Final Report on the research grant F/07 134B

The formation of molecules in star-forming regions of interstellar space

funded by the Leverhulme Trust through a grant to institutions for research

(a) The grant

The grant was awarded to support an interdisciplinary programme of research involving members of several research groups and research departments at University College London. The total grant awarded by the Trust was £190 330, and the start and completion dates were 1August 2000 and 31 July 2003. The funding was mainly to cover the employment costs of two research fellows; other costs met by the grant covered laboratory consumables, computing expenses, and travel and subsistence.

The Principal Applicant was Professor D A Williams (Department of Physics and Astronomy) on behalf of the members of the UCL Centre for Cosmic Chemistry and Physics. Those members most closely associated with the work supported by the grant, and the percentage of their effort committed to that work, were:

Professor D E Williams, Chemistry, 5%
Professor S D Price, Chemistry, 10%
Dr W A Brown, Chemistry, 20%
Professor D C Clary, 5%
Professor A J Fisher (Physics and Astronomy) 5%
Dr J M C Rawlings (Physics and Astronomy) 5%
Professor D A Williams (Physics and Astronomy) 5%

The main activities of the programme were carried forward by the research fellows funded by the grant:

Dr A J H M Meijer, 100%; Dr J Perry, 100%

Two research students working on the projects supported by the grant obtained their PhD degrees

Dr A J Farebrother (100%); Dr J Perry (100%)

Two research students began their studies while working on this research programme
Mr A Bolina (100%); Ms S Creighan (30%)

and one undergraduate project student was involved in the programme for four months
Mr T Paul (50%)

(b) Objectives

The formation of a star involves the gravitational collapse of a large cloud of gas at low density into a dense compact object. During the collapse, the gravitational potential energy of the cloud is released as heat; this heat must be radiated away, otherwise the rise in temperature and pressure that it would cause would terminate the collapse. The most effective coolants at the very low temperatures of interstellar clouds are molecules, and it is through their emissions that astronomers can most easily trace the collapse process.

Interstellar molecules are formed through a variety of processes taking place in the gas phase and on the surfaces of interstellar dust grains. Many of the gas phase processes have been intensively studied, but there is little reliable information concerning the formation of molecules on surfaces at very low temperatures.

The **objective of our research** is, therefore, to gain understanding of the formation process of some astronomically important molecules on the surfaces of dust grain analogues, under conditions approaching those of the interstellar medium. This research represents new and fundamental work in surface science. It is carried out through a combination of laboratory experiments and theoretical studies. This combined approach gives benefits to the understanding of both experiment and theory, and to the application of the results to the astronomical situation. Our work has concentrated on addition reactions at surfaces, particularly the formation of molecular hydrogen, but also the formation of water, ammonia, and methanol.

(c) Research activity

Experimental work

The formation of molecular hydrogen (H_2) on graphite has been studied for graphite temperatures in the range 15 – 50 K in experiments in which a cooled beam of H atoms impinges on the cold graphite target. Analysis of the newly formed H_2 molecules shows that they are internally excited, the molecules being found in several rotational levels of vibrational levels v = 1 and 2. The experiments demonstrate that H_2 forms efficiently on low-temperature graphite and that a significant fraction of the energy released in the reaction appears as vibration-rotation excitation.

Preliminary experiments have also been performed in which water vapour is allowed to form an ice layer on the graphite. Such a system is applicable to the grains found in dense clouds. Preliminary work has also been carried out to study the formation of carbon monoxide on surfaces. Development of a deuterium atom source has been carried out; experiments to form HD will provide an important independent check on the H_2 work.

In separate experiments studies of the heterogeneous formation of water, methanol, ammonia and carbon dioxide have been initiated. The surfaces used in these experiments will include graphite, silicates, and water ice. These experiments probe the nature of the surface species *in situ* through reflection – absorption infrared spectroscopy and through temperature programmed desorption.

Theoretical work
We have developed *ab initio* quantum dynamics calculations of the interaction of a free H atom with another H atom that is chemically bound to a graphite surface. To gain further insight into the nature of the reaction we have performed similar calculations involving a deuterium atom. The results predict that the product molecules should be formed very efficiently and with considerable vibration – rotation excitation, and that there are distinct isotope effects.

In the astronomical situation the surface coverage with H atoms may be high, and the reaction to form hydrogen molecules may be influenced by the neighbouring surface atoms. We have therefore completed a study of hydrogen molecule formation in which the surface coverage is high and have shown that the internal excitation in the molecule is reduced by the coupling to the surface states.

A study of H_2O formation on graphite has also been completed (but not yet published).

Astronomical implications
A search for emission lines from newly formed internally excited molecular hydrogen has been made using the UK InfraRed Telescope on Hawaii. The predicted intensity was at the limit of sensitivity of the instruments on this telescope. No detections were made, and the upper limit deduced may suggest that the level of excitation is less than that measured in the experiment and determined by theory. The chemical consequences of internal energy in H_2 in promoting otherwise endothermic reactions in the interstellar medium have also been explored.

