

# Desorption of Molecules from Grain Mantles

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**Abstract.** As a prerequisite to returning their molecular inventory to the gas phase, icy grain mantles must desorb from the refractory core material of the grain. This desorption process can be instigated through interactions with photons or cosmic rays but can equally well be thermally driven. In this invited paper, the application of thermal desorption techniques borrowed from ultrahigh vacuum surface science to problems of astronomical interest will be discussed. The experimental methods employed by surface scientists to probe thermal desorption processes will be described and the analysis of the resulting empirical data outlined. The results of recent laboratory measurements from a number of groups will be highlighted.

**Keywords.** astrochemistry — ISM: molecules — methods: laboratory — molecular processes

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## 1. Introduction

Icy grain mantles formed from a combination of reactive accretion and condensation from the gas phase are observed in the infrared along many lines of sight toward dense molecular clouds (Whittet *et al.* 1996; Gibb *et al.* 2000). These icy mantles act as a reservoir of volatile small molecules that are returned to the gas phase in the early stage of pre-stellar core collapse and aid in radiative cooling (Williams 1998). The mantles also act as chemical nanofactories wherein these simple molecules are subject to energetic processing induced through interaction with photons and cosmic rays, converting them into more complex chemical species (for example Bernstein *et al.* 2002; Muñoz Caro *et al.* 2002; Gerakines, Moore & Hudson 2004; Loeffler *et al.* 2005; Holtom *et al.* 2005). These in turn may be returned to the gas phase as core collapse proceeds. Once there, such complex molecules could be detected if there is a sufficiently high concentration (Kuan *et al.* 2003). Alternatively, grain-grain collisions can consolidate the material into larger grain clusters that may eventually evolve into the comets capable of seeding a nascent planet with a watery ice rich in potentially pre-biotic materials (Wang *et al.* 2005).

As return of material from the icy grain mantle to the gas phase is crucial to their astronomical role, it becomes important to understand this process. In quiescent, dark regions only desorption processes associated with the interaction of cosmic rays and penetrating high-energy photons with grain mantles are likely to be important. Laboratory studies and theoretical models of the sputtering process associated with direct collisions between cosmic ray nuclei and mantle molecules are well developed (Baragiola *et al.* 2003; Vidal, Teolis & Baragiola 2005). Less so is our understanding of desorption induced by the secondary electron cascade associated with the passage of such high-energy particles through an ice film. This is also likely to be crucial in quantifying desorption induced by the high-energy photons (X-rays and  $\gamma$ -rays) that can penetrate optically dense regions. In optically less opaque regions, visible, ultraviolet and vacuum ultraviolet photon-stimulated desorption becomes feasible. Laboratory investigations of such photon-stimulated desorption are also well developed (Westley *et al.* 1995; Bergeld *et al.*

