

Physicochemical Processes on Surfaces: The Gas-Dust Interaction in Interstellar Molecular Clouds

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Introduction

It has become increasingly clear that the gas-grain interaction plays a crucial role in the chemical evolution of interstellar molecular clouds [1]. This programme was amongst the first to directly seek to address key questions relating to the gas-grain interaction using the tools of modern surface physics and chemistry. As such, it had two central aims that can be summarised as below,

- (i) To construct a state-of-the-art UHV system supporting suitable diagnostic and sample handling facilities to permit the investigation of processes mimicking the gas-grain interaction in the interstellar medium under realistic conditions.
- (ii) To investigate the adsorption and desorption of simple molecules of relevance to the interstellar medium on surfaces mimicking those of solid grains.

Within the formal period of this programme, we have made substantial strides towards achieving both of these aims. Furthermore, we feel that our efforts in the fledgling discipline of surface laboratory astrophysics have helped to establish the precedent that such measurements are both practical, from the experimental standpoint, and relevant, from the standpoint of potential users of our results. The success of our programme to date, as described below, is even more striking given that nearly £35,000 was cut from the original equipment budget by the Astronomy Research Assessment Panel. Only with additional support from the University of Nottingham and the School of Chemistry of the University of Nottingham to the order of £42,300 was it possible to achieve as much as we have done.

Scientific Results

Central to the work of this research programme has been the development of the laboratory apparatus necessary for the study of model gas-grain interactions under realistic conditions. The apparatus is described in some detail in the following section. Subsequently, we describe the application of this apparatus in studies of the thermal desorption of water ice and of carbon monoxide from water ice surfaces. We are confident that our new measurements represent a significant advance in our understanding of these interactions.

A Laboratory Apparatus for Studies of Ultracold Molecular Ice Surfaces

The apparatus, shown in **Figure 1**, comprises a 30 cm diameter stainless steel chamber (Instrument Technology Ltd.) pumped by a combination of liquid nitrogen-trapped oil diffusion pump (Edwards High Vacuum Ltd.) and titanium sublimation pump (Instrument Technology Ltd.). After a typical bake of 48 to 60 hours at 120 °C (limited by the presence of viton o-rings in a number of differentially pumped seals), a base pressure of better than 2×10^{-10} mbar (corresponding to a number density of *ca.* 5×10^6 cm³), is easily achievable. The chamber is equipped with a precision XYZ θ manipulator (Caburn-MDC Ltd.) supporting an UHV-compatible closed cycle helium cryostat (APD Cryogenics) capable of achieving a base temperature of less than 10 K. Attached to the cryostat tip is the substrate onto which we deposit material introduced into the gas phase in the chamber *via* a pair of fine control leak valves (VG Ltd.). This comprises a small quartz single crystal disc onto which a 5 mm diameter gold electrode has been

deposited. This disc forms the sensing element of a sensitive cryogenic quartz crystal microbalance (QCM) (Oxford Applied Research Ltd.).



Figure 1. The Nottingham Apparatus for studies of molecular ice surfaces in ultrahigh vacuum at cryogenic temperatures.

The nature of species adsorbed on the surface of the microbalance can be investigated by utilising the experimental probes available to us. These are specifically, Fourier transform reflection-absorption infrared spectroscopy (FT-RAIRS) utilising a standard laboratory benchtop FTIR spectrometer (Biorad Ltd.), and temperature programmed desorption (TPD) utilising a line-of-sight configured quadrupole mass spectrometer (Hiden Analytical Ltd.) [2]. The microbalance itself, of course, giving us a measure of the mass of the ultrathin film that we are studying.

The design of the system is highly flexible. For example, infrared access to the cold substrate can be achieved at a range on angles of incidence (6° , 15° and 45°), such that it is possible from RAIR measurements to obtain detailed information on the variation of the optical constants of thin films as a function of wavelength across the entire mid-IR. In addition, access to the surface is also provided, but currently not utilised, for interaction of the cold substrate with UV light, electrons, ions (of energies less than 5 kV) and reactive atomic or molecular species simultaneously with FT-RAIRS probing of the surface and mass spectroscopic monitoring of the gas phase. We simply need to integrate the appropriate sources to our system. This combination of probes with the considerable potential for extension of our system, and our understanding of surface physicochemical processes gained from other measurements within our group, places us in a very strong position in comparison to the few competitor groups that exist elsewhere.