(d) Conclusions and achievements

The original objectives with regard to the study of H_2 formation on graphite surfaces have largely been met. While the qualitative agreement between the experimental and theoretical programmes is highly satisfactory, qualitative differences have suggested that additional factors may need to be taken into account. While some these newer lines of enquiry have already been explored (e.g. the effects of surface coverage) other effects (e.g. surface mobility) are projects for the future. Graphite is an important likely component of interstellar dust, and our results are valuable for astronomical applications, but work on other grain materials must also be carried out. The experimental and theoretical results obtained for H_2 and HD formation on low temperature graphite are important results in surface science; the information about the internal excitation is unique. Studies of the formation of other molecular species in surface reactions are making good progress, and work done on this grant will be exploited in future studies.

(e) Publications and dissemination

Time-dependent quantum mechanical calculations on the formation of molecular hydrogen on a graphite surface via an Eley-Rideal mechanism
A J H M Meijer, A J Farebrother, D C Clary, A J Fisher
J Phys Chem A (2001) **105** 2173-2182

Isotope effects in the formation of molecular hydrogen on a graphite surface via an Eley-Rideal mechanism
A J H M Meijer, A J Farebrother, D C Clary
J Phys Chem A (2002) **106** 8996-9008

Time-dependent wave packet calculations on parallel computers
A J H M Meijer
Computer Physics Communications (2001) **141** 330-341

Surface coverage effects on the formation of molecular hydrogen on a graphite surface via and Eley-Rideal mechanism
A J H M Meijer, A J Fisher, D C Clary
American Chemical Society, in press

Detection of rovibrationally excited H_2 formed through the heterogeneous recombination of H atoms on a cold HOPG surface
J S A Perry, S D Price Astrophys and Space Science (2003) **285** 769-776

An apparatus to determine the rovibrational distribution of molecular hydrogen formed by heterogeneous recombination of H atoms on cosmic dust analogues
J S A Perry, J M Gingell, K A Newson, J To, N Watanabe, S D Price
Measurement Science and Technology (2002) **13** 1414-1424

Physics and chemistry of icy particles in the universe: answers from microgravity
P Ehrenfreund, H J Fraser, J Blum, J H E Cartwright, J M Garcia-Ruiz, E Hadamcik, A C Levasseur-Regourd, S Price, F Prodi, A Sarkissian
Planet. Space Science (2003) **51** 473-494

A RAIRS and TPD investigation of the adsorption of methanol on the HOPG surface
A S Bolina, T A Paul, W A Brown
In preparation

Investigations of the growth of amorphous and crystalline ice on the HOPG surface
A S Bolina, T A Paul, W A Brown
In preparation

Observational indicators of formation excitation of H_2
S Tine, D A Williams, D C Clary, A J Farebrother, A J Fisher, A J H M Meijer, J M C Rawlings, C Davis
Astrophys and Space Science (2003) **288** 377-389

Chemical effects of H_2 formation excitation
R T Garrod, J M C Rawlings, D A Williams
Astrophys and Space Science (2003) **286** 487-499

Recent progress in astrochemistry
D A Williams, S Viti
Annual Reports of Progress in Chemistry, section C, (2002) **98** 87-120

Other forms of dissemination of this work include presentation of results at national and international conferences through invited lectures (at least eleven invited lectures have been given) and through many poster presentations. The work receives a high profile at regular meetings of the UK Astrophysical Chemistry Group, a special interest group of the Royal Society of Chemistry and the Royal Astronomical Society. We have applied to EPSRC for funding to establish a proposed Network in “Surface Science Applications in Laboratory Astrophysics”. A proposal has been made to the Royal Society for a display at the summer exhibition focusing on the chemistry that occurs on dust grains in space.

Professor Price was awarded the 2003 Royal Society of Chemistry Corday-Morgan Medal in part for his work on laboratory studies of astrochemistry.

(f) Future research plans in this field

The support of the Leverhulme Trust has been invaluable for the prosecution of this research programme by the UCL Centre for Cosmic Chemistry and Physics. Members of the Centre are most grateful to the Trust for its support of our interdisciplinary programme. The publication record shows that many of the aims of the proposal have been met, but that this work has also opened up many new and fundamental lines of enquiry. The UCL Centre will continue with the general thrust of its present programme on heterogeneous chemistry arising in astronomy, as it has developed from the work reported here. We have obtained research council support for part of the future programme, and are actively seeking further support from research councils for other parts of our programme. The coordinated theoretical/experimental approach has been found to be valuable and will continue. The programme that started from astronomical motivations is providing new and fundamental insight into surface science, and this cross-disciplinary benefit is expected to continue.

Some personnel changes have occurred. In particular, Professor Clary is now at the University of Oxford, and Dr Meijer has taken up a lectureship at the University of Sheffield. Both intend to maintain their collaborations with the UCL Centre. Thus, the Centre is becoming in effect a national grouping, so we are taking steps to formalise this wider interest in astrochemistry with several UK universities. The UCL Centre will, however, continue at about its present level of activity, and will be a major node within the national scene in astrochemistry.