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Surface Science Investigations of Icy Mantle Growth on Interstellar Dust Grains in Cooling Environments

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Abstract

Experimental measurements on the thermal and non-thermal behaviour of water and other simple molecules, including organic compounds such as methanol and benzene, on model interstellar dust grain surfaces and on solid water surfaces using surface science

other simp model inte techniques and methodologies are reviewed. A simple qualitative model of the early stages mantle growth arising from a synthesis of the results of such investigations from our own laboratory and others is presented.

Keywords

Icy grains, molecular clouds, thermal desorption, diffusion, non-thermal desorption, electroninduced chemistry, water ice

1 Introduction

As a dust grain journeys from a diffuse to a dense interstellar environment, the temperature drops as the density of the local environment increases. As this proceeds, water (H_2O) reactively accretes from its constituent atomic components and assuming a low enough temperature, H_2O is accommodated on the surface. To date, H_2O in the ISM is known to be formed via three types of reactions: 1^{-5} 1) ion-neutral reactions, that dominate at low temperatures and proceed with no activation barrier, 2) neutral-neutral (radical) reactions, that are known to dominate around room temperature and above, and 3) solid state (grain catalysed) chemistry lowering significantly the activation barrier for the radical reactivity allowing a rich chemistry even at low temperatures. It is interesting to note that for the chemistry occurring on the surface of the interstellar grains, many reactive pathways proceed via H_2O_2 formation that is then readily converted in OH and H_2O . Moreover, several of the reactions that convert the adsorbed O to OH, H₂O and O₂ on dust can result in their direct release into the gas phase. Here, these species can further react or be re-adsorbed on the grain surface. An interesting question to ask is; how does H₂O behave once adsorbed on a dust grain surface? Temperature-programmed desorption (TPD) experiments are able to answer part of this question as TPD probes the interactions between adsorbates and surfaces and between the adsorbed molecules themselves. TPD experiments^{6–8} of sub-monolayer and

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multilayer quantities of H_2O have consistently shown zero-order, multilayer desorption from surfaces ranging from amorphous silica ($aSiO_2$), Au, sapphire and Ru/Al. This means that H_2O must become mobile on the surface to form clusters or islands through diffusion at some temperature before it leaves the substrate. However, the existing model for the structure of icy grain mantles, the Onion Model,^{9,10} visualises the icy coat as organised in layers where the core dust grain material is fully covered by a thick, multilayer of H_2O . Atop this, other species adsorb or reactively accrete depending on temperature. This means only a relatively pure layer of H_2O interacts directly with the dust grain surface while other species, such as CO, will interact with water. However, as dust grains travel from diffuse, "hot" regions toward dense, "cold" environments and H_2O is reactively accreted then the H_2O molecules themselves must be mobile on the grain surface. The Onion model, thus, may not be an accurate depiction of interstellar ice. In fact, if H₂O molecules are mobile at temperatures around 10 K then both H_2O surface and bare dust grain surface would be available for other species to adsorb onto. Our argument for a more realistic model for the ice mantle on dust grains will be developed in this work. It is noteworthy to stress that the picture of interstellar icy grains that will be discussed here is limited to the stage of the life of a molecular cloud before star formation is triggered, and hence not in the hot cores or hot corinos regions near massive and low-mass proto-stars.

Laboratory measurements such as those reported and referenced in this work can significantly improve our understanding of astrochemical phenomena such as icy mantle accretion on interstellar grains in diffuse, translucent and dense clouds. However, the impact of such findings must be properly assessed *via* elaborate theoretical models in order to extrapolate their implications to astrophysical contexts. As part of this process astrophysical modellers have turned to simulating laboratory experiments as a step towards more realistic and accurate models of astrophysical environments and processes. For instance, the first off-lattice Monte Carlo kinetics model of interstellar dust grain surface chemistry presented by Garrod¹¹ was initially constructed *ab initio* with no emphasis on laboratory data. However, a subsequent version of the model was tuned to reproduce certain key experimental values before extrapolation to conditions appropriate to proto-planetary disks.¹² Further examples of this approach can be found in the literature. The large scale Monte Carlo model of Vasyunin and Herbst,¹³ describing both gas-phase chemistry and the chemistry occurring in the icy mantles of interstellar grains, accurately describes the desorption behaviour of the icv manthe during the warm-up phase due to a close comparison and adjustment with laboratory TPD data of ice desorption. Another noteworthy case where simulations and experiments work hand in hand is the work of Karssemeijer *et al.*¹⁴ investigating the dynamics of CO in amorphous solid water (ASW). Particularly, the coverage dependence of the binding energy at sub-monolayer level that was previously extracted from TPD data¹⁵ is well reproduced by the simulations; and the energy barrier for diffusion is determined from both the simulations and the isothermal desorption experiments. The binding energy of volatile molecules (N_2, N_2) CO, CO_2, O_2, CH_4) on ASW and of NH_3 on crystalline water ice have been measured in the laboratory.^{16,17} The authors found that for most of these species the binding energies decrease with increasing coverage in the sub-monolayer regime and obtained values much larger than commonly used in gas-grain models. When the newly determined binding energy distributions are used in a simulation of gas-grain chemistry for cold cloud and hot-core models, the authors found that a fraction of the volatiles remain adsorbed on the grain surface to higher temperatures compared to other astrochemical models. These and other works^{18–21} provide large scale astrochemical modellers with important input parameters that would otherwise be overlooked.

Obviously, simulations have given us deep insight into the mantle accretion 13,22 and the methodologies employed are not the object of debate in this paper. Nevertheless, recent experimental findings show that there is still ample room for improvement in such simulations. The work of Dulieu and colleagues, 23,24 for example, highlighted the effect of a small

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difference in affinity between a certain species and a surface with respect to a second species on the same substrate during their co-deposition. At sub-monolayer levels, CO binds more strongly to water ice than N_2 and O_2 and hence CO displaces these two species from the most stable adsorption sites *via* a segregation mechanism. This means that both N_2 and O_2 will thermally desorb at lower temperatures when mixed with CO on solid water than when deposited as pure substances.

Our work can be contextualised within this framework, as we aim to highlight recent laboratory findings from our group and others that challenge our current picture of the icy mantle of the interstellar grains and can potentially improve the accuracy in prediction of large scale astrochemical models. We will specifically report on (1) thermal desorption and the impact of surface heterogeneity; (2) diffusion of H_2O on silica surface as probed by infrared spectroscopy; non-thermal desorption of small molecules through (3) photon absorption and (4) radiolytic interaction; and (5) efficient H_2 generation from ionisation of saturated C-containing species. Finally we will present a simple model to highlight how laboratory experimental findings can challenge and further our understanding of the interstellar icy grain structure and pave the route to future key experiments.

2 Experimental

The experimental apparatus, ancillary equipment and general methods employed have been described in detail previously.^{25–29} Herein only details specific to the reported measurements are given. Gas doses are reported in Langmuir units (1 L = 10^{-6} Torr s). These can be used to estimate the film thickness, d, from Eq. 1 based on the assumption of uniform film growth:

$$d = \frac{SPt}{\sqrt{2\pi m k_B T}} \frac{1}{\rho_s} = \frac{Z_W t}{\rho_s} \tag{1}$$

ACS Paragon Plus Environment where S is the sticking coefficient (assumed to be 1), P is the pressure recorded on the hot cathode ion gauge corrected for the molecular ionisation efficiencies, t is the time of exposure, k_B is the Boltzmann constant, T is the temperature of the dosed molecules, Z_W is the bombardment rate (the incident flux), ρ_S is the molecular volume density and m is the molecular mass. In Eq. 1, we first define the number of molecules deposited onto the substrate (N_{tot} , molecules per unit of surface area) during the dose ($N_{tot} = Z_W t$) and then divide this by the density (molecules per unit of volume).

