The astrochemical factory: A solid base for interstellar reactions

Ligterink, N.F.W.

Citation

Ligterink, N. F. W. (2017, December 18). *The astrochemical factory: A solid base for interstellar reactions*. Retrieved from https://hdl.handle.net/1887/58690

Author: Ligterink, N.F.W.
Title: The astrochemical factory: A solid base for interstellar reactions
Issue Date: 2017-12-18

V-UV

$CO{:}CH_3OH(s) \rightarrow CO(g) + CH_3OH(g)$

$CH_3CHO(s)$

$CH_3OCH_3(s)$ $CH_3CH_2OH(s)$

$CH_3(s) + NCO(s) \rightarrow CH_3NCO(g)$

$CH_3 + NH_2CO \rightarrow CH_3CONH_2$

$CH_3NH_2(g)$

$CH_2NH + H \rightarrow CH_3NH_2$

$NO + H \rightarrow NH_2OH$

$H + Br \rightarrow HBr$

1

Introduction

N.F.W. Ligterink

Astrochemistry is the study of chemical processes under the extreme conditions in the interstellar medium in which new stars and planets are born. This thesis deals with its three main research areas: laboratory experiments, astronomical observations and astronomical modelling. The common denominator between the chapters is the *interstellar icy dust grain*, a surface covered with frozen-out molecules on which much of the interstellar chemistry takes place. The introduction to this thesis follows the voyage that an icy grain takes through the cycle of star formation. Various interstellar phenomena interact with the ice layers of the grain and trigger physical and chemical processes. Laboratory, observational and modelling concepts and results will be introduced in this story along the way. The focus will be on the parts of the star formation cycle that are of particular interest to this thesis.

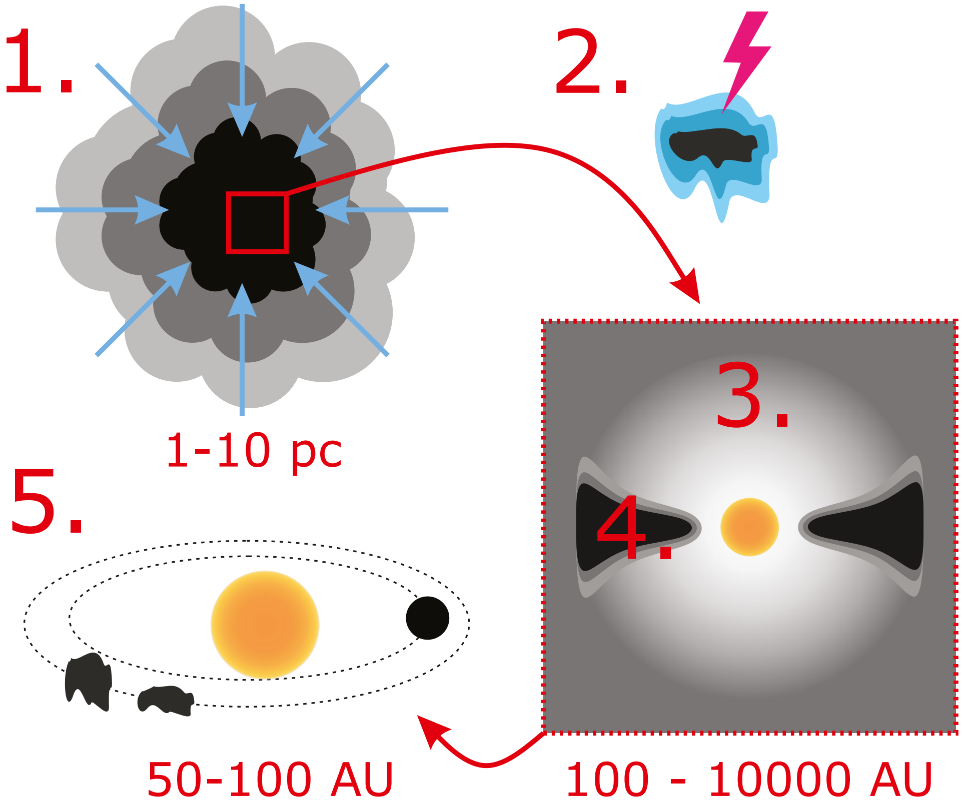

Figure 1.1: (1) Ice mantle formation on dust grains; (2) Energetic processing of ice mantles; (3) Gas-phase chemical complexity in the hot core after ice has thermally desorbed; (4) Non-thermal desorption processes in protoplanetary disks; (5) Formation of rocky bodies in the protoplanetary disk and the inheritance of ice from dust grains.

