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

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Introduction

Molecules are found throughout the universe.

The discovery of molecules in space opened up a window to the chemical complexity of the interstellar medium, enabling us to explore the embedded phases of star and planet formation as well as address the origins of life on Earth and maybe elsewhere in the universe. Indeed, since life as we understand it is molecular in nature, finding organic molecules in space and more specifically in regions where stars and planets form, prompts questions about the development of life elsewhere. The molecular inventory in the interstellar medium, the processes leading to molecule formation, stability and delivery to planetary bodies are thus key questions that astrochemists are answering through a combination of observations, simulations, and laboratory experiments. The presence of icy mantles on interstellar dust grains play a key role in the formation and observation of molecules at every stage of the star-formation process. It is the ice evolution through processes encountered in space and their link with the presence of observed organic species in the gas phase that this thesis addresses.

1.1 Interest for molecules in space

A great diversity of chemical species can be found in the interstellar and circumstellar media, going from atoms, simple diatomic molecules, to large carbon edifices like fullerenes, radicals and ions¹. The first evidence for the presence of molecular species in space were unidentified optical-UV interstellar lines that had no corresponding atomic signature (Merrill 1934). These lines have later been identified as electronic transitions of the CH and CN radicals (Swings & Rosenfeld 1937; McKellar 1940). Since then, more than 200 molecular species, including isotopologues, have been detected in outer space through their rotational, vibrational and/or electronic transitions. Their identification through their emission and/or absorption features are used by astrochemists to probe the physics of the environment in which they are found. Temperature, density, kinematics and energetic fields all have an impact on the molecular energy levels population and their line shape, making these molecular species useful tracers of conditions encountered in star-forming environments.

Chemicals are used to trace the physics but they also contribute to the physical processes. Molecules are efficient coolants in the interstellar medium that are necessary to

1. See http://en.wikipedia.org/wiki/List_of_interstellar_and_circumstellar_molecules for a complete list and references.

form stars as we know them. During the gravitational collapse of dense clouds inducing the formation of a protostar, the gas pressure increases and the gas temperature should rise due to the frequent collisions of atoms and molecules. The heating of the collapsing cloud poses a dilemma: since the heated gas wants to expand, the cloud collapse could be stopped or even reversed. Molecules found in the cloud gas play thus a significant role as they can effectively transport energy outside of the cloud through collisional excitation followed by radiative de-excitation, producing photons that can escape. The photons carry this energy away thus allowing the cloud to collapse. Dominant molecular coolants include CO, O₂, H₂O (e.g. Goldsmith & Langer 1978; Neufeld et al. 1995; Goldsmith 2001).

From an astrobiological point of view, the discovery of molecules in space, and especially the complex ones has changed society's view on the origins of life, seeding the idea in people's mind that life on earth may have emerged from interstellar molecules and that our solar system might not be the only planetary system harboring a rich chemistry in the universe. Molecules are observed at every stages of star formation and complex ones are expected to be present in disks where planets and comet form. It is thus likely that they are incorporated into planetary bodies during their formation (Ciesla & Sandford 2012). Studying the chemical processes in star-forming environments and understanding the origin of molecular complexity would thus provide clues on the ordinary nature of our life-hospitable solar system.

1.2 Ices in the interstellar medium

1.2.1 The need for an ice - gas connection

Organic molecules are often associated with hot-core/corinos regions observed around high and low-mass protostars, respectively. Molecules like CH₃OH, CH₃CN, CH₃OCH₃, CH₃CHO, H₂CO, HCOOH, CH₃CH₂OH, or CH₃CH₂CN are typically observed through their rotational emission in these regions where densities are higher than 10⁷ cm⁻³ and temperatures above 100 K (e.g. Blake et al. 1987; Cazaux et al. 2003; Fuente et al. 2005). If ion-neutral reactions can explain the presence of molecules like CO, CS and small hydrocarbon chains in the interstellar medium (Herbst 1997), the high abundance of complex species in core regions around young stellar objects at relatively early stage of their formation requires other explanations since reactions rates are too low (Horn et al. 2004; Geppert et al. 2006). In addition, a fraction of these species are deuterated at levels that defy explanations by gas phase reactions alone (e.g. Ceccarelli et al. 2001; Parise et al. 2006). Ice-covered dust grains found in star-forming environments, do allow us to successfully explain these observations however, since they can act as catalyst for surface reactions.

1.2.2 The presence of ices

Submicron-sized dust grains are widely found in the interstellar medium and present distinguishable absorption features in the infrared and emission features in the submillimeter. They are composed of carbon, silicates, PAHs (e.g. Draine 2003) and are the remnants of stellar death. In the dense clouds where young stars form, they

