LABORATORY STUDIES OF DESORPTION FROM MODEL INTERSTELLAR ICES USING SURFACE SCIENCE METHODOLOGIES

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Abstract. Desorption of condensed species is a key process in controlling the balance of material between the solid and gaseous phases in the interstellar medium. Therefore, a quantitative understanding of desorption in astrophysical environments, by both thermal and non-thermal mechanisms, is essential for development of the field of astrochemistry. This paper briefly reviews recent progress in the study of desorption by experimental and computational methods, and identifies some areas with potential for development in the near future.

1 Introduction

Molecular synthesis on grain surfaces, and on and in icy grain mantles is but the first step in a complex sequence of processes that may ultimately lead to the participation of these molecules in the chemical evolution of astrophysical environments. Returning these molecules to the gas phase from the cold dust surface and icy grain mantles is likely to be the key step in coupling the chemistry of the grains and mantles to the astrophysical gas phase, and thus, in their observation. This paper will briefly review the various thermal and non-thermal mechanisms that contribute to this important process, and that are being, or are potentially capable of being, investigated with the computational and experimental tools of modern laboratory astrochemistry.

2 Desorption mechanisms — a summary

A substantial literature exists on potential desorption mechanisms operating in astrophysical environments. That literature is increasingly being supplemented by

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sophisticated computational and experimental investigations of individual desorption mechanisms, which deliver a detailed understanding of the phenomena and their complexity. From that literature, four basic desorption mechanisms can be identified: (i) desorption promoted by reaction enthalpy release; (ii) desorption promoted by collision; (iii) desorption promoted by heating; and (iv) desorption promoted by electronic excitation. These processes operate in parallel. In particular environments, however, a particular mechanism or mechanisms may come to dominate. For example, in quiescent dense gas an excess concentration of heavy molecules is sometimes observed in the cold, dense core regions. Desorption promoted via cosmic ray induced electronic excitation, either by direct interaction or indirectly by interaction with the VUV radiation field associated with recombination following cosmic ray ionisation of H_2, is the likely mechanism for returning molecules to the gas phase from the solid state in such environments (Herbst & Cuppen 2006). Similarly, heating of the gas by core collapse promotes thermal desorption, and the role of this thermal desorption in promoting chemistry in the gas phase in such hot cores and hot corinos is increasingly well understood (*e.g.* Viti *et al.* 2004).

2.1 Desorption promoted by reaction enthalpy release

Many chemical reactions in astrophysical environments are exothermic. In the gas phase, the energy released by reaction can appear as translational or rovibrational excitation of the reaction products and is eventually lost to the heat bath as relaxation to local thermodynamic equilibrium occurs. On grain surfaces, the exothermicity can be substantial; *e.g.*, recombination reactions of atoms to form H_2, O_2 and N_2 which respectively release $\sim$436 kJ mol^{-1} (4.52 eV), 498 kJ mol^{-1} (5.16 eV) and 946 kJ mol^{-1} (9.80 eV). This energy release is coupled into the underlying substrate. However, for species such as these which are only weakly physisorbed (*i.e.* surface binding energies of typically $\ll$ 50 kJ mol^{-1} or 0.5 eV), this coupling is likely to be relatively weak. Consequently, the reaction energy release can promote desorption with the appearance of significant amounts of excitation in the gaseous molecule, as has been demonstrated for H atom recombination both experimentally (Creighan *et al.* 2006), and theoretically (*e.g.* Meijer *et al.* 2003).

Molecules formed by atom and free radical recombination in icy grain mantles are essentially solvated. Enthalpy release in this instance is likely to be quickly dissipated (on the ps timescale) into the heat bath provided by the surrounding icy solid. Only where this recombination occurs within the selvedge of the icy mantle is there likely to be a contribution to desorption of the surrounding solvent. Desorption of this type has been included within astrochemical models for many years (Schutte & Greenberg 1991; Shen *et al.* 2004). However, such processes are inherently difficult to investigate experimentally. Recent work on vibrational state-resolved product energy distributions in photodissociation dynamics in liquids may point to potential experiments in the future (Rose *et al.* 2011).