Schematically the journey of an interstellar dust grain from *diffuse cloud* to *protoplanetary disk* is depicted in Fig. 1.1. The numbering corresponds to the following sections and specific environments and processes they describe. Section 1.1 follows the collapse of clouds of gas and dust to dense *dark clouds*, while dust grains simultaneously build up an ice mantle. Section 1.2 discusses energetic processes in the interstellar medium, especially $far-UV$ irradiation, and how this enhances the chemical complexity on dust grains. In section 1.3 the transition from dark cloud to *protostar* is described and the effect this has on its surroundings. Specifically the *hot core* is important, which is an environment where the ice mantles are thermally desorbed and give a snap shot of the chemical complexity that was attained on the icy dust grain. Section 1.4 discusses the protoplanetary disk, mainly in the context non-thermal desorption mechanisms that cause the release of molecules to the gas-phase. In section 1.5 the final stage of star formation is discussed, when large rocky bodies, comets and *protoplanets* form in the protoplanetary disk. The comets retain the remnants of the earliest stage of star formation, the dust grains and their ice mantles, and are therefore link the beginning and the end of star formation.

1.1. Forming an icy dust grain

Dust grains consist of iron and magnesium containing silicates and carbonaceous material. Their size is small, ranging from nanometres to millimetres. Dust grains are the remnants of dying stars, but also may be formed through condensation and growth in the interstellar medium.

Grains reside in large low density diffuse clouds together with gas phase atoms and molecules. Typical densities are $n \sim 100$ cm^{-3} and extinctions of $A_v \approx 1$ magnitude (mag, 1 mag = 2.5 times reduction in intensity), caused by absorption and scatter of incoming radiation by dust. The gas is dominated by H, H_2 and He, followed by traces of carbon, nitrogen and oxygen. Even smaller fractions of small molecules can be present, such as CO, CN and HCO^+. Diffuse clouds are relatively warm at around 100 K and subject to the intense radiation of the interstellar radiation field (ISRF, Mathis et al. 1983), the combined radiation field of all the stars at a typical location in the galaxy. Under these conditions molecules are readily destroyed and therefore mainly atomic gases with small abundances of molecules are present, mixed with dust grains.

Perturbations to the diffuse cloud, for example caused by shocks from supernovae, can locally increase the density of gas and dust. This local over-density gravitationally attracts more material and at some point the cloud becomes dense enough to shield its inner regions from the ISRF. This is accompanied by a decrease in temperature, which results in a gradual freeze out of atomic and molecular gas phase species. The cloud passes through a *translucent cloud* phase (10^3 cm^{-3}, $A_v \approx$ 1-5 mag) and eventually becomes a so-called *dense* or *dark cloud* ($n \sim 10^4$-10^6 cm^{-3}, $A_v \gg 5$ mag). External visible and ultraviolet light does not penetrate this type of cloud. The temperature keeps decreasing to as low as 10 K and most atoms and molecules freeze out onto the dust grains. Only substantial amounts of H_2, H and He stay in the gas phase (Herbst & van Dishoeck 2009).

The frozen out species do not remain idle on the surface of the dust grains. Diffusion is possible and various reactions can occur. One of the most prominent and well-studied reactions are those involving H-atom additions, so called hydrogenation reactions. Hydrogen atoms stick on the grain, diffuse over the surface and find a species with which they can react. Due to this so-called

Langmuir – Hinshelwood mechanism a large part of the atomic carbon, nitrogen and oxygen reservoir is converted to methane (CH_4), ammonia (NH_3, Hidaka et al. 2011; Fedoseev et al. 2015b) and, fractionally the most abundant, water (H_2O, Oba et al. 2009; Ioppolo et al. 2008; Dulieu et al. 2010; Cuppen et al. 2010; Lamberts et al. 2014) in a non-energetic way. Via similar diffusion reactions carbon dioxide (CO_2) is formed from radical-molecule reactions between CO and OH, and to a lesser extent from CO + O reactions (Ioppolo et al. 2011, 2013).

