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Article (Published Version)

Williams, D A, Brown, W A, Price, S D, Rawlings, J M C and Viti, S (2007) Molecules, ices and astronomy. *Astronomy and Geophysics*, 48 (1). ISSN 1366-8781

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Molecules, ices and astronomy

David A Williams, Wendy A Brown, Stephen D Price, Jonathan M C Rawlings and Serena Viti of University College London review how far experimental work on molecular synthesis can be applied to the interstellar medium – and how it is becoming a tool for the understanding of astrophysical processes.

Over the past 40 years, about 140 distinct molecular species have been detected in a wide range of astronomical locations (see <http://www.cv.nrao.edu/~awooten/allmols.html>). We now know that molecules are present within our galaxy in the atmospheres of cool stars, in stellar envelopes, in planetary nebulae, in the ejecta of novae and supernovae, in diffuse and dense clouds in the interstellar medium (see figures 1 and 8), and in star-forming regions (figure 2) (Fraser *et al.* 2002, Williams and Viti 2002). Molecules are also found locally in the solar system: in planetary atmospheres, in comets, meteorites, interplanetary dust and even (rather briefly) in sunspots. Molecules are present in external galaxies too, and have been identified in objects at redshifts up to 6.4. In fact, as a crude rule of thumb, we may expect molecules to be present in cosmic gas in which the temperature is not too high (say, less than 4×10^3 K) and the density is not too low (say, more than one hydrogen atom per cm^3). These conditions are easily met for gas in many locations in the Milky Way and other galaxies. Most significantly, the giant molecular clouds in the galaxy – which contain most of the non-stellar baryonic matter – are almost entirely molecular

ABSTRACT

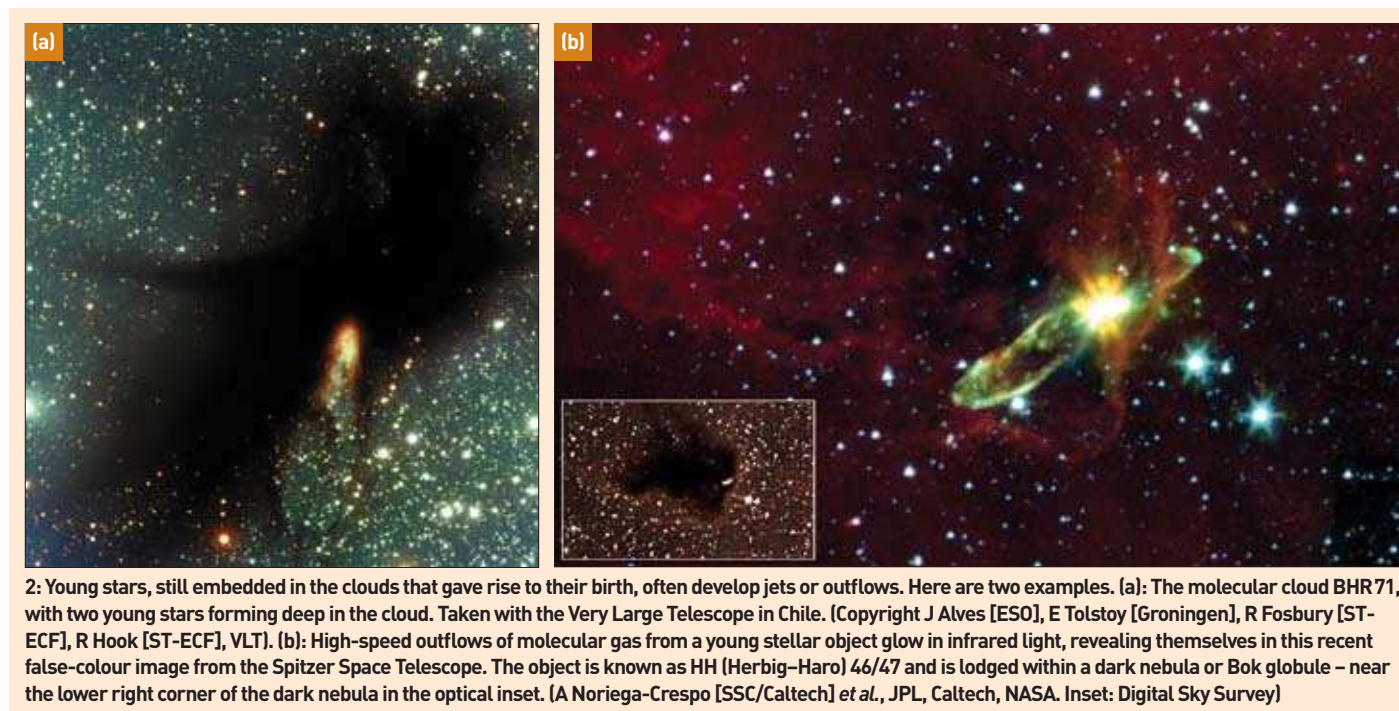
Molecules in interstellar gas and in interstellar ices play a fundamental role in astronomy. However, the formation of the simplest molecule, molecular hydrogen, is still not fully understood. Similarly, although interstellar ice analogues have received much attention in the laboratory, the evolution of ices in the interstellar medium still requires further study. At UCL we have developed two separate experiments to address these issues and explore the following questions: How is H_2 formed on dust-grain surfaces? What is the budget between internal, kinetic and surface energies in the formation process? What are the astronomical consequences of these results? For ices, we ask: How do molecules desorb from pure and from mixed ices in regions warmed by newly formed stars? What can molecules released from ices tell us about the star-formation process? We put our results in the context of other laboratory work and we describe their application to current problems in astronomy.

1: The star-forming region IC1396. This image shows extensive regions of low-density gas (red), rich in atomic hydrogen, and high-density (black) interstellar gas, rich in molecular hydrogen. Star formation is occurring in the high-density gas, but is shielded from view by the dust mixed in the gas. Scattered light from the newly forming stars emerges around the edges of the dark cloud. (Image taken by Nick Wright of UCL for the IPHAS consortium)

(figure 3). Thus, the matter that is the main reservoir from which new stars are formed in galaxies is molecular, and the process of star formation and the means by which we study it – emission in rotational transitions – is essentially molecular.

Emission in rotational lines

Molecules provide a rich spectrum of transitions by which we can trace the presence of the gas at various temperatures and densities in these locations. This is often achieved by mapping the emission in rotational lines of various molecules. These emissions are found to be important cooling mechanisms, without which the heat generated in gravitational collapse of clouds, for example, could not be radiated away. Thus, molecules have an important



2: Young stars, still embedded in the clouds that gave rise to their birth, often develop jets or outflows. Here are two examples. (a): The molecular cloud BHR71, with two young stars forming deep in the cloud. Taken with the Very Large Telescope in Chile. (Copyright J Alves [ESO], E Tolstoy [Groningen], R Fosbury [ST-ECF], R Hook [ST-ECF], VLT). (b): High-speed outflows of molecular gas from a young stellar object glow in infrared light, revealing themselves in this recent false-colour image from the Spitzer Space Telescope. The object is known as HH (Herbig–Haro) 46/47 and is lodged within a dark nebula or Bok globule – near the lower right corner of the dark nebula in the optical inset. [A Noriega-Crespo [SSC/Caltech] *et al.*, JPL, Caltech, NASA. Inset: Digital Sky Survey]

active role in star-forming regions. But, more than that, if we can understand the processes by which the molecules are formed, we can learn in great detail about the physical conditions in the molecule-bearing regions.

So, how are these molecules formed under interstellar conditions in which the gas pressures and temperatures are generally low compared to terrestrial conditions? Theories developed in the 1970s – and supported by a huge effort in laboratory chemistry – have shown that cosmic chemistry (unlike terrestrial) in the gas phase occurs largely by two-body ion–molecule and neutral-exchange reactions. However, such schemes are known to be incomplete and it is now clear that there is an important class of reactions that involve the surfaces of dust grains, either as catalytic agents or as substrates on which interstellar ices can be deposited. However, there is a severe lack of reliable data associated with surface processes under conditions relevant to the interstellar medium. Therefore, a decade ago we formed the UCL Centre for Cosmic Chemistry and Physics (UCL CCCP) to address – through experiment, theory, astronomical observations and modelling – some of the fundamental problems arising in astrochemistry. This article presents some of our work, puts it in the context of other related work, and applies our results to detailed studies of the interstellar medium.