The issue of solvation is also important in relation to interactions of thermal gas phase ions with icy surfaces. The solvation enthalpy of the proton is exothermic by 1150 kJ mol^{-1} (11.9 eV) (Tissandier *et al.* 1998). This is significantly more than the energy release from any atom or radical recombination. At thermal energies, it might be expected that H_2O desorption subsequent to ion solvation would be common. However, the only report in the literature of H^+ interactions with H_2O ice at low energies (<10 eV) points to some unusual chemistry with H_2^+ ions as the primary detected product (Bag *et al.* 2011).

2.2 Desorption promoted by collision

Atoms and molecules colliding with surfaces can in principle transfer energy to adsorbates on the surface.   In cold, dense regions thermal collision energies of $\sim$0.1 kJ mol^{-1} ($\sim$0.1 meV) are likely too small to promote desorption, given that typical binding energies at surfaces even for the most weakly interacting species are of the order of a few kJ mol^{-1}. In shocked regions, thermal energies may be significantly higher, approaching 1000 kJ mol^{-1} ($\sim$10 eV), which is sufficient to promote collision-induced desorption of even some weakly chemisorbed species. Although not directly relevant to astrochemistry, the sputtering of water and other species (*e.g.* Killelea *et al.* 2012) nicely illustrates desorption promoted by collisions. This might be particularly important as a means of desorbing reactive molecules and radicals where thermal processing may well result in the chemical transformation of the adsorbate prior to thermal desorption. Measurements using this methodology would be a powerful probe of such atom and radical interactions at model grain surfaces, and would potentially provide a means of benchmarking the sophisticated computational methodologies now being used to investigate surface reactions of relevance in astrochemistry.

Perhaps the most obvious form of collision-promoted desorption process to consider is that associated with cosmic ray interactions with the dust and icy grains. There is little doubt that with kinetic energies in the keV and MeV ranges, well in excess of typical surface binding energies, cosmic rays can promote desorption. This is *cosmic ray sputtering*. Cosmic rays interact with solids in two ways, by scattering from the electrons in the material and by scattering from the nuclei. The proportion of scattering into each channel is dependant on the energy of the cosmic ray and on the nature of the material. Codes such as SRIM and TRIM allow us to estimate relevant *stopping ranges* (Ziegler *et al.* 2008), and suggest that for the most common cosmic ray energies electron stopping (scattering) is by far the dominant mechanism. Nuclear stopping (scattering) and hence nuclear collision promoted desorption (sputtering) is a minor channel for returning material to the gas phase. This simple process is very readily modelled by simple billiard ball dynamics and is embedded in codes like SRIM and TRIM to predict sputtering yields (Ziegler *et al.* 2008). However, in ignoring the vibrational dynamics in molecular solids such codes have some difficulty in reproducing observed yields. In reality, molecular dynamics (MD) simulations, even those utilising simple empirical molecular mechanics force fields, would provide a more realistic picture of this

process. MD simulations typically ignore the secondary electron processes that are the product of electron stopping (scattering), the principal channel for cosmic ray interaction. Techniques combining quantum mechanical treatment of the electronic interaction with molecular mechanics to describe the subsequent energy disposal could provide a more realistic picture of this complex process. Empirical benchmarking of such computational methods against experiment would remain essential.

Raising the scale from the molecular to that of grains themselves, in some astrophysical environments grain-grain collisions may be important as a mechanism from returning material to the gas phase. While there have been studies of the impact of icy films on the stickiness of such collisions (and the accretion of grains into clusters) (Wang *et al.* 2005), there are no reports of laboratory studies of desorption promoted by this process. However if we consider typical particles (100 nm diameter with a density akin to that of amorphous solid water) with modest relative collisions velocities ($\sim$1 m s^{-1}) then collision energies of at least 100 times the typical hydrogen bond strength in water are not unrealistic. Desorption should occur in such collisions and would be enhanced in environments where large relative grain velocities can be achieved, *e.g.* in proto-planetary disks around young stellar objects. Simulations might help in understanding such processes but such mixed scale simulations are difficult and would require careful benchmarking by experiment.