Not only atoms, but also molecules can be hydrogenated, in particular carbon monoxide (CO). This molecule can be efficiently converted to formaldehyde (H_2CO) and eventually methanol (CH_3OH, Watanabe & Kouchi 2002; Fuchs et al. 2009). Contrary to the previously mentioned molecules, CO itself is mainly formed in the gas phase. Due to its very volatile nature carbon monoxide only freezes out at the coldest temperatures of the dark cloud stage, often after water, ammonia and methane have already formed. This results in a distinct water-rich and CO-rich layer and explains how a prototypical icy dust grain is build up: a silicate/carbonaceous core, covered by a water layer with methane, ammonia and some carbon dioxide, which is surrounded by a second mantle that consists of mainly CO, CO_2, H_2CO and methanol (Boogert et al. 2015 and references therein, Fig. 1). Note that CO_2 is the only molecule that has substantial abundances in both layers.

These examples of water, ammonia and methanol formation show the importance of the dust grain as a catalytic surface, although not in the traditional chemistry sense. It is often found that gas-phase reactions are not efficient enough at low temperatures to account for the observed abundances of these molecules. The surface of a dust grain acts as a molecular reservoir that brings species together, promotes reactions to form these products and acts as a third body to take away excess energy of a reaction. Therefore an interstellar icy dust grain is of great importance not only to form these simple species, but, as we will see later, also much more complex molecules.

InfraRed (IR) observatories like the *Infrared Space Observatory* (ISO) and *Spitzer*, together with ground-based telescopes, have been fundamental in understanding the general structure and composition of interstellar ice (Gibb et al. 2004). Besides the main components also the spectral signatures of a number of other solid state species, such as OCN^-, OCS and possibly NH_4^+, have been identified (Grim & Greenberg 1987; Palumbo et al. 1995). Even more species have been tentatively identified, for example ethanol (CH_3CH_2OH), the formate ion ($HCOO^-$), formamide (NH_2CHO) and acetaldehyde (CH_3CHO, Schutte et al. 1999; Raunier et al. 2004; Öberg et al. 2011). Although less abundant than the main ice species, these molecules are interesting because they can potentially tell us more about the chemical and physical processes that take place in the ice mantles that lead to their formation. Table 1.1 gives an overview of all ice species identified so far, also showing their relative abundances and a comparison with comets.

So-called Complex Organic Molecules (COMs) are only observed in the gas-phase, but their formation must have taken place in the solid state. The James Webb Space Telescope (JWST) with its higher spectral resolution and detection sensitivity will enhance our view of the Icy Univserve, by identifying for the first time also their solid state signatures. Combining the gas phase and

