

LABORATORY SURFACE SCIENCE – THE KEY TO THE GAS-GRAIN INTERACTION

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ABSTRACT

Icy mantles on dust grains in molecular clouds play an important role in the chemistry of these regions, and their influence on the star formation process can not be underestimated. Quantification of fundamental processes occurring on grain surfaces is an essential step in pursuing a fuller understanding of the role of ice in the ISM. We have developed an interdisciplinary programme that brings together laboratory surface science with molecular astrophysics and astronomy in researching aspects of such processes in our laboratory. Using a combination of reflection-absorption infrared spectroscopy, mass spectrometric techniques and nanogravimetry, our studies to date have focussed on the adsorption and desorption behaviour of simple molecular species commonly observed in the interstellar medium under conditions where the simple physical processes dominate and chemical reactivity is negligible. In this paper, we summarise these results and make a more general case that if we are to fully understand the role of the gas-grain interaction, then we must employ surface science, its tools and methodologies to these studies.

Subject Headings: infrared: ISM: molecules --- ISM: lines and bands--- line: profiles --- methods: laboratory

1. INTRODUCTION

It is widely recognised by the astronomical community that understanding the chemical processing of molecular gas clouds is the gateway to understanding key aspects of the physics of star formation (Williams 1993, Williams 1998), and possibly to understanding the origin of life itself (Bernstein, Sandford & Allamandola 1998). Central to this is the recognition that physical and chemical processes occurring at the surfaces of interstellar grains are crucially important. Grains provide surfaces upon which a variety of reactions occur that are vital to the chemical evolution of molecular clouds. Gaseous molecules may condense onto these surfaces which, when irradiated by photons and cosmic rays, are chemical nanofactories in which the complex molecules of life may be synthesised from simple ices. Of course, the key to this chemistry is an appreciation of the role of the adsorption and desorption of atoms and molecules from the grains themselves, under both reactive and non-reactive conditions.

As a field of research, surface science has existed for roughly forty years, since the development of vacuum technology sufficient to achieve ultrahigh vacuum (UHV) conditions. One of the main forces driving the field has been the study of heterogeneous catalysis for industrially important reactions. In such research, a reductionist approach is required – an extremely complex system is simplified to a level where parameters can be controlled and varied individually. The behaviour of the complex system is then understood through a knowledge of the behaviour of the system's many components. There are many examples of how surface science research using this philosophy have led to advances in the chemical industry, the development of nickel-gold catalysts by Nørskøv and Chorkendorff (Bengard et al 1999) being a prime example.

In some respects, interstellar ices are not dissimilar systems to those involved in heterogeneous catalysis. They are complex mixtures with a composition and structure that is variable and not yet fully characterised. The chemistry that occurs within such ices and on its surface, while perhaps not strictly heterogeneous catalysis, can most readily be studied by reducing the ice matrix to a controlled and simplified system.

The conditions of low temperature and pressure in the ISM make interstellar ice analogues ideally suited for study in a cryogenic UHV apparatus using existing surface science techniques. Indeed, the value of surface science to the study of these aspects of astrophysics has been recognised. Of forty eight articles in a recent volume the journal *Surface Science*, which was dedicated to a review of the future directions of the field, three dealt with astrophysical applications (Greenberg 2002, Williams & Herbst 2002, Madey, Johnson & Orlando 2002).

2. STRUCTURE OF INTERSTELLAR ICES

The layered structure of ice mantles on interstellar dust grains is often compared to the layers of an onion. The dust grain itself is composed of silicate or carbonaceous materials, or perhaps a mixture of both. Initially, a layer of hydrogenated (polar) ice is formed by reaction of atomic hydrogen and other species which are adsorbed on the surface. An outer layer of dehydrogenated (apolar) ice is subsequently adsorbed when atomic hydrogen has been depleted. Water and carbon monoxide are the most abundant molecules in the hydrogenated and dehydrogenated ice layers respectively (Allamandola et al 1999). For this reason, our experimentation has commenced with these two species.

