion-Rowe, D. Travers, P. Bocherel, B. R. Rowe and I. W. M. Smith, "*Ultralow temperature kinetics of neutral-neutral reactions: the technique and results for the reactions CN + O_2 down to 13 K and CN + NH_3 down to 25 K*", *J. Chem. Phys.,* **1994**, *100*, 4229. (157 citations)

[5] I. R. Sims and I. W. M. Smith, "*Gas-phase reactions and energy transfer at very low temperatures*", *Ann. Rev. Phys. Chem.,* **1995**, *46*, 109. (83 citations)

[6] D. Chastaing, P. L. James, I. R. Sims and I. W .M. Smith, **"***Neutral–neutral reactions at the temperatures of interstellar clouds Rate coefficients for reactions of C_2H radicals with O_2, C_2H_2, C_2H_4 and C_3H_6 down to 15 K***"**, *J. Chem. Soc. Faraday Discuss*., **1998**, *109*, 165. (81 citations)

Much of the work at the UoB was supported by EPSRC research grants in the 1990s, *e.g.* GR/J87503/01 "*Reactive and Inelastic Processes In The Gas-Phase At Ultra-Low Temperatures*", £353k. The UoB/Rennes team was awarded one of the first Descartes prizes for this work, and Professor Smith was awarded the Royal Society of Chemistry Polanyi and Tilden Medals.

References 3, 4 and 5 best indicate the quality of the underpinning research.

4. Details of the impact

The impact achieved from these research findings has been through significantly influencing the policies and priorities of the world's most active space agencies in terms of the scientific objectives of their space exploration programmes, in mission design and on the instrumentation carried on spacecraft. Leading individuals at the European and US agencies (ESA and NASA) have confirmed that Smith and Sims' findings on low-temperature gas-phase chemistry and kinetics have made a material contribution to their understanding of interstellar chemistry and thus helped determine the approach to current and planned exploratory missions.

The impact extends into the decision-making and practice of the world's foremost space agencies.

It has influenced how these agencies conceptualise their missions, deploy very large sums of public money and plan their future programmes. Given the length of time involved in planning and executing space missions, any significant impact is likely to be visible across a longer period than a five year window; nevertheless, it can been seen here that although these impacts started prior to 2008, they have continued to be important to the current Rosetta mission, as well as on the Herschel mission which launched in 2009 and to ongoing work in the development phase of further planetary exploration.

Impact on Missions Probing the Interstellar Medium
Our Sun was formed from the condensation of an interstellar cloud, complete with all the complex molecules that it contained, about 4.5 billion years ago. The proto-solar nebula then evolved into the Solar System. Exploration of the Solar System and the understanding of Earth's place in it, including its evolution and biosphere, are fundamental rationales for ESA and NASA. Such exploration is extremely expensive – a typical interplanetary mission can cost 1bn Euro – and is only undertaken with a thorough analysis of the mission's scientific objectives and feasibility. Indeed the planning, design and development stages typically span a decade or more prior to the actual operational phase.

Knowledge of the types of complex molecules formed within interstellar clouds serves as an important starting point in the search for organics and ultimately life elsewhere in the Solar System. ESA's infrared astrophysics missions [ISO (1995-1998) and Herschel (2009 – 2013)] together with NASA's Spitzer mission (2003-2012) were the pathfinders for establishing the detailed organic component of the interstellar medium, with their observations informed by the published research conducted at UoB into reaction rates at low temperatures. Professor R. E. Griffiths, the Program Scientist for Physics of the Cosmos at NASA has stated: "*This work, exemplified by that performed by Smith and Sims, is seminal to our understanding of the low-temperature reactions which lead to the production of complex molecules within interstellar clouds, molecules which are evidenced by observations made using instruments on space telescopes*". [source 1]

A Rosetta Mission Project Scientist, Rita Schulz (see below) also confirmed that the Herschel Space Observatory, launched in 2009, has the study of the low temperature chemistry of complex organics in molecular clouds as a key objective, and that this is a further example of a mission where benefits will rely on this research.

Impact on Comet Missions: ESA's Rosetta mission
Having knowledge of the composition of interstellar clouds allows designers of Solar System exploration missions to include instrumentation that can search for these various species on or in planetary and smaller bodies (asteroids, comets, moons). It is here that the published work of Smith/Sims has had the most impact, affecting instrument design, spacecraft operations and instrument configurations during the exploration phase. Building on the results from ESA's GIOTTO mission, the Rosetta mission to rendezvous and land on a comet in 2014 has the study of these complex organics as a key objective.