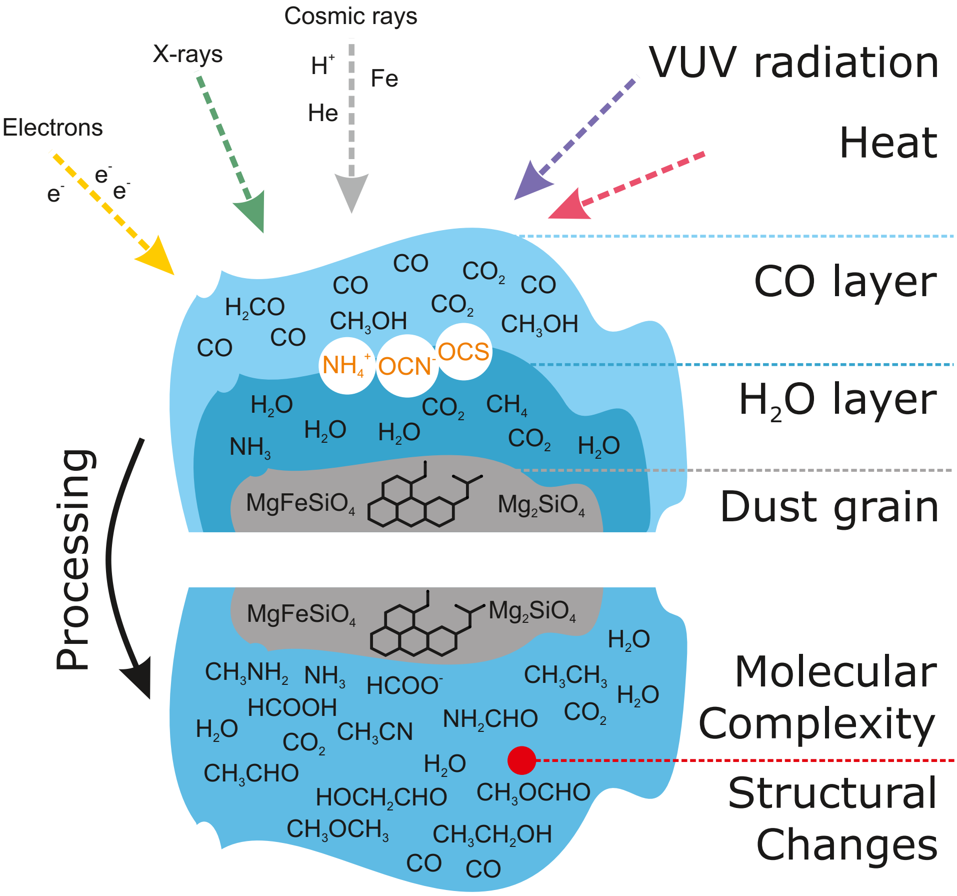

Figure 1.2: Schematic representation of an interstellar dust grain. The top half shows the dust grain surrounded by the water-rich and CO-rich layer. The species NH_4^+, OCN^- and OCS are separately depicted, because they are not clearly attributed to either layer. Various energetic processes are shown which can lead to greater molecular complexity and structural changes in the ice, as is shown in the bottom part of the image.

Table 1.1: Interstellar ice species

Molecule	MYSO[a]	LYSO[b] %[H_2O][c]	Comets
Securely identified			
H_2O	100	100	100
CO	3-26	(<3)-85	0.4-30
CO_2	11-27	12-50	4-30
CH_3OH	(<3)-31	(<1)-25	0.2-7
NH_3	∼7	3-10	0.2-1.4
CH_4	1-3	1-11	0.4-1.6
Likely identified			
OCN^-	0.1-1.9	(<0.1)-1.1	-
OCS	0.03-0.16	≤1.6	0.1-0.4
H_2CO	∼2-7	∼6	0.11-1.0
Possibly identified			
HCOOH	(<0.5)-6	(<0.5)-4	0.06-0.14
CH_3CH_2OH	∼HCOOH	-	-
$HCOO^-$	0.3-1.0	∼0.4	-
CH_3CHO	$HCOO^-$ × 11	-	-
NH_4^+	9-34	4-25	-
SO_2	(<0.9)-1.4	∼0.2	0.2
PAH	∼8	-	-
HNCO	<0.3-0.7	-	0.02-0.1
NH_2CHO	<1.5	-	0.002

Notes. [a]Massive Young Stellar Objects and [b]Low-mass Young Stellar Objects. [c]Values represent the full range of abundances w.r.t. water (100). Table reproduced from Table 2 & 3 of Boogert et al. (2015).

solid state data may answer the question how the two phases are physically connected. Chapter 5 shows the spectroscopic data of the interstellar relevant COMs acetaldehyde, ethanol and dimethyl ether, that can be used to guide future JWST observations.

1.2. Energetic processing of ices

1.2.1. Types of energetic processes

The chemistry taking place on a dust grain in a dark cloud is not limited to non-energetic hydrogenation reactions. Energetic processes, taking place simultaneous with hydrogenation, play a part as well and can explain the formation of the larger, more complex species on the grains. These larger species will become ″visible″ in the gas-phase following ice sublimation.

There are a number of processes that can release energy in the ice mantle of the dust grain. Cosmic rays are highly energetic particles such as protons, H^+, helium and various heavy metal nuclei that are found throughout the interstellar medium. They are able to transfer large amounts of energy into an icy dust grain upon collision and in this way cause chemical reactions. Electrons, either moving through space freely or as secondary particles from a hydrogen-cosmic ray collision, can do the same. X-rays can penetrate dark clouds and cause chemical reactions as well. Also, far-UV (often denoted by experimentalists as Vacuum-UV or VUV) radiation causes chemical reactions, although this may seem unexpected, since UV radiation does not penetrate deep into a dark cloud. However, a dark cloud has an internal source of VUV radiation that stems from cosmic ray ionization of gas-phase H/H_2 to form energetic electons, that in turn excite H_2, which then decays to its ground state by emitting a far UV photon (Prasad & Tarafdar 1983; Heays et al. 2017). For atomic hydrogen this is a photon of 121.6 nm, the so-called Lyman-α wavelength. Excited H_2 can emit photons in a large number of discrete lines as well as a broad emission spectrum between 140 and 165 nm. In dark clouds this results in a VUV flux of $\sim 10^4$ photons cm^{-2} s^{-1} (Shen et al. 2004). Hydrogen plasma VUV lamps are known to mimick this radiation field closely and considerable laboratory effort has been put into characterizing laboratory VUV sources (Chen et al. 2014; Es-Sebbar et al. 2015; Ligterink et al. 2015, see Chapter 3 of this thesis). The laboratory work conducted in this thesis focuses on chemistry induced by VUV radiation.