2.3   Desorption promoted by heating

Thermally-promoted desorption is perhaps the least complex desorption mechanism associated with astrophysical processes. Gravitational collapse of dense gas in star-forming regions warms the gas and hence the icy grain population, returning their icy inventory of molecules to the gas phase. To produce a chemical clock for the star formation processes from observations and simulations of the gaseous chemistry in such environments requires a detailed understanding of the thermally-promoted desorption process. Fortuitously, this understanding can be obtained from Temperature Programmed Desorption (TPD), a standard laboratory surface science technique, and the past 15 years has seen significant progress in the area.

Initial experiments naturally focussed on the most common icy mantle components, H_2O and CO. The porous morphology of amorphous solid H_2O, which is evident for vapour deposited films studied in the laboratory (*e.g.* Collings *et al.* 2003a) and predicted for ice formed reactively from H and O atoms in astrophysical environments (Cuppen & Herbst 2007), plays a crucial role in thermally-promoted desorption processes. As illustrated in the cartoon in Figure 1a, the collapse of metastable porosity competes with CO surface diffusion and desorption with the consequence that substantial quantities of CO can become entrapped in solid H_2O films. Rather than a single CO desorption, four distinct features are observed, corresponding to desorptions of solid CO, of CO adsorbed on the H_2O ice surface, of CO trapped in pores released during crystallisation (*i.e.* a molecular volcano) and
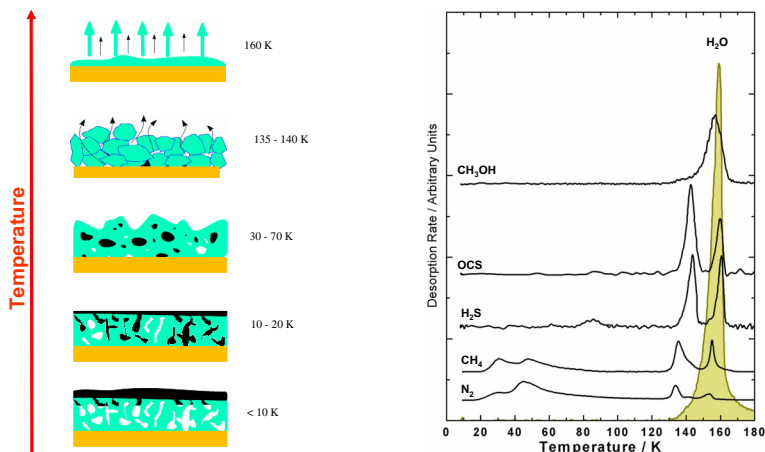
Fig. 1. (a) A cartoon illustration of the complex sequence of processing occurring during thermal processing of CO (black) adsorbed on a porous amorphous solid H_2O (green) at 10 K (Collings *et al.* 2003a). (b) TPD of some icy grain mantle components mixed in amorphous solid H_2O (Collings *et al.* 2004).

of CO coincident with the H_2O desorption (Collings *et al.* 2003a, 2003b). Subsequent experiments on a wider range of likely icy mantle components (Fig. 1b) revealed behaviour that could be qualitatively interpreted on a similar basis, yielding a simple classification of adsorbed and absorbed mantle components (Collings *et al.* 2004): (i) weakly bound species with a similar behaviour to that of CO, *e.g.* N_2, CH_4, etc.; (ii) intermediate species, which have a limited ability to diffuse out of a mixture but which show trapping behaviour when overlayered, *e.g.* H_2S, OCS, etc.; (iii) species which strongly hydrogen bond to solid H_2O, *e.g.* CH_3OH, etc., and therefore when mixed with H_2O show only coincident desorption; and (iv) refractory species, *e.g.* metals, sulfur, *etc.*, which desorb only at high temperatures (100 s of °C). This categorisation can be introduced into simple models of astrophysical regions where thermally-promoted desorption is important (Viti *et al.* 2004).