H_2 is the most abundant molecule in the universe and is the key partner in many of the reactions of cosmic chemistry; therefore, it is fair to say that the most important reaction involving cosmic dust grains is the formation of molecular hydrogen from incident atomic hydrogen. It has now become possible to investigate, in the laboratory, reactions on surfaces at low temperature and low pressure that mimic those occur-

TABLE 1: INVENTORY OF COSMIC ICES

Data from G A Blake (2006, unpublished). Abundances are expressed by number of molecules relative to H_2O . HH46 is a region of low-mass star-formation; W33A is a region of high-mass star-formation; Hale-Bopp is a comet.

	HH46	W33A	Hale-Bopp
H_2O	100	100	100
CO	20	1	23
CO_2	30	3	6
CH_4	4	0.7	0.6
H_2CO	–	2	1
CH_3OH	7	10	2
HCOOH	2	0.5	0.1
NH_3	9	4	0.7
OCS	–	0.05	0.4

ring on cosmic dust. Our aim at the UCL CCCP is to understand the nature of those reactions, to determine their efficiency in the interstellar medium, their energy budget, and their consequences in the interstellar medium.

Molecular ices are detected in the interstellar medium along lines of sight through somewhat denser-than-average gas. The composition of the ices varies from one line of sight to another (see table 1). The ices are made up of molecules formed *in situ* (e.g. H_2O), accreted directly from the gas (e.g. CO), or processed in some way within the ice (e.g. the formation of CO_2 and CH_3OH from CO). It is unclear to astrophysicists at present what triggers the deposition of these ices and how chemistry occurs within them. Therefore, our aim at the UCL CCCP is to understand *in situ* formation, adsorption from the gas, and surface processing of ices. In this article we describe the results we have obtained so far, the

context of related work, and the implications of adsorption and surface reactions for astronomy.

Molecular hydrogen formation

In 1997 we began a combined programme of experimental and theoretical work to study the formation of H_2 and HD from atomic hydrogen and deuterium on astrophysically relevant surfaces. This section presents a review of experimental work carried out at UCL. A brief overview of the complementary experimental work carried out by other groups is summarized in box 1. Space prohibits a detailed discussion of the extensive theoretical work performed, both at UCL and elsewhere, which complements our measurements (Farebrother *et al.* 2000, Meijer *et al.* 2002, Meijer *et al.* 2003, Meijer *et al.* 2001). However, a brief overview of theoretical studies of the formation of H_2 on graphite is presented in box 2. A more detailed review of the theoretical studies of atomic recombination carried out at UCL is in preparation.

The experiments at UCL focus on measuring the internal energy content of newly formed hydrogen molecules – an approach that complements other experimental investigations of this phenomenon (see box 1). We use the internal excitation of H_2 as a signature of the formation process. Our experimental technique (figure 4), which has been described in detail in the literature (Creighan *et al.* 2006, Perry *et al.* 2002), involves continuously irradiating a cryogenically cooled highly orientated pyrolytic graphite (HOPG) surface with beam(s) of incident H (and D) atoms. These atomic beams are generated by microwave dissociation of H_2 (D_2). The nascent product molecules desorbing from the surface are detected by state-selective laser ionization and the resulting H_2^+ and HD^+

signals can be transformed into the relative populations of the nascent ro-vibrational states formed at the surface.

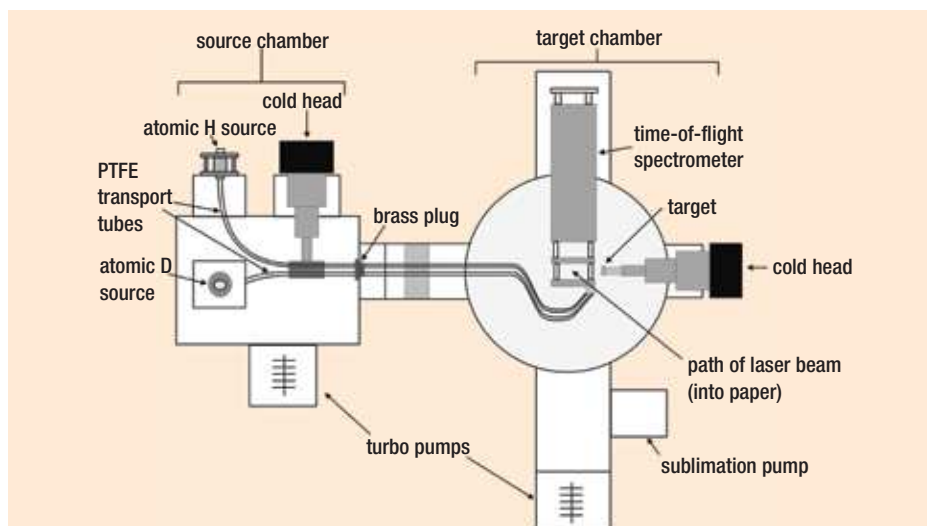
We initially performed experiments to study H_2 formation using just an atomic beam of H atoms (Creighan *et al.* 2006, Perry *et al.* 2002). In these experiments, a small fraction of the H atoms and undissociated H_2 molecules from the microwave source are piped up to the HOPG target. This transport of the atoms (via PTFE tubing) means that they are translationally thermalized, via collisions with the walls of the tube, and will reach the target with a translational temperature of approximately 300 K. For the experiments studying the formation of H_2 it is important to note that we have shown experimentally that we do not observe any vibrationally excited H_2 molecules in the beam of gas emerging from the PTFE tube (Creighan *et al.* 2006, Perry *et al.* 2002). In order to extend our apparatus to allow studies of the formation of HD on the HOPG surface, a second atom source was commissioned, to create D atoms. Both H and D atom beams are separately piped up to the HOPG target surface through PTFE tubes. The atom beams do not interact until they reach the target and we have carefully determined that vibrationally excited HD does not form in the dissociation cells or transport lines (Creighan *et al.* 2006, Perry *et al.* 2002).

The HOPG target can be cooled to astrophysically relevant temperatures, with a lower limit of 13 K, using a closed-cycle helium cryostat. The target can also be resistively heated for cleaning. The product molecules desorbing from the surface are detected by state-selective ionization, above the surface, using laser-induced (2+1) resonance enhanced multi-photon ionization (REMPI) requiring photons with wavelengths of between 200 and 230 nm. A typical REMPI spectrum for HD formation is shown in figure 5. The positive ions produced from the REMPI process are detected using a time-of-flight mass spectrometer. Considerable experimental attention has been paid to confirming that the H_2 and HD signals we detect from the REMPI process are dominated by molecules generated on the HOPG surface (Creighan *et al.* 2006, Perry *et al.* 2002). Hence, the ion counts we detect can be processed to determine the nascent ro-vibrational distribution of H_2 (HD) molecules formed on the HOPG surface. We are currently in the process of adapting our apparatus to determine the nascent velocity of the molecules we detect, by installing a position-sensitive detector in the mass spectrometer.