Finally, thermal processing is the last form of energetic processing mentioned here. Its relevance to dark clouds is limited, due to the low temperature of this stage. However, it becomes more relevant as the system starts evolving towards a protostar and temperatures start increasing. Certain acid-base reactions proceed more efficiently at elevated temperatures and in some cases neutral molecules react as well (van Broekhuizen et al. 2004; Bossa et al. 2009; Danger et al. 2011). Radicals become more mobile at higher temperatures, which increases the reaction rate. Photodissociation or other processes can produce energetic products which have enhanced reaction rates.

An icy dust grain experiences all these energies over its life time, but their importance relative to each other remains under debate. The energy input can cause the breaking of molecular bonds, diffusion of species on the grain surface and to overcome reaction barriers. Also structural changes may occur, such as phase changes from amorphous to crystalline ice and ice segregation (Fig. 1.2 bottom).

1.2.2. Laboratory investigations

Laboratory Equipment

Many laboratory experiments have been conducted to simulate ice mantles and processes in various ways (e.g., Muñoz Caro et al. 2010; Allodi et al. 2013; Ioppolo et al. 2013; Paardekooper et al. 2014). The experimental set ups are at their basis often similar. They consist of (ultra-)high vacuum chambers with a cryogenically cooled surface. This surface can either be a transmission window or a reflecting metal, carbon or silicate surface and is meant to act as dust grain analogue. A gas inlet mechanism ensures that gases or gas mixtures can be deposited on this surface. A source to process the ice, for example a VUV lamp, particle accelerator or synchrotron, is attached to the set-up. Chemical and physical changes in the ice sample are monitored in-situ with IR or UV/Vis spectroscopy, mass spectrometry and laser interferometric techniques. In some cases ex-situ Nuclear Magnetic Resonance (NMR) spectroscopy and gas chromatography techniques are used as well, although these usually have the drawback that a sample needs to be extracted from the set-up and exposed to atmosphere before analysis. A more detailed description of the inner workings of a representative laboratory set-up and the VUV lamp as irradiation source for energetic processing as used in this thesis can be found in Chapters 2 and 3, respectively.

Experiments

Experiments often start from the known, most abundant, interstellar ice components: H_2O, CO_2, CO, CH_3OH, NH_3, CH_4 and/or HNCO/OCN^-. Some of the earliest laboratory astrochemistry experiments investigated the VUV processing of complex mixtures, such as $CO:NH_3:H_2O:CO_2$, $H_2O:CO:NH_3:CH_4$ and $H_2O:CH_3OH:NH_3:CO$ showing the formation of radicals like HCO, NH_2 and HOCO and more complex molecules such as HNCO, NH_2CHO, HCOOH and H_2CO (Hagen et al. 1979; D'Hendecourt et al. 1986; Allamandola et al. 1988). More recent papers show the formation of even more complex species in similar ice mixtures. The VUV irradiation of a $H_2O:CH_3OH:CO:NH_3$ mixture by Bernstein et al. (1995) demonstrates not only the formation of species like ethanol, formamide, acetamide and nitriles, but also very complex molecules like hexamethylenetetramine, polyoxymethylene and a host of more complex alcohols, ethers, aldehydes and amides. Experiments conducted by Muñoz Caro et al. (2002) show that the residue of an irradiated $H_2O:CH_3OH:NH_3CO:CO_2$ mixture contains amino acids and a host of other complex molecules.

Although these experiments show the direction interstellar ice chemistry might take, they give little quantitative information in terms of reaction networks, kinetics and reaction rates. To get this information a bottom-up approach must be taken. First the behavior and chemistry of interstellar relevant molecules in pure form must be studied (Gerakines et al. 1996; Collings et al. 2004; Raunier et al. 2004; Bennett et al. 2007; Öberg et al. 2009a; Paardekooper et al. 2016). Methanol is particularly noteworthy in this respect, because on its own it can lead to a vast oxygen-bearing chemical complexity. VUV processing of methanol leads to species like acetaldehyde, formic acid, dimethyl ether, ethanol and methylformate. For the nitrogen-bearing species, HNCO/OCN^- is of great interest, since VUV processing of this species leads to the formation of, among others, formamide, one of the most abundantly observed complex nitrogen-bearing species in the gas-phase and smallest amide or peptide-bonded molecule. The other abundant nitrogen-bearing species in interstellar ice, NH_3, does not form complex species on its own, but small species species like N_2H_4 and N_2. It does however also produce the NH_2 radical, which can react with other species.