The results reported in Section 3 are from experiments conducted in two ultrahigh vacuum (UHV) chambers, both are shown in Figure 1. The first UHV system (Figure 1 panel 1) is capable of reaching pressures of 2×10^{-10} mbar pumped by a liquid nitrogen trapped 6" diffusion pump backed by a rotary pump. The sample is an oxygen free high conductivity (OFHC) copper block coated with an amorphous silica $(aSiO_2)$ layer (ca. 300 nm thick) deposited by electron beam evaporation as described by Thrower $et \ al.^{25}$ resulting in a very rough surface with peak-trough variations of up to *ca.* 60 nm. This sample is mounted on the end of a closed-cycle helium-cooled cold finger with a base temperature of 15 - 20 K. A cartridge heater (Heatwave Labs Inc.) placed inside the copper block is used to uniformly heat the $aSiO_2$ surface. The surface and cold finger temperatures are monitored using KP-type (Au-Chromel) thermocouples connected to IJ-6 temperature controllers. The UHV chamber is equipped with a pulse-counting quadrupole mass spectrometer (QMS, Hiden Analytical Ltd, HAL301), residual gas analyser mass spectrometer (RGA, SRS 200) and reflection-adsorption infrared spectroscopy (RAIRS, Varian 670-IR FTIR spectrometer) apparatus. Also attached to the main chamber are two doubly differentially pumped atomic beam chambers. Each of these chambers is split into plasma and beam chambers by an internal wall fitted with a 5 mm collimator flange. The base pressure in the plasma chambers routinely reaches below 5×10^{-10} mbar when the beams are not in use. Each plasma cham-





Figure 1: Schematic of the UHV chambers used for the experiments conducted at Heriot-Watt University. Panel 1 shows the Ice Rig used for the experiments reported in Section 3.2. Labels in this panel are: 1a - quadrupole mass spectrometer; 2a - Sample mount with substrate; 3a and 4a -KBr windows for IR spectroscopy. Panel 2 shows the Beam Rig used for the electron irradiation experiments described in Sections 3.4 and 3.5. Labels in this panel are: 1b - rotating quadrupole mass spectrometer; 2b - Sample mount with substrate; 3b and 4b -KBr windows for IR spectroscopy; 5b - Residual gas analyser; 6b - electron gun; 7b - viewport. Both set-ups have two levels where the sample can be located by adjusting its height. Only the level where the experiments were conducted is displayed for the two chambers in the panels. The other level is not shown for clarity, but it is worthwhile noting that it is equipped with viewports to allow visual access to the chamber and with leak valves for background dosing.

ber is equipped with a radio frequency (RF) powered plasma source (Oxford Scientific, RF OSPrey) and a fibre optic spectrometer (Ocean Optics, USB4000). Molecular beam modulation spectrometry (MBMS) analysis can be performed allowing the identity and intensity of gaseous species during the beam irradiation part of an experiment to be obtained. Although most of these species would be from the beam or background contaminants, other species may be detected that were formed through surface reactions and desorbed upon formation. As a consequence, this technique provides more detailed kinetic data of the processes occurring on the surface that would otherwise be missed using other analytical techniques. TPD measurements can also be performed using the QMS. An alternate method for introducing molecules is through background deposition of gases and liquids using designated and differentially pumped glass gas handling lines.

The substrate used in the UHV chamber (Figure 1 panel 2) for electron irradiation experiments was a polished stainless steel disc coated with *ca.* 200 nm aSiO₂ deposited by electron beam evaporation.²⁵ The substrate was cooled through contact with a liquid nitrogen reservoir, reaching a base temperature of 112 ± 2 K as measured by a K-type thermocouple spot-welded to the edge of the stainless steel disc. Layered ices were obtained by sequential background deposition using benzene (C₆H₆; Fluka, 99.5%), de-ionised water (H₂O), methanol (CH₃OH) (Sigma-Aldrich, HPLC grade 99.9% pure), or diethyl ether (CH₃CH₂OCH₂CH₃, Sigma-Aldrich, Chromasolv grade 99.9% pure). All the chemicals were stored in glass vials and purified by repeated freeze-pump-thaw cycles before use. Crosscontamination was avoided by collecting the vapour phase from the liquids using two independent manifolds each interfaced to its own dedicated leak valve (Vacuum Generators MD95).

Sample irradiation was performed using an electron gun (Kimball Physics, ELG-2) incident at $ca. 30^{\circ}$ with respect to the substrate normal with a 1 mm² beam spot size. Desorption

of the species was followed using a quadrupole mass spectrometer (VG Microtech PC300D, further modified by ESS) with a home-made line-of-sight tube facing the sample. Several control experiments revealed evidence of substrate charging during the irradiation of the ices with electrons. The incident electron current decreased by up to 30% after 600 s of exposure to the beam giving a typical average flux of $(9 \pm 2) \times 10^{13}$ electron cm⁻² s⁻¹. However, this had little impact on the quality of the reported measurements as the relevant events occur either in the first 50 s, when the flux can be assumed to be constant at around $(1.1 \pm 0.2) \times 10^{14}$ electron cm⁻² s⁻¹ (ϕ_1), or at longer times, when the flux has reached a limiting value of $(7.5 \pm 0.5) \times 10^{13}$ electron cm⁻² s⁻¹ (ϕ_2).

Electron trajectories in the investigated ices were calculated *via* Monte Carlo simulations consistent with the experimental conditions and were published elsewhere.^{28,29} The results indicate that the calculated penetration depth of 250 eV primary electrons has a maximum around the uppermost 5 nm of the ices. Thus, all the binary layered systems reported here have an overall thickness larger than the primary electron maximum penetration depth. The sole exception was found for the thinnest ice (70 L H₂O topped with 5 L of C₆H₆, *ca.* 8 nm thick), although the fraction of primary electrons reaching the substrate remains negligible.^{28,29}

3 Results and discussion

3.1 Thermal Desorption by Temperature-Programmed Desorption

TPD has been widely used over the last two decades to determine the binding energies of molecules on grain surfaces;³⁰ a crucial input to our understanding of the gas-grain interaction in the interstellar medium. For the most part, simple analyses are presented in the literature for desorption of ultrathin solid films of pure mantle components assuming zero order kinetics or for sub-monolayer quantities of adsorbed mantle components on model grain surfaces (*e.g.* silica, graphite or water ice films) assuming first order kinetics. Such studies typically report a single binding energy and, sometimes, the pre-exponential factor for desorption. However, such analysis is inaccurate especially where the surface from which the molecules desorb is heterogeneous, as multiple binding sites result in a range of binding energies. Kay and co-workers were the first to report a simple inversion analysis which advanced the interpretation of sub-monolayer desorption data on grains.³¹ Work by Dulieu, Lemaire, Kay, McCoustra, Vidali, and Zacharias illustrates this procedure.^{23,32–36} Table 1 summarises this state-of-the-art in TPD.

Table 1: Binding energy ranges of small molecule on silica, graphite and water surfaces obtained from TPD data. Values for water ice on Au, sapphire, Ru/Al, Al_2O_3 surfaces have also been reported. Note that *n.a.* stands for not available.

Species	Surface	Binding Energy / kJ mol ^{-1}		Reference
		Sub-monolayer	Multilayer	-
	$aSiO_2$	n.a.	49.3±2	37
H ₂ O	Graphene	n.a.	46.0 ± 3	38
	Au	n.a.	46.6-48.0	6
	Sapphire	n.a	$49.4{\pm}0.8$	7
	$\mathrm{Ru}/\mathrm{Al},\mathrm{Al}_2\mathrm{O}_3$	n.a.	46.9-48.3	8
	H ₂ O	$9.6 {\pm} 0.5$	n.a.	15
СО	$aSiO_2$	7.2-12.2	6.9-7.3	$15,\!37,\!39,\!40$
	Graphene	7.6-12.5	$7.6 {\pm} 0.4$	41
N_2	H ₂ O	$9.6 {\pm} 0.5$	n.a.	41
	$aSiO_2$	8.8-13.4	6.6-6.9	$37,\!39$
	Graphene	6.5-11.2	7.2 ± 0.4	41
O_2	H ₂ O	7.6-9.7	7.5-7.8	15
	$aSiO_2$	7.7-8-11.9	7.4-7.6	$15,\!37,\!39,\!40$
	Graphene	8.6-11.8	$8.6 {\pm} 0.4$	41
CH_4	H ₂ O	11.4 ± 0.6	10.5 ± 0.5	41
	$aSiO_2$	n.a	n.a.	
	Graphene	10.5 - 14.9	$9.9{\pm}0.5$	41
CO_2	H_2O	18.3-21.0	18.8-19.6 15,42	
	$aSiO_2$	18.9-25.0	18.7 ± 0.7	15
	Graphene	19.8 ± 2.9	23.0-24.8	38,42