For surface temperatures between 15 K and 23 K, we have detected H_2 molecules formed in their first ($\nu=1$) and second ($\nu=2$) excited vibrational states while irradiating the HOPG surface with hydrogen atoms (Creighan *et al.* 2006, Perry *et al.* 2002). Similarly, when both H and D atom beams are illuminating the target, we have

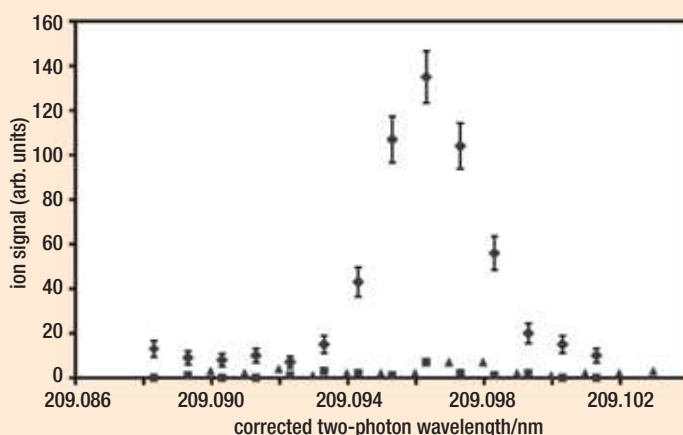


3: M83, the Southern Pinwheel galaxy with giant molecular clouds. This galaxy, like the Milky Way, shows the distribution of giant molecular clouds and their associated star-forming regions along the spiral arms. (FORS Team, 8.2 m VLT, ESO)



4: A schematic diagram of the UCL experiment to study the formation of H_2 (HD) molecular hydrogen on cold interstellar surfaces using laser spectroscopy. H and D atoms from microwave discharges hit a cooled graphite surface. (Reused with permission from Susan C Creighan, James S A Perry and Stephen D Price 2006 *J. Chem. Phys.* 124 114701. Copyright 2006, American Institute of Physics)

5: REMPI spectrum of ro-vibrationally excited HD ($J=1 \nu=1$) on graphite. \blacklozenge shows the signal when both atom sources are on, \blacksquare with the H source on but the D source off and \blacktriangle with the D source on but the H source off. (Reused with permission from Susan C Creighan, James S A Perry and Stephen D Price 2006 *J. Chem. Phys.* 124 114701. Copyright 2006, AIP)



1: The UCL H₂ and HD work in the context of related recombination experiments on relevant surfaces

● **Experiment of Vidali and colleagues**, Syracuse, New York (Biham *et al.* 1998, Katz *et al.* 1999, Manico *et al.* 2001, Perets *et al.* 2005, Pirronello *et al.* 1997a, 1997b, 1999, 2000, Roser *et al.* 2002, 2003, Vidali *et al.* 1998, 2004a, 2004b): HD formation from cool H and D beams on surfaces of olivine, amorphous carbon, and water ice at 5–20 K; a period of dosing is followed by temperature programmed desorption (TPD). HD is detected both during the dosing, to detect “promptly” formed HD, and after the dosing to study “delayed” formation. Efficiencies of both processes are measured.

Results for amorphous carbon surfaces:
 (i) “Prompt” formation efficiency is fairly flat over the range of surface temperature 5–20 K.
 (ii) “Delayed” formation efficiency falls from 0.5 to 0.1 over a similar temperature range.
 (iii) Nascent molecules have low translational energy and there is significant energy transfer to the surface.

Comparison with the UCL experiments:
 (i) Agreement that surface morphology significantly affects molecular hydrogen formation.
 (ii) The UCL surface is non-porous, so nascent molecules do not thermalize in pores; hence, a high “prompt” fraction is expected with high internal (ro-vibrational) energy (as detected in the UCL experiment).
 (iii) The UCL experimental upper limit of 1 eV on translational energy is in accord with these experimental measurements of low translational energy.

● **Experiments of Hornekaer and colleagues**, University of Odense and University of

Aarhus, Denmark (Hornekaer *et al.* 2003, Hornekaer *et al.* 2005, 2006): HD formation on both amorphous and non-porous water-ice surfaces studied by TPD, and on graphite surfaces studied by scanning tunnelling microscopy.

Results:
 (i) Nascent molecules are fully thermalized on porous amorphous water-ice.
 (ii) Nascent molecules are rapidly desorbed from non-porous surfaces, and internal excitation is expected.
 (iii) Two distinct dimer adsorption structures are possible for chemisorbed H atoms on graphite, and recombination is only possible for one of these states.

Comparison with the UCL experiments:
 (i) Detection in the UCL experiment of ro-vibrational excitation in nascent molecules is consistent with the interpretation that molecules do not fully thermalize with non-porous surfaces.

● **Experiment of Baurichter and colleagues**, University of Odense (unpublished): HD formation on graphite by dosing with H and D beams, followed by TPD.

Results for graphite:
 (i) Detection of “delayed” fraction is weak, implying the “prompt” channel is dominant.

Comparison with the UCL experiments:
 (i) Results are consistent and confirm that the nature of the surface (porous/non-porous) is important.

● **Experiments of Zecho and colleagues**, MPI Garching and University of Bayreuth (Guttler *et al.* 2004a, 2004b, 2004c, Zecho *et al.* 2002a, 2002b, 2003, 2004): Reactions of hot

(2000 K) H and D atoms, which have enough energy to chemisorb on graphite.

Results for graphite surface:
 (i) Sticking coefficients determined for chemisorbing H and D atoms. Confirmation of barrier to chemisorption.
 (ii) Recombination of chemisorbed atoms on the surface is relatively insensitive to the level of defects on the surface, indicating that chemisorption occurs mainly at the planar surface of the graphite.

Comparison with the UCL experiments:
 (i) Implication is that the UCL experiments measure the reactions of physisorbed atoms, although reactions at chemisorbed sites involving defects on the surface cannot be excluded.

● **Experiments of Govers and colleagues**, University of Waterloo (Govers 2005, Govers *et al.* 1980, Marengo *et al.* 1972): Pioneering experiments studying H₂ (D₂) adsorption/desorption and H, D atom recombination on a cryodeposit on a liquid helium cooled bolometer.

Results for “ice” surface:
 (i) Sticking probability and accommodation coefficient determined as a function of coverage.
 (ii) Recombination observed to be efficient down to 4 K. Recombination desorbs other H₂ molecules from the surface. Nascent H₂ is ro-vibrationally excited.

Comparison with the UCL experiments:
 (i) Agrees with observation of ro-vibrational excitation. “Prompt” recombination reactions are important down to very low temperatures.

detected HD molecules formed in $v=1$ and $v=2$ when the target temperature is 15 K (Creighan *et al.* 2006). Recently recorded experimental data also clearly show the formation of HD in $v=3$ and $v=4$ from a 15 K HOPG surface. Qualitative indications are that the relative number densities of nascent H₂ molecules in the $v=1$ and $v=2$ states are comparable (Creighan *et al.* 2006). A similar situation exists for the formation of HD. It is important to note that the experimental REMPI signals are proportional to the number density of the molecules in the ro-vibronic state being probed. Obviously, to transform these densities into relative fluxes we need the velocity of the molecules. Other experimental measurements indicate that these molecular products possess a low translational energy, an energy comparable with the surface temperature. Therefore, if we assume that the molecules in the different vibrational states have the same translational

TABLE 2: CHARACTERISTIC TEMPERATURES FOR HD AND H₂

Fitted rotational temperatures $T_{\text{Rot}}(v'')$ for the $v''=1$ and $v''=2$ states of HD formed on HOPG at a surface temperature T_{Surf} .

Product	T_{Surf}/K	$T_{\text{Rot}}(v''=1)/\text{K}$	$T_{\text{Rot}}(v''=2)/\text{K}$
H ₂	15	–	364 ± 37
H ₂	23	314 ± 9	309 ± 41
HD	15	246 ± 24	282 ± 31

temperature, our experimental results indicate that the product fluxes in the $v''=1$ and $v''=2$ vibrational states are similar. Preliminary indications are that the product fluxes in $v''=3$ and $v''=4$, for the formation of HD, are, if anything, larger than for $v''=1$ and $v''=2$.