It is well known from laboratory studies that water ice can exist in a number of phases under conditions of low temperature and pressure (Jenniskens & Blake 1994, Jenniskens et al 1995). Water adsorbed at temperatures prevalent in most molecular clouds (< 30 K) will form a high density amorphous phase, I_{hda} , which has a highly porous structure (Stevenson et al 1999, Kimmel et al 2001a). When this phase is heated, a transition to less porous, low density amorphous phase, I_{lda} , occurs gradually over the 32 ~ 80 K temperature range (Jenniskens & Blake 1994, Lu et al 2001). Water ice adsorbed in this temperature range will also show a graduated mixture of the two phases. At higher temperatures, the I_{lda} phase crystallises to a cubic structure, I_{c} , (Smith et al 1997) which, under conditions applied in our laboratory, occurs at approximately 140 K.

3. EXPERIMENTAL

Experiments were performed in a UHV chamber that has been described in detail elsewhere (Fraser et al 2002). Briefly, the apparatus features two analytical techniques – temperature programmed desorption (TPD) and reflection-absorption infrared spectroscopy (RAIRS). This form of infrared spectroscopy has both advantages and disadvantages over the more commonly used transmission infrared spectroscopy. The principle disadvantage is that astronomical spectra are of the transmission form, and therefore experimental RAIRS spectra can not be compared directly with them. However, as RAIRS is performed in grazing incidence from a metal substrate, the resulting enhancement of the p-polarised electric field at the surface confers a sensitivity advantage of the order of fifty-fold, and introduces an additional metal surface selection rule that can provide information on the orientation of molecules at the surface. Thus, in a surface analysis experiment, RAIRS can be considered a more powerful technique than transmission infrared spectroscopy.

The growth of ice films is calibrated against adsorption on a quartz crystal microbalance (QCM). A value of mass per unit area is obtained, which can be converted to a film thickness using literature values of density and porosity (Jenniskens & Blake 1994, Kimmel et al 2001b). A copper plate covered by a film of polycrystalline gold serves as a sample. This can be cooled to a base temperature of less than 8 K by a closed cycle helium cryostat, and heated to well above room temperature while the cryostat is still operating. A base pressure of 10^{-10} mbar is routinely achievable in the chamber, while adsorption of ices is usually performed in the 10^{-6} – 10^{-7} mbar range.

The base pressure of 10^{-10} mbar (corresponding to particle density of $\sim 2 \times 10^6 \text{ cm}^{-3}$) is several orders of magnitude higher than most dense regions of molecular clouds. However, H_2 is by far the most abundant molecule contributing to the background pressure in our experiment, and so the conditions in the UHV chamber remain a reasonable approximation of the molecular cloud environment.

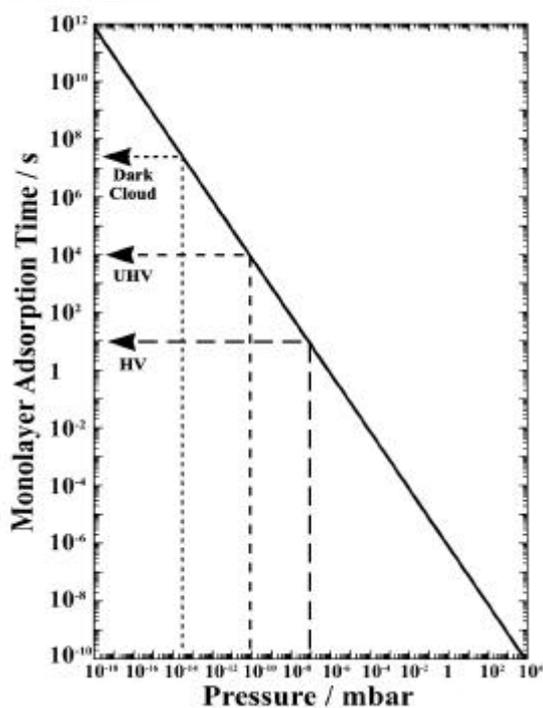


Figure 1. The rate of accumulation of H_2O at room temperature as a function of pressure, assuming a sticking probability of 1 and a surface density of 10^{19} m^{-2} .