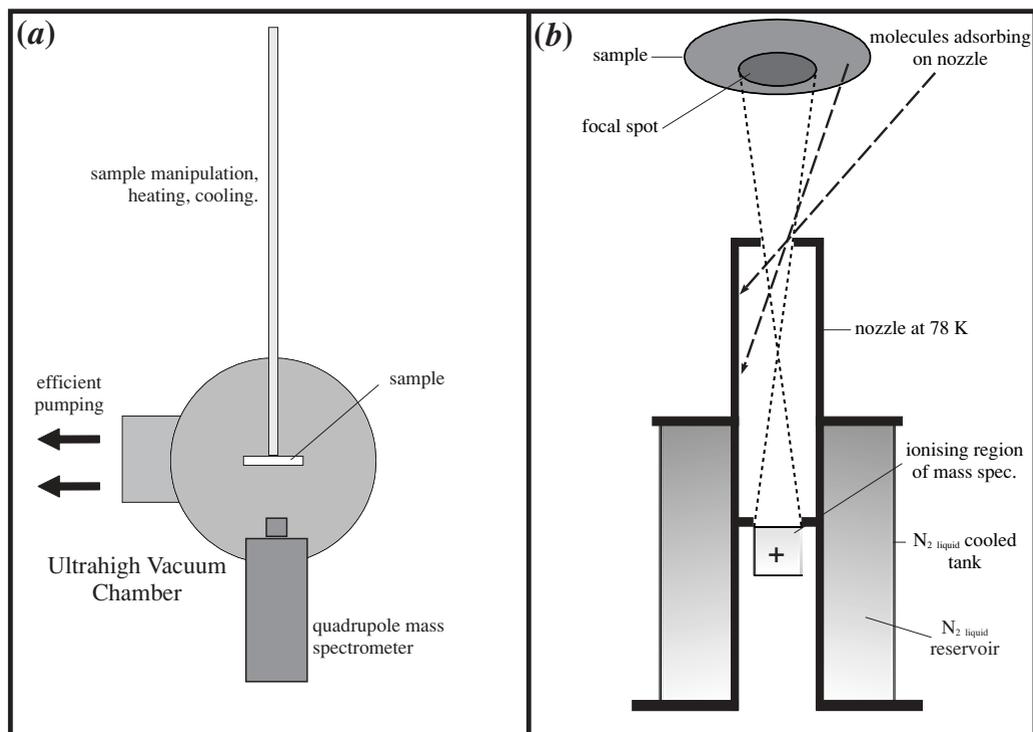
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2004). However, in star-forming regions simple thermally-promoted desorption probably dominates as pre-stellar cores collapse and warm. Laboratory studies of the thermal desorption process have been reported in the astrochemical literature for a number of years (Sandford & Allamandola 1988; Hudson & Donn 1991; Notesco & Bar-Nun 2005). These have generally utilised high vacuum ( $\sim 10^{-7}$  mbar) techniques coupled with, for example, transmission infrared spectroscopic measurements of the icy film itself, total pressure measurements using an ion gauge or low-quality mass spectrometric studies of the desorbing mantle materials. However, as we have demonstrated previously, high-vacuum techniques are insufficient if the purpose of the experiment is to probe the interactions occurring at the grain surface (Collings *et al.* 2002). In high vacuum, a surface at low temperature will be completely covered by adsorption of background species (mostly water) in roughly 10 s. However, in ultrahigh vacuum ( $\sim 10^{-10}$  mbar), saturation of a cold surface takes in the order of  $10^4$  s. Therefore, experiments can be completed before surface contamination becomes an overwhelming problem. To this end, we describe the application of ultrahigh vacuum (UHV) temperature-programmed desorption (TPD) techniques to the study of the thermally promoted desorption of icy grain mantles. Specifically we will review desorption of single-component ices and report on the issue of ice morphology as highlighted in our own recent work.

## 2. Experimental

The technique of temperature programmed desorption is thoroughly described in the surface science literature (Woodruff & Delchar 1994, Chapter 5; Kolasinski 2002, pp. 193–201; King 1975). The basic apparatus is shown schematically in Figure 1(a), while a practical realisation of the ideal can be found in our own work (Fraser, Collings & McCoustra 2002). In the experiment itself, the sample is heated uniformly at a constant rate. The gases evolved from the surface are detected mass spectrometrically and displayed as a plot of mass spectrometer signal *versus* temperature. At this stage, we must realise that the efficiency with which the desorbing gas is removed from the UHV chamber is crucial to the quality of the resulting TPD traces. This is illustrated in Figure 2(a) which presents simulated TPD data for carbon monoxide chemisorbed on a platinum surface. At low pumping speeds, the desorbate accumulates in the UHV chamber. This is the so-called flash desorption limit, when the pumping speed is small compared to the rate of desorption. As the pumping speed is increased, in Figure 2(a) by a factor of 10 at each step, we see a transformation from the sigmoidal curve characteristic of flash desorption to the peaks characteristic of true TPD experiments. We should also note that within the TPD regime, increasing the pumping speed further simply reduces the detected yield of desorbate requiring that we increase the sensitivity of the mass spectrometer.

Likewise, the sample heating can play a significant role in determining the quality of the recorded TPD data. Figure 2(b) illustrates the effect of increasing the heating rate on the same system as considered in Figure 2(a). At low heating rates, good quality TPD peaks can be observed if highly-sensitive mass spectrometric detection is employed. As the heating rate increases, the TPD peaks broaden and move towards a shape more characteristic of flash desorption. Of course, this behaviour assumes that the substrate is heated evenly. In real systems, uneven sample heating as a consequence of sample size, sample mounting or heating method may give rise to peak asymmetry or even multiple TPD peaks for a system that is chemically simple. Reducing the sample size, careful design of sample mounts and optimising the heating rate to achieve uniform heating across the sample can reduce these problems. However, to eliminate them entirely,



**Figure 1.** Schematic diagrams showing the typical layouts of (a) a TPD experiment in UHV, and (b) a line of sight TPD apparatus.