The rotational populations in the vibrational

states of HD and H₂ we detect (figure 6) are reasonably well modelled as Boltzmann distributions with the characteristic temperatures listed in table 2 (Creighan *et al.* 2006). Note that these rotational temperatures are much greater than the surface temperature. Indeed, for recombination on metals it is often, but not always (Kubiak *et al.* 1985), observed that such rotational distributions are approximately Boltzmann, sometimes with a rotational temperature that is higher than the temperature of the surface (Murphy and Hodgson 1996, Schroter *et al.* 1991, Winkler 1998, Zacharias 1988). The rotational temperatures we observe for HD formed on a 15 K HOPG surface in both $v''=1$ and $v''=2$ are very similar to those we observe for H₂ at all the surface temperatures investigated. Our results do not show any clear evidence of the isotope effects predicted for these processes in some theoretical studies (Meijer *et al.* 2003). However, it is again

important to emphasize that to date we have only observed the formation of H_2 and HD in $v''=1$ and $v''=2$. Thus, our measurements give no information on the occupation of higher vibrational levels that may perhaps be better candidates for detecting differences in relative vibrational populations as a monitor of isotopic differences in the formation of H_2 and HD (Meijer *et al.* 2002).

With our experimental arrangement it is difficult to investigate the nascent population of the lower rotational states in the $v''=0$ level of H_2 , since these signals are swamped by those from the background H_2 gas that enters the target chamber from the H atom source. We have not yet searched extensively for the formation of H_2 ($v''=0$) molecules in rotational states ($J'' > 7$) which are energetic enough not to be masked by the signals from the background gas. We also detect weak signals from HD ($v''=0$) when the microwave supply to either of the atom sources is turned off. This observation suggests that some of the HD generated in the target chamber accumulates on the experimental surfaces and the residual desorption of these thermalized HD molecules yields a background signal for HD $v''=0$. This background signal masks any signals from nascent HD $v''=0$ molecules in low J'' states.

In summary, our experiments demonstrate that hydrogen molecules (H_2 or HD) are formed efficiently from atoms on graphitic surfaces at low temperatures, and are ejected promptly to the gas phase. The detection of ro-vibrationally excited H_2 and HD molecules from the cold HOPG surface indicates that some of the binding energy released upon the formation of the H–H (or H–D) bond is converted into internal excitation of the molecule. Considering the energy budget for H_2 formation (a total of 4.5 eV per molecule formed), the temporal widths of the H_2^+ and HD^+ signals in our time-of-flight mass spectra place an upper limit of 1 eV on their translational energy. Combining this upper limit on the translational energy with the internal energy of the (v'' , J'') levels we observe to be populated suggests that an upper limit of approximately 40% of the binding energy released upon the formation of H_2 (and HD) goes into internal and translational excitation of the molecules we detect, with the remainder of the energy flowing into the HOPG surface (Creighan *et al.* 2006). As described above, we put our results into the context of other work in boxes 1 and 2.

Application of results to astronomy

What are the consequences for astronomy of these experimental results? The first and most important result, that H_2 forms efficiently on low-temperature graphitic surfaces, is supported by other experiments and has been extended by others to silicate and ice surfaces (see box 1). The main routes by which this formation occurs

2: UCL work in the context of quantum dynamical studies of H_2 and HD formation on surfaces

Calculations have looked at both physisorbed (weak physical bonding between the atom and the surface) and chemisorbed (stronger chemical bonding between the atom and the surface) H atoms.

● **Eley–Rideal mechanism** (an incident atom in the gas phase reacts with an atom chemisorbed on the surface) (Farebrother *et al.* 2000, Jackson and Lemoine 2001, Meijer *et al.* 2001, 2002, 2003, Morisset *et al.* 2003a, 2003b, 2004b, Parneix and Brechignac 1998, Ree *et al.* 2002, Rutigliano *et al.* 2001, Sha and Jackson 2002, Sha *et al.* 2002): The cited studies all refer to reactions on graphite surfaces or models of graphite surfaces. These studies generally predict a high reaction probability and significant ro-vibration populations in nascent molecules, but sometimes give less information on the energy transfer to the surface.

Relevance to the interstellar medium and to the UCL experiments:

(i) The Eley–Rideal mechanism may apply for chemisorbed atoms at surface defects on dust in cool interstellar regions, and for chemisorbed atoms on perfect graphite

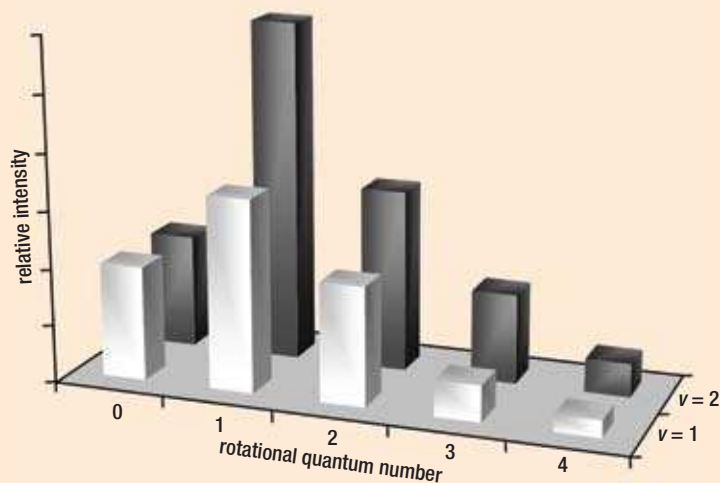
surfaces in hot regions (e.g. post-shock regions) of the interstellar medium. The UCL experiment is probably probing more directly the reaction of physisorbed atoms, so these quantum studies may not be directly relevant. However, the relatively low rotational excitation detected in the experiment is in accord with several of these studies.

● **Langmuir–Hinshelwood mechanism** (reactions between two physisorbed atoms on a graphite surface) (Morisset *et al.* 2004a, 2005): These also predict internal excitation of the product molecules, but perhaps greater excitation than the Eley–Rideal mechanism.

Relevance to the interstellar medium and to the UCL experiment:

(i) This mechanism may be more relevant to the interstellar medium and to the UCL experiment, where low surface coverage and low temperatures apply. The experiment detects approximately equal molecular abundances in the lowest two excited levels, which calculations indicate should be less strongly populated than higher lying vibrational levels that have not been probed experimentally at UCL to date.