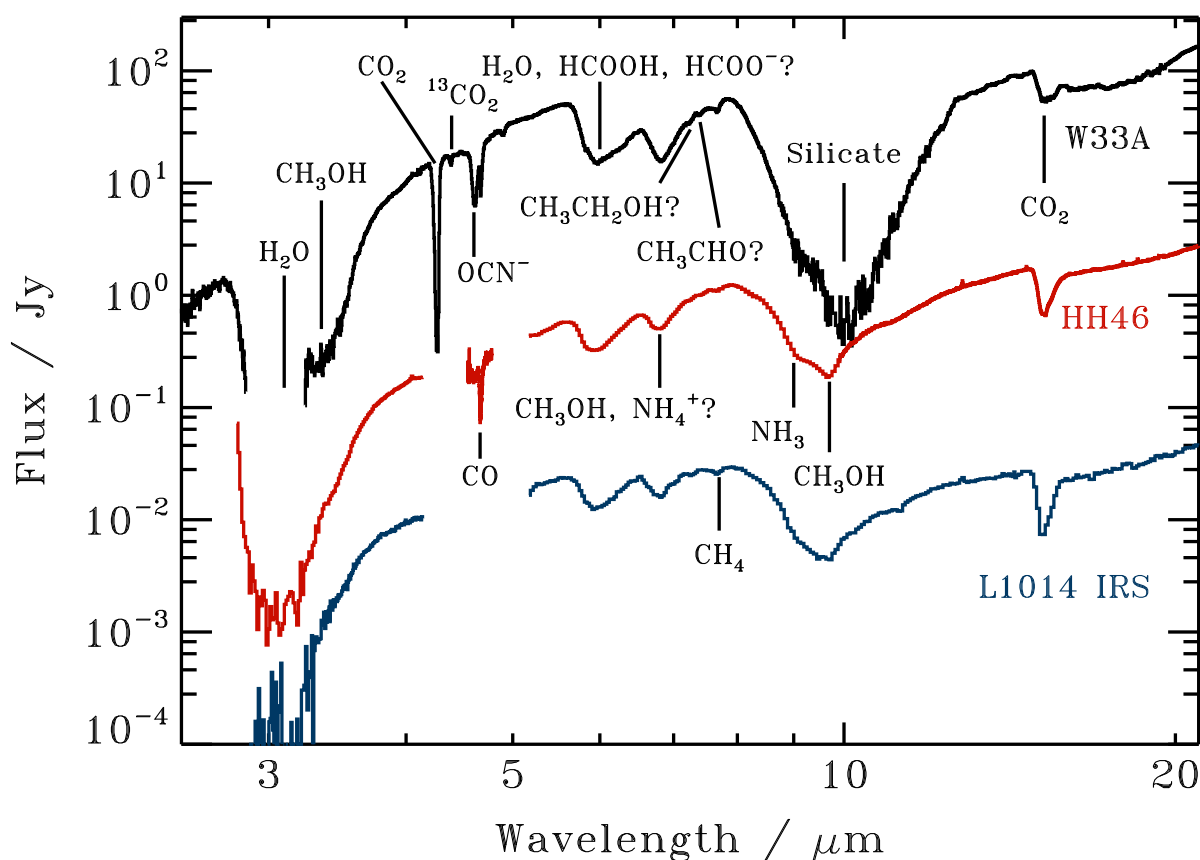


Figure 1.1: Infrared Space Observatory (ISO) spectrum acquired by the Short Wavelength Spectrometer (SWS) of the star forming region W33A, HH46, and L1014 IRS, covering the 2.5 to 20 microns region. A variety of ice mantle and refractory grain core features are evident.

account for 1% of the cloud composition ; the rest of the matter consists of gas, mainly H_2 . It is on the surface of these dust grains that most molecules will form or freeze-out in the cold regions of molecular clouds.

The hypothesis of the dust grains catalyzing molecule formation has been proposed very early on by van de Hulst (1949), who suggested that the molecular abundances should be directly related to the elemental abundances. Even though the gas grain interplay induces a more complex chemical inventory, the contribution of molecule formation mediated by the grains has been confirmed and adopted with the observation of condensed molecules along the lines of sight towards protostellar environments. The first observational evidence was the detections of solid H_2O , identified through its O-H stretching vibration at 3.08 microns (Gillett & Forrest 1973; Merrill et al. 1976). During the following decades, careful observations of ice features have been successful in identifying NH_3 , CO , OCN^- , CH_4 , CH_3OH among others as well as the presence of mixed components hinting for parent-daughter molecular relations or similar formation mechanisms. The atmospheric lines, however, prevented comprehensive surveys for ice from ground-based facilities. Breakthroughs on the relative ice mantles compo-

Table 1.1. Abundance medians^a and lower and upper quartile values of ices and individual ice components with respect to H₂O ice (Öberg et al. 2011a).

Ice Feature	Low Mass	High Mass	Background
H ₂ O	100	100	100
CO	38 ₂₀ ⁶¹ (29)	13 ₇ ¹⁹	31
CO ₂	29 ₂₂ ³⁵	13 ₁₂ ²²	38 ₃₂ ⁴¹
CH ₃ OH	7 ₅ ¹² (3)	8 ₈ ¹⁶ (4)	8 ₇ ¹⁰ (4)
NH ₃	5 ₄ ⁶	16 ₁₀ ¹⁷ (5)	...
CH ₄	5 ₄ ⁷	4 ₂ ⁴ (2)	...
XCN	0.6 ₀ ^{0.8} .2 (0.3)	0.8 _{0.4} ^{1.4} (0.6)	...
Pure CO	21 ₇ ³⁶	3 ₂ ⁶	...
CO:H ₂ O	13 ₇ ¹⁹	10 ₅ ¹²	...
CO:CO ₂	2 ₁ ³	1.3 _{0.4} ^{1.6} (0.3)	...
Pure CO ₂	2 _{0.3} ⁴	2 ₁ ²	...
CO ₂ :H ₂ O	20 ₁₅ ²³	9 ₆ ¹⁵	24
CO ₂ :CO	5 ₄ ⁷	5 ₂ ⁶	6
CO ₂ shoulder	0.8 _{0.4} ^{1.1}	1 ₁ ²	...
OCN ⁻	0.4 _{0.3} ^{0.4} (0.2)	0.6 _{0.4} ^{1.4}	...

Note. — ^a Values in parentheses include upper limits in the median calculation using survival analysis.

sitions have been obtained with the space-based Infrared Space Observatory (ISO) and its Short-Wavelength Spectrometer (SWS) instrument, allowing for spectral acquisition in the entire 2.5 - 45 microns window where vibrations of condensed molecules are intense. This survey investigated in a comprehensive way the ice abundances found along the lines of sight of intermediate to high-mass protostars (Dartois 2005, Gibb et al. 2004, and references therein). Examples of ice spectra are shown in figure 1.1 for three different interstellar regions. The ice composition is derived by subtracting the emission background due to the emitting YSO (or background star) and fitting the ice features with laboratory spectra for which the associated band strength is thus known (available for example in the Leiden data base for ice²). A follow-up ice composition survey around low-mass protostars environments and in pre-stellar cores have been realized using the Spitzer space telescope and its InfraRed Spectrometer (IRS) 5 - 30 microns (Boogert et al. 2008; Pontoppidan et al. 2008; Öberg et al. 2008; Bottinelli et al. 2010; Öberg et al. 2011a).

