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UV Photodesorption and photoconversion of interstellar ices: the laboratory perspective

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1 Introduction

Until 1992, our knowledge about planets was limited to the nine planets (at that time) in our Solar System (Wolszczan & Frail 1992). Since then, our view of stellar systems has been revolutionized by detections of thousands of planets surrounding other stars. These exo-planets exhibit an incredible diversity, in terms of size, composition, and distance to their star, illustrated in Figure 1.1. The characteristics of these new distant worlds significantly defy the known extremities: gas giants larger than Jupiter, planets locked in permanent freeze or extremely hot rocky bodies with their surface covered in hot lava. Among these, are also planets which are Earth-like, with a similar rocky composition and a temperature allowing to sustain liquid water. This invites to revisit the questions asked since the dawn of times: is it possible that life originated on other planets as well?

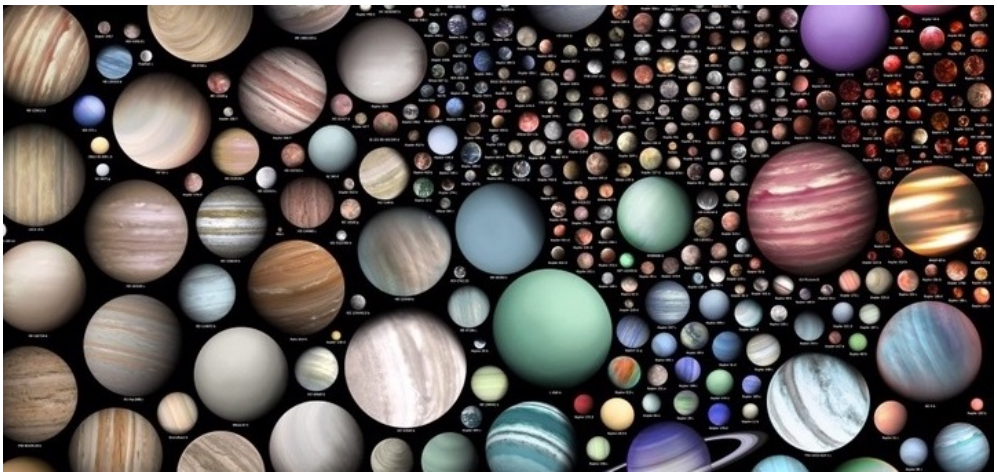

Figure 1.1: Diversity of worlds. Recreated with permission from the artist: Martin Vargic.

To address this question, it is important to understand the chemical evolution of matter during the process of star and planet formation. This process starts already in the large and highly dilute interstellar clouds that fill the space between stars. The subsequent formation of prestellar cores and protoplanetary disks ultimately results in the formation of a young stellar object surrounded by one or more newly born planets. More specifically, we need to understand how the physical conditions along this evolutionary track govern chemical processes that result in the molecular species that

are needed to create life, as we know it, e.g. small molecules like water, but also more complex organic molecules, like sugars and amino acids.

The interstellar medium (ISM) consists of regions which can be linked to particular stages of a star formation cycle, beginning in molecular clouds. The relevant local physical conditions span a wide range in density (10^2 - 10^6 particles cm^{-3}), temperature (10 - 10^3 K), and exposure to different types of radiation and particles (cosmic rays, ultraviolet (UV) photons, free atoms and energetic electrons). These conditions determine the ongoing chemistry, both in the gas phase and in the solid state, that is in icy mantles that cover the surface of micrometer sized dust grains. Such icy grains provide a chemical reservoir that also acts as a catalyst for surface reactions. These involve mostly radicals, which are produced upon 'energetic' processing, or via hydrogen addition and abstraction reactions (referred to as 'non-energetic' processing). The balance in molecular abundances between ice and gas phase is controlled by accretion and desorption processes, and the latter are triggered by an increase in temperature (sublimation), or via non-thermal mechanisms: photodesorption, electron stimulated desorption, or a release of energy following a chemical reaction (e.g. Hollenbach et al. 2009; Thrower et al. 2010; Acharyya et al. 2020).

Radiation from the interstellar radiation field, typically in the vacuum-UV (VUV), or at later stages emitted by young stellar objects, plays a special double-sided role at each stage of the stellar evolution cycle. It can cause molecules to fragment (dissociation), with the resulting fragments reacting to form other molecules and increasing the chemical complexity in the ice (photoconversion, see Herbst & van Dishoeck 2009), or it triggers a non-thermal desorption of ice mantles. This thesis provides an experimental study to quantitatively determine the role of VUV radiation on interstellar ice analogues, in the context of the early stages of the stellar formation cycle. Topics that are discussed focus on the formation of new complex molecules, accurate photodesorption rates as well as an explanation for the large amounts of molecular oxygen ice found on comets in our solar system.

1.1 Ices during star formation sequence

The composition of the ISM is divided by mass, between gas (99%) and dust (1%). The gas-phase component is dominated by hydrogen and helium, with only a small fraction of heavier elements (∼0.1%). The dust grains are mostly made of silicates or carbonaceous material with their sizes varying between 10 nm - 0.5 μm. Billions of stars in our Galaxy participate in a continuous recycling of this material in the ISM. The stars (and planets) are formed from the available matter, through gravitational collapse of a large interstellar cloud, and after a number of evolutionary stages (prestellar core, protoplanetary disk and planetary system) matter is ejected back into the ISM when a star explodes at the end of its life. Depending on the size of the star, this process can span periods ranging from several hundred millions of years up to several tens of billions of years. The formation and evolution of the low-mass stars (less than two solar masses) has been previously described in detail (Shu et al. 1987; Draine 2010; Tielens 2005) and the results presented in this thesis concern processes along this evolutionary track. The processes taking place during high mass star formation differ to some extent (Zinnecker & Yorke 2007).

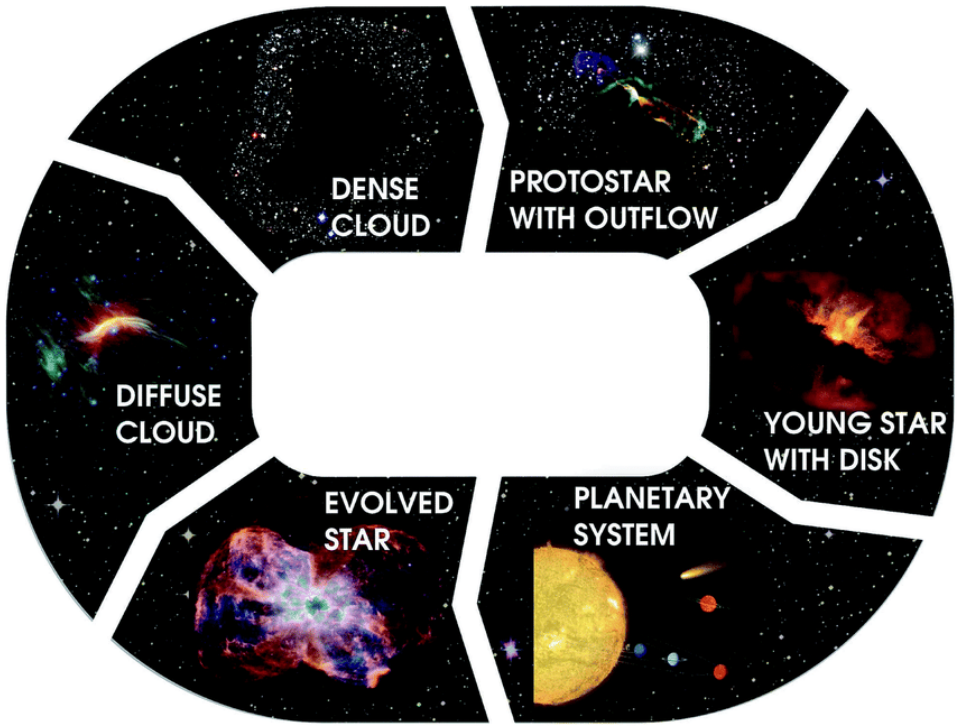

Figure 1.2: Recycling of matter in the ISM during the star and planet formation sequence. Credit: M. Persson, NASA/ESA/ESO/ALMA