This simple preliminary assessment has been followed by an increasingly substantial literature detailing measurements on specific systems, over a range of relative abundances and on an increasing complexity from the simple binary $CO + H_2O$ system to ternary systems, such as $CO + H_2O + CH_3OH$ (Burke & Brown 2010, 2012). As the complexity is increased, it is becoming increasingly clear that a simple phenomenological model as above is a gross over simplification. Complex thermodynamic (*e.g.* phase transitions and separation) phenomena coupled into a kinetic environment control thermally-promoted desorption. Theoretical descriptions of this complexity have yet to be explored.

Another important question to consider is the impact of substrate on the morphology of the adsorbed layer and on desorption. Work on model systems comprising benzene (C_6H_6) on amorphous silica and C_6H_6 on amorphous solid H_2O
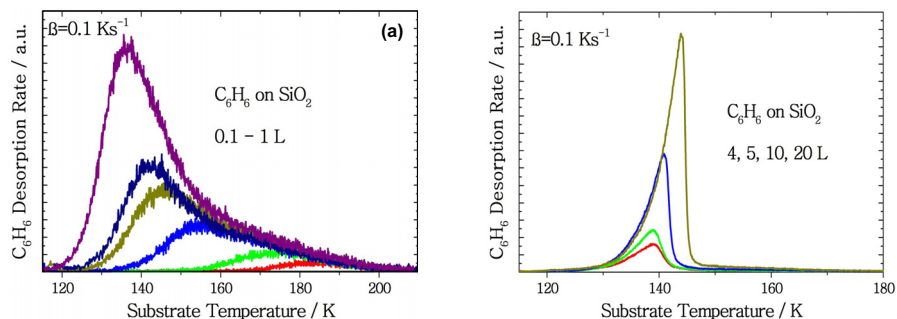
Fig. 2. TPD of (a) sub-monolayer exposures (0.1 to 1 L); and (b) multilayer exposures (>5 L) [1 L ≡ 10^{-6} mBar s]; of C_6H_6 from an amorphous silica substrate (Thrower *et al.* 2009b).

illustrate this. C_6H_6 may be thought of as a model for polycyclic aromatic hydrocarbon (PAH) compounds. Since PAHs are a major sink for carbon in the ISM, they are likely to be adsorbed on grains and within icy grain mantles. Amorphous silica and H_2O ice are, respectively, good representations of a silicate grain and its icy mantle. With increasing exposure in the sub-monolayer regime, the TPD data of C_6H_6 from amorphous silica exhibit broadening and a steady decrease in the peak desorption temperature (Fig. 2a) consistent with desorption from a surface that presents a distribution of binding energies with the most strongly bound sites being filled first. Desorption of the multilayer begins at around 140 K when the monolayer is complete at exposures in excess of 1 L. For the first few multilayers, the lack of leading edge coincidence points to a fractional desorption order. Only when layers are much thicker do we see the leading edge coincidence characteristic of zeroth order desorption kinetics (Fig. 2b) (Thrower *et al.* 2009a,b). In contrast, the TPD data for sub-monolayer exposures of C_6H_6 on H_2O ice grown at ∼100 K show no evidence for multiple binding sites, and indeed growth of the multilayer seems to occur from the lowest of concentrations with straight forward zero order kinetics. C_6H_6 interacts with both the silica and H_2O surfaces via π-hydrogen bond interactions. The C_6H_6 molecules are more strongly bound to the silica surface than to other C_6H_6 molecules; *i.e.*, C_6H_6 wets the surface and grows a distinct monolayer. C_6H_6 molecules are less strongly bound to the water surface than to other C_6H_6 molecules, and hence dewet from the surface to form 3-dimensional islands. Such behaviour is not uncommon and would be expected in many systems.