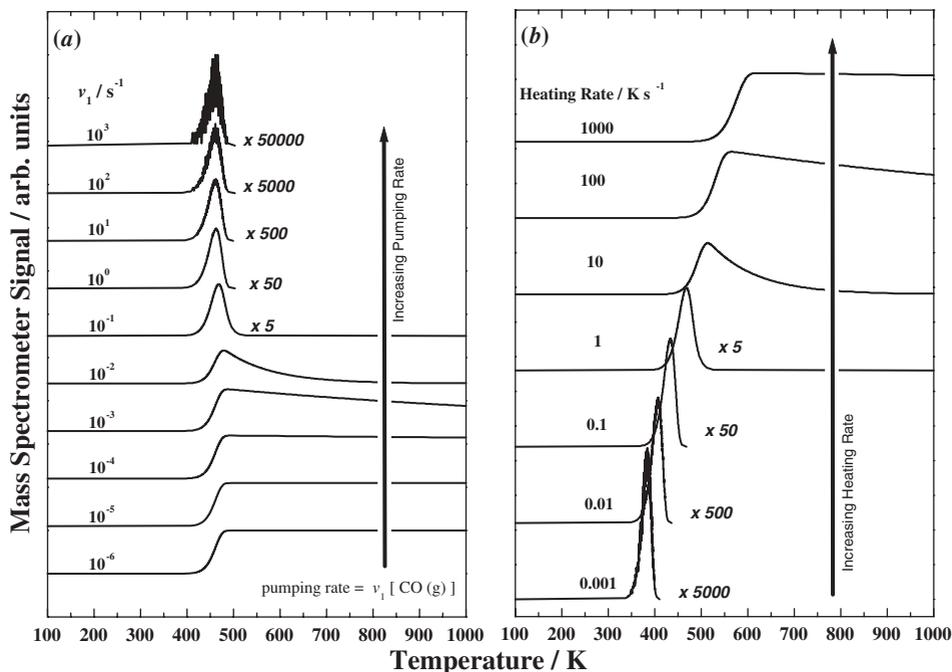
line-of-sight TPD methods as championed by Jones and co-workers can be adopted (Jones & Turton 1997; Jones & Fisher 1999), as illustrated in Figure 1(b).

### 3. Results and Discussion

Temperature programmed desorption is a kinetic technique. There is no simple relationship between the positions of peaks in a TPD trace and the energetics of the desorption processes under investigation other than a simple statement that the more strongly a species is bound to a surface, the higher the temperature at which it will desorb. Analysis of TPD data requires that we develop a kinetic model for the desorption process. This is based on the Polanyi-Wigner equation,

$$-\frac{dC_s}{dt} = \nu_{des} C_s^n e^{-E_{des}/RT} \quad (3.1)$$

where the rate of desorption ( $-\frac{dC_s}{dt}$ ) is related to the surface concentration of adsorbate,  $C_s$ , and surface temperature,  $T$ , through the order of desorption,  $n$ , the activation energy for desorption (the surface binding energy),  $E_{des}$ , and the pre-exponential factor for desorption,  $\nu_{des}$ . The activation energy and pre-exponential factor for desorption potentially can depend on the adsorbate surface concentration; *i.e.*  $E_{des}(C_s)$  and  $\nu_{des}(C_s)$ . The order of desorption, activation energy for desorption and the pre-exponential factor for desorption are all experimentally determined and can, at least in principle, be recovered by appropriate analysis of TPD data as a function of the initial surface concentration of the desorbate. To illustrate this we will look at two examples: our own work on desorption of



**Figure 2.** Model TPD spectra for a monolayer of CO desorbing from a platinum substrate illustrating the effects of (a) increasing the relative speed at which the desorbing CO is removed by pumping from the UHV chamber, and (b) increasing the heating rate. The binding energy of CO on the Pt surface is assumed to be  $125 \text{ kJ mol}^{-1}$  and a pre-exponential factor of  $10^{13} \text{ s}^{-1}$  is assumed for the first order desorption of CO from the Pt surface. The heating rate,  $\beta$ , is fixed at  $1 \text{ K s}^{-1}$  in (a), and the pre-exponential factor for pumping,  $\nu_1$ , is fixed at  $0.1 \text{ s}^{-1}$  in (b).