The importance of UHV conditions is demonstrated by considering the rate of adsorption of background gas as a function of pressure. The rate of accumulation of adsorbed material in monolayers per second is given by

$$\text{rate} = s n P / (2 \pi m k_B T)^{1/2} \quad (1)$$

where s is sticking probability, n is the surface density of the adsorbate layer (m^{-2}), P is pressure (Pa), m is the mass of the molecule (kg), k_B is the Boltzmann constant, and T is temperature (K). The time required for adsorption of a complete monolayer from the background gas is plotted in figure 1 as a function of pressure, for molecules of mass $0.018 \text{ kg mol}^{-1}$ (i.e. water) at room temperature, assuming a sticking probability of 1 (reasonable for a surface at $< 100 \text{ K}$) and a surface density of 10^{19} m^{-2} . As is shown, a complete monolayer of adsorbate is accreted in several hours at UHV pressures. At a base pressure typical of high vacuum (HV) experiments (10^{-7} mbar), this occurs in only a few seconds. Over many hours of an experiment, this may represent many thousands of layers of background contaminant. This may dramatically alter the nature of catalytically important surface sites.

4. RESULTS

The results of temperature programmed desorption of water have been published previously (Fraser et al 2001). Figure 2a shows experimental data for water desorption compared with a model created using a simple stochastic integration package¹. The model uses two reaction steps; firstly, the desorption of solid ice to the gas phase, and secondly, the pumping of gas phase water out of the chamber. It is evident that this zeroth order model fits the experimental desorption trace well. A first order model (not shown) does not reproduce the desorption characteristics observed for water. By optimisation of the model, the kinetics of desorption for water ice can be obtained from the first step:

$$\text{desorption rate} = v [\text{H}_2\text{O}(s)]^n \exp\{-E_a / R T\} \quad (2)$$

where the pre-exponential factor, v , is $10^{30 \pm 2} \text{ molecules cm}^{-2} \text{ s}^{-1}$, the activation energy for desorption, E_a , is $48.0 \pm 0.5 \text{ kJ mol}^{-1}$, and the reaction order, n , is 0, so that the desorption rate is independent of the surface concentration of water molecules, $[\text{H}_2\text{O}(s)]$. A single desorption peak is observed, with no distinction between multilayer (solid) and monolayer (interfacial) water. This behaviour is the result of hydrogen bonding, which induces a stronger interaction between neighbouring water molecules than exists between water and the gold surface. The slight bump in the experimental data at 140 K results from the more rapid desorption of the amorphous water phase prior to its crystallisation (Smith et al 1997).

The model can be adjusted to demonstrate the desorption of water in the ISM. The gas phase pumping step is removed, so that the model output is gas phase concentration. A step is added to allow for re-adsorption of water from the gas phase, although this was not found to have a significant impact on the results. The heating rate was reduced to 10^{-9} K s^{-1} , which is typical of heating in some hot core regions (Viti & Williams 1999). The results show a sharp desorption of water at near to

¹ Chemical Kinetics Simulator (CKS), Version 1.0, IBM Almaden Research Center, 650 Harry Road, Mailstop ZWX1D1, San Jose, CA, USA. Further information may be obtained from the CKS website at <http://www.almaden.ibm.com/st/msim/ckspage.html>