2.4 Desorption promoted by electronic excitation

Chemical transformations in models of icy mantles induced by electronic excitation (*i.e.* through photon absorption or charged particle interactions) have been the subject of intensive study (*e.g.* Ehrenfreund *et al.* 1997; Palumbo *et al.* 1999; Hudson & Moore 2004; Bernstein *et al.* 2004). These have for the most part

employed high vacuum matrix isolation methods, although some recent studies, in particular of electron-promoted chemistry (*e.g.* Bennett *et al.* 2011), have utilised ultrahigh vacuum. Under high vacuum conditions, where the growth of water ice films is typically $\sim$0.1 nm s^{-1}, measurements of the rate of loss of material from the icy surface, and of other physical processes such as phase change, can not readily be made. Nevertheless, these undoubtedly important experiments yield detailed information on the spectroscopic evolution of the model mantles as a means of assigning potential bands in the infrared spectra of astronomical objects. There are relatively few exceptions (*e.g.* Westley *et al.* 1995; Öberg *et al.* 2009) which address the fundamental question of how much of the electronic excitation energy is driving processes other than chemistry. Furthermore, research in this area has largely focussed on the impact of short wavelength vacuum ultraviolet radiation and high energy ($>$1 keV) ions and electrons. It has ignored the wavelength dependence of the photophysics and photochemistry of the solid state and surface, and the impact of low energy secondary electron-driven processes at the surface and in the solid state. This is in stark contrast to the deep understanding of desorption and other physicochemical processes promoted by electronic excitation that exists within the surface science community. Here, methodologies exist to investigate the photon and electron energy dependences of the cross-section for desorption, the products of desorption, and the disposal of energy into those products. Much of this surface science literature has focussed on metallic substrates where hot electron, photoelectron and charge exchange processes driven by interactions with the metal dominate the physics and chemistry at the surfaces. However, buried interface techniques (Street *et al.* 1997) allow us to study model grain surfaces with the same simple methodologies as might be applied to metallic surfaces.

As the interstellar radiation field (ISRF) is at its strongest in the range extending from the near-UV to the mid-IR (Mathis *et al.* 1983), it is logical to consider the impact of such radiation. Solid H_2O absorbs strongly at the red end of this region. Organic species present in the icy grain mantles, *e.g.* PAHs, absorb from the blue end of this region, with increasing unsaturation of the molecule pushing absorption further into the visible spectrum. Photon absorption by molecules present in the ice (adsorbate- or absorbate-mediated, whether at the surface or in the bulk) and by the H_2O solid itself (substrate-mediated) can result in desorption. Recent work in which layered C_6H_6-H_2O systems were irradiated with photons at around 250 nm demonstrates this through observation of the desorption of C_6H_6 and H_2O molecules, and $(H_2O)_x$ clusters (Thrower *et al.* 2008a,b, 2010). This wavelength corresponds to the lowest lying electronic transitions of C_6H_6. Solid H_2O has a negligible absorption cross-section in this region. The desorbed molecules were found to be translationally energetic, with temperatures in excess of 1000 K, while the clusters were much cooler. The desorbates, the desorption yield and translational energy release can be explained with a simple model in which the photon energy is resonantly absorbed by the C_6H_6; non-radiative transitions then promote unimolecular decomposition of a π-facially hydrogen bonded $C_6H_6...(H_2O)_x$ surface cluster yielding C_6H_6, H_2O and $(H_2O)_x$ clusters consistent

with the observations. Time-dependent measurements of desorption yield allow estimation of the cross-sections for photon-stimulated desorption, which were found to be 4×10^{-19} cm^2 for C_6H_6 and 1×10^{-19} cm^2 for H_2O (Fig. 3a) at 250 nm, and scale appropriately with the absorption cross-section as the excitation wavelength is changed within this absorption band system. Recent measurements of CO desorption under VUV radiation (Fayolle *et al.* 2011) confirm the resonant nature of photon-promoted desorption. However, a single wavelength measurement of the photon-promoted desorption rate is, of course, a gross underestimate of the real rate in the relevant radiation field. This should be represented as a sum of the product of the radiation flux, $\psi_{h\nu}$ in cm^{-2} s^{-1}, and desorption cross-section, $\sigma_{\mathrm{des},h\nu}$ in cm^2, across the wavelength range of the radiation field.