The main stages of the stellar formation cycle for a solar-type system are represented in Figure 1.2. The cycle begins in molecular clouds, which can be further divided based on their density, between diffuse, translucent and dense dark clouds. The diffuse clouds have a typical density of 50 - 100 particles cm^{-3}, and a visual extinction (A_V) of less than 1 ($A_V < 1$ mag, where 1 mag = 2.5 times reduction of intensity), allowing the interstellar radiation field (ISRF) to penetrate the cloud. The ISRF represents the average radiation in a galaxy, with multiple components including stellar UV radiation between 6 - 13.6 eV, with a photon flux equal to 10^7 $cm^{-2}s^{-1}$ (Mathis et al. 1983). The interstellar medium is also pervaded by cosmic rays, energetic (>10 MeV/nucleon) particles (Gredel et al. 1989). The diffuse cloud composition is a mixture of bare dust grains with mostly atomic (H, C, O, N) and ionic species (C^+), and weak traces of simple molecules, such as H_2, CO and H_2CO (Snow & McCall 2006; Liszt & Lucas 2001). It is likely that also larger species reside in these clouds, giving rise to diffuse interstellar bands (DIBs), which remain largely unassigned (Snow 2013).

Density fluctuations within a diffuse cloud (e.g., upon stellar winds or supernovae explosions) lead to local over-density regions, where gravity starts playing a role. The result is a dense, gravitationally bound cloud with its interior shielded from the external UV radiation. The local physical parameters with the densities around 10^3 - 10^4 cm^{-3}, A_V of 1 - 5, and temperatures around 10 - 20 K, are typical for a dense

molecular cloud. The low temperature results in a gradual freeze-out of atomic and molecular species on top of dust grains, that also start reacting with each other. This marks the onset of interstellar ice formation, which has a profound impact on the chemical inventory available during star formation, discussed further in Section 1.3 (Herbst & van Dishoeck 2009). In parallel, a low temperature gas-phase chemistry largely based on ion-molecule and radical-radical reactions results in the formation of diverse species (Bergin & Tafalla 2007). The chemical composition at this stage is regulated by UV radiation, which results in a competition between molecular dissociation and formation (Bergin et al. 2004). The edge of dense clouds, fully exposed to the ISRF, is referred to as a photon dominated region (PDR). At its front only atomic and ionic species survive, however, behind the front, efficient gas-phase chemistry results in molecular complexity (Hollenbach & Tielens 1997; Guzmán et al. 2014).

The inner region of the dense cloud reaches a density above 10^5 cm^{-3} and cools down to temperature of 10 K (Pagani et al. 2007). This substructure is referred to as a cloud core, and it is where the star will eventually form. Under these physical conditions, all species, except for H and H_2, rapidly freeze-out on top of the dust grains, forming multilayered icy mantles. The low temperature gas-phase chemistry continues, however, it is accepted that for these conditions with generally low gas-phase reaction efficiencies, the chemical evolution is largely steered by solid state processes, that is reacting molecules that are part of the icy mantles coating small dust grains. Solid state astrochemical reactions within the dense clouds can take place upon impacting particles (atoms, electrons, cosmic rays) or upon UV photolysis. The external UV field does not penetrate the dense cloud, however, there exists an alternative source of VUV photons. The interactions of cosmic rays with molecular hydrogen lead to its ionization or excitation. This creates a cascade of secondary electrons as well as VUV photons, generating a so-called secondary UV field. The VUV spectral energy distribution includes a strong Ly-α emission at 121.6 nm, a large number of discrete H_2 lines and a broad molecular emission between 140 and 165 nm (Prasad & Tarafdar 1983). The cosmic ray-generated photon flux in dense clouds is a few orders of magnitude lower compared to ISRF, and equals (1-10) $\times$ 10^3 cm^{-2}s^{-1} (Gredel et al. 1989; Shen et al. 2004a). The interactions of the VUV photons, with the icy mantles results in a number of processes, introduced in more detail in section 1.3.2, and these are discussed throughout this thesis.

As the dense core becomes more massive (density of 10^5 - 10^7 cm^{-3}), it becomes opaque and starts to heat up as gravitational collapse occurs. The resulting protostar is surrounded by a debris disk, comprising of leftover dust and gas that carries the chemical inheritance from the diffuse and dense cloud stages, all embedded within a large molecular envelope. In order to preserve angular momentum, disk formation is accompanied with perpendicular outflows. At this point, the cloud character of the region is lost and the object is referred to as a young stellar object (YSO). The newly formed protostar emits infrared radiation and rapidly heats up its surrounding to a temperature above 100 K, which triggers a complete sublimation of the nearby icy mantles. This region around a low mass protostar is referred to as a hot corino (for high mass stars it is called a hot core). Over the last few decades a highly diverse chemical complexity has been found towards these sources, based on gas phase identifications. It is generally assumed that these species, or at least a substantial fraction provides a good representation of the chemical composition of icy mantles (for an overview, see Jørgensen et al. 2016; Drozdovskaya et al. 2019).

Over the following 1 - 10 millions of years the protostellar system evolves and the remaining material from the molecular envelope is either dispersed of accreted. This leaves a pre-main sequence star surrounded by a protoplanetary disk. The chemical composition of the disk is of great interest, as it determines the chemical inventory available for planets. This includes access to water and molecules relevant for life (reviews by Williams & Cieza 2011; Öberg & Bergin 2021). The chemical structure of the protoplanetary disks is less known due to their compactness, and weak molecular emission, however, some smaller complex organic molecules have already been detected, such as CH_3OH and CH_3CN (Öberg et al. 2015; Walsh et al. 2016; Booth et al. 2021). These detections demonstrate that species linked to prebiotic molecules are present at the onset of planet formation. Their origin, however, is not firmly constrained (Drozdovskaya et al. 2014). The leftover material, which does not get incorporated into planets and their moons, ends up in other celestial bodies, such as comets, asteroids, or boulders and dust. In particular comets are very interesting objects, as these are frozen remnants of the protoplanetary disks, and provide the most pristine view on the chemical composition of the Solar System (Mumma & Charnley 2011).

Depending on how massive the star is, it can live for several billions of years. Once the star burns through most of its fusion material, its outer atmosphere becomes a factory ejecting dust and other species back into the interstellar medium. This material provides the (chemically enriched) constituents required for the next generation of stars to be formed.

1.2 Interstellar ices

The focus in this thesis is on interstellar ices. Their presence has been first proposed by Eddington (1937), however it was not until the 1970s, when the first solid state signature of water was identified (Gillett & Forrest 1973). Since then, astronomical observations of ices on interstellar dust grain surfaces, and combined with dedicated laboratory data, allowed to identify other components of interstellar ices in various stages of star formation sequence. The dominating components of interstellar ices, as shown in Figure 1.3, include: H_2O, CO_2, CO, CH_4, CH_3OH, and NH_3. Some other constituents are less abundant or still under debate (see Table 1.1). It is expected that with the upcoming James Webb Space Telescope (JWST) mission, new ice constituents will be identified, possibly also including complex organic molecules. This is important, as the interstellar ice species are subject to energetic and non-energetic processing, and it is generally expected that this transforms simple solid state precursors into larger species, but observational evidence is still lacking (e.g. Terwisscha van Scheltinga et al. 2018). In addition, the desorption of species present in the ice via thermal and non-thermal mechanisms affects the ice-gas balance in the ISM.