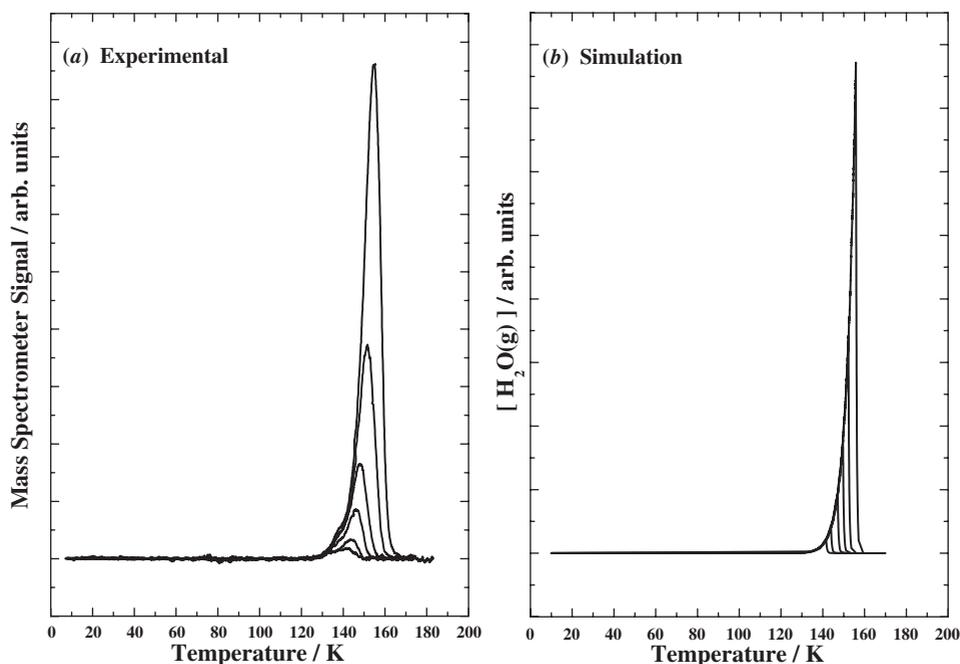
water ice (Fraser *et al.* 2001) and recent work from the group of Brown and co-workers on desorption of methanol ice (Bolina 2005; Bolina, Wolff & Brown 2005a).

Figure 3(a) illustrates the TPD of water ice films of increasingly thickness in the range up to *ca.* 25 nm reproduced from Fraser *et al.* (2001). The TPD traces show a characteristic overlap of their exponential-like leading edges and monotonic increases in peak desorption temperature with film thickness. These observations are consistent with the water desorbing from the gold substrate in our apparatus with zeroth order kinetics, *i.e.*,

$$-\frac{dC_s}{dt} = \nu_{des} e^{-E_{des}/RT} = k_{des,ice} \quad (3.2)$$

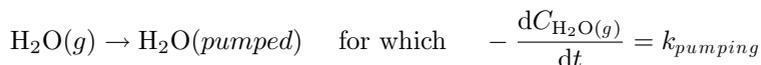
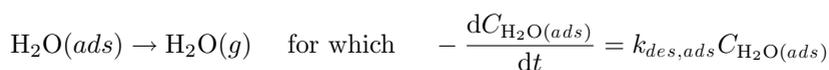
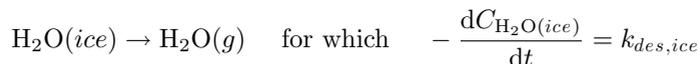
The desorption rate is independent of the amount of water ice on the substrate. The TPD of bulk solid materials is generally observed to follow zeroth order kinetics. The desorption of monolayers of intact molecules in contrast is generally taken to be first order, while the recombinative desorption of dissociated molecules is second order.

As a starting point, we then assumed the binding energy for water to a water ice multilayer from the work of Kay and co-workers (Speedy *et al.* 1996) and equivalent to the latent heat of sublimation of water ice. We also assumed that this value is independent of the water ice film thickness. The only unknown in our rate equation was therefore



**Figure 3.** (a) A sequence of TPD spectra for water ice films for exposures of the cold substrate to 1.2, 2.4, 6.1, 12, 24 and 61 Langmuirs (L) of water vapour,  $\beta = 0.02 \text{ K s}^{-1}$ .  $1 \text{ L}$  ( $10^{-6} \text{ mbar s}$ ) is approximately equivalent to 1 monolayer. (b) Kinetic simulations of the TPD of water ice films of thickness equivalent to Figure 3(a), using the simple model described in the text.