Low energy secondary electron production is the predominant scattering mechanism in the interaction of high energy charged particles with surfaces and solids. Knowledge of the energy distribution of the cosmic ray flux (Shen *et al.* 2004) and of the electron stopping power of materials (Ziegler *et al.* 2008) allows us to estimate the yield of secondary electrons produced by high energy charged particle interactions with icy mantles. The energy distribution within that yield ranges from near zero to several hundred eV with a broad maximum around 200 to 400 eV (Long & Paretzke 1991; Rudd *et al.* 1985). Probing electron-promoted desorption should therefore focus in this region. Such electrons strongly interact with matter. Typical inelastic mean free paths are of the order of 1 nm (Briggs & Seah 1990). As such, these electrons rapidly lose energy by generating excitons within the solid state with energies corresponding to valence electronic excitations (*e.g.* Ashley 1980; Petrik & Kimmel 2005); *i.e.* a few eV in organic solids, and around 8 to 14 eV in H_2O solid. Desorption promoted by secondary electrons will therefore be largely restricted to the solid selvedge while those species excited in the bulk will likely relax *in situ* or undergo chemical transformations (Abdulgalil *et al.* 2013).

Again, consider the C_6H_6-H_2O layered system as an example illustrating low energy electron-promoted desorption. Desorption of C_6H_6 is significantly enhanced by the presence of solid H_2O. Desorption from solid C_6H_6 islands on the H_2O solid surface has a cross-section of $\sim 5 \times 10^{-17}$ cm^2 in the 200 to 400 eV range (Thrower *et al.* 2010, 2011). The presence of water enhances that cross-section and desorption of isolated C_6H_6 diffusing between islands has a massive cross-section of around 2×10^{-15} cm^2 in this energy range. This we believe is associated with the generation of long-lived excitons in the water film which are able to diffuse rapidly to the surface (*e.g.* Petrik & Kimmel 2005). Build-up and long time decay processes observed in the data are associated with diffusive refilling of the inter-island isolated C_6H_6 phase and competitive desorption from the selvedge of the C_6H_6 islands. In contrast to the photon-promoted situation, the electron-promoted desorption of H_2O solid itself is independent of the presence of the C_6H_6. Figure 3b shows typical electron-promoted desorption data obtained using a combination of TPD and infrared absorption spectroscopy, with a cross-section of $\sim 5 \times 10^{-18}$ cm^2, that is independent of the electron energy and of the C_6H_6 coverage at exposures where C_6H_6 forms islands. Desorption of the H_2O is attenuated and eventually
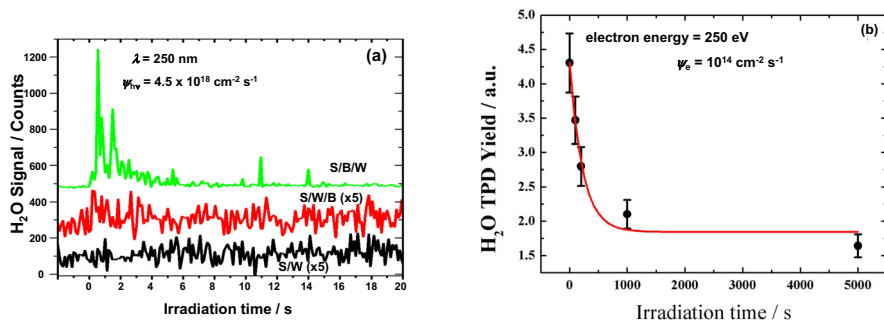
Fig. 3. Time-dependence of the H_2O signal in (a) the photon-promoted desorption of layered C_6H_6 (B) and H_2O (W) on a sapphire (S) substrate − the presence of C_6H_6 is clearly necessary to promote desorption of the H_2O and capping the H_2O layer with a layer of C_6H_6 (S/W/B system) obviously results in attenuation of the H_2O signal (Thrower *et al.* 2009a,b); (b) the electron-promoted desorption from a thick layer of amorphous H_2O beneath islands of C_6H_6 (10 L average) on an amorphous silica substrate (Thrower *et al.* 2010, 2011).