The typical ice compositions along the line of sight derived from all of the available ice surveys and for the various environments are presented in table 1.1 (Öberg et al. 2011a). H₂O, CO, and CO₂ are the main ice components along the line of sight of most objects. The other ice components generally found are NH₃, CH₄, CH₃OH and XCN. Interstellar ices are far from simple since some of the molecules are found in pure

2. <http://www.strw.leidenuniv.nl/lab/databases/databases%202007.htm>

phase, in water-dominated (polar) and/or in water-poor (apolar) ice phases. Moreover some of the absorption features cannot be unambiguously attributed to a single species due to the intrinsic broadness of vibrational features in the solid phase and because of the overlap in vibrational frequencies of molecules presenting similar chemical functions. Comparing the ice composition variation and abundances between star-formation stages and low- and high-mass protostellar environments provided information on the formation of the ice components and processes accompanying the ice evolution across star-formation. These findings are developed in the following subsection.

1.2.3 Ice evolution during star formation - ice sublimation affects the chemistry

A cartoon depicting the current understanding of ice evolution during star formation is presented in Fig. 1.2. At the prestellar stage, before the star is formed, molecules like H_2O , CH_4 , NH_3 form at the surface of the grain through atomic and small molecule collision and diffusion on the grains. The formation of CO_2 together with H_2O at the prestellar stage is consistent with CO_2 observed mainly in a polar environment (Knez et al. 2005). When the cloud gravitationally collapses to form the star, the temperature decreases and molecules that were initially in the gas phase freeze-out on top on the H_2O -rich layer. Since the main species to deplete at this stage is CO , an apolar layer will form on top of the already present polar ice mantle (Pontoppidan et al. 2003). At this early stage the dominant chemical reaction occurring on ices is hydrogenation since the regions are cold and deeply-embedded in the dark cloud, preventing efficient UV penetration. The hydrogenation of the CO -rich ice top layers will result in the formation of more complex species like H_2CO and CH_3OH (e.g. Tielens & Hagen 1982; Watanabe & Kouchi 2002). The observed amount of CH_3OH is in good agreement with model predictions based on CO hydrogenation schemes (Pontoppidan et al. 2003; Cuppen et al. 2011).

At the protostellar stage, the newly formed star will grow from the collapse of its envelope, inducing changes in the ice composition. The heat induced by the star will lead to thermal reactions mainly activated by diffusion within the solid. Moreover the UV radiation resulting from the interaction of cosmic rays with H_2 gas will induce in the ice a very rich chemistry since the radicals created will diffuse and react to form more complex species (Garrod & Herbst 2006; Garrod et al. 2008). In addition to the chemical changes, the icy grains will undergo sublimation induced by the protostar heating and energetic particles, which will affect the chemistry occurring on both the grains and in the gas phase. In warm regions close to the protostar where $T > 100$ K, most of the ice material on the grains sublimates into the gas phase, leading to a rich gas phase chemistry activated by the higher temperatures and densities (e.g. Charnley et al. 1992).

Some of the grains may not reach the 100 K sublimation zone but instead, follow a trajectory where they are incorporated into a disk forming around the protostar (Visser et al. 2009). In this disk, the temperatures encountered are such that ices can survive in the middle plane. The icy material will be processed by the UV and X-ray photons coming from the central object, as well as by possible vertical mixing, resulting

in ice sublimation, freeze-out cycles, and inducing a complex ice structure and composition that is yet to be understood. The dust grains in the disk coagulate to form planetesimals and some of the ice material may end up in the planets, satellites, and comets of mature planetary systems (Okuzumi et al. 2012). Understanding the evolution of the icy mantle composition and in particular the presence of complex molecules would provide valuable insights into the incorporation of prebiotic molecules during the planet and comet formation process.

1.2.4 Testing the ice to gas link

Molecules observed in the gas phase in star-forming environments are tightly linked to the physical and chemical processes occurring in the solid state. According to Herbst & van Dishoeck (2009), the formation of organics species of 6 or more atoms, so called complex organics, could either result from 1) reactions on grains through atomic bombardment during the prestellar stage and early protostellar stage (0th generations of organics), 2) energetic processing and / or heat-activated chemistry creating a the 1st generation of organics, 3) sublimation of the precursor from the ice and formation of 2nd generation of organics in the warm and dense gas-phase through neutral-neutral or ion-neutral reactions (see Fig. 1.2). In all cases, the ice composition should be linked to the observed organics in the gas phase, provided that other factors such as UV-fields are not drastically influencing the organic chemistry in the gas-phase. The presence of an ice - gas link could validate the organic formation scenario presented above but is yet to be confirmed. The small number of sources having both ice observations and gas-phase observation prevented until now the search for correlations between gas-phase organics and parent species in the ice. Chapter 7 presents new insights on how to extend this number of sources and provides tentative ice-gas correlations.

Since part of the ice organic content will end-up in planet forming regions, it is important to understand the details of this organic chemistry and particularly where the different species are formed and how. It is, however, very difficult to observe organics in the solid state due to confusion between their broad vibrational features ; the features cannot thus be unambiguously attributed to a single species. Instead, one must rely on gas phase observations where lines are quite distinct. Spatially resolved observations together with a careful analysis of the molecule excitation conditions can provide good constraints on the classification of organics into 0th, 1st, and 2nd generation as the first two will be found in the cold gas phase due to possible non-thermal desorption and the 2nd generation will only be present in the warm gas phase close to the protostar (see Fig. 1.2).

Observational constraints on the spatial location of organics and excitation conditions can be used to test chemical models predicting abundances and evolution in the ice and gas phase. Such detailed gas-grain models, require, however a good understanding of the molecular physics in the ISM. If data on gas-phase processes are mostly available, processes occurring on the grains are difficult to include in models since reaction rates, diffusion, sublimation mechanisms and efficiencies are yet to be fully constrained. It is the main goal of this thesis to investigate gas-grain processes in order to support astrochemical models.