1.2.1 Ice demographics

The identification and determination of abundances of interstellar ice components relies on infrared absorption spectroscopy. Species present in the ices absorb the light emitted by a background source, such as a protostar (or YSO), at molecule-specific wavelengths in the near- and far- infrared regime. Each molecule has a series of char-

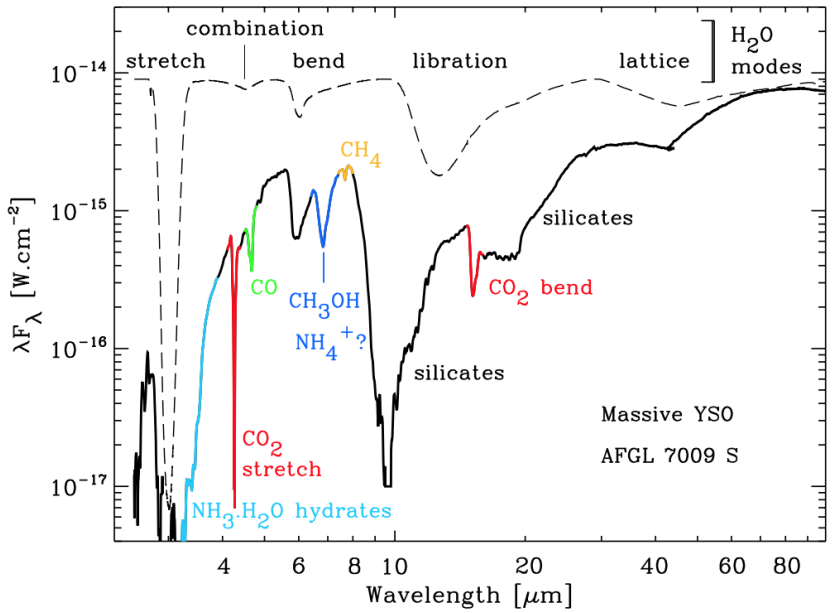

Figure 1.3: An ice spectrum towards the massive YSO AFGL 7009S, published by Boogert et al. (2015). The major interstellar ice components are identified with the marked vibrational modes. A complete vibrational signature of pure H_2O ice is shown at the top of the figure.

acteristic absorption features, the molecular spectrum, that in the infrared region corresponds to the excitation of intrinsic vibrational modes. In the ice, the molecules are immobilized, hence only (hindered) vibrations are possible, which are excited by the infrared radiation (e.g. Hagen et al. 1980; Gerakines et al. 1995; Gibb et al. 2004). In principle, it is also possible to investigate electronic transitions in ices (e.g. Bouwman et al. 2009), but recent applications involve mainly polycyclic aromatic hydrocarbons (PAHs) and this is beyond the scope of this thesis.

Ground observations of ices in the IR are obstructed by the strong telluric pollution of atmospheric H_2O and CO_2. This can be overcome by using space-based or air-born telescopes. The Infrared Space Observatory (ISO) and the Spitzer Space Telescope (SST), have opened up the required infrared spectral windows, in the range of 2.3 - 200 μm (see e.g., Whittet et al. 1996; Gibb et al. 2000, 2004), and 3 - 37 μm, respectively (see e.g., Boogert et al. 2008; Öberg et al. 2011a; Boogert et al. 2015). The interpretation of the resulting astronomical observations was only possible following accurate laboratory experiments recording interstellar ice spectra for different species and for different temperatures (e.g. Hudgins et al. 1993; Gerakines et al. 1995; Ehrenfreund et al. 1996; Bisschop et al. 2007a; Terwisscha van Scheltinga et al. 2018). Currently, many of the available ice data are summarized and available online through the Leiden Database for Ice[1] or NASA Goddard Cosmic Ice Laboratory IR spectra database[2].

A typical ice absorption spectrum collected towards a YSO is shown in Figure 1.3, with clear assignments of features to the main components of the interstellar ices, as

[1] https://icedb.strw.leidenuniv.nl
[2] https://science.gsfc.nasa.gov/691/cosmicice/spectra.html

Table 1.1: Interstellar ices and (a range of) their abundances normalized to the water ice column density (in %).

	Species	MYSOs	LYSOs	Mol. clouds	Comets
Secure	H_2O	100	100	100	100
	CO	3 - 26	<3 - 85	9 - 67	0.4 - 30
	CO_2	11 - 27	12 - 50	14 - 43	4 - 30
	CH_3OH	3 - 31	<1 - 25	<1 - 12	0.2 - 0.7
	NH_3	∼7	3 - 10	<7	0.2 - 1.4
	CH_4	1 - 3	1 - 11	<3	0.4 - 1.6
Likely	OCN^-	0.1 - 1.9	<0.1 - 1.1	<0.5	-
	H_2CO	∼2 - 7	∼6	-	0.11 - 1.0
	OCS	0.03 - 0.16	<1.6	<0.22	0.1 - 0.4
Possibly	HCOOH	<0.5 - 6	<0.5 - 4	<2	0.06 - 0.14
	CH_3CH_2OH	<0.5 - 6	<0.5 - 4	<2	0.06 - 0.14
	$HCOO^-$	0.3 - 1.0	∼0.4	<0.1	-
	NH_4^+	9 - 34	4 - 25	4 - 13	-
	SO_2	<0.9 - 1.4	∼0.2	-	0.2
	PAH	∼8	-	-	-
	O_2	<15	<39	-	2 - 5.4[a]
	H_2O_2	<2 - 17	-	-	-
	CH_3CN	-	-	-	0.008 - 0.04[a]
	N_2	-	-	<0.2 - 60	0.07 - 0.11[a]

Notes. The table is adapted from Boogert et al. (2015) and references therein, with added cometary ice abundances from Rubin et al. (2019) ([a]) and references therein; upper limit values are marked by "<" signs.

well as "likely" and "possibly" identified carriers (Boogert et al. 2015). To securely identify a constituent of an interstellar ice, its observational spectrum should provide an excellent fit to the laboratory data. This is often challenging due to the large width of ice absorption features in the solid state and an overlap of typical vibrational modes (e.g., C-H or C-O stretching mode), originating from different species and complicating unambiguous identifications. This problem increases with increasing molecule size. Moreover, there is an uncertainty in the exact position of absorption features as these shift depending on the ice morphology (ice composition and ice structure and temperature). Finally, the derived ice column density needs to be balanced with the gas-phase abundance. Species which are "likely" in the ice mantle, such as OCN^-, require only one securely identified band, however, their complete signature needs to fit into the full absorption spectrum along with the derived abundances. The "possibly" identified species, such as CH_3CN or PAHs, lack a convincing full profile fit, or have been detected in an indirect way, for example, in the gas phase in a region dominated by sublimating ice species.

The column density of an ice species is determined by integrating the optical depth of a characteristic band and dividing it by the integrated band strength, measured in the laboratory. The resulting column density of water ice ranges between 10^{17} - 10^{19} cm^{-2} for different YSOs. The abundances of other ice components are often normalized to water. The composition of ice mantles can vary between different molecular clouds, however, certain trends are observed. Table 1 shows the ice abundances rel-

ative to water ice in different environments - massive young stellar objects (MYSO), low and intermediate young stellar objects (LYSO), dense clouds and cores, as well as comets. The table is divided into three sections, with secure, likely and possible identifications of species, as explained earlier. Water is the most abundant constituent in all environments, and the median relative amount of species such as CO or CO_2 is within the same range, although the variation for each type of an environment can be by a factor of a few. The observations of a molecular cloud as a function of depth into the cloud, show the layered structure of the icy mantles with the H_2O-rich layer coated by a CO-rich ice. This is due to the fact that CO is highly volatile and only freezes out at higher densities and very low temperatures. In the literature the H_2O-rich layer is called the polar ice phase, the CO-rich layer is referred to as the a-polar ice phase.