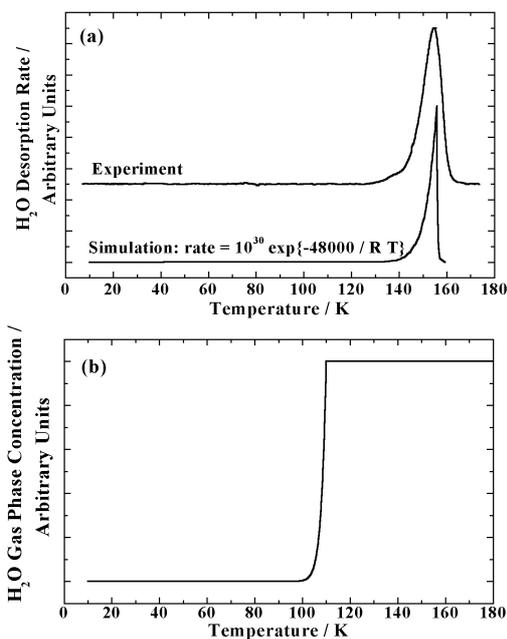


Figure 2. (a) Experimental TPD and a zeroth order simulation for a $1.8 \mu\text{g cm}^{-2}$ ($\sim 0.06 \mu\text{m}$) H_2O film, heating rate = 0.01 K s^{-1} ; (b) Zeroth order simulation converted to output a gas phase concentration (see text for details), heating rate = 10^{-9} K s^{-1} .

110 K, somewhat higher than predicted by the first order model usually applied (Sandford & Allamandola 1988).

Temperature programmed desorption studies were also performed for an ‘ice mantle’ consisting of a layer of I_{hda} with a layer of CO adsorbed on top of it. This represents an simple model of an ‘onion layered’ ice mantle with an inner layer of hydrogenated ice (H_2O) and an outer layer of non-hydrogenated ice (CO). The desorption characteristics of the water layer were not effected by the presence of the CO, and are not presented. In this experiment ^{13}CO was used to avoid any interference from contaminant N_2 . However, experiments with ^{12}CO (not presented) show no difference between the labelled and unlabelled CO. There are four distinct desorption phases in the TPD traces shown in figure 3. Firstly, a zeroth order desorption occurs for higher CO exposures at about 25 K. Comparison to our TPD results for CO adsorbed on the gold surface alone,

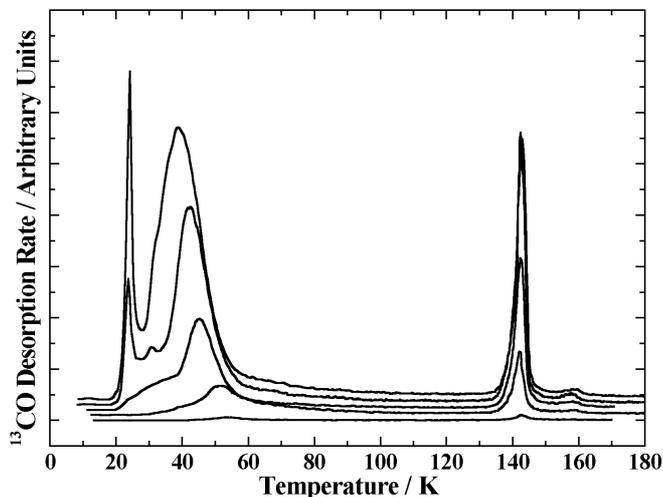
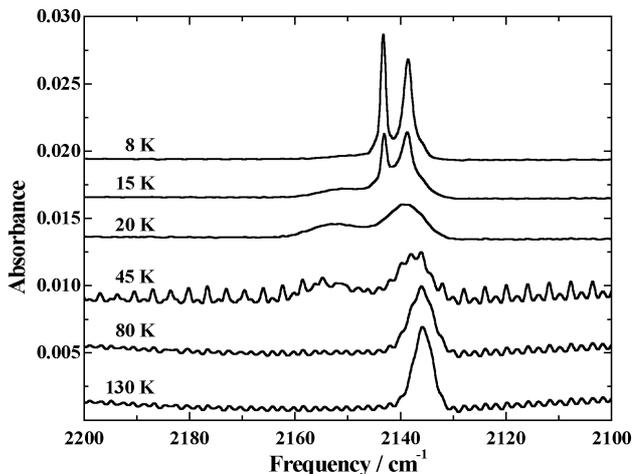


Figure 3. TPD of increasing exposures of ^{13}CO (up to $0.4 \mu\text{g cm}^{-2}$) adsorbed at 8 K on to H_2O ($17 \mu\text{g cm}^{-2}$ – $0.2 \mu\text{m}$) adsorbed at 8 K, heating rate = 0.08 K s^{-1} .