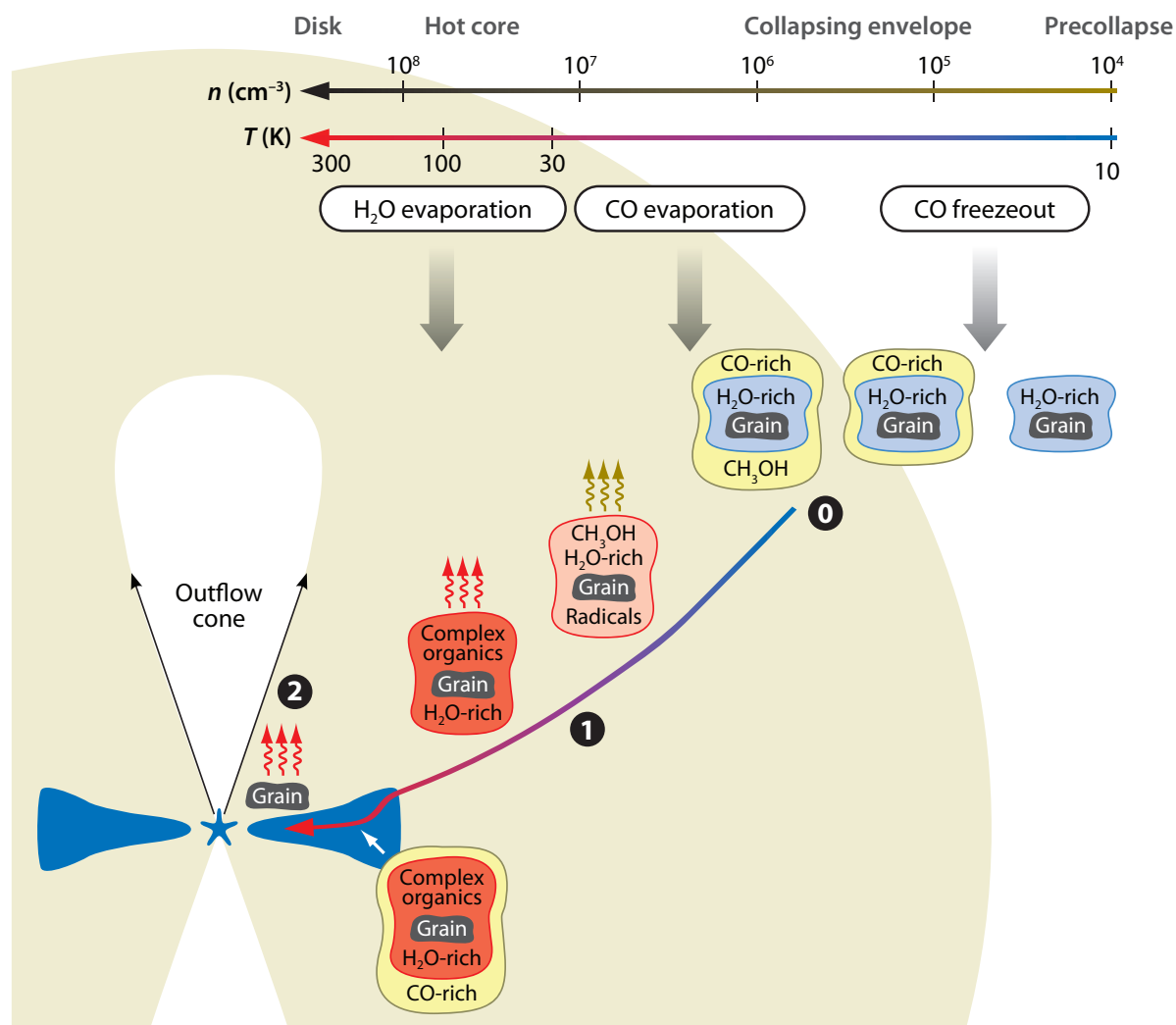


Figure 1.2: Cartoon representation of the ice evolution from the prestellar stage, through the collapsing envelope, and into a protoplanetary disk. The prestellar stage will see the formation of the first H₂O-dominated ice mantle, followed by gas-phase freeze-out during cloud collapse, forming a CO-rich 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 sublimate when grains reach the 100 K region, giving rise to an active hot-core chemistry. Alternatively some of the icy grains will flow in the mid-plane of protoplanetary disks where planets and comets are formed, and the grains will be incorporated into their composition. Stages where 0th, 1st, and 2nd generation of organic molecules form are indicated. Credit E. van Dishoeck and R. Visser.

1.3 Ice sublimation in the laboratory

Ice sublimation plays an important role in the chemical evolution of star forming regions as it regulates the amount of species able to participate in the chemistry on the

grains or in the gas phase. The state in which molecules are found also provides valuable information from a physical point of view as it depends on the density, temperature, radiation conditions of the medium. Different kinds of sublimation can be distinguished: thermally-induced, photon-induced, electron-induced, high-energy particle induced (sputtering) and chemically-induced. If all of these mechanisms can trigger ice desorption to a certain extent, some of them will dominate in different regions of the ISM. The thermally-induced and UV-photon induced desorption are developed in this thesis.

1.3.1 Thermal desorption of ices

Thermal desorption of ices is the sublimation process that dominates the gas-grain interactions during the protostellar stage where the envelope collapses onto the newly formed star. The icy grains flow towards the young star and the ice mantles are warmed up. This will induce thermal desorption of the ice into the gas phase according to the binding energy of the desorbing molecules onto the surface. The thermal desorption process depends highly on intermolecular interactions and on the kinds of desorbing sites. Thus one molecular component in mixed interstellar ice is very unlikely to desorb at only one single temperature. It is not straightforward to model the desorption process in astrochemical simulations since ice parameters such as molecular composition, ice thickness, internal arrangement, must be taken into account in addition to the physical parameters of the warm-up.