The Rosetta spacecraft will be the first to undertake the long-term exploration of a comet at close quarters and also the first mission to land on a comet. The craft comprises a large orbiter, which is designed to operate for a decade at large distances from the Sun, and a small lander. The craft carries a total of 21 instruments (11 in the Orbiter, 10 on the Lander) designed to complete the most detailed study of a comet ever attempted. [source 2] Three of these instruments carry out activities that draw significantly on the work at Birmingham.

[redacted] the Rosetta Mission Project Scientist confirmed the contribution of the Birmingham research to the Rosetta mission as follows: "*Three mass spectrometers, two on the Lander (COSAC and PTOEMY) and one on the Orbiter {COSIMA), are designed to study in–situ the composition of comet refractories specifically focussing on organic macromolecules. They will measure molecular numbers of CHON particles from which certain chemical groups may be identified. However, to be able to conclude on a specific derivate or clearly attribute the results to specific organic molecules, laboratory measurements are required that allow to determine the* *probability of their synthesis in a low temperature environment.*

Important work was done at Birmingham University's School of Chemical Sciences on low-temperature gas-phase chemistry and kinetics. Many of the ion-neutral and neutral-neutral processes studied and reaction rates determined by Smith, Sims and Rowe have been particularly helpful in view to understanding interstellar chemistry and its relations to volatiles in comets. I believe that without the research work from Birmingham University over the past some twenty years we would have a poorer Rosetta mission – particularly as much of it was conducted during the mission's critical design and build phase in the 90's. Furthermore on arrival at our target comet the past efforts of the School of Chemical Sciences related to low temperature reaction rates will be invaluable in interpreting the chemistry that will be underway as our comet makes its way ever closer to our sun." [source 3]

Impact on Planetary Missions: Mars and the Jovian moons

Comets are one end of the exploration spectrum. Planetary bodies, particularly Mars and the moons of Jupiter such as Europa and Ganymede, are the other and have recently become centre of attention. Current and planned missions to Mars by NASA, ESA and the Russian Space Agency RKA have the search for life, extinct or extant, as a key aim, with complex organic molecules now a precursor in that search. The same can be said of the study of the Jovian moons, a mini solar-system in its own right. Mission designers, instrument developers and spacecraft/payload operations all have the work of Smith and Sims at the UoB underpinning their scientific objectives.

[redacted] the former Head of ESA's Science Technology and Future Science Missions Department, has confirmed the continuing impact of the Birmingham research on these programmes as follows: "*… future missions in their early preparatory phases such as the exploration of the Jovian moon Europa or Exoplanet characterisation, instrument and mission design will again be influenced by the search for organic molecules. Without the research of Smith and Sims, these mission concepts would be much more limited. But now the search for complex organics and potential bio-chemical signatures is on the agenda. In short, studies of the constituents of the interstellar medium and the exploration of our solar system owe a debt to the work of Smith and Sims. Without their research we would still be designing missions with for astronomy a mainly exploratory focus and for the solar system an emphasis on geophysics. This readjustment of the scientific objectives will have far reaching implications on mission design, instrument complement and ultimately cost."* [source 4]

NASA and ESA are currently pursuing separate missions (JUNO and JUICE respectively) to the Jovian system acting as precursors with a key long-term science objective to search for evidence of life – indeed JUICE will search for evidence of habitability on these moons. If one of these missions does discover biological signatures this will have a profound impact on mankind's place in the Solar System and the Universe. While the goal of these major missions is such a return, they are underpinned by the fundamental scientific research on low temperature reaction rates and species production conducted by Smith, Sims and their co-workers.

5. Sources to corroborate the impact (indicative maximum of 10 references)

1. Corroborating statement received from Program Scientist for the Physics of the Cosmos, Astrophysics Division, Science Mission Directorate, NASA HQ, Washington DC 20546, USA
2. http://www.esa.int/Our_Activities/Space_Science/Rosetta/Lander_Instruments
3. Statement from Rosetta Mission Project Scientist, Directorate of Science and Robotic Exploration, European Space Agency, ESTEC, Keperlaan 1, 2201 AZ Noordwijk The Netherlands dated 10/7/2012
4. Corroborating statement from former Head of ESA's Science Technology and Future Science Missions Dept (2000-2007) dated 29/4/13