1.2.2 Rosetta revolution

While the ice abundances in regions outside of the solar system (MYSOs, LYSOs, molecular clouds) are largely derived based on their IR signatures, different options apply for the comets whose orbits come closer to Earth, providing a unique opportunity to probe their composition *in-situ*. Space missions *Giotto* and more recently *Rosetta* probed the cometary comae of comets 1P/Halley (1P) and 67P/Churyumov-Gerasimenko (67P), respectively. *Rosetta* mission followed the comet 67P, illustrated in Figure 1.4, along its orbit around the Sun, measuring the release of gas and dust during the different phases. The composition of the coma was used to derive the composition of the nucleus of the comet, that could be considered to be a large dirty snowball. The measurements were done with an on board mass spectrometer, the Rosetta Spectrometer for Ion and Neutral Analysis (ROSINA). This detection method solves (some) of the challenges inherent to IR ice spectroscopy, and provides a more sensitive and unambiguous identification technique. The analysis of the data from the ROSINA instrument resulted in an impressive number of different species, doubling the number of previously detected cometary molecules (currently 66), including small COMs (e.g. CH_3OH, CH_3CN), polycyclic aromatic hydrocarbons (PAHs), sugars (glycolaldehyde, ($HC(O)CH_2OH$)) and even the simplest amino acid (glycine, NH_2CH_2COOH) (Altwegg et al. 2016, 2017; Rubin et al. 2019). Approximately two-thirds of the species detected in comets, have been previously detected in clouds of low and high mass stars. In addition, the relative abundances of the species detected at the early evolutionary stages are similar to the cometary values, supporting the primordial (inherited from prestellar stage) origin of the cometary chemical composition (Altwegg et al. 2019).

One of the surprising results from the *Rosetta* mission was the detection of a large amount of molecular oxygen (O_2), at level of a $\sim$3% with respect to H_2O ice (Bieler et al. 2015). This finding motivated a re-analysis of the data from the *Giotto* mission, which resulted in a similarly high ratio in comet 1P (Rubin et al. 2015). These cometary O_2/H_2O values were significantly above the expected gas-phase ratio in the interstellar medium (ISM) (Woodall et al. 2007; Yıldız et al. 2013). The origin of the high abundance of O_2 in the cometary ice is still debated (Luspay-Kuti et al. 2018), and it may be that it is inherited from the ices formed in the dense molecular clouds (Bockelée-Morvan et al. 2000; Cleeves et al. 2014; Drozdovskaya et al. 2014). The two comets originate from different parts in the Solar System, with chemically and physically different conditions. 1P has its origin in the Oort cloud and 67P is considered a Kuiper Belt Object (Balsiger et al. 1995; Altwegg et al. 2015). The consistent relative

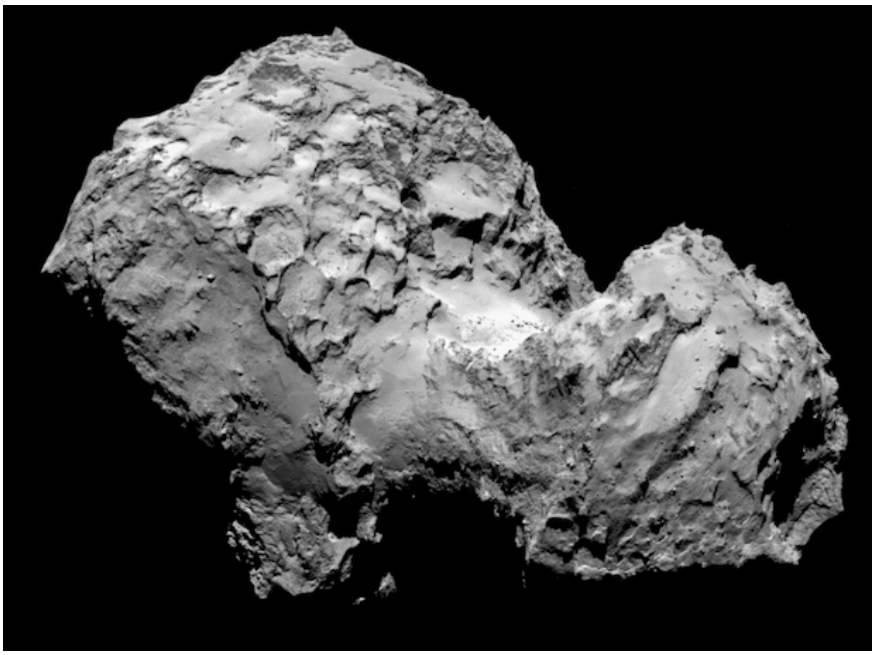

Figure 1.4: Image of comet 67P/Churyumov-Gerasimenko taken by Rosetta's OSIRIS narrow-angle camera on 3 August, 2015 from a distance of 285 km. Copyright: ESA/Rosetta/MPS

O_2 abundances for both bodies is in line with a common (primordial) origin of the observed O_2. The primordial origin of O_2 ice cannot be observationally verified, due to its homo-nuclear diatomic nature, which turns this molecule nearly invisible in the infrared and millimeter wavelength regime.

1.3 Complexity in interstellar ices

Icy dust grains in space provide a surface where molecules 'accrete, meet and greet', that is, where they freeze-out forming a molecular reservoir, where they can interact, directly or following diffusion in the ice (Linnartz et al. 2015). The ice mantle supports the increase in chemical complexity in two major ways. It acts as a solid state sink of gas phase atoms and molecules, where species have a higher chance to meet (compared to the gas phase). In addition, the icy surface acts as a chemical catalyst, providing a third body that allows to absorb energy from an exothermic reaction, stabilizing the reaction product. As stated earlier, different chemical triggers are at play, both leading to a formation of radicals in the ice, so called 'non-energetic' (dark) and 'energetic' (light) processing. Radicals are highly reactive species containing at least one unpaired electron in the valance shell. The dark chemistry is driven by atom and radical addition/abstraction reactions and is dominant during early stages of star formation, in dark and dense molecular clouds. The 'energetic' processing of ices is expected to play a larger role in the later stages of stellar evolution, triggered by im-

pacting cosmic rays, X-rays, UV photons, or energetic electrons. Another trigger for chemistry is an increase in temperature, which takes over when ices are heated (but not sublimated yet). All these processes have been studied in specialized laboratory experiments, providing the driving mechanisms and parameters needed for astrochemical modelling (e.g. Watanabe & Kouchi 2002; Muñoz Caro et al. 2002; Fuchs et al. 2009; Öberg et al. 2009c; Fillion et al. 2014; Dulieu et al. 2019). In the next sections several of these studies are discussed.

1.3.1 Dark ice chemistry

In dark clouds ice chemistry is mostly driven by atom addition reactions at temperatures typical for molecular clouds (10 - 20 K) between the most abundant elements: H (D), O, C, N. The involved chemical reactions are experimentally demonstrated and reviewed by Linnartz et al. (2015). The dominant abundance of H atoms promotes the importance of hydrogenation reactions, where H atoms stick on the grain, diffuse over the grain surface and find species to react with. This so-called *Langmuir-Hinshelwood* mechanism is used to explain the formation of abundant interstellar ice molecules: H_2O, CH_4 and NH_3 (Ioppolo et al. 2008, 2010; Qasim et al. 2020; Fedoseev et al. 2015b). For example, the formation of water ice proceeds via sequential hydrogenations of O atoms (or O_2 and O_3), which has been also verified by chemical modelling (Cuppen et al. 2010; Lamberts et al. 2013). In parallel, CO_2 ice is formed via reactions between CO and the OH radicals (O + H), and to a lesser extent between CO and O (Oba et al. 2010; Garrod et al. 2008; Ioppolo et al. 2011). Formation of more complex methanol, has been suggested and verified to proceed via hydrogenation reactions of the solid CO, particularly during the a-polar ice stage, when CO forms an ice coating (Tielens & Hagen 1982; Watanabe & Kouchi 2002; Fuchs et al. 2009).

Upon further hydrogenation of these species (H_2CO and CH_3OH) larger radicals are formed in the ice, such as HCO, CH_3O and CH_2OH (Chuang et al. 2016). The following radical-radical reactions result in the formation of COMs, such as methyl formate, glycolaldehyde, ethylene glycol, and even glycerol - a three carbon containing species necessary for the formation of membranes of living cells (Chuang et al. 2016; Fedoseev et al. 2017). A schematic representation of a part of the involved chemical network is provided in Figure 1.5. Finally, it has been recently shown that species as complex as the amino acid glycine, can be formed with 'non-energetic' chemistry in a water-rich ice. The final chemical step leading to NH_2CH_2COOH formation is between the NH_2CH_3 radical and HOCO (Ioppolo et al. 2021). Whereas methylamine (NH_2CH_3) as a precursor species has been identified in the ISM, the detection of glycine in dense molecular clouds remains to be confirmed (Kaifu et al. 1974).