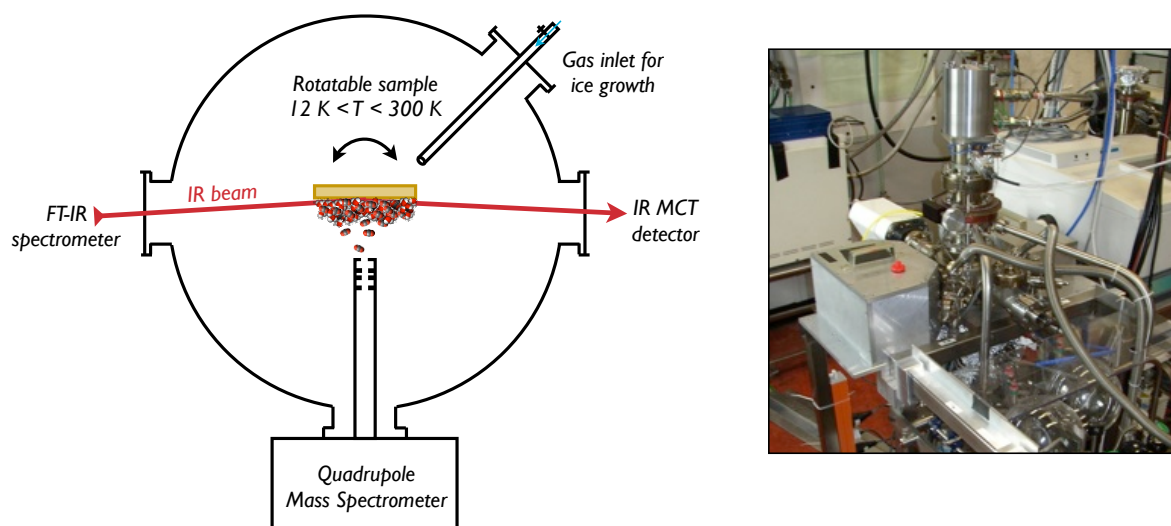


Figure 1.3: The CRYOPAD experiment from the Sackler Laboratory for Astrophysics used to perform the thermally-induced desorption experiments presented here.

Fortunately laboratory experiments based on surface science techniques can provide insights on thermal desorption mechanisms that icy grain undergo. Most of the experiments performed in this respect are done by means of Ultra-High vacuum experiments, like the set-up CRYOPAD (CRYOgenic Photoproducts Analysis Device) devel-

oped by Fleur van Broekhuizen in the Sackler Laboratory for Astrophysics in Leiden (See figure 1.3). In this low pressure environment ($\sim 10^{-10}$ mbar, $\sim 10^7$ particles per cm^{-3}), a gold sample cryogenically cooled can reach temperatures as low as ~ 12 K. Molecular ices can be grown with monolayer precision onto the sample by injecting pure or pre-mixed gas into the chamber through a capillary tube perpendicular to the sample. A heater can regulate the temperature and warm-up the sample. For the study of ice desorption, the Temperature Programmed Desorption (TPD) technique is used and consists of linearly warming-up the ice sample. The rates employed here fall between 0.5 and 5 K min^{-1} but TPD rates vary from groups to groups according to the literature. The molecules desorbing from the ice into the gas phase can be detected in CRYOPAD by Quadrupole Mass Spectrometry (QMS, model Balzers QMA 200) and Reflection Absorption InfraRed Spectroscopy (RAIRS) using a Fourier transform infrared (FTIR) spectrometer over the $4000 - 900 \text{ cm}^{-1}$ region. The infrared set-up is also used to quantify the ice thickness and ice loss during warm-up. Following the desorbing molecules from the ice (or the ice loss) with respect to the temperature provides insights on their binding energies and desorption mechanisms. These information are further incorporated into kinetic models that can be run under astrophysical warm-up time-scales, in the order of few Kelvin per century.

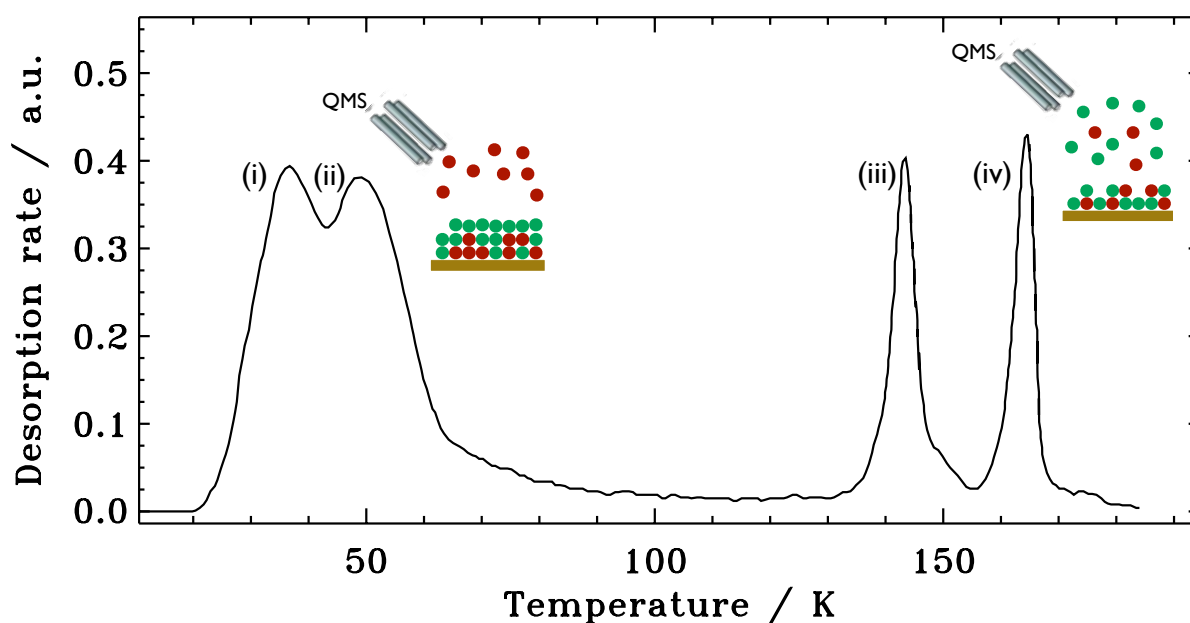


Figure 1.4: Desorption of CO from water-rich ice monitored by mass spectrometry. The four CO desorption peaks originate from (i) desorption from CO rich surface, (ii) H_2O rich surface, (iii) desorption during H_2O phase change, (iv) co-desorption with H_2O . The cartoons show the QMS detection of CO at low temperature and CO trapped with water. CO is depicted as the red species and H_2O as the red species.