Typically, this analysis starts by direct inversion of the Polanyi-Wigner Equation, Eq. 2:

$$r_{des} = \frac{\mathrm{d}N_{ads}(t)}{\mathrm{d}t} = N_{ads}(t)^n \,\nu \, e^{-\frac{E_{des}}{k_B T}} \tag{2}$$

where r_{des} is the desorption rate (which is equivalent to the rate of change of surface concentration, N_{ads}), ν is the pre-exponential factor, n and E_{des} are the desorption order and energy respectively, k_B is the Boltzmann constant and T is the surface temperature. Rearranging Eq. 2 yields Eq. 3:

$$E_{des}\left(N_{ads}(t)\right) = -k_B T \ln\left(\frac{r_{des}}{\nu N_{ads}(t)^n}\right)$$
(3)

 $N_{ads}(t)$ can be determined from an estimate of the total number of molecules, N_{tot} , adsorbed on the surface as discussed for Eq. 1. Knowing this, the TPD data can be normalised since also the integral of the TPD curve up to a certain time is the number of desorbed molecules up to that time value. Subsequently, the variation of E_{des} with respect to N_{ads} can be used to yield the probability of finding a particular desorption energy $(P(E_{des}))$ (Eq. 4):

$$(P(E_{des})) = -\frac{\mathrm{d}N_{ads}}{\mathrm{d}E_{des}} \tag{4}$$

Even this methodology is limited by the assumption that the pre-exponential factor is fixed at 10^{12} s⁻¹ (for a physisorption interaction) or 10^{13} s⁻¹ (for chemisorption). Recent work by Kay and co-workers^{43,44} has revealed the weakness of this assumption that goes back to the classical Redhead analysis⁴⁵ and can be attributed to an over-simplification of the transition state theory description of desorption which neglects transition state rotational motion. This more recent and complete analysis suggests a pre-exponential factor of around 10^{17} s⁻¹ for C₆H₆ desorbing from graphene using their optimised inversion procedure.⁴⁴

The impact of surface heterogeneity can also be seen in the vibrational spectroscopy of simple molecules on model grain surfaces in the broadening of the spectral features. This is nicely illustrated in the study of Taj *et al.*⁴⁶ on the line profiles of sub-monolayer quantities

of CO on $aSiO_2$ and porous amorphous solid water (p-ASW) ice, which explored the impact of surface heterogeneity on the frequency of the CO vibration assuming broad distributions of CO binding sites on these surfaces. The authors also investigated the CO deposition mechanism in considering both ballistic deposition, where a species is unable to diffuse once adsorbed and diffusive deposition, where species can diffuse across the substrate. Through comparison with experimental IR spectra, this work showed the propensity of CO to diffuse on $aSiO_2$. For CO on p-ASW, the interpretation is less clear as both the diffusive and ballistic models appear to fit the observed IR CO line shape.

3.2 Surface Diffusion probed by RAIRS

As H_2O is generally the most abundant component of the solid state materials on interstellar dust grains, desorption of multilayer H_2O has been studied on surfaces ranging from sapphire to polycrystalline and single crystal metals^{6,8,47} including dust grain mimics such as $aSiO_2^{37}$ and graphene.⁴³ Many of these studies report zero, or near-zero, order desorption for all H_2O coverages. As zero order desorption kinetics is associated with multilayer desorption, this indicates that H_2O molecules must diffuse and agglomerate into clusters and islands on the surface before or during the desorption. This also implies that the H_2O - H_2O interaction is stronger than the H_2O -substrate interaction. Experimentally, H_2O molecules at sub-monolayer coverages have been shown to be mobile on model dust grain surfaces at temperatures as low as 17 K;⁴⁸ exhibiting an activation energy for diffusion of about 2 kJ mol⁻¹.

The data in Figure 2 are illustrative of the de-wetting and agglomeration experiments of H₂O on aSiO₂ obtained using reflection-absorption infrared (RAIR) spectra of the ν OH stretching vibration.⁴⁸ This figure shows how the intensity of the ν OH stretching band increases over a period of 5 hours at a temperature of 18 K before a final annealing to 100 K for 20 minutes producing a fixed "infinite time" spectrum. The peak is constant in



Figure 2: RAIR Spectra of the OH stretching region of a sub-monolayer quantity of H_2O deposited on $aSiO_2$ at 17 K and warmed for the indicated times to 18 K. The infinite time corresponds to annealing for 20 minutes at 100 K. Reproduced from reference 48 with permission from the PCCP Owner Societies.

position and the dangling O-H modes cannot be clearly observed. Shifts in ν OH are known to occur in particle growth up to diameters of 4 nm.⁴⁹ The absence of such shifts in Figure 2 would suggest that this initial growth phase is complete before our first measurement is made. In addition, the presence of heavy spectral contamination by gas phase water rovibrational bands from our instrument purge gas will make observation of the dangling bonds difficult. This is not uncommon in studies of H₂O ice. Control experiments conducted under the same conditions, where the partial pressure of H₂O in the UHV chamber was significantly less than 10⁻¹³ mbar, indicated negligible H₂O film growth. Consequently, the only explanation for the increase in ν OH intensity is an increase in the oscillator strength of the band. Formation of hydrogen-bonds (of the type H···O-H) is known to increase the ν OH oscillator strength.⁴⁹ Thus, H₂O must be diffusing over the aSiO₂ and highly oriented pyrolytic graphite (HOPG) surfaces to form hydrogen-bonded clusters that eventually desorb following zero order kinetics. Assuming first order kinetics, the rate constant for this dewetting process can be calculated from data such as those presented in Figure 2. Table 2 summarises the rate constants for this agglomeration process on both surfaces over the range

of temperatures probed in the experiment.

$T_{anneal} \pm 0.3$ / K	k (aSiO ₂) / s ⁻¹	k (HOPG) / s ^{-1}
17	$2.432 \times 10^{-5} \ (\pm 8\%)$	-
18	$3.640 \times 10^{-5} \ (\pm 15\%)$	-
21	$5.188 \times 10^{-4} \ (\pm 14\%)$	-
24	$8.894 \times 10^{-4} \ (\pm 4\%)$	$1.488 \times 10^{-3} \ (\pm 21\%)$
27	$8.788 \times 10^{-4} \ (\pm 9\%)$	-
29	-	$1.572 \times 10^{-3} \ (\pm 1\%)$
30	$1.508 \times 10^{-3} \ (\pm 15\%)$	-
33	-	$3.703 \times 10^{-3} \ (\pm 51\%)$
40	$2.046 \times 10^{-3} \ (\pm 12\%)$	-
50	$1.392 \times 10^{-3} \ (\pm 10\%)$	$5.865 \times 10^{-3} \ (\pm 36\%)$
60	$1.300 \times 10^{-3} \ (\pm 11\%)$	-
70	-	$3.289 \times 10^{-3} \ (\pm 16\%)$
100	$1.400 \times 10^{-3} \ (\pm 27\%)$	$4.330 \times 10^{-3} \ (\pm 51\%)$

Table 2: Agglomeration rate constants for H_2O on the $aSiO_2$ and HOPG surfaces taken from reference 48. The numbers in brackets are estimated relative error on the measurements.

Figure 3 presents the data reported in Table 2 for the $aSiO_2$ surface in the form of an Arrhenius plot. At temperatures below 25 K, there is a 2 kJ mol⁻¹ barrier for the agglomeration process, which disappears at temperatures above 25 K. This de-wetting and agglomeration process has been shown to be enhanced by atomic O bombardment as molecular O₂ forms and releases energy (reaction enthalpy).⁵⁰ It is likely that the formation of other molecules would also enhance this process.

Figure 4 shows the results of a simple kinetic simulation in which a sub-monolayer equivalent quantity of gaseous H_2O randomly adsorbs onto a surface as the surface temperature decreases while the surface presents a barrier to agglomeration as estimated above. Mechanistically, we treat this with the following series of kinetic processes;



Figure 3: Arrhenius plot of the data in the $aSiO_2$ column in Table 2 illustrating the change in activation barrier for H₂O agglomeration as the surface temperature changes. Replotted from reference 48 with permission from the PCCP Owner Societies.

$$H_2O(g) \to H_2O(ads)$$
 (5a)

$$H_2O(c-ASW, s) \to H_2O(CSW, s)$$
 (5b)

$$H_2O(ads) \to H_2O(CSW, s)$$
 (5c)

$$H_2O(ads) \rightarrow H_2O(c-ASW, s)$$
 (5d)

Adsorption will primarily be to isolated H_2O molecules, $H_2O(ads)$, on the substrate surface (Eq. 5a). The model recognises that agglomeration at high temperature will lead to crystallisation and the formation of crystalline solid water (CSW) agglomerates (Eq. 5b and Eq. 5c). At temperatures below 80 K, H_2O deposition leading, *via* agglomeration, to the compact amorphous solid water (c-ASW) particles becomes the dominant channel (Eq. 5d). The simulations also show that the surface concentration of $H_2O(ads)$ is almost negligible as H_2O is able to agglomerate on timescales substantially shorter than that of deposition.