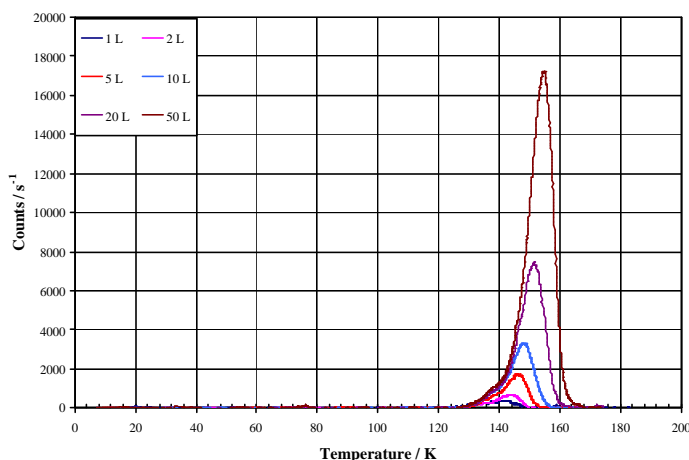
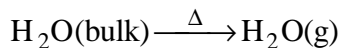


Figure 2. A sequence of TPD spectra of water ice films of increasing thickness (1 L is equivalent to an exposure of 10^{-6} mbar s) showing the coincidence of leading edge consistent with zero order desorption kinetics.

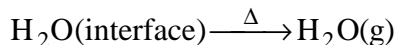
Our preliminary work has focussed on understanding some simple, yet key, gas-grain interactions. In the first instance, we investigated the nature of water ice films deposited from the gas phase on to the surface of our cryogenic QCM using a combination of TPD and FT-RAIRS. A typical set of TPD measurements for increasing amounts of water ice grown on the QCM substrate is shown in **Figure 2**. These are entirely consistent with spectra reported in the literature by others [3]. The TPD process, and hence these observations, can be modelled using a simple rate equation approach assuming zero order kinetics for the desorption of bulk ice,



with a rate of formation of gaseous water given by

$$\frac{d[\text{H}_2\text{O}(\text{g})]}{dt} = v_0 e^{-E_{\text{des,bulk}} / RT}$$

where v_0 is the zero order pre-exponential factor and $E_{\text{des,bulk}}$ is the heat of desorption of the bulk ice, and first order kinetics for ice at the interface with the gold,



with a rate of formation of gaseous water given by

$$\frac{d[\text{H}_2\text{O}(\text{g})]}{dt} = v_1 \theta_{\text{H}_2\text{O}(\text{interface})} e^{-E_{\text{des,interface}} / RT}$$

where v_1 is the first order pre-exponential factor, $E_{\text{des,interface}}$ is the heat of desorption of the interfacial ice and θ is the surface density of the interfacial ice. The value for the bulk heat of desorption is constrained by previous studies [3] and so in modelling the TPD, we have simply varied the remaining parameters to best reproduce the experimental observations. The results of these simulations are given in **Table 1**. From an astronomical standpoint, the most relevant figures are those relating to the desorption of bulk ice.

Table 1. Summary of the kinetic data obtained from the analysis of water ice TPD spectra such as displayed in Figure 2.

Reaction	Pre-exponential Factor	$E_{\text{des}} / \text{kJ mol}^{-1}$
Bulk Desorption	$10^{30 \pm 2} \text{ cm}^{-2} \text{ s}^{-1}$	48 ± 3
Interfacial Desorption	$10^{13 \pm 1} \text{ s}^{-1}$	42 ± 3

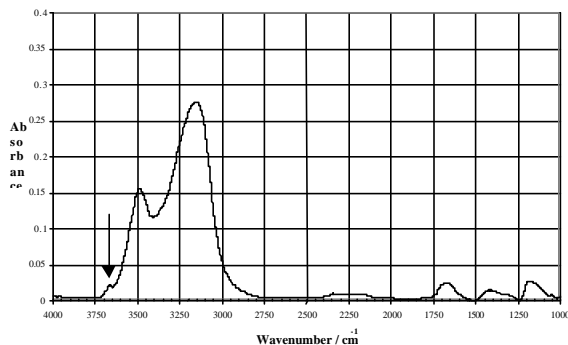


Figure 3. RAIR spectrum of an ultrathin film of water ice deposited at 7 K. The dangling bond feature is arrowed.

A typical infrared spectrum of an ultrathin ice film is shown in **Figure 3**. We can clearly see the sharp dangling OH bond feature to the high wavenumber side of the bulk OH stretching band. It is

interesting to note, however, that the feature appears to be split. A weaker shoulder is seen at high wavenumber in a position consistent with the clean water ice surface (3692 cm^{-1}) [4], while the sharp feature occurs at a shorter wavelength consistent with that observed by Devlin and co-workers for a water ice with molecular nitrogen (N_2) adsorbed on top (3664 cm^{-1}) [5]. The origin of this N_2 contamination, which we can confirm by TPD, is as yet unclear. It may be dosed into the system with the water or may represent the accumulation of several small sources of nitrogen associated with differentially pumped seals on the system. Measurements are in progress to elucidate the origin of this contamination.