Since the main component of interstellar ices is water, the thermal desorption study of molecules mixed in a water matrix is very relevant for protostellar environments

(Viti & Williams 1999). Collings, Brown, Barnun, Kimmel, among others, studied the desorption characteristics of such systems through TPD (Burke & Brown 2010). In the case of volatiles species like CO mixed with water (see for example TPD profile in 1.4), desorption of CO molecules mixed in a water matrix can occur from (i) CO surface, due to possible diffusion and segregation of volatile component to the top of the ice, (ii) from mixed CO-H₂O surface, (iii) volcano desorption during H₂O ice phase change from amorphous to crystalline, and (iv) co-desorption with H₂O. The first two release mechanisms occur around the desorption temperature of pure CO ice (starting around 30 K) while the last two occur in temperature regions where H₂O desorbs. There is thus a clear difference between the volatile material that desorbs at low temperature and the rest that stays trapped within the water ice until its desorption. This last "trapped" fraction of molecules will stay longer on the grains and can participate in surface chemical schemes while the species released at lower temperature are available for gas phase reactions (Viti et al. 2004). Quantifying and predicting the amount of volatile material that stays trapped within the water ice under astrophysical condition is thus a crucial for a good estimation of the protostellar chemical evolution and will be addressed in the chapter 2 of this thesis through laboratory experiments and modeling.

1.3.2 Non-thermal desorption induced by UV photons

In interstellar regions where the temperature is low but UV photons are present, sublimation of molecules can occur through non-thermal processes driven by UV-photons. This non-thermal desorption process can be responsible for the presence of cold gas in environments where molecules should be frozen out onto dust grains. Thus it regulates the ice-gas balance (Hollenbach et al. 2008). In particular, Willacy & Langer (2000); Dominik et al. (2005); Oka et al. (2012) among others showed that this mechanism was necessary to explain H₂O observation in protoplanetary disks. The photon distribution in star-forming environments (See Fig. 1.5) has different origins: 1) photons from the InterStellar Radiation Field (ISRF) generated by surrounding stars can penetrate the first layers of molecular clouds depending on their density (Mathis et al. 1983), 2) in inner regions shielded from the ISRF, it is the interaction of cosmic rays with H₂ that generates a local UV field composed of the Lyman and Werner photon series (e.g. Gredel et al. 1987), 3) when the protostar turns on, it will also emit UV photons that may reach the ice and 4) in protoplanetary disks, the accretion of material onto the protostar will generate a UV field dominated by Lyman- α and other characteristic emission lines (Bergin et al. 2003). These typical profiles will be altered through gas absorption and dust scattering as the photons travel to the ice regions and radiative transfer codes are necessary to predict the exact UV profiles inducing photodesorption (Guzmán et al. 2011; Fogel et al. 2011).

The photodesorption process has been studied in the laboratory and efficiencies for the main ice components have been quantified. The first detailed study that provided photodesorption rates for the interstellar medium was published by Westley et al (1995a,b) on pure H₂O ice. They found a strong dependence to the ice temperature, thickness and photon dose. To derive a photodesorption rate, they used an

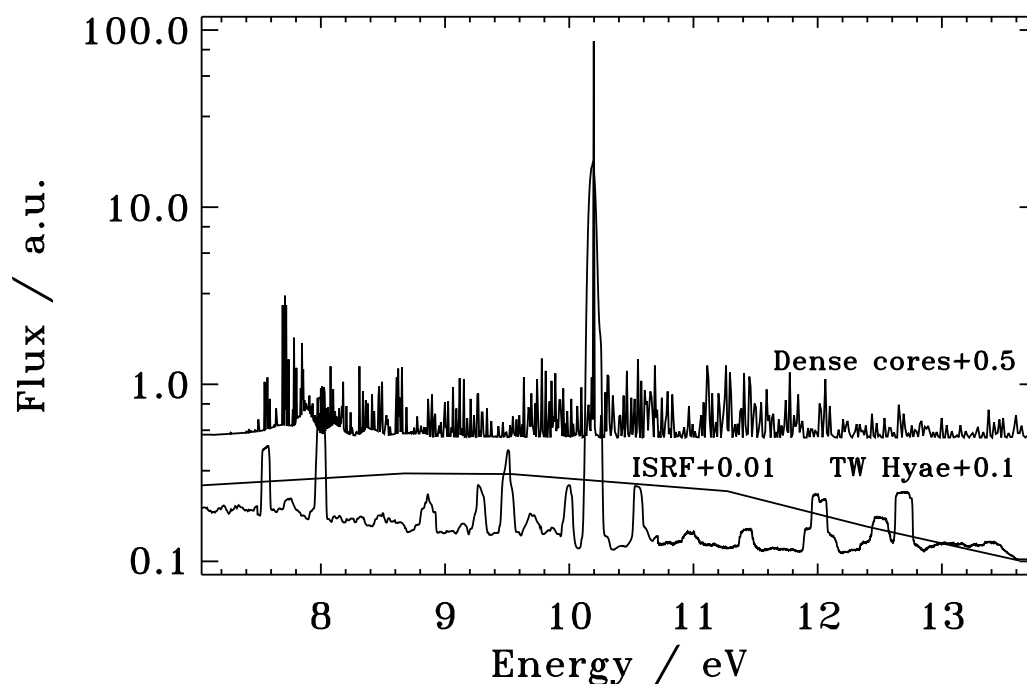


Figure 1.5: Characteristic UV fields encountered in the ISM. The dense cores spectrum is derived by Gredel et al (1987), the ISRF by Mathis et al (1983) and the protoplanetary disk TW Hydrae by Herczeg et al (2002), Valenti et al (2003) and Johns Krull & Herczeg (2007). The integrated area of each spectrum is normalized to 1 and offsets are used for clarity.