1.3.2 Energetic processes

Different forms of energetic particles (cosmic rays, photons, electrons) interact with solid state species, both on the ice surface and in the bulk. Dense dark clouds, even though shielded from the ISRF, are penetrated by the cosmic rays, highly energetic particles, which produce energetic electrons and a secondary UV (VUV) field in the inner regions of the molecular clouds. These trigger dissociation, followed by radical-driven chemistry forming other species, including larger COMs, which become detectable

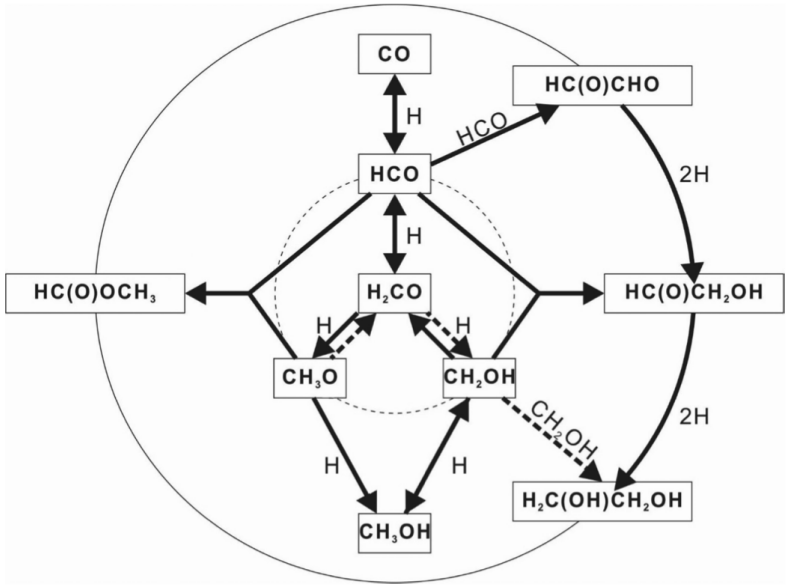

Figure 1.5: Non-energetic formation pathways showing sequential hydrogenation of CO, leading first to formaldehyde (H_2CO) and methanol (CH_3OH). Subsequent radical-radical or radical-molecule recombinations, or hydrogenation of reaction products result in the formation of methyl formate ($HC(O)OCH_3$), glycolaldehyde ($HC(O)CH_2OH$) and ethylene glycol ($H_2C(OH)CH_2OH$). The latter COMs have been identified in the gas phase in the ISM. Figure taken from Chuang et al. (2016).

following an ice sublimation. Alternatively, energetic processing of ices results in a non-thermal desorption mechanism regulating the balance between ice and gas in cold regions of the ISM. The focus of this section will be on processes following the irradiation of an ice analogue with VUV photons, as this is the main topic of this thesis.

Figure 1.6 shows a simplified overview of feasible processes following VUV photolysis of solid state species on a grain surface in cold regions in the ISM or in laboratory experiments on an ice formed on a gold-coated copper substrate. A molecule in the ice matrix is electronically excited following an absorption of a VUV photon (1). The photon absorption cross-sections of the main constituents of interstellar ices have been derived experimentally and all species except for (a possible constituent) N_2 absorb efficiently in the VUV range (Cruz-Diaz et al. 2014a,b). The energy released upon the relaxation of the excited molecule to its ground state (2), can have different outcomes. If its transferred to the neighboring molecule, it can result in neighbor's indirect desorption from the ice (3a, e.g. Bertin et al. 2013). Alternatively, the excited molecule can use its energy to directly photodesorb (3b, Fayolle et al. 2011) or photodissociate and form radicals (4). The formed radicals species can participate in dissociative or reactive photodesorption, where the excited radicals desorb from the ice surface (3c, Muñoz Caro et al. 2010; Andersson & van Dishoeck 2008), or 'kick-out' their neighbor (molecule or fragment) into the gas phase (3d, Andersson & van Dishoeck 2008). Finally, the formation of radicals can also result in their recombination into new molecules (6, photochemistry), which either stabilize in the ice or desorb (3e, photochemidesorption as in Martín-Doménech et al. 2016). Photoconversion is char-

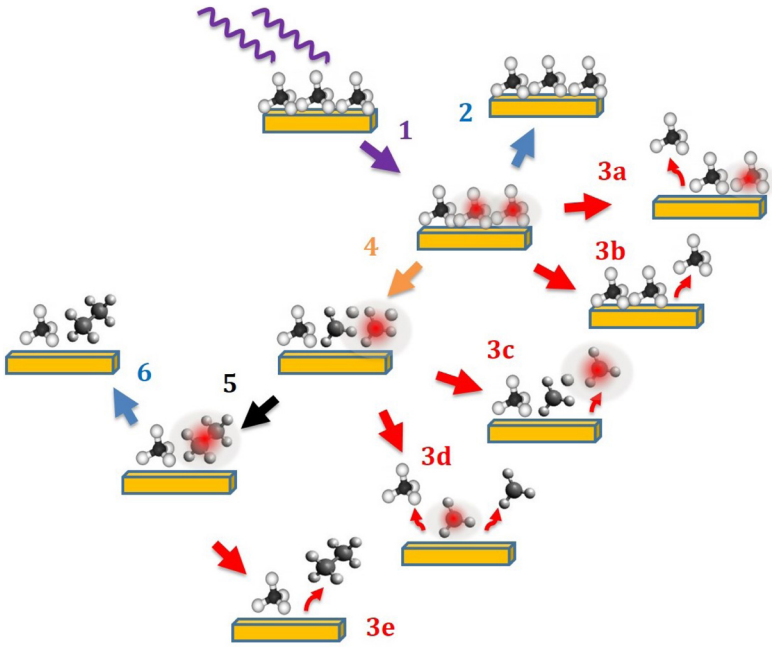

Figure 1.6: Competition between processes taking place in solid state species upon an absorption of a VUV photon. Photodesorption processes (in red) are only possible for the top layers of the ice. All other processes can happen in both the ice bulk and on the surface. The schematic applies to ices at a temperature excluding thermal desorption, typically $\leq$ 20 K. Figure from (Bulak et al. 2020).

acterized by a combination of photochemistry (6), and reactions of nondissociated, photoexcited molecules (1), with neighboring neutral species. Both types of reactions provide formation pathways of many of the observed simple and complex species (e.g. Gerakines et al. 1996; Jin & Garrod 2020).

The desorption processes described above (3a - 3e) are expected to be possible only in the top few layers of the ice. In case of CO and H_2O, the top 3 ML (1 ML = 10^{15} molecules cm^{-2}) participate in photodesorption (Andersson & van Dishoeck 2008; Bertin et al. 2012). The photodissociation branch (4) is accessible when an absorbed photon carries enough energy to dissociate the molecule in the ice. This threshold is given by a molecular bond dissociation energy, BDE. The main constituents of interstellar ices, such as H_2O, CO_2, CH_4, NH_3, CH_3OH, have their BDE in the energy range between 4 - 10.2 eV allowing to be dissociated by the VUV field. An exception to this is the CO molecule, which requires 11.2 eV to be dissociated. Upon photodissociation, radicals are formed and their mobility in the ice is dependent on the temperature. At 20 K, H atoms are expected to diffuse through the ice, however, larger radicals, such as CH_3, OH, CH_2OH or CH_2CN have limited mobility, in a range up to a few layers (Andersson et al. 2006; Garrod et al. 2008). The following radical-radical and radical-molecule interactions in the ice, result in many detected complex organic species, including alcohols, sugars, nitriles, amides, and the building blocks of life - aminoacids, (e.g. Bernstein et al. 1995; Muñoz Caro et al. 2002; Öberg et al. 2009c; Ligterink et al. 2018a; Bulak et al. 2021). The separation and quantification of

these competing processes (photodesorption and photoconversion) is an experimental challenge for pure ices, and even more so, for ice mixtures. This is another topic that is addressed in detail in this thesis.