Crucially, we believe that our laboratory spectroscopic measurements have allowed us to make a preliminary identification of the dangling OH bond feature in astronomical spectra from at least two objects. Dartois and d'Hendecourt in a recent publication report IR spectra in the OH stretching region of a number of objects recorded using the Short Wavelength Spectrometer (SWS) on the IRAS satellite [6]. In at least two of these objects, Elias 16 and GL2136, we believe that we have identified the dangling OH feature at a position consistent with a clean ice surface. We are currently in discussion with the group of Professor van Dishoeck (Leiden University), recognised experts on the IRAS SWS systems, in an effort to confirm our preliminary identification.

Beyond these important initial measurements, within the period of the grant, we conducted preliminary studies towards understanding the interaction of carbon monoxide (CO) with the water ice surface. **Figure 4** below shows a typical TPD measurement from these studies. The two sharp features at

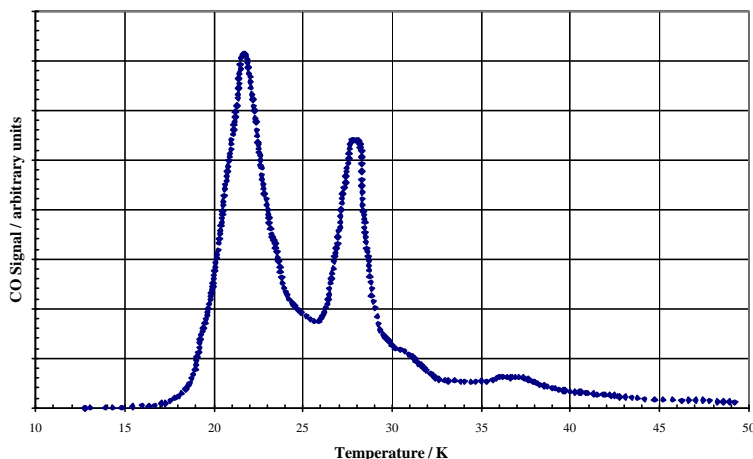


Figure 4. TPD spectrum of CO (as $m/z = 28$) of an ultrathin multilayer of CO deposited on an ultrathin film of water ice deposited at 7 K.

low ($< 30\text{ K}$) temperature we can assign to the desorption of multilayers of CO (at *ca.* 22 K) and of small quantities of adsorbed N_2 that we have evidence for from our RAIR measurements (at *ca.* 28 K). This latter observation is also consistent with the TPD measurements of N_2 desorption from ice of Kay and co-workers [7]. The broad feature centred around 37 K, we believe is associated with the desorption of CO directly hydrogen bonded to the ice surface. It may also, however, contain some fraction of N_2 desorption [7]. Measurements utilising isotopically labelled ^{13}CO ($m/z = 29$) are currently underway to confirm this assignment. A very preliminary kinetic analysis of these CO desorption data would suggest a binding energy for the monolayer CO on the ice layer of approximately 10 kJ mol^{-1} , *cf.* 6.81 kJ mol^{-1} for the latent heat of sublimation of multilayer CO. Simple *ab initio* quantum mechanical calculations suggest that this value is not inconsistent with a weak $\text{CO-H}_2\text{O}$ hydrogen bonding interaction.

Conclusions

Our research programme is progressing rapidly now with detailed measurements currently being undertaken on the adsorption and desorption of CO on a range of hydrogen bonding surfaces (water ice, ammonia ice and methanol ice) and on the interaction of ammonia itself with the water ice surface. We are confident that the quality of the results presented above and the quality of the work that we are currently undertaking are comparable to that originating from competing groups elsewhere in the world.

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CONFERENCE PRESENTATIONS AND INVITED TALKS ARISING FROM GR/L57562

1. From Gases to Dust: Cosmic Chemistry
H. J. Fraser,
2nd Annual Chemical Physics Meeting, University of Birmingham, UK, July 1999
2. Novel Laboratory-based Studies of Interstellar Ice Grain Mimics
H. J. Fraser, M. R. S. McCoustra and D. A. Williams,
Proc. IAU Symp. 197, Sogwipo, South Korea, 1999, 209.
3. Laboratory Astrochemistry
H. J. Fraser,
Invited Contribution to the Molecular Cloud and Star Formation Group Progress Meeting,
UCL, London, January 2000
4. From Gases to Dust: Surface Interactions in the Interstellar Medium
H. J. Fraser,
Seminar in the Centre for Astrophysics, Harvard University, Boston, USA, March 2000
5. From Gases to Dust: Surface Interactions in the Interstellar Medium
H. J. Fraser,
Seminar in the Chemistry Department, Brookhaven National Laboratory, New York,
USA, March 2000
6. From Gases to Dust: Surface Interactions in the Interstellar Medium
H. J. Fraser,
Seminar in the Chemistry Department, University of California, Berkeley, USA, March
2000
7. From Gases to Dust: Surface Interactions in the Interstellar Medium
H. J. Fraser,
Seminar in the Department of Space Sciences, NASA Ames Research Centre,
Moffett Field, USA, March 2000
8. Laboratory Astrochemistry
H. J. Fraser,
Seminar in the Department of Physics and Astronomy, University of Leeds, UK, April
2000
9. From Gases to Dust: Surface Interactions in the Interstellar Medium
H. J. Fraser, M. R. S. McCoustra and D. A. Williams,
Proc. 5th NATO Summer School on Astrochemistry, Erice, Sicily, June, 2000
10. From Gases to Dust: Surface Interactions in the Interstellar Medium
H. J. Fraser,
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5. From Gases to Dust: Surface Interactions in the Interstellar Medium
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2000
12. Surface Chemistry and Reactions of Molecular Ices in an 'Interstellar' Environment