H_2 discharge lamp as the UV source, emitting mainly at Lyman alpha and a quartz microbalance to follow the ice loss. Their derived photodesorption rates are in the 10^{-3} molecules desorbed per incoming photons range, assuming that H_2O is the main species desorbing from the ice. Following studies on $\text{H}_2\text{O}/\text{D}_2\text{O}$ (Watanabe et al. 2000, Yabushita et al. 2009, Öberg et al. 2009b), CO (Öberg et al. 2007, 2009, Muñoz Caro et al. 2010), N_2 (Öberg et al. 2009), CO_2 (Öberg et al. 2009, Baragiola et al. 2012, Yuan & Yates 2013) confirmed the high photodesorption rates and investigated the various dependencies to the experimental parameters and the impact of photochemistry. Molecular dynamics simulations have also contributed to the microscopic understanding of the photodesorption process (Andersson et al. 2005, 2006, 2008, Arasa et al. 2010, 2011). For the case of CO ice, both Öberg et al. (2007, 2009) and Muñoz Caro et al. (2010) derived efficiencies that are temperature dependent but thickness and dose independent, hinting for a surface mechanism. For the absolute photodesorption values, the first study derived a rate in the 10^{-3} molecules photon $^{-1}$ range while the other derived a higher efficiency in the 10^{-2} molecules photon $^{-1}$. These values are still under debate but the discrepancy could be due to different UV irradiation profiles.

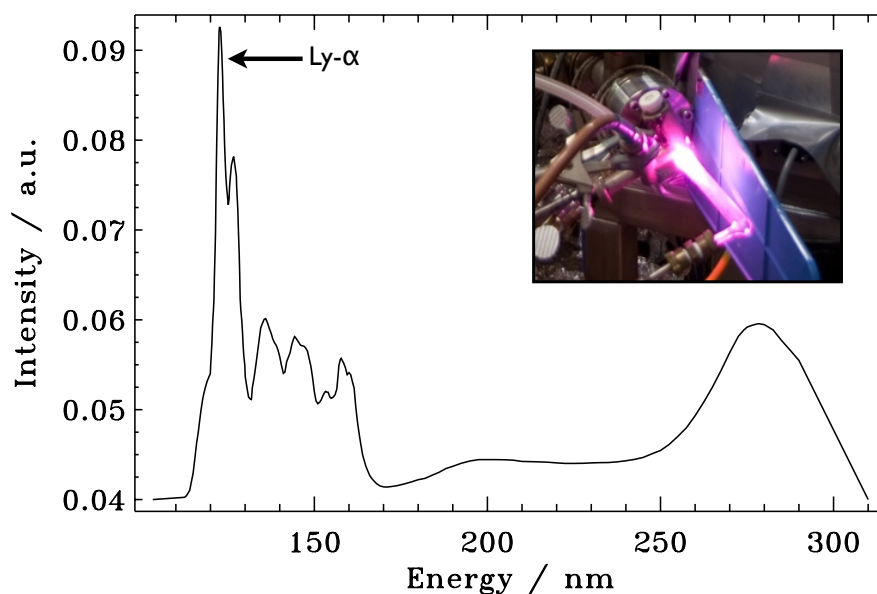


Figure 1.6: The emission profile of a broadband H₂ discharge lamp peaking at lyman alpha (Muñoz Caro & Schutte 2003).

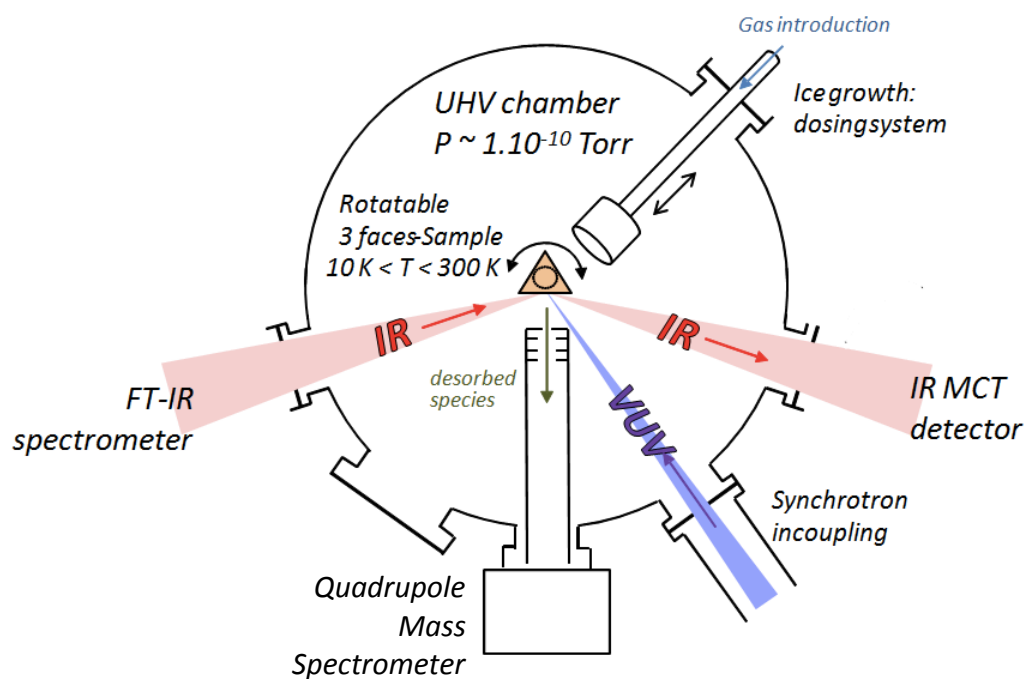


Figure 1.7: Schematic view of the set-up SPICES from the LPMAA used for the monochromatic irradiation of interstellar ice analogues at the SOLEIL synchrotron on the DESIRS beamline.

The UV energy distribution impacts on the measured photodesorption efficiency since it is the electronic excitation of molecules that induces the desorption. The pho-

photodesorption of interstellar ice analogues is traditionally studied in the laboratory using an H₂ microwave discharge lamp as source of UV photons. The set-up CRYOPAD described in the previous section is dedicated to the study of photo-processes using an H₂ lamp. Such a UV source, based on the excitation of H atoms, presents a flux high enough to induce processes that can be monitored on experimental time-scales. Figure 1.6 presents the spectrum of one of these lamps. It peaks at Lyman- α but other radiative features, in particular at 160 nm can come from the de-excitation of H₂. The spectrum profile is very sensitive to the conditions in which the lamp is used, namely H₂ pressure, microwave power, residual vacuum. Thus, a comparison of photodesorption efficiencies between experiments set-ups requires the knowledge of the lamp spectrum used for irradiation.