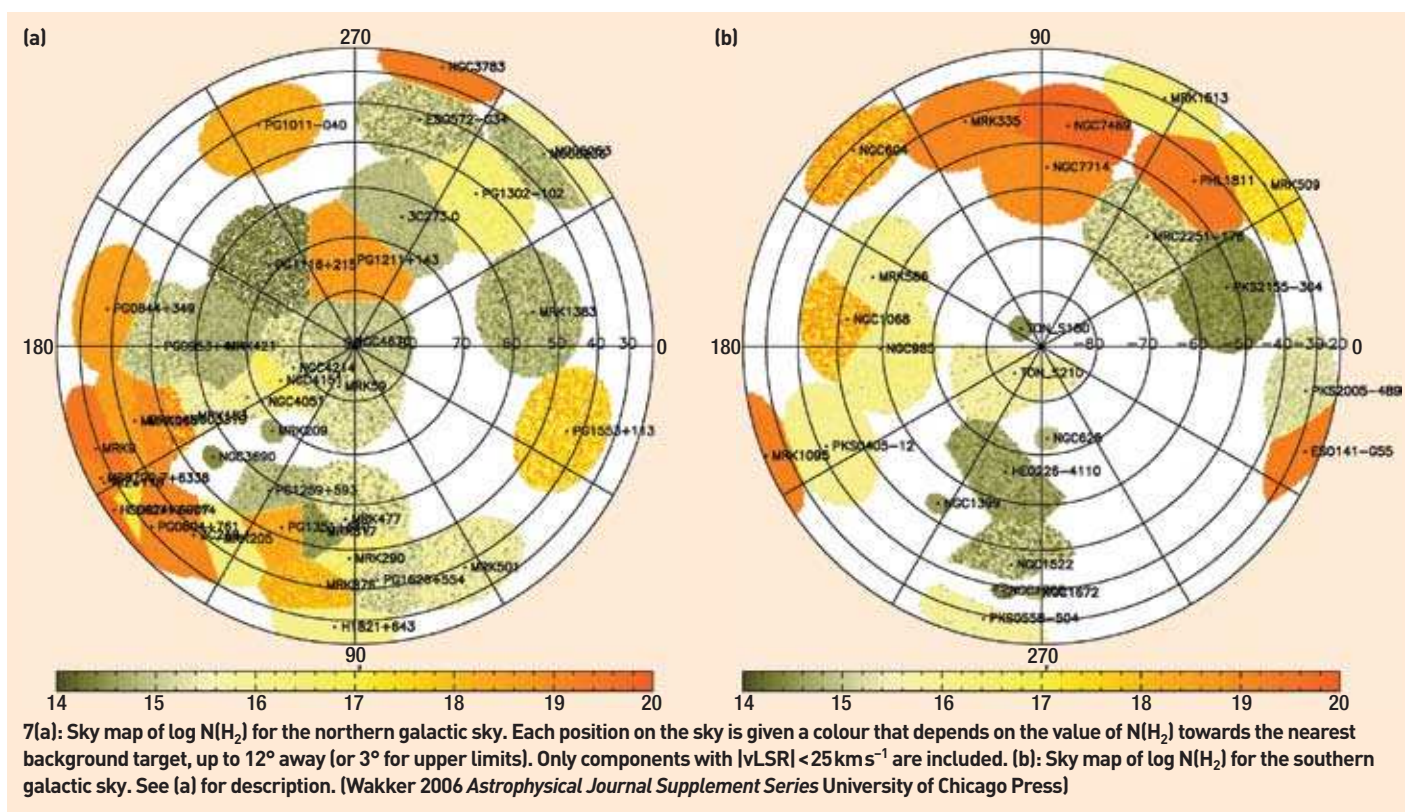
6: The relative populations of the $v=1$ and $v=2$ states of HD formed by recombination of H and D atoms on a graphite surface at 15K. The relative intensities for both $J=0$ states have been normalized to unity.



have been investigated theoretically (see box 2). A high value for the H_2 formation rate was predicted long ago on the basis of observations of atomic and molecular hydrogen along the same line of sight (Jura 1975) and the widespread existence of H_2 is confirmed by recent observations using the Far Ultraviolet Space Explorer (figure 7) (Wakker 2006). The assumption of efficient H_2 formation has been the basis of all models of interstellar chemistry for the last 30 years, and we shall not discuss this result any further – except to note that the temperature dependence of the formation rate over a relevant temperature regime has not yet been investigated

experimentally. There are situations (especially in regions of massive star formation) where the relevant surface temperatures may be several hundreds of kelvin, rather than the 10–20K typically found in interstellar clouds.

The second result is that a potentially significant fraction of the newly formed H_2 is rotationally and vibrationally excited. Indeed, in the UCL experiment this excitation is used as the signature of molecule formation. Our experiment confirms and (to some extent) quantifies predictions of internal excitation made by many authors. Relaxation from excited levels under interstellar conditions generates a well-defined



discrete line spectrum. In shocked interstellar regions the excited levels are populated by collisions (Burton *et al.* 1989), but in quiescent regions at low temperature these populations arise from UV excitation in the Lyman and Werner bands, in collisions with non-thermal electrons, as well as from the formation process. Thus, in principle, observations may be able to constrain the efficiency and excitation states arising in the formation process. Tiné *et al.* (2003) predicted the relaxation spectrum for a particular model of H_2 formation, and they searched in quiescent interstellar regions of low UV intensity. However, those observations appeared to lack sufficient sensitivity and new observations are planned.

There are some interesting chemical consequences in the interstellar medium of the internal excitation of newly formed H_2 . Reaction channels that are inhibited for ground-state H_2 may be opened when the H_2 is internally excited. For example, reactions of O atoms and C^+ ions with H_2 are suppressed at low kinetic temperature but are efficient for H_2 in states $v=1$ or higher, to form OH and CH^+ , respectively. Both of these species are detected in the interstellar medium. However, the short radiative lifetimes of these excited states of H_2 (Black and Dalgarno 1976) imply that the abundance enhancements of these species are small, except possibly in strong isothermal shocks (Garrod *et al.* 2003).

The experimental results place an upper limit of 1 eV on the translational energy of the desorbing H_2 (HD) molecules; this means certainly that the translational energy of the desorbing H_2 is not above 1 eV and could be considerably below



8: Molecular cloud Barnard 68. Dark clouds such as B68 are regions in which ices are detected. The freeze-out of gas-phase species on to dust grains is partially offset by desorption mechanisms such as that driven by the formation of molecular hydrogen on dust-grain surfaces. (FORS Team, 8.2m VLT Antu, ESO)

that limit, as observed by the Syracuse group (Roser *et al.* 2003) for recombination on water ice. Alternatively, the nascent molecules might be moderately translationally excited. If there is translational excitation at the limit of 1 eV, there are two consequences in the interstellar medium. First, since most of this energy, ϵ , is shared elastically with H, H_2 and He, this constitutes a heating rate of about $5 \times 10^{-29} n(\text{H})n_{\text{H}} (\epsilon/1 \text{ eV}) \text{ erg cm}^{-3} \text{ s}^{-1}$. This may be compared with the heating rate arising from the photoelectric effect on dust grains. The heating rate from kinetically excited H_2 may become competitive if ϵ is near unity and the photoelectric efficiency

is as low as 10^{-4} . The second effect is chemical: these kinetically excited H_2 molecules may undergo reactions with C^+ ions and O atoms. The decay lifetime of the kinetic excitation through collisions in low-density gas is several orders of magnitude longer than the radiative decay. Therefore, the steady-state population of kinetically excited H_2 is greater than that of internally excited H_2 . If the amount of kinetic energy in the H_2 is sufficient to overcome the barrier in the reactions of C^+ and O with H_2 , then this route may become significant for the formation of CH^+ and OH molecules in the diffuse interstellar medium.

Energy from formation

The final important result from the UCL experiment on H_2 formation is the implication that at least 1.5 eV of energy is deposited into the surface for each H_2 ($v=1,2$) formation event. If this energy were immediately diffused over the whole grain, then any effect on the grain temperature would be minimal. However, interstellar grains are likely to be amorphous materials with a high degree of porosity. The localization of even such a small amount of energy as 1 eV or so will cause a local rise in temperature that may be significant in desorbing weakly bound molecules such as CO and N_2 . A detailed study by Roberts *et al.* (2007) has shown that desorption by H_2 formation on dust grains within dark clouds, such as B68 (figure 8), is likely to be the most effective means of limiting the loss of molecules from the gas phase by freeze-out on to dust. It appears to be more effective than the heating caused by the occasional passage of a

cosmic ray through a dust grain in limiting ice-mantle growth if one CO molecule is desorbed per hundred H₂ formations. This seems to be a very modest requirement.

We conclude that efficient H₂ formation events on dust grains into internally and kinetically excited states, with significant deposition of energy into the underlying grain surface, has major consequences for interstellar physics and chemistry in both diffuse and dense interstellar clouds.

Laboratory studies of molecular ices

In 2002 the laboratory work at UCL was expanded to include studies of interstellar ices, especially the adsorption and desorption of astrophysically relevant molecules from model grain surfaces. The ultra-high vacuum apparatus we use for this purpose has been described in detail elsewhere (Bolina and Brown 2005, Bolina *et al.* 2005a, 2005b). The molecular ices under investigation are adsorbed onto a graphite surface cooled to 80–90 K using liquid nitrogen. Although this temperature is not as low as that found in the interstellar medium, where temperatures are usually around 10–20 K, it still allows us to understand the adsorption and desorption of relevant species. A brief review of other experiments investigating the adsorption and desorption of molecular ices is given in box 3.