H. J. Fraser,

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13. From Gas and Dust to ... The Chemistry of Interstellar Grain Surfaces
M. R. S. McCoustra
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17. The Interaction of Carbon Monoxide with Hydrogen-bonding Molecular Ice Surfaces
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Abstr. 47th Nat. Symp. Am. Vac. Soc., San Francisco, USA, 2001,
Submitted.

PUBLICATIONS ARISING FROM GR/L57562

Please note that a copy of each paper is appended, if available at the time of submission of this report.

1. Thermal Desorption of Water Ice in the Interstellar Medium.
H. J. Fraser, M. P. Collings, M. R. S. McCoustra and D. A. Williams
Mon. Not. Roy. Astron. Soc., submitted
2. The Molecular Universe - A Simple Guide to Astrochemistry.
H. J. Fraser and D. A. Williams
Astronomy and Geophysics, in preparation
3. A New Apparatus for Laboratory Studies of Gas-Solid Processes Relevant to the Interstellar Medium.
H. J. Fraser, M. P. Collings and M. R. S. McCoustra
Rev. Sci. Instrum., in preparation

SCIENTIFIC SUMMARY

PPARC Research Grant GR/L57562

Physicochemical Processes on Surfaces: The Gas-Grain Interaction in Interstellar Molecular Clouds

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Probing the Physics and Chemistry on Star Dust

Star dust is the birthplace of molecules. The formation of complex molecular species in the vast spaces between the stars and in the cold, dark clouds that are the birthplaces of the stars themselves is governed, for the most part, by complex gas phase chemical reactions. However, it has been increasingly realised of late that the physical and chemical interactions between atoms and simple molecules from the gas phase with cold, nanoscale ($\ll 1 \mu\text{m}$ across) dust grains must play a crucial role in the evolution of complex organic molecules. Such gas-grain interactions are perhaps even responsible for the manufacture of the molecules associated with the development of life itself!

Given their potential importance, little is really known of the physics and chemistry of gas-grain interactions. However, much is known of the possible structure and composition of such star dust from observations. Those, in particular, made in the infrared utilising the UK Infrared Telescope (UKIRT) and the Infrared Space Observatory (ISO) have proven to be especially valuable in this respect. These observations tell us that our star dust is likely to comprise of a silicate or carbonaceous core a few tens of nanometres across, with a surrounding mantle composed of the frozen ices of a few simple molecular species. Amongst these ices, water (H_2O) and carbon monoxide (CO) are dominant, but ammonia (NH_3), carbon dioxide (CO_2), methanol (CH_3OH) and a few others are also observed. In the first instance, therefore, the laboratory investigation of the interaction of interstellar atoms and molecules with models of the likely grain surface can focus on their interaction with molecular ice surfaces. This is the route we have adopted in constructing a novel new experimental apparatus designed to mimic the extremely low pressures and temperatures of the interstellar medium in the laboratory (see Figure 1) and to permit infrared spectroscopic and mass spectrometric investigations of the interaction of gases with cold surfaces.



Figure 1. The “Nottingham Star Dust Machine” for studies of molecular ice surfaces in ultrahigh vacuum at cryogenic temperatures.

Utilising this apparatus, we have carried out a number of initial investigations of simple physical processes important in the gas-grain interactions. Principally, we have re-investigated the desorption of water ice, a process key to the evolution of molecular clouds into stars. Contrary to the existing astronomical literature, which reports this process as occurring at temperatures below 100 K, our measurements unequivocally demonstrate that water is likely to remain stuck to grains at temperatures some 20 to 30 K higher! This will undoubtedly have implications for those modelling the formation of stars. Further measurements currently underway on the interaction of CO with H_2O , NH_3 and CH_3OH ices and NH_3 with H_2O and CH_3OH ices are too revealing their secrets.

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