Figure 4: Results of a toy model simulating the deposition of gaseous H_2O and including diffusive agglomeration on a dust grain surface. The model assumes that agglomeration at high temperature will lead to crystallisation. Reproduced from reference 48 with permission from the PCCP Owner Societies.

With H_2O de-wetting, the dust grain surface previously covered by H_2O , as in the traditional Onion Model, is now exposed. This creates a duality of environments on interstellar dust on which other molecules can adsorb. As demonstrated, the small binding energy differences between CO on $aSiO_2$ and ASW result in differential adsorption.⁴⁶ This is equally true of many volatile species, *e.g.* there is as much as 1 kJ mol⁻¹ variation for O_2 on different surfaces.¹⁵ Such alterations in binding energies could result in greater lifetimes of molecules in the solid state, possibly explaining the lack of observable abundances of certain molecular species. For example, O_2 lifetimes on a bare dust grain surfaces have been shown to reach values of 10⁹ years suggesting that bare grain surfaces may act as a sink for O_2 .³⁷ O_2 , incidentally, has also been shown to diffuse across model interstellar surfaces with a diffusion barrier of 2.4 kJ mol⁻¹.⁵¹

Can we see evidence of this behaviour? Observations of CO in H_2O poor environments have been shown to produce three features at; 2143.7 cm⁻¹, 2139.9 cm⁻¹ and 2136.5 cm⁻¹.⁵¹ The first two features were assigned to CO molecules interacting with other CO molecules. Page 17 of 61

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The latter feature at 2136.5 cm⁻¹ was left unassigned. However, this feature compares favourably with laboratory experimental results of CO adsorbed directly onto $aSiO_2$. Additionally, the invariance of sub-monolayer CO RAIR spectra with deposition temperature leads to the inference that adsorbed CO is mobile on $aSiO_2$ at cryogenic temperatures.³⁷ Diffusion of CO on cold interstellar analogue surfaces is further supported through the line profile simulations reported by Taj *et al.*⁴⁶ The launch of the James Webb Space Telescope may open additional windows on to this issue.

Experimental and theoretical work from Cuppen and co-workers^{20,52} has shown the propensity for CO to diffuse on and in H₂O films while TPD experiments inform us that CO fills all adsorption sites on a surface to form a complete monolayer before building a multilayer.^{15,37} In forming that monolayer, CO must also diffuse across the surface given the evidence above. This leads us to a picture of the evolving interstellar grain where the grain surface is slowly populated by mountainous H₂O agglomerates while some parts of the grain surface remains bare. Both the H₂O and bare grain surfaces are covered by thin films of CO. Hydrogenation of CO yields methanol, CH₃OH,^{53,54} and methanol, in turn, has been shown to exhibit a preference for those binding sites that lead to a stronger adsorption interaction with the SiO₂ surface at low temperature but exhibiting de-wetting and diffusion behaviour at elevated temperatures.⁵⁵

As an aside, the formation of multilayer CO through diffusion and deposition produces a material that spontaneously exhibits an intense electric field; known as a spontelectric field.^{56,57} This field, and its impact on the magnetic support of the dense medium, have been proposed to play a crucial role in determining the rate of star formation in dense cold, dense environments.^{58,59}

3.3 Non-thermal Desorption through Photon-absorption

It is well established that photo-processes (namely photo-dissociation, photo-ionisation, and photo-desorption) are important to interstellar and circumstellar chemistry. Traditionally, the focus has been on photo-processes driven by vacuum ultraviolet (VUV) radiation as the radiation field near a star is dominated by Lyman- α (121.6 nm). Even in dense objects, cosmic rays can excite Lyman- α emission *via* radiolysis of H₂. Numerous laboratory investigations have employed microwave-discharge hydrogen-flow lamps (MDHL) in order to simulate the photon-irradiation of astrophysical ices.^{60–81}

Such studies have contributed significantly to understanding non-thermal processes in interstellar environments. However, while the MDHL is a realistic radiation source, it does not exclusively emit Lyman- α and contributions to the emission from molecular hydrogen around 160 nm are observed.^{82,83} Indeed, recent work has demonstrated that the MDHL emission spectrum is actually very sensitive to the operational conditions, especially the intensity ratio of atomic H to molecular H₂ emission.^{82,83} This has led to disagreements between measurements from almost identical experiments employing MDHL by different groups. Measurements on photo-desorption of CO are the perfect example as CO photodesorption yields have been reported with values ranging from 3 × 10⁻³ to 6.4 × 10⁻² CO molecules per photon.^{60,61,82,84-87}

Clearly, the utility of broadband MDHL sources is brought into question unless careful characterisation of the source is performed. Better insight into mechanisms, rates and yields can be obtained using a wavelength-resolved approach. The works led by Bertin⁸⁸ and Fayolle⁸⁷ investigate photo-desorption of CO with unprecedented detail using monochromatic synchrotron emission in the photon energy range 7 - 13.6 eV (117 - 91 nm) and gas-phase detection of the photo-desorbed CO by QMS. Follow-up studies on other species have allowed generalisation of the main conclusions drawn from the case of CO, which was extensively

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investigated also in mixed ices (*e.g.* N_2 , CH_4 , CO_2 and CH_3OH).^{88–91} While we will focus the following discussion on CO due to the abundance of experimental evidence, we will highlight the main differences and the similarities when relevant. The key results of these experiments can be summarised as follows:

- The photo-desorption spectrum reflects the photo-absorption spectrum of solid CO,⁹² and hence the photo-desorption yield is modulated by the same wavelength dependence observed for the transition from the ground state of CO (X¹Σ⁺; v = 0) to vibrational levels of the first allowed electronic state (A¹Π). A strikingly similar conclusion was recently reported for the study of the photodesorption of NO ices. Also in this case, the desorption spectrum reflects the absorption spectrum of solid NO from Lu *et al.* (2008) in the 5 and 11.5 eV range.⁹³ This kind of photon-stimulated desorption (PSD) energy dependence was also observed for CO₂, CH₄, O₂ and N₂^{88-91,94} strengthening the idea that the electronic excitation responsible for desorption takes place in the condensed molecular film, and not in the substrate.
- CO PSD is driven by a three-step indirect Desorption Induced by Electronic Transition (DIET) process requiring: (i) electronic excitation of a sub-surface CO molecule by absorption of a UV photon; (ii) excitation of intermolecular vibrational modes following the rearrangement of neighbouring CO molecules around the excited molecule; and (iii) ejection of a surface CO molecule into the gas-phase. The data collected using layered binary ices made of ¹²CO topped with ¹³CO clearly show that the initial excitation step occurs within the 2 to 3 topmost molecular layers and hence, in order for this mechanism to occur, there have to be at least three monolayers of CO molecules. This conclusion also bears another important consequence, which is that the mechanism is independent of the thickness of the CO ice and of the substrate upon which the CO ice is grown. However, we need to stress here that other mechanisms might contribute to the overall desorption yield when the ice film is thin, *e.g.* a few monolayers, and hence when the excitation can reach the underlying substrate. This is the case for

the substrate-induced dissociative electron attachment (DEA) desorption mechanism of ices grown on graphite as reported by Chakarov *et al.*.^{95,96} Complementary to this, the synchrotron studies on the DIET process show that, as long as the CO ice layer is thick enough, the three-step DIET process will take place with the same efficiency whether the substrate is a metal (polycrystalline gold), HOPG, solid water (SW) ice, both p-ASW and CSW.

