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From ice to gas : constraining the desorption processes of interstellar ices

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English summary

Ices in star-forming environments

Molecules are present throughout our universe. In the inter- and circumstellar medium, the highly dilute space in between and around stars, a wide variety of molecules have been observed ranging from diatomic species to organic molecules, large PAHs, ions and radicals. Studying their formation, and destruction pathways in the laboratory provides us with clues on the physical environment in which they are found. This constitutes one of the main goals in astrochemistry, the science that focuses on chemical processes in space.

Star-forming regions are typically composed of molecular gas and submicron-sized dust particles. In the cold regions such as prestellar cores, outer parts of protostellar envelopes and mid-planes of protoplanetary disks, molecules can form on or freeze-out onto dust grains, forming an icy mantle. The ice composition along the lines of sight of various star-forming environments can be inferred through mid-IR spectroscopy. Interstellar ice consists mainly of H₂O, followed by CO and CO₂ and also includes NH₃, CH₄, OCN⁻, CH₃OH. Even bigger organic species still have to be identified. The presence of molecules in polar and apolar ices and molecular abundance variations during the various stages of star formation provide valuable clues on their possible formation pathways. The focus in this thesis is on the physical and chemical processes that take place in interstellar ice, and their characterization through dedicated laboratory experiments.

Figure 8.4 presents a simple schematic summarizing the current understanding of how ices form and behave during star formation. Simple ices form at the prestellar stage through accretion of atoms and small gas phase molecules onto the grains. The main molecules that form at this stage are CO₂ and the hydrogenation products H₂O, CH₄, and NH₃. When the core gravitationally collapses to form the protostar, the temperature drops and molecules that were still in the gas phase, mainly CO, will freeze out on top of the first water-rich layer, resulting in an apolar mantle. During the protostellar stage, the newborn star feeds on its accreting envelope, resulting in a warm-up of the icy dust grains. This phase will see the formation of more complex species through heat-activated reactions and through the increase in mobility of rad-

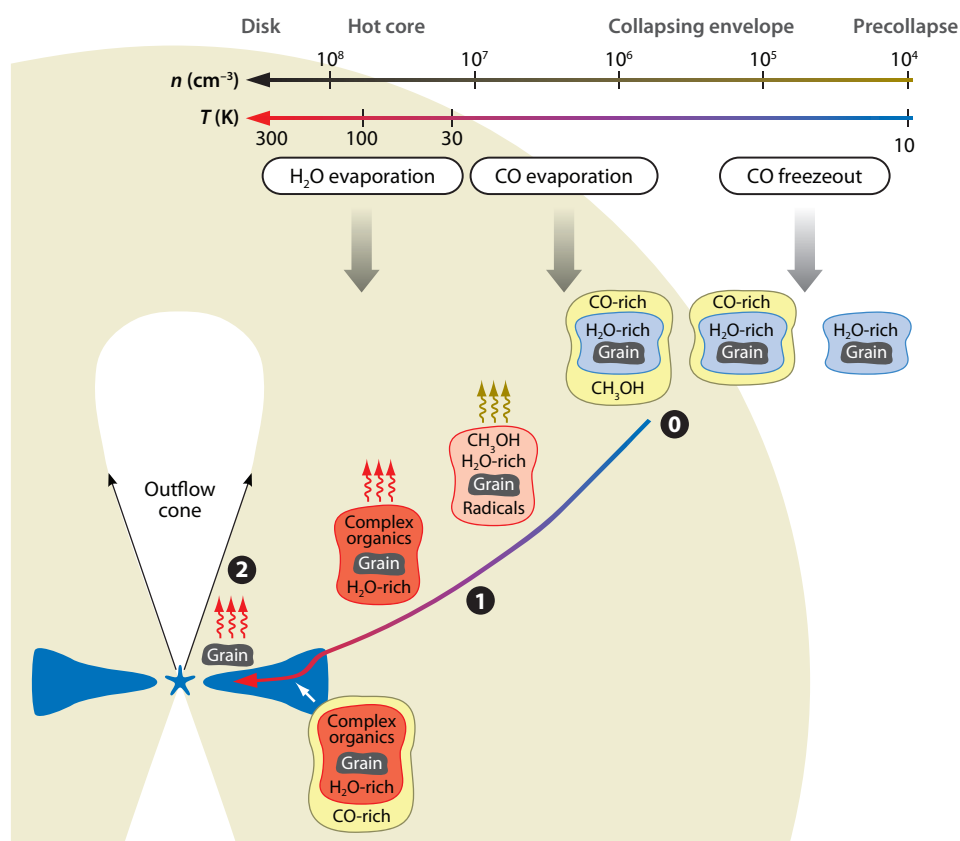


Figure 8.4: Cartoon representation of the ice evolution from the prestellar stage through the collapsing envelope into a protoplanetary disk. The prestellar stage will see the formation of the first H₂O-dominated ice mantles, followed by gas-phase freeze-out during cloud collapse, forming a CO-rich mantle. The icy-grains will undergo hydrogenation, heat and UV activated reactions in the protostellar phase while flowing towards the star. Most of the icy mantle will evaporate when grains reach the 100 K regions, giving rise to an active hot-core chemistry. Alternatively some of the icy grains will flow into the mid-plane of protoplanetary disks where planets and comets are formed and become incorporated into these bodies. Figure by E. van Dishoeck and R. Visser.