prevented by completion of the C_6H_6 overlayer, as might be expected. As with the photon-promoted desorption, the rate of electron-promoted desorption in principle depends on the electron flux, ψ_e in $cm^{-2} s^{-1}$, and desorption cross-section, $\sigma_{des,e}$ in cm^2, across the energy range of the secondary electron flux.

3 Astrophysical implications

To illustrate the impact of non-thermal desorption mechanisms some simple "toy" simulations were conducted on a model H_2O solid with a column density of 10^{17} cm^{-2}, assuming four desorption mechanisms operating in parallel: (i) photon-stimulated desorption involving the background VUV field produced by cosmic ray ionisation; (ii) photon-stimulated desorption involving photons from the ISRF and assuming solid state absorption cross-section of the icy grain akin to that of C_6H_6 in the 250 nm region and the desorption quantum yield of unity; (iii) electron-stimulated desorption associated from secondary electrons produced by cosmic ray interactions with icy grains; and (iv) thermal desorption occurring with kinetics as determined by Fraser *et al.* (2001). Desorption promoted by reaction enthalpy release and collisions is not included in these simple simulations. At a steady-state temperature of 10 K, photon-promoted desorption due to the ISRF unsurprisingly dominates for a visual extinction of 0. However, when the conditions within a molecular cloud are reproduced by application of an ISRF equivalent to a visual extinction of 6 (Fig. 4a), the total desorption rate is barely distinguishable from that due to electron-promoted desorption alone, with a timescale for return to the gas phase of some 10^8 years. As expected, the rate of thermal desorption is essentially zero at both extinctions. When warming of
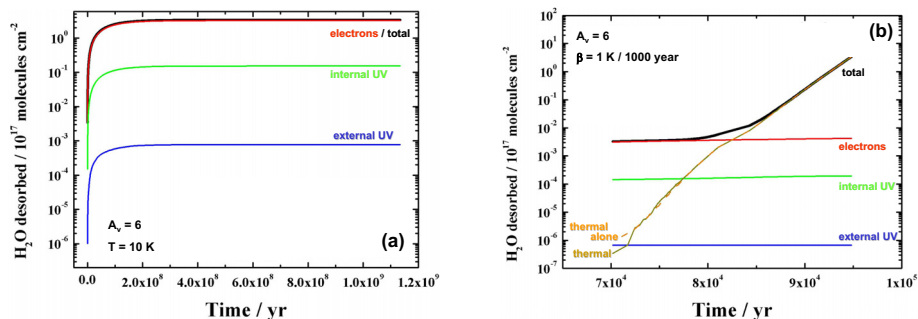
Fig. 4. "Toy" simulations to illustrate the impact of non-thermal desorption on a model icy grain population, (a) at steady state; and (b) in a warming molecular environment, using the approach described in the text and a simple stochastic integration tool (Hinsburg & Houle 1996).

the cloud at a rate of 10^{-3} K year^{-1} is added to the model, the thermal channel remains insignificant at a visual extinction of 0, but dominates desorption after some 8×10^4 years for a visual extinction of 6 (Fig. 4b).

4 Conclusions

Surface Science techniques (both experimental and theoretical) can help us understand heterogeneous chemistry in astrophysical environments, especially in relation to desorption processes. We are still at an early stage in our understanding of these processes, and much more work is needed, requiring a close collaboration between laboratory surface scientists (both experimental and computational), chemical modellers and observers.

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