The conclusion that CO photo-desorption involves only the upper layer and is triggered by vibronic excitation of a sub-surface CO molecule is supported by classical Molecular Dynamics (MD) simulations.⁹⁷ These calculations, however, reveal that there are two CO photon-stimulated desorption mechanisms occurring upon irradiation of the CO ice: a direct process and an indirect one (the kick-out mechanism). The former involves only CO molecules at the vacuum interface, and competes with the indirect process making its observation difficult. In fact, the work of Hemert et al.⁹⁷ shows that electronic excitation of the CO molecule promotes rotation and induces a rearrangement of the neighbouring molecules before relaxation to the ground state *via* internal conversion follows. This leaves the originally excited molecule in an unfavourable configuration with respect to the neighbouring species while also possessing a high degree of vibrational excitation. It is the unfavourable orientation and position that triggers desorption rather than the vibrational excitation. Hence, molecules in the next top layer contribute to desorption through a "kick-out" mechanism through which a neighbouring molecule in the covering layers desorbs while the originally excited molecule stays in the ice. This is akin to the "Newton's Cradle" mechanism proposed by King and Arnold from studies of ultrafast C_6H_6 desorption from C_6H_6 films.⁹⁸ The simulations show that there is hardly any vibrational energy transferred after the internal conversion, so the photo-stimulated desorption is caused by a disruption of the local configuration around the excited CO molecule, or in other words "by the differences in anisotropy of ground and excited-state interaction potentials".⁹⁷ This mechanism is consistent with the laboratory findings, although, by contrast, the original model proposed on the basis of the Page 21 of 61

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experiments only⁸⁸ states that at least part of the energy of the excited sub-surface CO molecule is transferred to the upper species *via* the excitation of intermolecular vibrational modes. One might argue that in the case of the kick-out mechanism, the desorbing surface molecule would be vibrationally, rotationally and translationally cold, whereas in the other mechanism the escaping species would be vibrationally hot. Unfortunately, there is currently no experimental evidence to support these conclusions and further investigations are warranted.

One thing is certain, intermolecular interactions play an important role in determining the effective photon-stimulated desorption yield. Subsequent studies of more complex binary CO and N₂ ices demonstrated that the measured photo-desorption rate is not modulated by the absorption spectrum of the desorbing molecule. Instead the wavelength dependence results from a combination of the absorption profiles of the surrounding species which are present deeper in the ice. Thus, the efficiency of the indirect DIET process driving photonstimulated desorption depends on the nature of the species, being very effective for N₂ with CO, less effective⁸⁹ for CH₄ with CO or CO₂ with CO,⁹⁰ and negligible⁹¹ for CH₃OH with CO or for H₂O and CO.⁸⁸ It should be noted that comparing the studies of CH₄/CO and N₂/CO reveals some evidence in support of a DIET mechanism that excludes a pure kick-out process. In fact, as Fillion and coworkers point out, CH₄ is lighter than N₂ so momentum transfer only originating from the excited sub-surface CO molecule would result in a more efficient desorption of the lighter CH₄ contrary to experimental observations.⁸⁹

It is clear now that:

- Photon-stimulated desorption is a wavelength-dependent process,
- and that care must be taken in using the measured photon-stimulated desorption rates for pure ices in complex astrochemical models because the molecule that is lifted off the surface is not necessarily the one that absorbs the photon.

The latter concept was first reported in the work of Thrower *et al.*^{99,100} in near-UV irradiation of binary layered ices of C_6H_6 and H_2O . The study nicely illustrates how adsorbatemediated indirect photo-desorption of H_2O can occur subsequent to resonant electronic excitation of the C_6H_6 adsorbate on the H_2O ice through unimolecular decay on the ground electronic state surface of a cluster in which C_6H_6 is π H-bonded to a number of H_2O molecules in the surface. To the best of our knowledge, this experimental investigation was one of a very few^{101,102} to measure the kinetic energy of the desorbing molecules upon photon irradiation of ices of astrophysical interest. There remain exciting challenges ahead of us in studying, both experimentally and theoretically, the partitioning of energy into translational, rotational and vibrational degrees of freedom of the photodesorbed species, and how the excess energy can affect the low temperature chemistry in the gas phase of dark clouds.

Finally, the work of Thrower *et al.*^{99,100} also highlighted the potential importance of wavelengths longer than 200 nm when considering photo-processes in unsaturated, conjugated and aromatic molecules. Indeed, the wavelength dependence of astrophysically relevant radiation fields have an overall higher intensity between 200 - 600 nm than at shorter wavelengths (100 -200 nm).¹⁰³

3.4 Radiolytic Interactions: Highly Efficient Electron-promoted Desorption of Small Molecules from Solid Water

Regardless of the growth mechanism of the icy shell coating interstellar grains, observations clearly confirm that H_2O is the dominating chemical species in the solid phase ISM.¹⁰⁴ Therefore, once the diffuse clouds evolve into dense molecular clouds, grains have accrued a thick water-rich mantle. From a physicochemical point of view, it is well known that the three dimensional network of molecules constituting solid H_2O possesses a rather unique feature: a strong intermolecular interaction, namely hydrogen-bonding (H-bonding), that affects both macroscopic and microscopic properties in comparison to other simple molecular solids (*e.g.* CH_4 , CO).

Recent experimental investigations have highlighted how H-bonding is intimately intertwined with the efficient capability of solid H_2O in propagating non-thermal excitations through the ice itself, particularly from the bulk to the vacuum interface.^{28,29,105} The case study is the irradiation of layered binary ices of ASW topped with benzene (C_6H_6) using electrons in the range of 100-350 eV. The results show an efficient non-thermal desorption mechanism (electron-promoted desorption, EPD), for C_6H_6 from solid H_2O . Regarding these experiments, one should recall that $C_6H_6-H_2O$ complexes have been shown to display two different types of hydrogen bonds. In fact, the aromatic molecule can act either as a hydrogen bond acceptor or as a hydrogen bond donor. In the former case, the π -electron density interacts with the OH group of H_2O , while in the latter case the C_6H_6 molecules bind with the lone pair of the O-atom, via a CH···O interaction.^{28,105–115} Therefore, the C_6H_6/H_2O system is a convenient model for the far more complex (in composition) water-dominated interstellar icy mantles. However, such simplification (of using binary ices) is necessary to probe the processes occurring solely at the ASW/C_6H_6 interface and the transportation of excitations from the depths of the water bulk to the C_6H_6 (or vacuum) interface. In both cases, H-bonding plays a key role. It is important to stress that analogous experiments looking at C_6H_6 on a bare aSiO₂ surface result in negligible EPD. This intimately links efficient EPD with H_2O and the H-bonding network in the solid H_2O . Further evidence of this important conclusion and its implications for the icy mantle growth of interstellar grains will be reported later on in this section.

Assuming first-order kinetics for the EPD process, a typical EPD trace²⁸ is shown in Figure 5, where the experimental data (black full circles) is fitted by a bi-exponential function (solid blue line) that explicitly contains two desorption components:



Figure 5: C_6H_6 EPD signal obtained for 5 L of C_6H_6 on 11 nm (100 L) thick c-ASW. The experimental data are represented by black closed circles while the solid blue line is the result of fitting a two component decay model to the data as described in the text. Decay time constants are displayed in plot. Irradiation was conducted with 250 eV electrons and initial beam current of 180 nA. Reproduced from reference 28 with permission of the PCCP Owner Societies.

$$I(t) = I_1 e^{-\sigma_1 \phi_1 t} + I_2 e^{-\sigma_2 \phi_2 t} + I_\infty$$
(6)

here σ_i are the desorption cross-sections in cm² for the fast (i = 1) and slow (i = 2) component, I_i is the corresponding amplitude, and I_{∞} is the residual.

In order to understand the physical meaning of the two components, a series of electron irradiation experiments was performed for ASW/C₆H₆ ices as summarised in Figure 6. In all cases, first a compact film of amorphous H₂O was deposited on top of a silica substrate at *ca*. 110 K which was then capped with C₆H₆. The binary system was subsequently bombarded with electrons while the QMS was employed to detect desorbing aromatic molecules during the irradiation. In panel A, the thickness of the ASW under-layer is kept constant to a thick film regime while C₆H₆ exposure is progressively increased (0.5 L, 5 L, 50 L, 200 L) from a sub-monolayer to the multilayer regime.²⁸ The observed desorption trace is shown to change significantly depending on the overlayer thickness as clearly displayed by Figure 7.



Figure 6: Cartoon summarising the EPD experiments for ASW/C_6H_6 ices by changing: the C_6H_6 coverage (panel A); electron energy (panel B) and the thickness of the H₂O underlayer (panel C).