icals created by energetic reactions. The icy grains are also subject to sublimation as they get closer to the star. The relationship between ice composition and observation of complex organics around high-mass protostars is the subject of chapter 7. Around $T = 100$ K, most of the molecules sublime into the gas phase and participate in gas phase reaction networks. Alternatively, some of the icy grains will flow to the protoplanetary disk. Molecules formed at previous stages are thus most likely at the origin of the molecular complexity as observed in planetary systems. In regions where thermal desorption does not occur, energetic particles and especially UV-photons can also induce ice desorption. This is the case in prestellar clouds, before the star is formed, in the outer parts of the protostellar envelope and in the mid-planes of protoplanetary disks.

Constraining thermal and non-thermal desorption processes is crucial to understand the gas-grain interactions in star-forming environments. Molecules in the gas phase are widely used by radio astronomers as tracers of physical conditions. Thus it is vital to understand the parameters - temperature, radiation fields, ice composition, etc - that govern the transition of molecules from the icy grains into the gas phase. From a chemical point of view, a good estimate of the ice and gas partitioning is crucial since chemical reactions are drastically different in both phases ; some daughter species may form in one phase more than in the other. The main goal of this thesis is to experimentally constrain the thermally- and photon-induced desorption processes under conditions that are relevant to the interstellar medium.

Thermal desorption of ice

Thermal ice desorption is a crucial process during the protostellar stage when the young star feeds through the infall of its envelope. The icy grains from the envelope warm up as they flow towards the star and molecules go from solid to gas-phase according to their binding efficiencies to the icy surface. Laboratory experiments simulating the sublimation of the ice mantle are used to understand how the desorption of interstellar ices occurs. Specifically, chapter 2 focuses on how H_2O , the main component of interstellar ices, affects the thermal release of more volatile ice components. $\text{H}_2\text{O}:\text{CO}_2$ ice mixtures of various thicknesses and ratios are grown on a cold substrate, mimicking the cold grain surface, and under ultra-high vacuum to simulate the density conditions encountered in star forming environments. The ice sample is then warmed up at a linear rate and desorbing molecules are monitored by a mass spectrometer with respect to the temperature. CO_2 in pure ice desorbs around 70 K, but when it is mixed with H_2O , only a certain fraction will desorb at 70 K. The rest desorbs around 140 K together with the water molecules. It is this 'trapping' phenomenon that is captured in chapter 2 through an extended 3-phase model of the ice (see figure 8.5).

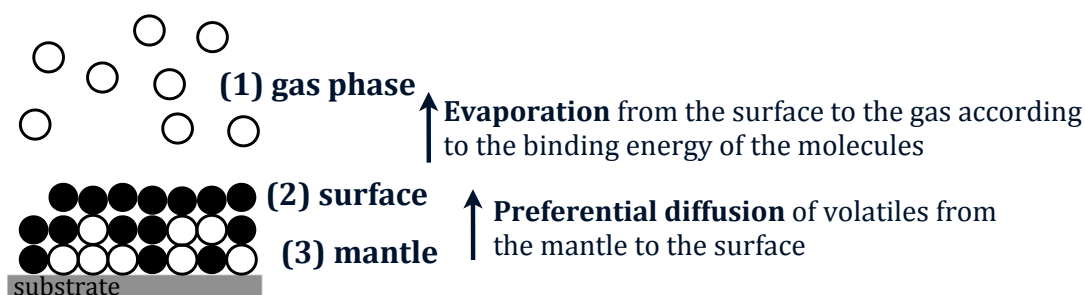


Figure 8.5: Principle of the 3-phase desorption model for volatiles (open circles) in water-rich ice (full circles). Desorption of molecules to the gas phase occurs from the surface according to the binding energy of the molecules and mantle molecules replenish the surface after each desorption event. The replenishment depends on the ability of molecules to diffuse from the bulk to the surface and is more favorable for volatile species since these are less bound to their surroundings.

The laboratory experiments are used to constrain the migration of volatile molecules from the mantle to the surface of the ice. This process is not statistical and instead depends on molecule specific diffusion in water matrix. Using this model, the amount of volatile species trapped within the water can be predicted for various ice thicknesses, mixing ratios, and warm-up rates typical for protostellar environments. Coupling this model to current gas-grain simulations allows for a better estimate of the ice to gas partitioning and thus improve the understanding of both the solid-state and gas-phase chemistry in protostellar environments.

Photon-induced desorption of ice

In cold regions where molecules are expected to totally freeze out, some of them are still observed in the gas-phase due to non-thermal desorption processes. For instance, non-thermal desorption induced by UV photons has been invoked to explain these molecular abundances in protoplanetary disks. Laboratory experiments have been performed to measure the efficiency of photodesorption and investigate its mechanism. Most photodesorption studies so far used an H₂ microwave discharge lamp to induce desorption as it mainly produces Lyman-alpha radiation. The emission profiles of these lamps is, however, very sensitive to the experimental conditions and thus the measured photodesorption efficiencies may depend on the lamps specific emission profile.