The role of the remaining type of energetic processing, thermal, is activated upon the formation of the protostar, when its environment begins to heat up resulting in processing of the surrounding icy mantles. Prior to the sublimation, the increased ice temperature results in more efficient diffusion or radicals and molecules, ultimately increasing the reaction rates. It also allows some acid-base reactions to proceed more efficiently (van Broekhuizen et al. 2004; Theulé et al. 2013). In addition, structural changes to the ice may occur, such as crystallization (transition from the amorphous to crystalline ice phase) and ice segregation (Ehrenfreund et al. 1998; Öberg et al. 2009a; Isokoski et al. 2014).

1.4 Link between ice and gas

1.4.1 Thermal desorption of COMs

The local composition of ice and gas in the warm regions (above 20 K) is regulated by thermal desorption characteristics of interstellar ices. One of the implications is related to the chemical inventory available for exoplanet formation. In particular, a temperature gradient in protoplanetary disks (decreasing temperature as a function of distance from the protostar), results in a varied gas phase composition linked to sublimation of water (temperature of 135 K) and CO (20 K). The location of these so-called snowlines determines the gas phase C/O ratio, which is available to be incorporated into new planetary systems (Öberg et al. 2011b).

Sublimation of interstellar ices is also linked to the first detections of COMs. In a massive-star forming region, where the young stars heat up their surroundings (hot cores), both CH_3OH and CH_3CN could be detected (Ball et al. 1970; Solomon et al. 1971). In these environments, the ice mantles are sublimated rapidly, hence the gas phase composition of hot cores is thought to give a good representation of the composition of the interstellar ices. Examples of high mass star forming regions are Orion KL and Sagittarius B2, while their low-mass equivalents include IRAS-16293 and NGC 1333-IRAS2A.

Since the 1970s, over 50 COMs have been detected in different environment associated with star formation, from prestellar cores, through hot cores and corinos, to protoplanetary disks and comets (e.g., Bisschop et al. 2007b; Öberg et al. 2010a; Jiménez-Serra et al. 2016; Calcutt et al. 2018). The gas phase species are studied with (sub)millimeter wave telescopes such as *Herschel*, or *Atacama Large Millimeter/submillimeter Array* (ALMA) and detections of new molecules continue on a yearly basis (McGuire 2018). Recent highlights include species detected in hot corinos containing three carbon atoms, such as acetone and propanal (Lykke et al. 2017), and species of prebiotic interest such as glycolaldehyde (Jørgensen et al. 2012) and formamide (Kahane et al. 2013). The wealth of the observations is summarized in (Jørgensen et al. 2020). These detections reinforce the importance of understanding the low-temperature grain surface chemistry for the formation of prebiotic molecules seen in hot corinos in the gas after sublimation of the entire ice mantle. Further evidence supporting the (partial) solid state origin of (some) COMs is found in astrochemical

models. The models have shown that gas-phase chemistry alone cannot explain the observed abundances of COMs. This includes methyl formate, dimethyl ether, glycolaldehyde, and ethanol, for which solid state formation schemes have been investigated and for which accurate solid state spectra have become available (Garrod et al. 2008).

The high spatial resolution of observation of COMs in star forming regions can provide additional chemical hints about their origin, that is a grain surface production and sublimation versus gas-phase formation scenario. This is illustrated by figure 1.7, where emission lines from several oxygen- and nitrogen- bearing COMs (O-, and N-bearing COMs) are mapped out. A spatial differentiation of COMs is clearly visible, with the N-bearing COMs (e.g., cyanides) peaking toward the protostar, while the O-bearing COMs (alcohols) toward two spots offset from the protostar (Csengeri et al. 2019). The N-bearing COMs demonstrate a typical thermal sublimation of ices possibly followed by warm gas-phase chemistry, while the O-bearing species peak at locations associated with accretion shocks (Csengeri et al. 2019). A similiar spatial differentiation has been seen towards other sources, such as a massive YSO NGC7538 IRS9 (Öberg et al. 2013). Here, the analysis of the emission of CH_3OH, CH_3CN, and CH_3CCH toward the YSO revealed a change in COM chemistry at temperatures above 25 K, likely reflecting the onset of an efficient ice chemistry above this temperature. Recent studies discussing detections and interpretations of varying distributions of O-, and N-bearing COMs are found in van Gelder et al. (2020a) and Nazari et al. (2021), respectively.

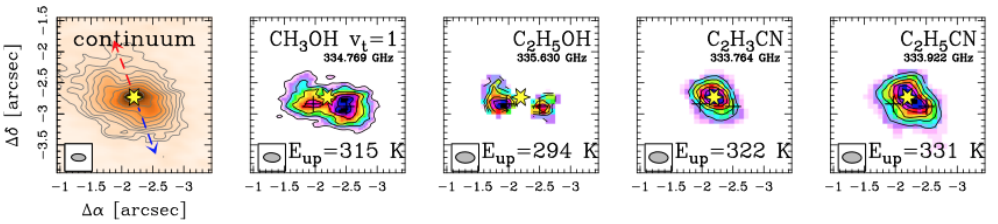

Figure 1.7: Continuum emission (left panel) and integrated intensity maps of transitions of several COMs (other panels) toward the young high-mass protostar G328.2551-0.5321 obtained with ALMA. O-bearing COMs (CH_3OH and CH_3CH_2OH trace two spots (black crosses) offset from the protostar (yellow star) that are associated with the accretion shocks. In contrast, the emission of N-bearing COMs (CH_2CHCN and CH_3CH_2CN) peaks on the protostar. Figure adapted from Csengeri et al. 2019.

The low-temperature grain-surface chemistry leading to O-bearing COMs, such as CH_3CH_2OH, or CH_3OCH_3, HCOOH, $HCOOCH_3$ is often linked to energetic processing of CH_3OH ice (Bennett et al. 2007; Öberg et al. 2009c; Paardekooper et al. 2016a). For the N-bearing COMs (cyanides, amides, amines) the dominant solid state precursors and chemical pathways are less clear. The structural equivalent of CH_3OH in nitrogen chemistry is acetonitrile (CH_3CN), which has been been indirectly detected to be a part of interstellar ices (e.g. Lee et al. 2019). Its potential as a precursor, mixed with H_2O and irradiated by ion bombardment has been tested by Hudson et al. (2008). The resulting residual material was extracted and analyzed *ex-situ*, following acid hydrolysis, yielding a range of amino acids. Despite demonstrating a potential to form building blocks of proteins, it was not possible to disentangle the involved chemical pathways or *in-situ* low-temperature ice chemistry. In another experiment, VUV

processing of interstellar ice constituents $HNCO/OCN^-$ mixed with CH_4 has been demonstrated to form species with a peptide bond (which build up amino acids), such as acetamide (CH_3CONH_2), formamide (NH_2CHO) and urea NH_2CONH_2 (Ligterink et al. 2018a). Photoprocessing of NH_3 was also tested and while it does not lead to a formation of large molecules on its own, it provides the NH_2 radical, which in combination with, for example CH_3OH, can yield a plethora of N-bearing COMs (Muñoz Caro et al. 2014). Mixtures containing NH_3 and CH_3OH are not expected to be abundantly present in the interstellar ices. Despite the ubiquity of large N-bearing species found towards different sources and their prebiotic potential, formation pathways (in the solid state or gas phase) towards already detected pecies, such as CH_3CH_2CN, $HOCH_2CN$, $(CH_2CN)_2$, or (NCCN)/(CNCN), remain unclear, or unknown. In this thesis it is shown that VUV photolysis of CH_3CN ice (in water) provides solid state pathways to a number of CN-containing species.