which will be presented in a future publication, show that this peak is due to desorption of CO from a multilayer (solid) environment. A broad desorption in the 30 to 70 K range results from desorption of CO from interfacial sites on the H_2O surface. Assuming this desorption to have first order kinetics, a Redhead analysis (Redhead 1962) estimates an activation energy of 10 kJ mol^{-1} , in good agreement with theoretical calculations of the bonding strength of CO to H_2O (Allouche, Verlaque, & Pourcin 1998). There is evidence of multiple desorption states in this interfacial peak, however, detailed analysis will be presented in a future publication. A sharp desorption is also apparent at roughly 140 K, equivalent to a binding energy far too high to result from CO desorbing from an interfacial site. However, this temperature is co-incident with the temperature at which the amorphous water phase crystallises, suggesting that the peak is a ‘molecular volcano’ desorption occurring as trapped CO is released during the phase transition. Such behaviour has been previously studied with TPD using a $\text{H}_2\text{O}/\text{CCl}_4$ system (Smith et al 1997), and has also been observed for the $\text{H}_2\text{O}/\text{CO}$ system in other types of experiments (Sandford & Allamandola 1988, Notesco & Bar-Nun, 1996). However, in all of these cases, the trapped species was adsorbed below the water film, or as an intimate mixture. Here, the CO was absorbed onto the H_2O , implying the CO diffuses into the porous structure of the I_{hda} film, and by some mechanism becomes trapped. A small peak, barely visible on the scale in figure 3, occurs at near to 160 K, coincidental with desorption of H_2O . This indicates that not all of the CO that becomes trapped is released in the molecular volcano desorption.

The extent of CO entrapment was found to vary with the temperature of water adsorption (Collings et al 2002). In a set of experiments where the H_2O and CO exposures were kept constant at 57 and $0.07 \mu\text{g cm}^{-2}$ respectively, the H_2O film was adsorbed at varied temperature, then the sample cooled to 8 K before subsequent CO adsorption. In a I_{hda} film adsorbed at 8 K, close to half of the CO becomes trapped at above the desorption temperature for interfacial CO. However, as the temperature of water adsorption was increased over the 30 to 70 K range, which should have resulted in a gradual change in the structure to the I_{hda} phase, the extent of trapping was reduced to zero. Therefore, the mechanism that causes CO entrapment must be related to this amorphous phase transition.

The $\text{H}_2\text{O}/\text{CO}$ system has also been investigated by RAIRS. The RAIR spectrum of the CO stretch region for a CO overlayer on I_{hda} is shown in figure 4. Two sharp features at 2143.3 and 2138.6 cm^{-1} are, respectively, the longitudinal and transverse modes of the C-O stretch for solid CO (Chang, Richardson, & Ewing 1988). Lydane-Sachs-Teller (LST) splitting of this type can only be observed in transmission infrared experiments if a p-polarised radiation source is used. The film of CO and H_2O ice was then annealed for five minutes at progressively higher temperatures. Between each anneal temperature, the sample was cooled to 8 K, and an additional RAIR spectrum recorded. All changes in the spectra are, therefore, irreversible. Annealing to a temperature of 15 K, although too low to induce desorption of solid CO, results in the loss of intensity in the solid CO features and the growth of intensity in a new feature at 2153 cm^{-1} , which is associated with CO adsorbed on dangling bond sites on the surface of the water (Schmitt et al 1989, Devlin 1992, Palumbo 1997, Allouche, Verlaque, & Pourcin 1998). This behaviour is strong evidence for the diffusion of solid CO into the porous structure of the I_{hda} film. Annealing to 20 K results in the complete loss of the solid CO features, and the appearance of a two peak profile typical of CO in a water environment (Sandford et al 1988, Schmitt, Greenburg, & Grim 1989, Palumbo 1997, Allouche, Verlaque,