Figure 7: C_6H_6 EPD traces for (i) 0.5, (ii) 5, (iii) 50 and (iv) 200 L of C_6H_6 adsorbed on a thick c-ASW film. The ices were irradiated with 300 eV electrons with a beam current of 100 nA. Traces are offset for clarity with the dashed lines showing the zero lines for each. The desorption signal for 200 L is significantly reduced compared to the low coverage experiments. Reproduced from reference 28 with permission of the PCCP Owner Societies

As a relatively thick film of C_6H_6 (e.g. 200 L) accrues on top of the ASW ice, the desorption trace decreases significantly in intensity and the observed profile matches that observed with for bulk C_6H_6 on bare $aSiO_2$.^{28,105} This supports the hypothesis of the key role played by the c-ASW film in driving desorption of the aromatic molecules. In other words, the H₂O ice is a necessary substrate to observe the efficient desorption of the C_6H_6 molecules. Below the thick benzene film regime (e.g. 50 L), the typical observed desorption trace displays two components, each with particularly large cross-sections. A fast component (σ_1), with a cross-section up to 10^{-15} cm² can be attributed to desorption of isolated C_6H_6 molecules that are hydrogen-bonded to small clusters of water molecules on the ASW surface. This process is more evident in the low coverage experiments (e.g. 0.5 L). A slower component (σ_2), with a cross-section of ca. 10^{-17} cm², is attributed mainly to C_6H_6 desorption from larger C_6H_6 islands on the solid water surface, which is more relevant at intermediate coverage (≥ 5 L).

At intermediate exposures, where C_6H_6 forms islands, some molecules will still be Hbonded to the icy substrate leading to observations of both the fast and the slow desorption components. It follows that the latter does not only contain the contribution to the signal from C_6H_6 desorbing from multilayer C_6H_6 , but might be enhanced as a result of the islands disrupting, morphological changes within the ice. It is possible that non-thermal diffusion of islanded C_6H_6 towards the dangling OH at the interface can also intensify the desorption yield during the irradiation.

Panel B in Figure 6 represents another set of experiments investigating the energy dependence of the EPD decay profiles, and hence how the desorption cross-sections varies with the energy of the primary electrons (100 eV, 150 eV, 200 eV, 250 eV, 300 eV, 350 eV). The study concludes that the cross-sections of the two components remain relatively constant in that energy range.¹⁰⁵ However, irradiation of a 10 L C₆H₆ film on c-ASW at higher energies (250 eV, 300 eV, 350 eV) results in the growth component in the desorption profile at around 50-70 s and delaying of the slow component (see reference 105). A subsequent study²⁸ has linked this effect to morphological changes within the H₂O ice at these higher electron energies. When the electron energy is at its highest, amorphisation of the H₂O/vacuum interface is accompanied by disruption of the C₆H₆ islands producing more C₆H₆ H-bonded to the c-ASW surface which contributes to the rising signal in the profile and delays the slow desorption component.

Finally, in panel C (Figure 6), the C_6H_6 exposure is kept constant at 5 L while the thickness of the underlying c-ASW ice is varied. In this situation, the observed desorption profile at 250 eV remains unchanged in the range of the H₂O doses explored (70 L, 100 L, 200 L, 500 L). This confirms that the observed phenomena are not associated with the substrate on which the c-ASW is deposited on.²⁸

The mechanism that has been proposed is based on previous electron irradiation experiments of H₂O ices and on optical-absorption and electron-energy-loss spectroscopy (EELS) of solid and liquid water.^{116–123} The primary electrons, employed in the above discussed experiments, possess sufficient kinetic energy that the incident beam is transmitted, almost unaffected, through the entire C₆H₆ film for low and intermediate exposures (up to 50 L) reaching the bulk of the H₂O ice. Here a cascade of electronic excitations, ionisation events and secondary electrons results from inelastic scattering of the primary (and secondary) electrons with the water molecules. These cascade processes are compatible with electronic excitations of the O-atom lying at 8.7 eV, 10.4 eV and at 14.5 eV^{116,121,123} and result in the formation of long-lived excitons in the bulk of the c-ASW film. Most importantly, the extended three-dimensionality of the H-bonding network within c-ASW provides a transportation route for the excitons over large distances (potentially tens of nm) from the bulk to interfaces. Whereas the relatively weak H-bonding between C₆H₆ and ASW allows the excitation to be transferred to the aromatic ring *via* dangling OH groups and/or exciton

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relaxation and excitation of the hydrogen bond followed by desorption.

In conclusion, the observed EPD seems to be peculiar for adsorbates interacting with the H_2O surface via H-bonding. Further evidence supporting this hypothesis was obtained in a follow-up EPD experiments employing methanol (CH₃OH) and diethyl ether (CH₃CH₂OCH₂CH₃) ices rather than c-ASW as substrates.^{28,29} The decreased extent of the H-bonding network (or its absence as for CH₃CH₂OCH₂CH₃/C₆H₆ ices) limits the propagation of excitons from the bulk to the substrate/C₆H₆ interface. Therefore, only the outer CH₃OH layers could potentially promote the C₆H₆ desorption efficiently. Thus, it comes as no surprise that these experiments show that C₆H₆ EPD from CH₃OH or CH₃CH₂OCH₂CH₃ is a minor process with respect to the analogous system of ASW/C₆H₆ (Figure 8). Data originally published in reference 29 have been re-plotted and shown in Figure 8.



Figure 8: Comparison of the C_6H_6 EPD traces from solid H_2O (left panel), CH₃OH (central panel), and CH₃CH₂OCH₂CH₃ (right panel). The signal is significantly decreased, although still observed, when the substrate underlying the 5 L of C_6H_6 is made of C-containing molecules. These results support the idea that a three dimensional H-bonding network propagates the O-centred excitations within the ice, while introducing methyl (CH₃) and ethyl (CH₂CH₃) groups bring additional electron-rich centres capable of being excited by the primary and secondary electrons which channel this excitation to favour other processes over exciton migration and desorption. Cartoons visually show the efficiency of the proposed mechanism for the three ices. Data have been re-plotted from reference 29 with permission of the PCCP Owner Societies.

The cartoons in each plot highlight how, even assuming exciton formation in the CH_3OH and $CH_3CH_2OCH_2CH_3$ ices, the decreased extent of the hydrogen-bonding network limits the propagation of the excitation energy to the C_6H_6 over-layer promoting C_6H_6 desorption. Different mechanisms can be attributed to the observed signal for CH_3OH/C_6H_6 and $CH_3CH_2OCH_2CH_3/C_6H_6$ systems. A more detailed discussion can be found in the provided references.^{28,29}

On the basis of these data, the relevance of efficient EPD from ASW surfaces in the ISM can now be discussed. Clearly, as the icy mantles on ISM dust grains consist primarily of H_2O , non-thermal desorption of small molecules bound to the ice surface *via* a dangling OH group is entirely feasible given the presence of cosmic rays and other ionising radiations in relevant regions. However, two issues have to be addressed: (i) how the above reported laboratory results are appropriate for consideration in an astrophysical context, and (ii) what species could more likely be involved in such context.

Electron irradiation experiments can simulate the secondary electron flux forming subsequent to ionising radiation with interstellar ices. This statement is reasonable when one considers the differential cosmic ray flux for protons in the energy range 1-10⁶ MeV nucleon⁻¹ in the interstellar medium, ¹²⁴ which displays a relatively flat distribution between 1-100 MeV with a maximum around 40-50 MeV. In this energy range, the ions will deposit most of their energy in the ice through electron scattering events. ²⁸ These interactions produce an ionisation track within the mantle which is rich in secondary electrons having energy distributions in the low energy tail overlapping with the electronic excitation of condensed H₂O.^{125,126} In a similar fashion (inelastic scattering followed by ionisation), an analogous flux of secondary electrons to that associated with cosmic rays can form subsequent to irradiation with the primary electron beam used in the experiments as reported above. The recent work by Herbst and co-workers reinforces the importance of this type of radiation-induced physics and chemistry.¹²⁷

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The aforementioned EPD experiments were conducted using C_6H_6 which is not known to be particularly abundant in the ice of the ISM. However, it has been observed in the gas-phase through its ν_4 bending mode at 674 cm⁻¹.¹²⁸ Moreover, the recent detection of benzonitrile $(C_6H_5CN)^{129}$ in the ISM strengthens the idea that, although elusive, C_6H_6 -like molecules and polycyclic aromatic hydrocarbons (PAHs), are indeed present. It should be noted that, when the abundance of benzonitrile is computed in the cold-core Taurus Molecular Cloud 1 (TMC-1), the column density is smaller than that detected by nearly a factor of 4. However, the same model predicts abundances of cyanopolyynes that match the observations within a factor of 2. The authors explain this mismatch by stating that their model does not take into account cosmic-ray driven chemistry in icy grains, although for "such grain-surface processes to contribute to gas-phase abundances, there must exist efficient non-thermal desorption mechanisms".¹²⁹ In regards of this conclusion, the electron irradiation experiments of C_6H_6 could well support the idea that C_6H_5CN can also undergo the same processes with a similar high cross-section as for C_6H_6 . Thus, the EPD experiments could provide the missing route to liberate solid-phase synthesised species (e.g. C_6H_5CN) into the gas-phase provided they are weakly bound to the ASW surface via H-bond interactions.