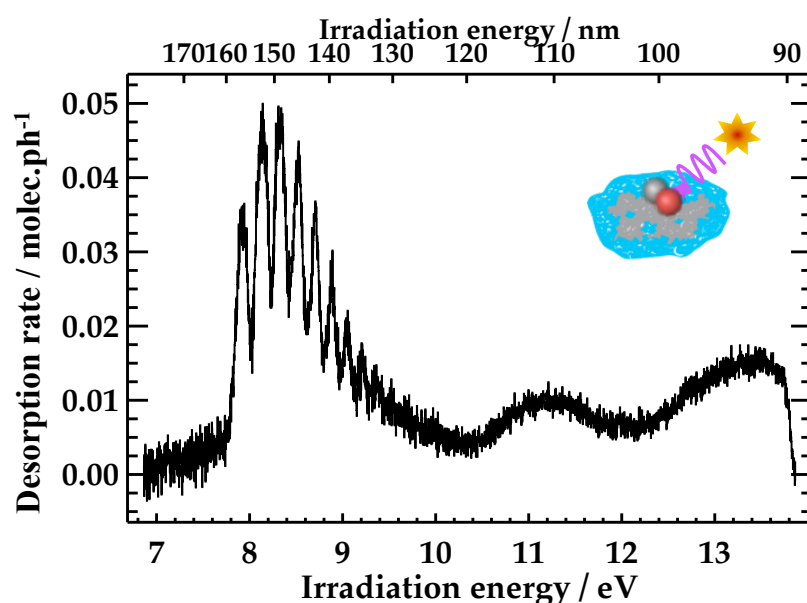


Figure 8.6: CO photodesorption spectrum for a 10 ML ice at 18 K. The vibrational progression below 10 eV correspond to excitation of the non-dissociative A¹Π state of CO.

Instead, a new approach used in chapters 3 to 6 relies on the use of tunable Vacuum-UV synchrotron-radiation to study the photodesorption of interstellar ice analogues. The DESIRS beamline at the SOLEIL synchrotron (Saint-Aubin, France) provides photons in the astrophysically interesting 7 - 14 eV spectral window at good flux and resolution to monitor photodesorption efficiency with respect to the incoming photon

energy. Such studies yield quantitative photodesorption rates for a wide energy range, which contributes to a better estimate of the photodesorption over different regions of space where UV fields can have various profiles. But more importantly, such a frequency resolved analysis of photodesorption provides valuable insights on the underlying molecular mechanisms. This is exciting from a physical-chemical point of view and also helps to incorporate this process into gas-grain astrochemical simulations.

The photodesorption of CO ice has been investigated first since CO is a rather well understood molecule and because CO-rich ice is found at the surface of interstellar grains (see figure 8.4). CO ice samples are grown under ultra-high vacuum at 18 K and then irradiated by photons which energy is ranging from 7 to 14 eV. The desorbing molecules are monitored by mass spectrometry with respect to the irradiation energy and yield the photodesorption spectrum presented in figure 8.6. The clear wavelength-dependence of photodesorption is due to the electronic structure of the CO ice; it is a Desorption Induced by Electronic Transition (DIET) process (chapter 3). Using isotopically-labeled layers of $^{12}\text{CO}/^{13}\text{CO}$ and the slight difference in energy observed for the vibrational levels of the excited state of the two isotopologues, it has been possible to go deeper than ever before in the understanding of this photodesorption process. It is found that the electronic excitation of molecules in the sub-surface induces a transfer of energy to the surface where it triggers their desorption (chapter 4). N_2 photodesorption mainly occurs in the same way as for CO below 10 eV. In the case of O_2 , the VUV irradiation induces dissociation in the 7 - 14 eV window and the photodesorption mechanism becomes much more complex since oxygen radicals can induce additional kick-out events, recombine, or induce chemistry affecting the photodesorption channels (chapter 5). In addition, non-dissociative photodesorption mechanism has been investigated for two distinct species in mixed iced: CO and N_2 . Understanding photodesorption for ice mixtures is crucial since interstellar ices are mostly mixed. Even though the photo-absorption spectra of the two species in the solid phase are completely different, their photodesorption spectra are the same when irradiating a 1:1 mixture. These similar desorption profiles are due to the electronic excitation of one specific species and subsequent energy transfer to the surface molecules, regardless of their nature. This has important astrophysical consequences as the photodesorption rates do not only depend on the nature of the species but also on the molecular environment. The exact nature of the energy transfer still remains an open question which will hopefully be answered in the coming years through laser spectroscopy of the desorbing species and measurement of ice fluorescence during irradiation. Finally, the photodesorption mechanisms of organics still have to be investigated, which is challenging, mostly because of the complex role of the radical created upon irradiation. Experimentally constraining the desorption of organics and observing it in the interstellar medium provides a fantastic tool to probe the chemical complexity of interstellar ices. This would definitely be a topic of future work.