The two experimental techniques we use to study the ices are reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD). RAIRS is an infrared technique that allows the identification of adsorbates from their vibrational frequencies, and also determines the orientation of the adsorbed species. TPD is a technique where the sample is heated at a constant rate and the desorbing species are detected using a mass spectrometer. We use TPD to determine the kinetic parameters (such as desorption order, desorption energy and pre-exponential factor) of the desorption process. With this information we can determine the desorption temperature for icy mantles on grain surfaces under astrophysical conditions and the molecular residence times of ices on the grain surfaces as a function of temperature (Brown and Bolina 2007). These results are important for models of astronomical desorption (Brown *et al.* 2006) (see next section). Systems that have been investigated to date include the adsorption and desorption of pure water (H₂O) (Bolina *et al.* 2005b) (the dominant interstellar ice molecule), pure ammonia (NH₃) (Bolina and Brown 2005) and pure methanol (CH₃OH) (Bolina *et al.* 2005a) from a graphite surface. We have also investigated the adsorption and desorption of layered and mixed ice systems including H₂O/CH₃OH (Wolff *et al.*) and H₂O/ethanol ices.

The adsorption and desorption of pure H₂O ice on the graphitic surface is complex (Bolina

3: Experiments on adsorption and desorption of ices

● **Experiments of Allamandola, Sandford and colleagues** at NASA Ames, USA (Sandford and Allamandola 1988, 1990a, 1990b, 1993a, 1993b, 1993c): Pure ices of CO, CO₂, H₂O, SO₂, H₂S, CH₃OH, NH₃ and H₂ deposited on a CsI substrate and probed by IR transmission spectroscopy. Binding energies and residence times derived indirectly from IR data. Results from UCL and the NASA Ames group agree qualitatively. However, the UCL experiments are performed on graphite surfaces – a more realistic dust-grain analogue. In addition, binding energies – and hence residence times – are derived directly from TPD data in the UCL experiments.

● **Experiments of van Dishoeck and colleagues**, Leiden University, the Netherlands (Bisschop *et al.* 2006, Oberg *et al.* 2005, van Broekhuizen *et al.* 2006): Studies of pure, layered and mixed morphologies of CO and N₂ ices on an Au-covered Cu substrate. RAIRS and TPD reveal that both materials have similar behaviour under astrophysically relevant conditions. The spectroscopy of pure, layered and mixed CO and CO₂ ices was investigated. UCL experiments have

investigated different ice mixtures, but show good agreement with Leiden results for systems with similar ices.

● **Experiments of McCoustra and colleagues**, University of Nottingham, UK (Collings *et al.* 2003a, 2003b, 2004, 2005, Viti *et al.* 2004): Studies of pure H₂O and CO/H₂O ices by TPD and RAIRS reveal that H₂O can trap CO and other species, and that this strongly affects CO desorption. Initial studies of a broad range of astrophysically relevant species also performed. Species classified according to desorption characteristics. UCL results generally in good agreement with Nottingham experiments, despite the different surfaces used in the two experiments. In combination, this work shows that the nature of the grain surface is not important in physisorbed ice systems.

● **Experiments of Bar-Nun and colleagues**, University of Tel-Aviv, Israel (Laufer *et al.* 1987, Notesco and Bar-Nun 1996, 2000, Notesco *et al.* 1999, 2003): Qualitative data recorded on mixed ice desorption. In comparison, UCL experiments give both quantitative and qualitative information.

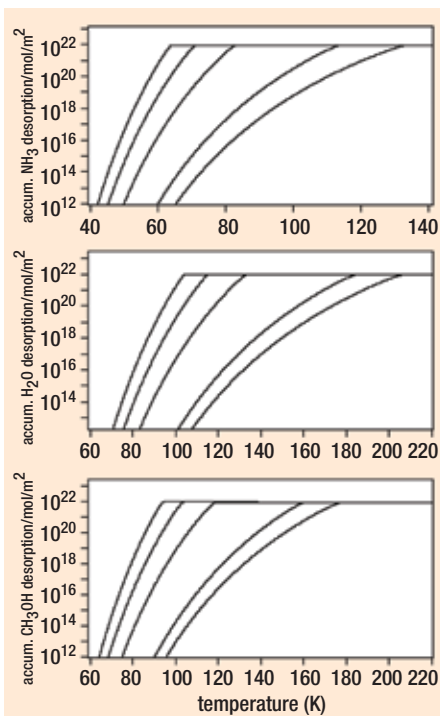
et al. 2005b). Since the H₂O is adsorbed onto the surface at ~90 K, the ice film grows initially in the form of low-density amorphous ice (Jenniskens *et al.* 1995). For very thin ices, TPD spectra show features that can be assigned to the formation of first two-dimensional, and subsequently three-dimensional, islands on the graphitic surface. H₂O does not wet the graphite surface and – evidently – clusters in hydrogen bonded islands. The adsorption of thicker ices leads to the observation of TPD peaks that can be assigned to the desorption of physisorbed H₂O multilayers (Bolina *et al.* 2005b). For thicker ices, TPD spectra also show peaks that can be assigned to the observation of the amorphous-to-crystalline and the crystalline-to-hexagonal ice phase transition. Isothermal TPD studies were also performed (Bolina *et al.* 2005b) and these show that the desorption of H₂O does not show perfect zero-order kinetics as previously assumed (Fraser *et al.* 2001). RAIR spectra confirm that H₂O is physisorbed on graphite at all thicknesses. RAIRS experiments at higher surface temperatures show marked changes in the infrared spectrum of the H₂O ice, which can be assigned to the observation of the amorphous-to-crystalline phase transition. Results show that RAIR spectra in the O–H stretching region of the spectrum can be used as a fingerprint of the phase (amorphous or crystalline) of the H₂O ice (Bolina *et al.* 2005b).

TPD spectra for the desorption of pure CH₃OH

ice from the graphitic surface also show complex behaviour with several peaks being observed as a function of increasing ice thickness (Bolina *et al.* 2005a). For very thin ices, the desorption of monolayer CH₃OH directly from the graphitic surface is observed. For thicker ices, the desorption of multilayers of CH₃OH is observed and – for the thickest ices investigated – the formation of crystalline CH₃OH is detected at high enough temperatures.

In contrast to the CH₃OH and H₂O ice films, pure NH₃ ice shows much simpler behaviour in both adsorption and desorption (Bolina and Brown 2005). RAIR spectra show very sharp bands, characteristic of the formation of physisorbed crystalline NH₃ ice on the graphite surface at ~90 K. TPD spectra also show the formation of physisorbed species. Unusually, the monolayer of NH₃ is observed to desorb at a lower temperature than the multilayer. This can be attributed to the extensive hydrogen bonding that occurs in the multilayer. NH₃ desorbs from the graphitic surface at a lower temperature than either the H₂O or CH₃OH ice.

For all of the pure ice systems described above, kinetic parameters for the desorption of the ices have been extracted from the TPD data using methods described previously (Bolina and Brown 2005, Bolina *et al.* 2005a, 2005b), see table 3. We have used these kinetic parameters to determine the desorption temperature of icy mantles from grain surfaces under astrophysical



9: Simulated cumulative desorption to the gas phase for pure NH_3 , H_2O and CH_3OH ices desorbing from graphite as a function of heating rate and temperature (Brown and Bolina 2007 MNRAS Blackwell Publishing). The simulations were run for an initial ice surface coverage of 9.5×10^{21} molecules/ m^2 , hence the cumulative gas phase desorption saturates at this value. Kinetic parameters were extracted from TPD data recorded for the desorption of H_2O (Bolina *et al.* 2005b), CH_3OH (Bolina *et al.* 2005a) and NH_3 (Bolina and Brown 2005) from the graphite surface. These kinetic parameters were then used to determine the gas phase concentration of these species as a function of the temperature of the grain surface. Note that the temperature at which desorption to the gas phase is complete is the temperature that would be the so called “peak” temperature for a TPD experiment at the corresponding heating rate. Simulations were performed for a range of heating rates including those observed in the laboratory and those expected under astronomical conditions. The spectra (from left to right) have a heating rate of 1 K century^{-1} , 1 K year^{-1} , 1 K day^{-1} , 0.2 K s^{-1} (0.5 K s^{-1} for H_2O and CH_3OH multilayers) and 10 K s^{-1} .

conditions (figure 9) and to determine the molecular residence times of the ices on the grain surfaces as a function of temperature (Brown and Bolina 2007).