the pre-exponential factor for the desorption process. A simple kinetic model was then constructed:



where  $\text{H}_2\text{O}(ice)$  represents water in the ice multilayer,  $\text{H}_2\text{O}(ads)$  represents water adsorbed directly on the gold substrate,  $\text{H}_2\text{O}(g)$  is water vapour and  $\text{H}_2\text{O}(pumped)$  is the water pumped out of the UHV chamber. Kinetic simulations were then run and fitted to our observed TPD data as function of film thickness allowing recovery of optimal values of  $E_{des,ice}$  and  $\nu_{des,ice}$  for the zeroth order desorption of water ice multilayers and  $E_{des,ads}$  and  $\nu_{des,ads}$  for the desorption of the water monolayer from our gold substrate. The kinetic parameters for the zeroth order desorption of water ice are summarised in Table 1, while Figure 3(b) illustrates the quality of the comparison between our experimental and modelled TPD data.

More recently, Brown and co-workers have adopted an analysis that avoids the assumptions of order and desorption energy used in our own work (Bolina 2005; Bolina, Wolff & Brown 2005a; Bolina, Wolff & Brown 2005b; Bolina & Brown 2005). Their analysis depends on recognising that the mass spectrometer signal as a function of temperature,

**Table 1.** Summary of the thermal desorption data for astronomically relevant ices recovered from analyses of UHV TPD experiments.

Species	$n$	$E_{des} / \text{kJ mol}^{-1}$	$\nu / \text{cm}^{-2} \text{s}^{-1}$
$\text{H}_2\text{O}^{a,b,c}$	0, 0, 0.26(0.02)	49.8, 48.0(0.5), 39.9(0.8)	$4.58 \times 10^{30}$ , $10^{30}$ , $5.5(4.5) \times 10^{31}$
$\text{CH}_3\text{OH}^d$	0.35(0.21)	31 ~ 40	–
$\text{NH}_3^e$	0.25(0.05)	23.3(1.2)	$8(3) \times 10^{29}$
$\text{CO}^{f,g}$	0	6.87(0.2), 7.11(0.21)	$7(2) \times 10^{26}$ , $10^{30(2)}$
$\text{N}_2^g$	0	6.57(0.21)	$10^{30(2)}$

Notes: Error values, where available, are shown bracketed. Data from (a) Speedy *et al.* (1996), (b) Fraser *et al.* (2001), (c) Bolina, Wolff & Brown (2005b), (d) Bolina, Wolff & Brown (2005a), (e) Bolina & Brown (2005), (f) Collings *et al.* (2003b), (g) Örberg *et al.* (2005). Citations to other examples where the kinetic parameters for desorption of these species are published can be found within these references. \*For simplicity, the units given for  $\nu_{des}$  relate to a zeroth order process; the actual units can be fractional and depend on the (non-zero) value of  $n$ .

$I(T)$  say, is proportional to the rate of change of surface concentration with temperature,

$$I(T) \propto \frac{dC_s}{dT} \quad (3.3)$$

where

$$-\frac{dC_s}{dT} = \frac{\nu_{des}}{\beta} C_s^n e^{-E_{des}/RT} \quad (3.4)$$

and  $\beta$  is the heating rate in  $\text{K s}^{-1}$ . Hence,

$$I(T) \propto \frac{\nu_{des}}{\beta} C_s^n e^{-E_{des}/RT} \quad (3.5)$$

In contrast to our own work on water ice, Brown and co-workers cannot determine the absolute surface concentration of their desorbate and therefore this expression must be re-cast in terms of relative coverage,  $\theta_{rel}$ , on the surface,

$$I(T) \propto \frac{\nu_{des}}{\beta} \theta_{rel}^n e^{-E_{des}/RT} \quad (3.6)$$

The relative coverage can be simply obtained by integrating the area under the TPD peaks of interest. Then at a fixed temperature,  $T_f$  say, the order of the desorption process can be recovered by plotting  $\ln[I(T_f)]$  versus  $\ln[\theta_{rel}]_{T_x}$ , while a plot of  $\ln[I(T)] - n \ln \theta_{rel}$  versus  $\frac{1}{T}$  can be used to obtain the activation energy for the desorption process, assuming that the value is independent of coverage. Using such an approach, Brown and co-workers have been able to determine orders and activation energies for desorption of water (Bolina 2005; Bolina, Wolff & Brown 2005b), methanol (Bolina 2005; Bolina, Wolff & Brown 2005a) and ammonia (Bolina 2005; Bolina & Brown 2005) from a graphite substrate.