A previous study on electron irradiation of CH₃CN on c-ASW using IR spectroscopy resulted in an EPD cross-section with a consistent value (10^{-17} cm^2) to that reported for the slow (second) component observed for C₆H₆ on c-ASW (σ_2). Unfortunately, the RAIRS experiment cannot probe fast processes, and hence measure the cross-section corresponding to the fast-decay in the EPD profile (σ_1). However, it still provides an important window on the long timescale processes where penetration of the electrons deep into the bulk solid, exciton transport and reaction product diffusion are important.¹³⁰ This result corroborates the intriguing idea that the exciton-driven mechanism, observed in the electron irradiation of ASW, can lead to non-thermal desorption of any small molecule sitting on top of the icy shell as long as there is a relatively weak intermolecular interaction (H-bonding) between adsorbate and ASW substrate. It follows that this might be the case of an abundant molecule like CO. The current view of the interstellar icy mantles pictures a CO layer on top of the ASW inner layers. Therefore, CO bound to H_2O could be ejected into the gas-phase by an efficient EPD process. Clearly, an additional efficient desorption step might potentially delay the mantle enrichment in CO, and hence its hydrogenation products including the formation of methanol (CH₃OH) and in turn, of other organic molecules.

As published elsewhere,²⁸ it was possible to tentatively estimate the rate constants for both EPD and PSD processes of isolated CO molecules (sub-monolayer and monolayer) Hbound to ASW in cold, dense objects. The resulting ratio between the two rate constants, k_{EPD}/k_{PSD} , suggests that the fast EPD process would be about one order of magnitude more efficient than PSD in returning CO to the gas phase in such environments.

A consequence of this is that in a cooling environment CO deposition is slowed on the water surface compared to the more weakly binding $aSiO_2$ surface as the latter does not exhibit the highly efficient EPD seen on an ASW surface. This is illustrated by the toy model calculations reported in the Section 4 of this article.

The presence of an additional efficient desorption channel influencing the gas-grain interchange cannot be ignored and should be taken into account for more realistic astrochemical models. However, this would benefit from further laboratory data. To date, the vast majority of electron/ion irradiation experiments on interstellar ice analogues focus on the chemistry induced upon exposure to ionizing bombardment;^{131–136} fewer look at the desorbing species.^{137–140} It is even rarer to see both processes compared, as in the work of Abdulgalil *et al.*¹⁴¹ This study reports that ion/electron induced chemistry is dominant in those environments where the ices are relatively thick (hundreds of layers thick), while EPD is significant when ices are thinner, which is the case as diffuse clouds transition to being dense clouds when reactive accretion has not yet reached a steady state.

3.5 Radiolytic Interactions: Efficient Hydrogen Production from Hydrogenated Carbon-containing Molecules

The efficiency of the C_6H_6 EPD from ASW, with respect to C_6H_6 EPD from CH₃OH and from CH₃CH₂OCH₂CH₃ surfaces with progressively decreasing degree of H-bonding in the substrate film, was discussed above. This work prompted a further question. What other processes are favoured over C_6H_6 desorption for organic substrates? Electron irradiation experiments on binary, layered ices comprising C_6H_6 on the three substrates were repeated while desorption of other species was monitored. The results, although preliminary, clearly show that electron-induced chemistry (EIC) leads to the formation of H₂ competitively with (in the case of H₂O) or dominating over (in the case of the organic substrates) C_6H_6 desorption.¹⁴² Indeed, H₂ formation and desorption are common processes to the three systems but are clearly more significant for organic-based ices than in ASW. Briefly, this remarkable difference can be addressed by considering the presence of electronic excitations localized around the C atom *versus* those involving the O atom, with the former favouring reactive routes. These results, along with work from other groups, ^{104,143,144} highlight two open challenges in astrochemistry:

- 1. the need to fully understand the distribution of products (branching ratios) of photonand charged-particle-induced physics and chemistry; and
- 2. the importance of looking at the nature of the species leaving the surface and not simply at what remains on and in the ice if we are to incorporate these processes into astrochemical models.

Consistency with what is known of the radiolysis of liquids and vapours^{145,146} would suggest that H/H_2 production is likely to be an important process in photolysis and radiolysis of both simple (*e.g.* water-rich) and complex (*e.g.* containing complex organic molecules; COMs) ices, ^{133,147–149} which leads to the question as to what extent does the formation and desorption of H/H_2 can contribute to hydrogen recycling in the ISM? At the early stages of dense cloud formation, gaseous H is depleted onto grains to form H_2O , NH_3 , and CH_4 by reacting with O, C and N atoms. Later, irradiation of these simple molecules as icy mantles accrue would promote EIC. On one hand, this yields radicals and enriches the ice in COMs but, on the other, seems to return H_2 to the gas phase, leaving residues that will potentially become increasingly unsaturated and with time probably aromatic. If this conclusion was to be confirmed, the formation and enrichment of the solid phase of conjugated systems will push the absorbance spectrum into the visible region, opening up, in turn, new channels for non-thermal desorption and photochemistry of other species interacting with the aromatic ring. Further experiments are required to reinforce these intriguing speculations.

4 Astrophysical Implications

Depending on the temperature and the nature of species involved, the mobility and diffusion of these species in the solid state may be possible on interstellar dust grains, as discussed. It is important to realise the consequences of the presence of binding energy distributions driving the gas adsorption on the ice. Differences in desorption energy reflect differences in adsorption sites. If a molecule is known to diffuse and to desorb from multilayers, then such molecules will behave differently to molecules known to desorb from the monolayer. Binding energies can therefore have a direct impact on how icy films are grown on a dust grain. The desorption behaviour of CO on dust grain surfaces and H_2O has been mentioned in the previous section and from the information therein reviewed Figure 9 can be made.

With H_2O present in clustered environments in the form of islands, bare dust grain surfaces will be available. As the surface temperature decreases while the dust grain travels toward denser regions of dust clouds, gas-phase CO (black curve) will begin to adsorb. The



Figure 9: The upper panel shows the number of CO molecules per unit of area (molecules cm^{-2}) in the gas phase (black line), adsorbed on water ice (red line), and adsorbed on $aSiO_2$ (green line) as a function of time (years). As the time increases, the temperature decreases. This is shown in the lower panel (blue curve). The labels a, b and c highlight three main stages of the simulation: an initial situation when the temperature is *ca.* 30 K and CO is mainly found in the gas-phase (a), the subsequent CO-freeze out due to the cooling down to *ca.* 10 K (b), and rearrangement and evolution of the system in isothermal conditions due to non-thermal desorption (c).

resulting kinetic model can be presented as below:

$$CO(g) \to CO_{SiO_2}(s)$$
 (7a)

$$CO(g) \to CO_{H_2O}(s)$$
 (7b)

$$CO_{H_2O}(s) \xrightarrow{\text{heat}} CO(g)$$
 (7c)

$$CO_{SiO_2}(s) \xrightarrow{\text{heat}} CO(g)$$
 (7d)

$$CO_{H_2O}(s) \xrightarrow{h\nu} CO(g)$$
 (7e)

$$\operatorname{CO}_{\operatorname{SiO}_2}(\mathrm{s}) \xrightarrow{h\nu} \operatorname{CO}(\mathrm{g})$$
 (7f)

$$CO_{H_2O}(s) \xrightarrow{e^-} CO(g)$$
 (7g)

In this toy model, we take into account:

- the parallel adsorption kinetics of CO on both ASW and aSiO₂ (Eq. 7a; Eq. 7b) the rate of which is simply determined by the gas temperature in Z_W (as defined in Eq. 1), with both species having a sticking coefficient of 1 (though the accommodation coefficient is determined by the balance of adsorption and desorption);
- 2. CO thermal desorption from both ASW and $aSiO_2$ surfaces using the most probable binding energies of 12 kJ mol⁻¹ and 8 kJ mol⁻¹ respectively³⁷ (Eq. 7c; Eq. 7d) assuming 10^{12} s⁻¹ for the pre-exponential factor. No account is taken for the distribution of the adsorption energies and there is no diffusion of either CO and H₂O built into this toy model. However, earlier in the text, an independent model for H₂O diffusion suggested agglomeration on a timescale of a few 1000s of years (Figure 4) leaving areas of $aSiO_2$ bare and directly accessible by other species such as CO. Therefore, this conclusion justifies the choice of considering adsorption-desorption mechanisms for CO and $aSiO_2$ in our simple model.
- 3. Furthermore, the simulation accounts for non-thermal desorption driven by VUV pho-

tons (Eq. 7e; Eq. 7f) and by secondary electron excitations (Eq. 7g) produced by cosmic ray interactions. The former was assumed to be temperature and substrate independent with a rate of 4.2×10^{-16} s⁻¹. This value was obtained by multiplying the yield of the process⁸⁷ (1.8×10^{-2}) by photon absorption cross-section for CO in the VUV range¹⁵⁰ between 120 nm and 160 nm (4.7×10^{-18} cm²), and by the estimated VUV flux in dense clouds, which is dominated by the emission from H₂ excited by cosmic rays, that is typically about 5×10^3 photon cm⁻² s⁻¹.^{124,151} The EPD CO rate was set to be 4.5×10^{-15} s⁻¹ as discussed in our previous work on C₆H₆/ASW,²⁸ and being active through a mechanism that takes place only for solid H₂O substrates and not for aSiO₂ surfaces in order to reflect that there is no evidence of exciton transport in the latter system. This may be an extreme assumption, which has been proven for C₆H₆^{28,105} but needs to be tested experimentally for CO.

As can be seen from this simple model, at first the temperature is too high for CO to efficiently adsorb on the icy grain (black curve, label **a** in Figure 9 and Figure 10), then, as the temperature drops below 30 K, CO will adsorb on both solid water (red curve, label **b** in Figure 9) and bare silica (green curve, label **b** in Figure 9).



Figure 10: Cartoons showing three limiting situations summarising the laboratory findings as discussed in the text. In panel a the grain surface temperature is too high for CO to condensate, but cold enough to have islands of water ice forming on top of the silica substrate that represents the grain. The cartoon in the middle (panel b) shows the CO freeze-out on top of ASW preferably than on top of $aSiO_2$ surfaces as the temperatures drops. Once the system is at 10 K the non-thermal desorption mechanisms drive the relocation of CO from the top of the ASW islands to the silica surface leading to the situation where $aSiO_2$ is predominantly covered by CO with respect to ASW, as shown in panel c.

From TPD data^{15,37,41,152} we know CO forms a full monolayer on solid H₂O and SiO₂ before a multilayer growth commences because binding sites for CO-H₂O are preferred over CO-CO and over CO with $aSiO_2$. Thus, CO will begin to grow on H_2O islands in these simple models while only 10% of CO adsorbs onto the bare silica surface (label **b** in Figure 9 and Figure 10). Interestingly, EPD and PSD of CO seem to have no notable effect at earlier times (and at higher temperatures than 10 K) in this simple model. This was tested by a control simulation with EPD and PSD channels switched off. However, non-thermal desorption becomes significant at later times, during the isothermal stage at 10 K of our simulation, (indicated by label \mathbf{c} in Figure 9) by favouring the depletion of CO from solid H_2O with respect to $aSiO_2$ surfaces, which are in turn covered by icy CO (label c in Figure 10). It is important to stress that the aim of presenting this simple toy model is not to replace far more elaborate existing models, but to highlight how experimental findings can challenge and further our understanding of the interstellar icy grain structure while exploring the physics of these systems and homing in on the future key laboratory experiments. For instance, a catalogue of how molecules interact with H_2O islands compared to dust grain surfaces, combined with their diffusion properties would provide a fuller picture of how icy mantles grow. Such a catalogue could also be used to determine the surface temperature of dust grains with sub-monolayer quantities of catalogued species. Determining if, e.g., CO is present solely on the H₂O surface would mean the dust grain temperature is hotter than if CO is found on bare dust grain surface.

5 Conclusions

The key results reported in this work can be summarized in the following bulleted list below.

 De-wetting, agglomeration and segregation of molecules on the cold surfaces of interstellar grains are important processes shaping the structure of the icy mantles. For simple systems, experimental evidence and literature reports of H₂O de-wetting the Page 39 of 61

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dust grain surfaces is reported. How might these observations be extrapolated to the range of potential grain surfaces that we might find in the interstellar medium? We would argue that the consistency of the agglomeration behaviour observed on silica and graphite in our work would suggest that similar behaviour would be expected for all substrates that show evidence of de-wetting of H_2O . This would include, for example, PAH films, hydrogenated amorphous carbon (HAC) and other carbonaceous materials. There may, however, be differences in the agglomeration where the diffusion barrier of H_2O over the substrate are significantly larger than that we have measured. Although, this does not take account of reaction-enthalpy release during H_2O formation promoting "hot molecule" behaviour on the surface. As H_2O slowly aggregates to form icy mountains, patches of the siliceous and carbonaceous grain surface are left exposed. It follows that both the freeze-out of gas-phase formed molecules, like CO, and the reactive accretion starting from adsorbed atomic species occur on a surface that is chemically inhomogeneous, displaying a variety of possible adsorption energies. However, when these substrates are covered by a sufficient number of layers of H_2O to decouple the H_2O solid surface from that of the substrate, a few nm at most, the surface processing will be dominated by the surface behaviour of the H₂O ice.

2. Towards the inner core of molecular clouds, where the temperature is the lowest, non-thermal processes play an important role in changing the icy structure and composition. In particular, the experimental findings for PSD and EPD have been reviewed and reported, respectively. Perhaps the most noteworthy conclusion is that, regardless of the type of energetic processing at play, the non-thermal desorption mechanisms can be complex because what desorbs is not necessarily what was directly excited to begin with. This implies that the energetic conditions required for the initial excitation to occur depend on the chemical nature of the substrate. The intermolecular interactions are also extremely important in efficiently transferring this excitation to the upper layer and hence, to the adsorbate at the vacuum interface that will be ejected into the

gas phase.

- 3. Interestingly, CH₃OH, an organic compound, displays a low photodesorption yield as an intact molecule and is found to be considerably less efficient with respect to H₂O in transferring the initial excitation across the ice during EPD experiments. By contrast, chemical reactivity (*e.g.* EIC) over physical processes is favoured. This means that in those parts of the interstellar ices where the mantle is C-rich, energetic processing results in the formation of radicals, COMs, and dehydrogenated residues that might become increasingly unsaturated while returning H₂ to the gas phase. It is important to stress that this process can be competitive with the hydrogenation of the adsorbed species due to H atom addition from the gas phase.
- 4. Finally, on the basis of several assumptions as discussed in the text above, a simple model exploring CO adsorption and the evolution of CO surface coverage on top of an icy grain with surfaces of both ASW and aSiO₂ was constructed. Despite the approximate approach in our simulation, the results highlight how CO binds predominantly to one of the two surfaces depending on the temperature and on the efficiency of the non-thermal desorption for the two possible substrates.

For clarity, we propose a simple cartoon (Figure 11) picturing the main processes so far discussed: agglomeration of water, PSD and EPD of small molecules, EIC leading to dehydrogenation of organic molecules and H_2 formation.

We would like to conclude by highlighting the key concept underpinning this work: the importance of intermolecular interactions whether these are established between the grain surface (*e.g.* aSiO₂) and the adsorbate (*e.g.* CO) or between two different species (*e.g.* CO and H₂O). Molecular interactions drive the icy mantle accretion and its chemical evolution by affecting the photochemistry, stabilizing charged species^{72,73} and transferring the excitation to the vacuum interface. Future laboratory experiments are encouraged to test the



Figure 11: Cartoon showing: formation of water rich areas *versus* organic and CO rich regions on top of the grain core; EPD of small molecules adsorbed on ASW, PSD of small molecules such as CO and CO₂ on top from CO rich ices (2-3 layers are required for the DIET mechanism); dehydrogenation of organic molecules (EIC) leading to H_2 formation. H_2 release has been observed also in the electron irradiation experiments of water ices, and hence here represented as well.

assumptions made in this work and investigate the dynamics of the discussed processes by measuring the branching ratios and the partition of the energy into translational, vibrational and rotational energy for each desorption channel in play.

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Graphical TOC Entry



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Legend:

Organic/CO-rich ice



Grain surface