As an alternative to H₂ lamps, the impact of the photon energy on the ice photodesorption efficiencies and photodesorption mechanism are investigated using a tunable monochromatic light source in the VUV. The outcome of these frequency-resolved studies is presented in chapters 3 to 6 of this thesis. Successful proposals for beamtime on the DESIRS beamline at the SOLEIL synchrotron allowed us to study the photodesorption mechanism of CO, N₂, and O₂ ices using the set-up SPICES developed at the LPMAA in Paris (depicted in Fig. 1.7). The ultra-high vacuum chamber is equipped with a cryostat that can cool down a rotatable 3-face sample to temperatures as low as 10 K. Ices are grown on a polycrystalline gold surface or on Highly Oriented Pyrolytic Graphite (HOPG) at submonolayer precision using a retractable dosing line. The changes in the solid state can be monitored using RAIRS and desorbing species can be probed using a QMS. The set-up is directly coupled to the undulator-based DESIRS beamline and photon fluxes measured by calibrated photodiodes reach the 10¹⁴ photon s⁻¹ range without the use of a monochromator and reach the 10¹² photon s⁻¹ range with the monochromator. Only photons in the 7 - 13.6 eV spectral range are used since a minimum of about 7 eV is required to induce electronic transition in the species studied here and photons above 13.6 eV are absorbed by hydrogen in the ISM. It is the acquisition of calibrated photodesorption spectra that allows for the derivation of photodesorption rates with respect to the UV fields encountered in space and that provides insight into the photodesorption mechanisms of pure ices (chapters 3 to 5) and binary mixtures (chapter 6).

1.4 This Thesis

This thesis presents studies on processes bridging ice and gas-phase content for the interstellar medium. It first presents thermal desorption of water-rich ices and describes how volatile species stay trapped within the water at temperatures above their own desorption temperatures. This mimics the thermal heating that icy grains undergo during the protostellar stage. The bulk of the thesis focuses on desorption induced by UV photons as it likely occurs at the edges of molecular clouds, in prestellar cores, in the cold outer part of protostellar envelopes and mid-plane of protoplanetary disks. Synchrotron light providing monochromatic radiation in the VUV is used to derive wavelength-dependent photodesorption rates and elucidate the underlying mechanism. Finally, an observational method to test a possible ice to gas connection

around massive protostars is presented in the last chapter.

– **Chapter 2** addresses the question of how volatile molecules like CO_2 and CO desorb from the water-rich icy mantle when they are warmed-up as it would be the case during protostellar envelope collapse onto a protostar. Most models including this process assumed that each ice component would desorb at its own desorption temperature but when interacting with water, some of the volatile content can stay trapped within the water ice and desorb together with the water molecules at higher temperature. Temperature programmed desorption experiments are performed on ices of different thicknesses, volatile concentration, for different volatile components in water and for various heating rates in order to parameterize a model reproducing the volatile trapped fraction. The gas-grain model distinguishes three-phases: gas, ice surface and bulk. The desorption process occurs from the surface only and the surface is replenished by the mantle molecules, according to the enhanced diffusion of volatiles compared to water.

– **Chapter 3** presents the first wavelength-dependent investigation of ice photodesorption. The photodesorption of thin CO ice films is induced by VUV monochromatic light and the resulting photodesorption spectrum is obtained by monitoring through mass-spectrometry the desorbing molecules versus the photon energy. The photodesorption profile is tightly linked to the absorption spectrum of the ice, hinting for a Desorption Induced by Electronic Transition (DIET) process which does not involve the substrate.

– **Chapter 4** investigates in more detail the CO photodesorption mechanism. There, the photodesorption spectrum of CO is analyzed for different ice thicknesses and on different substrates, which confirms the ice-only related process and the independence to the ice thickness proposed in chapter 3. This implies a mechanism occurring in the top-most layers of the ice. The use of isotopically labeled ice layers of CO ($^{12}\text{CO}/^{13}\text{CO}$) unveiled the indirect character of photodesorption: it is the excitation of the sub-surface molecules that triggers the desorption of the surface species. The photodesorption of CO on water is also investigated and reveals that the H_2O internal structure can highly quench the photodesorption of top CO layers.

– **Chapter 5** focuses on the photodesorption of N_2 and O_2 , two diatomic species that are infrared inactive. N_2 photodesorption occurs in the same fashion as CO photodesorption: it is the electronic excitation that induces the desorption. For O_2 , the photodesorption mechanism is less straightforward since the UV irradiation can induce dissociation. The formation of oxygen radicals and ozone can lead to photodesorption in addition to the indirect process of importance for CO and N_2 .

– **Chapter 6** investigates the UV irradiation of $\text{CO}:\text{N}_2$ binary ice, which presents a first step in understanding the photodesorption of more astrophysically relevant ices. There the photodesorption of both species is investigated for the case of mixed and layered ices. The indirect mechanism found in the case of pure CO and N_2 ices is valid for binary ices. When mixed in equal proportions, both species desorb with the

same photodesorption spectrum, which is the co-addition of the single species photoabsorption spectra. This indirect mechanism where CO excitation can promote the desorption of N₂, even at wavelengths where N₂ is transparent, can explain the observed anti-correlation of cold CO and N₂ gas in prestellar cores. This study beautifully emphasizes the crucial role of the ice composition and structure, which must be taken into account when modeling photo-induced processes.

– **Chapter 7** explores the link between ice composition and gas phase observations of organics molecules around high-mass protostars. A link between the ice and organics in the gas phase should exist since most of the organics form in the solid state or through gas-phase reactions involving the evaporated ice molecules. Observationally testing this link is difficult due to the small amount of sources with both ice data and bright organic line detections, like in hot-cores. Here, observations of organics in sources that do not possess a bright core and have ice data available is attempted in order to increase the ice-gas source sample. The combination of single dish data and interferometric observations allows for the differentiation between organics present in cold protostellar envelopes and the warm compact regions close to the protostar. By combining results obtained previously for hot-core sources and our high-mass protostars sample, tentative correlations supported by a gas-grain model are presented. This study shows that it is possible to explore the ice-gas connection with more observations of both the ice and gas content around non-hot core sources.