The key limitation of the analysis presented by Brown and co-workers is the inability of their analysis to recover the pre-exponential factor for desorption. This is a consequence of their lack of information on the absolute surface concentration of the adsorbed films. However, ices deposited at temperatures in excess of *ca.* 50 K are typically compact amorphous materials. This allows for an intuitive estimate of these pre-exponential factors to be obtained by considering the molecular packing density in the ice and the surface area of the substrate relative to that of a single adsorbate molecule. Brown and co-workers have on this basis estimated the relevant pre-exponential factors (Bolina 2005) and these are tabulated in Table 1 in comparison with other recent literature data relating to the TPD of astronomically relevant ices.

As is clear, neither of these methods is truly assumption free. Ideally, in performing TPD experiments, we would have the necessary surface concentration data to obviate the need for estimation of the pre-exponential factor. In that regime, a full kinetic analysis based on global fitting of TPD data from multiple initial surface concentrations made with no assumption as to desorption order, activation energy for desorption and pre-exponential factor (and any possible coverage dependence thereof) would permit recovery of these quantities.

While it is important to consider the single-component ices, there is little doubt from the observational data that the ice *in situ* is a mixture of components. This adds significantly to the problem of understanding the thermal desorption of icy mantles, for in addition to considering the issue of interaction between the ice components, we must also now consider the key issue of ice morphology. This is perhaps best illustrated by our work on the CO–H<sub>2</sub>O ice system (Collings *et al.* 2003a,b). Water ice film growth at temperatures around 10 K results in a material with high porosity (Stevenson *et al.* 1999). CO solid will spread into these pores covering the surface of the water as the temperature is raised towards and above 20 K. Strong binding of the CO to the water ice surface ( $E_{des}$  for CO from water is *ca.* 10.6 kJ mol<sup>-1</sup> as opposed to 6.8 kJ mol<sup>-1</sup> for a pure CO multilayer (Collings *et al.* 2003a; Collings *et al.* 2003b) and pore collapse at temperatures in the range 30 to 80 K, ensures that a significant amount of CO is trapped in the water ice matrix to elevated temperatures. Similar observations have been reported for other components of the interstellar ice inventory interacting with water ice (Collings *et al.* 2004), and for CO interacting with methanol ice (Chen *et al.* 2005). In fact for many species, release of trapped molecules is the dominant thermal desorption process, such that the binding strength of the adsorbate molecules to the water surface has an insignificant bearing on the desorption kinetics (Collings *et al.* 2004). The implications of this trapping process on gas-phase chemical networks in hot cores have been (Viti *et al.* 2004), and will continue to be the subject of investigation by astrochemical modellers.

Such systems can, of course, be interpreted using phenomenological kinetic models as we have demonstrated with the CO–H<sub>2</sub>O system (Collings *et al.* 2003a,b). However, this simply represents a starting point. There is much more to do in order to fully understand the microscopic processes occurring in these complex systems coupling thermal desorption kinetics, diffusion kinetics and morphological change.

#### 4. Conclusions

Temperature programmed desorption in UHV has been described. Certain experimental limitations relating to removal of the gaseous desorbate from the vacuum chamber and heating of the substrate have been outlined. The recent literature relating to the application of TPD to single-component molecular ices is summarised and methods of analysis described in detail. Orders of reaction, activation energies and pre-exponential factors for desorption of a number of species are tabulated. The problems associated with TPD of ice mixtures are introduced.

#### Acknowledgements

The authors thank PPARC, EPSRC, the University of Nottingham and the Leverhulme Trust for financial support for this work. We thank Dr. Helen Fraser, John Dever, Rui Chen, Simon Green and various final year undergraduate project students for their assistance and invaluable scientific contributions to our work discussed in this paper, Serena Viti and David A. Williams for helpful discussions, and Nico Bovet for assistance with graphics in this paper.

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## Discussion

D'HENDECOURT: Why not complement your studies on TPD by IR spectroscopy which, is more easily applicable to astrophysical problems? In particular, ice porosity does show up in the IR (around  $3700\text{ cm}^{-1}$ ), a feature which is not observed, for the moment, in protostellar spectra.

MCCOUSTRA: TPD has, since the 1960's, provided the surface science community with a relatively simple means of determining the binding energies of molecules on surfaces. Vibrational spectroscopy, on the other hand, provides us with useful complementary information in allowing us to characterize binding sites, in particular when we use good-quality computational chemistry to support both studies. Our work published in *Ap. J.* (2003, 583, 1058) and *A&SS* (2003, 285, 633) details how we have used this combination to probe the CO-H<sub>2</sub>O ice spectrum in some detail.



Photo: E. Herbst