1.4.2 Non-thermal desorption

In cold interstellar regions exposed to UV photons, the desorption of simple and complex species can occur via different non-thermal mechanism driven by UV photons (see Fig. 1.6). This process is responsible for the presence of cold molecular gas of molecules, such as CO and H_2O, in environments where molecules should be frozen out on grains. This conclusion is based on state-of-art gas-grain astrochemical models such as one of molecular cloud composition by Hollenbach et al. (2009). These complex studies derive the compositon of gas and ice as a function of depth into the cloud. The considered contributing effects include: thermal balance, gas-phase chemistry, simple surface chemistry, accretion of gas-phase species to grain surfaces, and various desorption processes such as photodesorption, thermal desorption, and cosmic-ray desorption. The model successfully reproduces the ice and gas abundances of H_2O, OH, O and (where relevant) O_2 towards molecular cloud B68, a star forming cloud in Orion, NGC 2024, and ρ Ophiuchus (Larsson et al. 2007; Hollenbach et al. 2009). The results show that UV-driven competition between photodissociation and photodesorption has a major effect on the gas phase chemical composition from the edge until intermediate depths into the cloud. At the onset of water ice formation, the majority (98%) of gas phase water is due to UV photodesorption of water from the grain surfaces. Deeper into the cloud, the percentage drops to 70%, and at intermediate depths into the cloud, goes up again to 92%. The photodesorption is also necessary to explain observed abundances towards other regions in the ISM: photon dominated regions of molecular clouds (Snell et al. 2000; Wilson et al. 2003), prestellar cores (Caselli et al. 2012), outer parts of protostellar envelopes (Schmalzl et al. 2014) and protoplanetary disks (Dominik et al. 2005; Willacy 2007; Hogerheijde et al. 2011).

The photodesorption process has been studied in the laboratory for the main constituents of interstellar ices: H_2O, CO, CO_2, CH_4, CH_3OH (Westley et al. 1995a; Öberg et al. 2007b; Paardekooper et al. 2016c; Fillion et al. 2014; Dupuy et al. 2017; Bertin et al. 2016; Cruz-Diaz et al. 2016). Despite the investigation of this topic for over 20 years, the photodesorption rates reported in the literature still vary by a few orders of magnitude. Among all ice constituents, the 'simple' case of CO photodesorption has been studied the most extensively, as CO does not dissociate upon VUV photolysis (Sect. 1.3.2). Fig. 1.8 shows an overview of all experimental studies on photodesorption of CO. There exist experimental differences between these studies

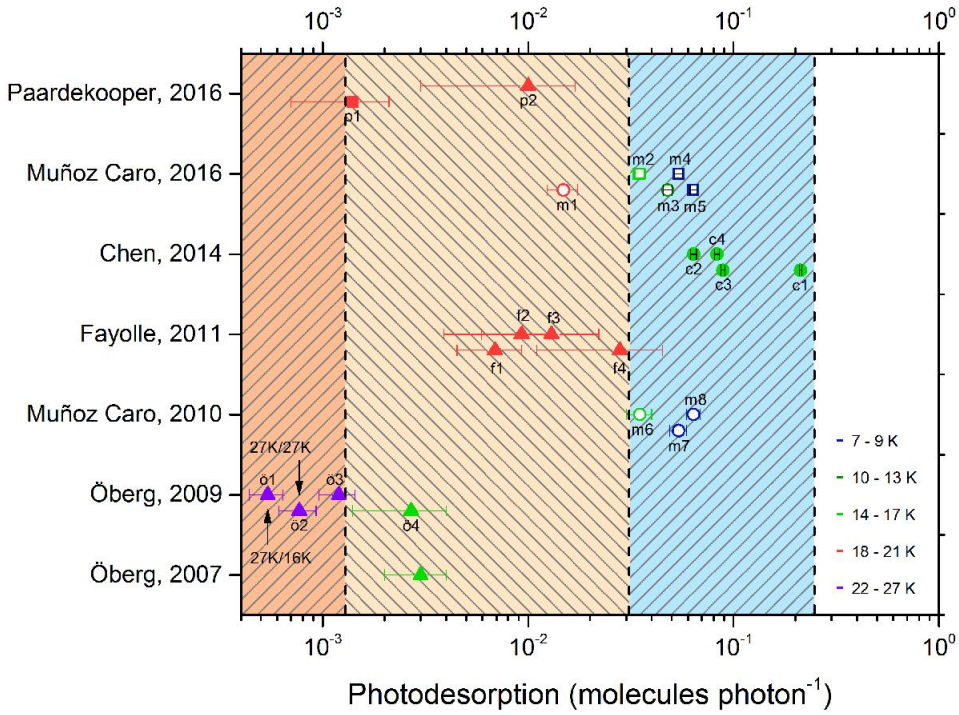

Figure 1.8: Overview of all the experimental CO photodesorption studies from (Paardekooper et al. 2016c). The colour code refers to the deposition and photolysis temperature. Studies at different photon energies by Fayolle et al. (2011) are labelled as: f1 = 10.2 eV, f2 = 11.2 eV, f3 = 9.2 eV, f4 = 8.2 eV. Flux calibration methods are distinguished with filled symbols (NIST photodiode) and empty symbols (actinometry). Detection technique; triangles and circles: IR spectroscopy; square: mass spectrometry. The labelling of c1, c2, c3, and c4 refer to different spectral energy distribution of a UV lamp in Chen et al. (2014). The labelling p1 and p2 refers to a direct measurement and derivation of the photodesorption rate in Paardekooper et al. (2016c).

explained in more detail in the next section, including the type of UV source, calibration methods, ice temperature and analytical techniques used to measure the rate. It is hard to understand, though, how these differences can account account for two orders of magnitude difference between the resulting rates of 2.3×10^{-1} molecules photon^{-1} (Chen et al. 2014) and 2.7×10^{-3} molecules photon^{-1} Öberg et al. 2009e). One should note, however, that photodesorption values of CO were set to 10^{-6} molecules photon^{-1}, before the experimental studies were performed. From this perspective, experiments still contributed substantially to a better quantitative understanding of this desorption process.

Besides broad band studies, also wavelength dependent photodesorption experiments have been performed using synchrotron facilities (Fayolle et al. 2011). In these experiments the molecular origin of the excitation mechanism - desorption induced by electronic transition - could be studied and also more information was obtained on the location of excited and desorbed ice species (Bertin et al. 2013).

The measurements of photodesorption of COMs, or smaller species that photodis-

sociate within the VUV energy range, is more challenging as it requires to separate the effects of photodesorption from photoconversion (see Fig. 1.6). This is reflected by missing photodesorption values for COMs, such as CH_3CN, CH_3CH_2OH, or HCOOH and differences in the reported values for intact photodesorption of CH_3OH (Öberg et al. 2009c and Bertin et al. 2016 or dissociative desorption of OH from H_2O ice ((Cruz-Diaz et al. 2018; Fillion et al. 2021)). These differences in the literature or the lack of measured photodesorption rates motivate further laboratory investigations of this mechanism, specifically for species which can be photoconverted in the VUV range.

1.5 Laboratory astrophysical approaches

A prime objective of laboratory astrophysical studies has been to record signatures of molecules allowing to identify the species in astronomical observations. In the case of interstellar ices, a few decades ago a typical laboratory system for solid state investigations comprised a chamber under high vacuum conditions (10^{-7} mbar) with a substrate cooled down below to 10 K and an IR spectrometer. In an experiment, after deposition of a pure or mixed ice of interest, infrared spectra of species were recorded using a Fourier transform infrared spectrometer (FTIR) and used for interpretation of observations, as shown in Fig. 1.3 (Hudgins et al. 1993). Today, these systems have been updated to ultra high vacuum conditions (10^{-10} mbar) and the infrared spectrometers to higher sensitivity and spatial resolution. This combination provides more accurate spectra of ice species in preparation for the JWST launch, planned towards the end of 2021 (e.g. Terwisscha van Scheltinga et al. 2018; Rachid et al. 2020).