More recently, we have undertaken studies of layered and mixed $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ ices (Wolff *et al.*). The layered systems were formed by depositing CH_3OH ice of various thicknesses onto the surface of a pre-deposited layer of amorphous H_2O ice. There is no detectable interaction between the layers on adsorption, however, heating the layered ice leads to mixing of the H_2O and CH_3OH layers. As expected, the results demonstrated that H_2O desorption was inhibited by the overlying layer of CH_3OH .

TABLE 3: DERIVED KINETIC PARAMETERS

The kinetic parameters previously derived for the desorption of pure H_2O , pure CH_3OH and pure NH_3 ices from an HOPG surface (Bolina and Brown 2005, Bolina *et al.* 2005a, 2005b). The kinetic parameters are described by the Polanyi–Wigner equation (de Jong and Niemantsverdriet 1990):

$$r_{\text{des}} = -\frac{d\theta}{dt} = \nu_n \theta^n \exp\left(\frac{-E_{\text{des}}}{RT}\right)$$

where r_{des} is the rate of desorption, ν_n is the pre-exponential factor for the desorption process of order n , θ is the surface coverage, E_{des} is the desorption energy, R is the gas constant and T is the surface temperature.

	Desorption order n	Desorption energy/K	Pre-exponential factor*/molec. $\text{m}^{-2}\text{s}^{-1}$
H_2O	0.26 ± 0.02	4799 ± 96	$1 \times 10^{27 \pm 1}$
NH_3	0.25 ± 0.05	2790 ± 144	$8 \pm 3 \times 10^{25}$
CH_3OH multilayer	0.35 ± 0.21	4931 ± 98	$6 \times 10^{25 \pm 3}$
CH_3OH monolayer	1.23 ± 0.14	5773 ± 95	$^{\S} 9 \times 10^{9 \pm 3}$

*The units given for the pre-exponential factors for H_2O , NH_3 and CH_3OH multilayers are those for zero order desorption, despite the fractional desorption order obtained from the data.

[§]The units given for the pre-exponential factor for monolayer CH_3OH are those for first order desorption (s^{-1}) despite the fractional desorption order obtained from the data.

The layered systems show evidence for the monolayer and multilayer features observed for pure CH_3OH (Bolina *et al.* 2005a). For thin layers of CH_3OH adsorbed on top of H_2O an additional desorption peak is also observed at high temperature; we assign this to CH_3OH trapped at grain boundaries between the amorphous H_2O ice and the crystalline H_2O ice, that form as the ice is heated during the TPD experiment. This trapped CH_3OH can only desorb from the surface along with the bulk of the H_2O ice.

As expected, co-deposited $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ layers, consisting of $\sim 10\%$ CH_3OH in H_2O , behave somewhat differently to either pure or layered ices. TPD data (figure 10) show that heating the mixed ice leads initially to desorption of CH_3OH molecules that are present on the surface of the ice. Further heating of the ice, beyond the amorphous-to-crystalline transition temperature of the H_2O , results in significant reordering of the ice which causes channels to open and close within the ice structure. These allow the percolation of CH_3OH molecules trapped in the bulk towards the surface of the ice where they then desorb. Once the crystallization of the H_2O ice is complete the channels become sealed and the remaining CH_3OH is trapped within the bulk of the H_2O ice and can only desorb when the H_2O desorbs, leading to the so-called co-desorption peak in the TPD spectra (figure 10). The behaviour of the H_2O within the mixed ice is little changed from that expected for pure H_2O . The infrared spectrum of the CH_3OH in the mixed ice is perturbed by the presence of H_2O in the ice, so that it is possible to distinguish CH_3OH trapped within the H_2O from that present on the surface of the ice.

In summary, we have studied some of the processes of deposition and desorption of molecules that are relevant to the formation and evaporation of interstellar ices. In the next sec-

tion, we apply this information to particular situations in astronomy.

Astronomical ices

Why is information about adsorption and desorption of ices important in astronomy? At first sight, such processes seem rather remote from the topics astronomers normally consider. However, ices are observed to be abundant in the interstellar medium, in the denser, cooler regions of molecular clouds. Their composition can be studied, and is found to vary from one location to another (see table 1 and figure 11), so evidently the ices respond to their environments. Of particular interest for current astronomical research is the behaviour of ices in star-forming regions. Here, a very young star is likely to be embedded in a shroud of dusty gas that absorbs all stellar radiation and re-emits it in the infrared region. This shrouded star therefore acts as a heat source for dense gas and dust in its vicinity. As the temperature of gas and dust near the star rise, the ices evaporate. Hence molecular tracers that were previously locked in the ices become available in the gas phase, and emissions from them allow us to explore regions very close to newly formed stars. These warm regions exist near all very young stars, but were first observed near massive stars; they are the so-called hot cores. One much-studied hot core is shown in figure 12.

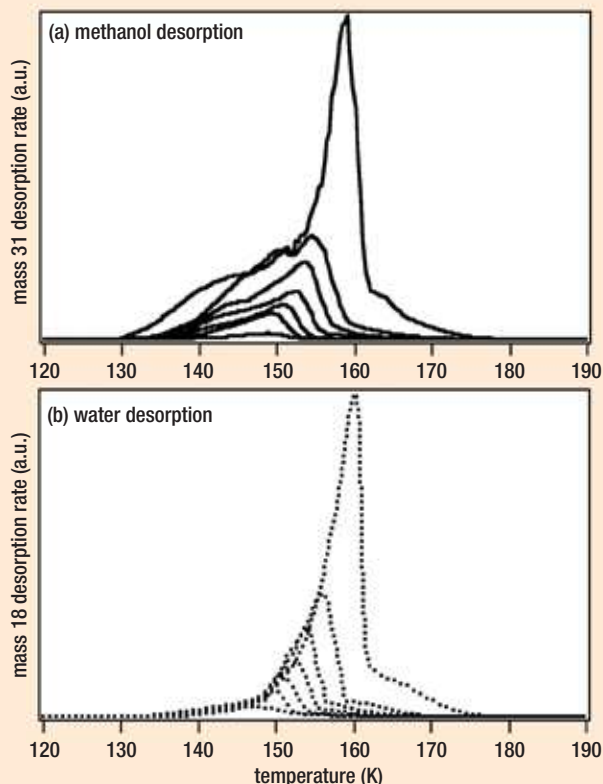
The region that becomes a hot core is heated from about 10 K to several hundred kelvin by the radiation of the nearby enshrouded star. How long does this take? The timescale must be related to the period over which the new star itself “switches on”. This switching-on is not instantaneous, but takes a finite time. During this warming period, the astronomical ices begin to evaporate, almost exactly replicating a TPD experiment in the laboratory, but over a longer timescale. Therefore, guided by those

10: TPD spectra recorded following the adsorption of an 8% CH₃OH in H₂O mixture onto a graphite surface held at 90 K. The spectra were recorded following increasing thicknesses of the mixed water/methanol mixture.

(a) Spectra for the desorption of methanol.

(b) Spectra for the desorption of water (Brown *et al.* 2006).