& Pourcin 1998, Collings et al 2002). The 2153 cm^{-1} feature is **Figure 4**, RAIR spectra of the CO stretch region of $0.35 \mu\text{g cm}^{-2}$ CO adsorbed over $57 \mu\text{g cm}^{-2}$ H_2O at 8 K; samples have been annealed for 5 minutes at the temperatures indicated; sharp features in the 45 K spectrum are due to gas phase CO transitions, resulting from contamination of the dry air in the purge of the IR optics; increased baseline noise in the 45 K, 80 K and 130 K spectra result from a slight mismatch between the sample spectrum and background spectrum used in data processing.

diminished and then disappears with annealing through the 30 to 80 K temperature range, as the amorphous phase transition occurs. This is unsurprising, as the less porous I_{hda} phase has a vastly reduced internal surface area. The spectra also show a strong CO feature present up to 130 K, indicating extensive CO entrapment.

The behaviour of the CO/ H_2O system under laboratory warm up conditions can be summarised as follows (Collings et al 2002). Water ice is adsorbed in the I_{hda} phase at 8 K. CO adsorbed onto the water forms a layer of solid CO. As the film is heated, solid CO becomes sufficiently mobile to diffuse into the porous structure of the film, at temperatures as low as 15 K. In the 20 to 30 K temperature range, this diffusion process competes with desorption of solid CO. By 30 K, CO remains adsorbed only in interfacial sites, both on the external surface of the water film, and the much greater area of the internal surface of pores within the film. Over the 30 to 70 K temperature range, desorption of CO from these interfacial sites competes with entrapment caused as the I_{hda} phase is transformed into I_{lda} . Trapped CO is released in an abrupt molecular volcano as the I_{lda} crystallises at 140 K, and as the crystalline water desorbs at 160 K.

In principle, the adsorption, diffusion, desorption and entrapment of CO on, in and from a I_{hda} film can be modelled using the kinetic simulation package, to examine the effect of entrapment under astrophysically relevant heating rates. However, this is a much more complex system, involving fourteen or more reaction steps, accounting for desorption from and readsorption to both solid and interfacial CO states, diffusion into pores, desorption and readsorption from and to the interfacial state within pores, diffusion of gas phase CO out of the pores, entrapment of both interfacial and gas phase CO in the pores, molecular volcano desorption of trapped CO, entrapment within the crystalline water phase, desorption of CO coincidentally with water desorption, and gas phase pumping. Before adapting the simulation to interstellar conditions, it is essential that we be confident that the simulation models the actual processes occurring in the ice, rather than just

successfully predicting the desorption characteristics observed in laboratory experiments. Only in this way can the simulations remain a valid prediction of behaviour of ices in the ISM. Work in this area is progressing and will be the subject of future publications.

5. IMPLICATIONS AND CONCLUSIONS

Our results demonstrate how our carefully designed and rigorous surface science experiment can contribute to the field of astrophysics, by providing accurate values for fundamental processes that occur on and in interstellar ices. The desorption kinetics of water have been evaluated in the laboratory and applied to interstellar conditions. The desorption behaviour of carbon monoxide has been shown to more complex than can be understood simply from a knowledge of binding energies and desorption kinetics. The retention and release of CO in the ISM at unforeseen temperatures may impact on temperature dependent chemistry in both the gas and solid phases, and influence the star formation process.

Some caution must be exercised when applying this model of CO desorption to the interstellar environment, as a variety of factors have yet to be incorporated. For instance, phase changes in water may be induced by UV irradiation and cosmic ray bombardment, and the effect of the substrate on the structure of accreted ice remains controversial. Interstellar ices are a complex mixture of compounds, and treating their behaviour as the sum of the behaviour of binary systems may be misleading. For example, the presence of low concentrations of methanol in the hydrogenated ice phase are known to have subtle effects on the behaviour of the dominant water component (Blake et al 1991). The reactively formed hydrogenated ice layer is currently studied by adsorption of ice. Although it seems unlikely that reactively formed ice should show significant structural differences to condensed ice, this has also yet to be experimentally verified. Such limitations to the model provide a direction for future research, as the complexity of the model and of our understanding of the system are built up through continued experimentation.

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