Since the identification of the main components of the interstellar ices, dynamical studies have been performed in laboratories, focusing on the involved solid state chemical processes, for example, by irradiating ice analogues with microwave discharge hydrogen lamps (MDHL), a source of VUV radiation, resembling the secondary UV field in the ISM. Photoconversion of simple ice species was investigated and the formation of new species during the UV photolysis was traced. In the very first studies by *ex-situ* investigation of remaining residues (Greenberg 1983; Bernstein et al. 1995), and later with *in-situ* methods, such as FTIR, which is well-suited for detection of molecules with a dipole moment (Gerakines et al. 1996). In complex ice mixtures, this technique is less powerful as the identification and quantification of species suffers from overlapping signatures of molecules with the same functional groups. For this reason, IR spectroscopy (in transmission or reflection-absorption mode, RAIRS) is often used in combination with quadrupole mass spectrometry (QMS) and temperature programmed desorption (TPD). Upon linear heating of the sample, ice constituents desorb into the gas phase, each at a characteristic temperature corresponding to the binding energy between molecules or molecule and the substrate (Collings et al. 2004). The desorbing species are detected with a QMS, which inherently measures an equilibrated gas-phase composition in the experimental chamber. This means that molecules, prior to being detected, may interact with the walls and other inner parts of the setup, which are typically at room temperature. Experiments with TPD can include the thermally induced processes, resulting in the chemical changes in the ice (Öberg 2009; Ioppolo 2010).

An alternative *in-situ* technique to these two methods has been implemented by Abplanalp et al. 2016, who have combined the TPD with a tunable single photon

ionization source and a time-of-flight mass spectrometer (TOF MS). The soft tunable ionization source, allows for minimal fragmentation and isomer-specific identification based on the ionization potential of the probed molecule. Successful application of this method allowed to identify the formation of polycyclic aromatic hydrocarbons from the energetically processed C_2H_2 ices (Abplanalp & Kaiser 2020).

Photodesorption of interstellar ices can be measured indirectly via monitoring the depletion of the ice or directly by measuring the photodesorbed species in the gas phase. Photodepletion of the ice - a decrease in abundance of the parent species as a function of UV photon fluence is a combined result of photodesorption and photoconversion. In the original photodesorption study by Westley et al. 1995a, the depletion of water ice was monitored by a quartz micro balance and linked to the photodesorption rate of H_2O. Over a decade later, Öberg et al. (2009d) monitored the depletion of the water ice with RAIRS and simultaneously measured the species in the gas phase with a calibrated QMS, detecting the dissociative desorption. In other studies (Fayolle et al. 2011) used the signal measured with a QMS to convert it to a photodesorption rate of CO. This method was later applied to other molecules (Bertin et al. 2016; Cruz-Diaz et al. 2018).

Most common laboratory UV sources are microwave discharge hydrogen lamps (MDHL), in which the excitation of H atoms (and H_2) results in emission of Lyman-α (121.6 nm) and features around 160 nm from de-excitaiton of H_2. The photon flux and spectral energy distribution of this lamp are sensitive to its operation conditions, described in detail by Ligterink et al. 2015. An alternative UV source is provided by tunable synchrotron radiation which allows to investigate the photodesorption efficiency as a function of UV photon energy (Fayolle et al. 2011).

The results of this thesis are based on experiments on MATRI^{2}CES - Mass Analytical Tool for Reactions in Interstellar ICES (Paardekooper et al. 2014). This setup follows a different experimental approach to quantitatively probe the composition of the ice as a function of VUV fluence at low temperatures (down to 20 K). The *in-situ* probing sequence is initiated by a desorption of the ice with unfocused laser shot, resulting in a gas phase plume representing the composition of the ice. The plume is ionized via electron impact and extracted into the time-of-flight mass spectrometer. This scheme is referred to as Laser Desorption Post Ionization Time-of-Flight Mass Spectrometry (LDPI TOF MS) and allows to simultaneously probe the effects of photoconversion and derive photodesorption rates of astronomically relevant ices in an ultra-sensitive manner. Much of the work described in the next chapters only became possible because of the experimental tools MATRI^{2}CES offers.

1.6 This thesis

This thesis is an experimental study of the UV irradiation of the interstellar ice analogues, relevant for the different stages of the star and planet formation sequence. It describes in detail photodesorption and photoconversion processes, and as such, contributes to worldwide efforts that aim at understanding how chemistry in space could have contributed to the origin of life on Earth and possibly planets around other stars. Our contribution to address this idea, is to investigate the potential of UV photolysis of astronomically relevant species as solid state precursors of the detected chemical

complexity, and molecules linked to life (photoconversion, Chapters 4 and 6). In parallel to photoconversion, UV photolysis triggers a non-thermal desorption mechanism which quantified, contributes to the ice - gas balance in cold regions of the ISM exposed to UV (photodesorption Chapters 3 and 5). The results from Chapters 3 and 5 can be used as a direct input for astrochemical modelling.

Chapter 2 details the experimental system MATRI^{2}CES, the apparatus used in this thesis to study the UV photoprocesses in ices. Under ultra high vacuum conditions (UHV), simple ice analogues are deposited and irradiated with vacuum UV photons. The chemical composition of the ice at low temperature is quantitatively traced as a function of UV photon fluence via laser desorption post ionization time-of-flight mass spectrometry (LDPI TOF MS), an *in-situ* experimental method, relatively new in the field of laboratory astrochemistry. The measurement toolbox on MATRI^{2}CES is described with examples of time-of-flight mass spectrometry traces contributing to the data analysis.

Chapter 3 presents a novel experimental approach to discriminate between photoconversion and photodesorption upon VUV photolysis of interstellar ice analogues. It is based on a comparison between the effects of photolysis of pure ices with ices coated with an Argon layer. The inert coating is transparent to the VUV photons (does not affect the UV fluence), but it quenches the photodesorption processes. A quantitative comparison of the photodepletion of the parent species between the (un)coated experiments is used to derive its total photodesorption rate. The method is first validated using the well-studied case of CO and extended to CH_4, CH_3OH, and CH_3CN.

Chapter 4 includes an investigation of a potential role of acetonitrile (CH_3CN) as a parent molecule to N-bearing COMs, motivated by its omnipresence in the ISM and structural similarity to another well-known precursor species, CH_3OH. In addition a mixture relevant to the interstellar ices, embedding CH_3CN in an H_2O matrix, is investigated. The UV photolysis of pure CH_3CN ice yields larger nitriles including NCCN/CNCN, CH_3CH_2CN and $NCCH_2CH_2CN$. The UV photolysis of an astronomically relevant H_2O:CH_3CN ice at 20 K, leads to the formation of larger (at least up to 6-7 C/N/O-containing) molecules with the functional groups of: imines, amines, amides, large nitriles, carboxylic acids, and alcohols. Many of these species already have been identified in gas phase studies, while other species that have not been identified yet may be well present in the ISM.

Chapter 5 is motivated by previous experimental and theoretical studies which provide a range of photodesorption rates for H_2O ice and hint at a convoluted competition between photodesorption and photoconversion. A novel experimental approach presented in Chapter 5 is applied to the case of water ice. The UV photolysis of porous amorphous water (H_2O) ice at 20 K water ice is repeated with an Argon coating and the chemical composition and ice thickness are traced with the LDPI TOF MS technique. The role of the Argon coating is to quench any type of photon-triggered desorption, with a minimal effect on photoconversion. Upon a comparison of the (un)coated experiments a photodesorption rate of water ice was derived, with an upper limit on intact, dissociative and reactive photodesorptions. The results can be used as direct input for astrochemical modelling. The main finding of this fully independent approach is

that the photo desorption value of water ice is close in the range of previously found values.

Chapter 6 explores a new (primordial) scenario which might (partially) contribute to the formation of the surprisingly large abundance of O_2 and its correlation with water in the cometary ices of comets 1P and 67P. In this chapter the formation of O_2 and (H_2O_2) is detected and quantified upon VUV irradiation of pure H_2O and mixed H_2O:CO_2 ice at 20 K. For an UV photon fluence representative of dense molecular clouds and innermost regions of protoplanetary disks ($\approx 10^{18}$ photons cm^{-2}), UV irradiation of porous amorphous H_2O ice at 20 K leads to formation of O_2 and H_2O_2 in the solid state at the maximum abundances of (O_2/H_2O) and H_2O_2/H_2O equal to (0.9 $\pm$ 0.2)% and (1.3 $\pm$ 0.3)%, respectively. The relative formation efficiency of (O_2/H_2O) increases with the presence of CO_2 in the initial mixture. The abundances of O_2/H_2O found in our experiments are sufficient to account for at least part of the observed cometary abundances.