The spectra show that the desorption of CH₃OH occurs in two main peaks. The sharp higher temperature peak is a so called “co-desorption” peak which occurs in coincidence with the desorption of the H₂O. The broader lower temperature peak is assigned to the desorption of CH₃OH that occurs during the phase transition of amorphous-to-crystalline H₂O ice (Brown *et al.* 2006). (Reproduced with permission of the Royal Society of Chemistry)

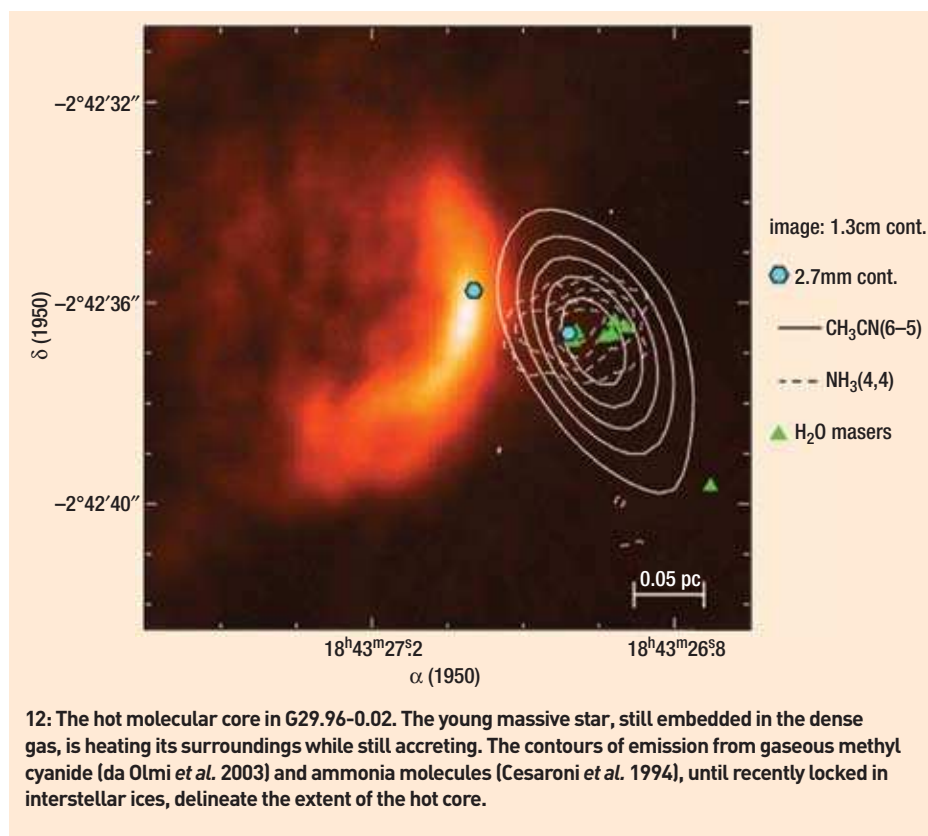


11: The dust and ion tails of Comet Hale-Bopp. Comets are rich sources of water ice (see table 1). Desorption of this ice by solar radiation, and photochemistry of these molecules, creates the familiar cometary tails. (Copyright John Gleason [Celestial Images])

experiments, we expect some molecules to desorb before others. In other words, the nature of the molecular emissions from a core that is warming up should be directly linked to the timescale over which the new star is formed, and that timescale is determined by the stellar mass. In principle, therefore, by observing the molecular emissions from a hot core that is warming up, we can say something about the mass of the newly forming star. This is important astronomical information that is probably unobtainable in any other way.

We are now learning how to make this connection between hot-core evolution and stellar mass. The first attempt was based on laboratory work at the University of Nottingham (Collings *et al.* 2004) in which the desorption of various mixed ices was studied by TPD and RAIRS. Those experiments showed that the desorption of molecules from mixed ices is a complex process; desorption of one molecular species may occur in several distinct temperature regimes, depending on the nature of the chemical binding of the molecule within the ice. For example, CO in a CO/H₂O ice is found to desorb at four distinct temperatures during the warm-up. Desorption data for various mixtures of molecules in H₂O ice were incorporated within a hot-core model (Viti *et al.* 2004) which demonstrated that distinct chemical peaks and associated molecular emissions should occur at particular stages during the warm-up process. Thus, a “molecular clock” defines the warm-up, which itself is related to the stellar mass.

The UCL experiments described above confirmed the general behaviour described by the Nottingham experiments. They also investi-



12: The hot molecular core in G29.96-0.02. The young massive star, still embedded in the dense gas, is heating its surroundings while still accreting. The contours of emission from gaseous methyl cyanide (da Olmi *et al.* 2003) and ammonia molecules (Cesaroni *et al.* 1994), until recently locked in interstellar ices, delineate the extent of the hot core.

gated the effects on desorption of varying the thickness of the ice layers. When these data were incorporated into a computational model (Brown *et al.* 2006) it was found that the desorption behaviour varied significantly only for ice thicknesses less than about 1 nm. Since ice thicknesses expected on dust in star-forming regions are much greater, the desorption behaviour

predicted for hot cores should not be affected. In addition, although the underlying substrates used in the Nottingham and UCL experiments were different, it appears that (for the likely ice thicknesses in the astronomical case) any differences in desorption from the two substrates are unimportant. This is an important conclusion that strengthens the laboratory basis for the

astronomical model of the warm-up phase.

However, the UCL experiment found a difference in behaviour for methanol-ice mixtures compared to that of the Nottingham experiment which predicted that methanol in such mixtures would only be released when the water itself evaporated. By contrast, the UCL experiment found that a fraction of the methanol (a significant component of interstellar ices, see table 1) was found to desorb at lower temperatures than that associated with H₂O desorption (Brown *et al.* 2006). Thus, in terms of predicting the “age” of a warming core, the detection of emission from methanol (and also methyl formate, which is derived from methanol in gas-phase reactions) would be a useful indicator that the core had not yet attained its maximum temperature and that ice-coated dust grains may still be present.

Evidently, the development of the picture by which we can infer the mass of a newly forming star from molecular emissions is not yet complete. Further laboratory work is required on mixed ice desorption, and the astronomical models incorporating these data need to be improved. Nevertheless, we can say that a feasibility study has now been completed.

Conclusions

Until relatively recently, laboratory techniques have been unable to address with adequate sensitivity the two examples of cosmic chemistry that we have discussed here: the formation of molecular hydrogen on the surfaces of cosmic dust, and the adsorption and desorption of interstellar ices on dust.

Ideas concerning the first of these have been discussed in the literature for about half a century, yet only now are we beginning to understand the complexities of the process, in terms of the nature of the surface on which the reaction occurs, the reaction efficiency, and the energy budget. Only now, therefore, can we begin to consider not merely unconstrained speculation but a proper analysis – well-constrained by experiment – of how the laboratory results apply in the interstellar medium. We can then investigate the astronomical consequences of that deeper understanding. The work reported here has shown that those consequences may be more profound than we had realized in terms of the relaxation spectrum of newly formed molecular hydrogen, the desorption of molecules from grain surfaces, and possibly interstellar chemistry with excited H₂.

The presence of dirty ices in dense interstellar clouds has been recognized for about three decades, since the detection of a strong absorption corresponding to the O–H stretch in H₂O ice. Over this period there has been considerable laboratory work on the spectra of dirty ices, so that the detailed chemical nature of the ice can be inferred. However, the processes by which the ices are deposited on dust grain surfaces, and by

which evaporation of those chemically mixed ices occurs, are poorly understood and have only rarely been investigated. The work reported here shows that the astronomical implications arising from such studies can be remarkably powerful, especially in giving detailed information about star formation.

Therefore, we conclude that if we wish to understand fundamental processes in astronomy, such as interstellar chemistry and the initial stages of star formation, and to explore their astronomical consequences, there is no alternative but to obtain the fundamental data of chemistry and surface science. Spectroscopic data of atoms and ions enable the understanding of stellar atmospheres, molecular data allow us to describe the chemistry of interstellar clouds; but for a fuller understanding of the evolution of interstellar chemistry and star-forming regions, fundamental data on surface and bulk processes are essential. ●

D A Williams, Dept of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK; W A Brown, Dept of Chemistry, UCL, 20 Gordon Street, London WC1H 0AJ, UK; S D Price, Dept of Chemistry, UCL; J M C Rawlings, Dept of Physics and Astronomy, UCL; S Viti, Dept of Physics and Astronomy, UCL. Corresponding author: w.a.brown@ucl.ac.uk

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