Processing of binary mixtures adds an extra degree of complexity to the system. Parent species, intermediate radicals and products of the pure species can all react with each other to form new, more complex species. In this way it is shown that for example methanol can be formed in processed $H_2O:CO$

mixtures or complex species like OCN^-, NH_2CHO, CH_3NCO and CH_3CONH_2 from NH_3:CH_3OH mixtures (Hudson & Moore 1999; Muñoz Caro et al. 2014; Henderson & Gudipati 2015). It must be noted however that observations indicate that the species in both these mixtures are found in distinct layers and therefore these mixtures likely do not explain the formation of these species. In this respect the formation of methylamine (CH_3NH_2) from electron irradiated C_xH_y:NH_3 mixtures is more likely to occur (Kim & Kaiser 2011). Methylamine is of particular interest because of its implied involvement in the formation of the smallest amino acid glycine. Several laboratory experiments hint that energetic processing of CH_3NH_2:CO_2 mixtures leads to glycine formation (Holtom et al. 2005; Bossa et al. 2009). This example shows that biologically relevant molecules, such as amino acids seen in the experiments of Muñoz Caro et al. (2002), can be explained in interstellar ices by a sequence of chemical reactions. However, for many other biologically relevant, or prebiotic, species such a pathway is not yet investigated. This is for example the case for amide molecules, species with a R_1-(C=O)-NH-R_2 bond, such as HNCO, NH_2CHO, CH_3NCO, CH_3NHCHO and CH_3CONH_2. Despite their potential importance to peptide chemistry, the formation mechanism(s) of, and links between these species have not yet been unravelled. Even for the simplest unit in this chain, HNCO, no consensus yet exists on its formation (Marcelino et al. 2010; Quan et al. 2010; Jiménez-Escobar et al. 2014). This thesis investigates several potential and plausible pathways for amide formation (Chapters 6 and 7).

1.2.3. Chemical modelling

Laboratory experiments thus give a wealth of information on the formation of molecular species and besides qualitative information also provide quantitative constraints to study the kinetics and infer reaction rates. These reaction rates are essential for theoreticians as input in chemical models. This allows to expand the conclusions drawn from experiments on a laboratory time scale to astronomical values (Cuppen et al. 2017). Simulation programs like GRAINOBLE, UMIST and the OSU/KIDA gas-grain network can study dark cloud chemistry based on dozens of molecules, many thousands of reactions and a variety of processes (Garrod et al. 2008; Wakelam et al. 2012; McElroy et al. 2013; Taquet et al. 2015). The systems that can be studied in this way are thus also much larger than what can be handled in a laboratory set-up.

Both laboratory and modelling are used for a better understanding on what kind of chemical complexity can be attained from relatively simple ices observed on icy dust grains. This makes it possible to connect astronomical observations of different objects, linking chemical snapshots in time. They explain some of the more complex components found in interstellar ices and help to understand molecular complexity observed in the gas-phase, subject of the following section.

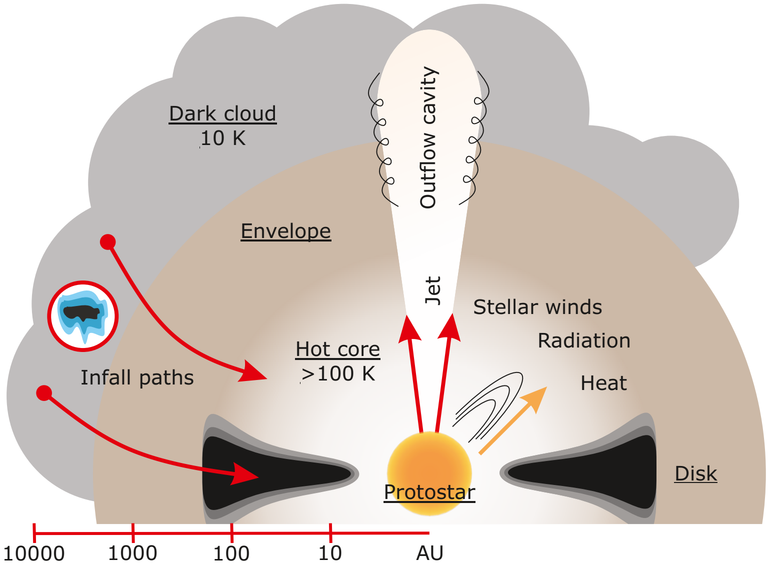

Figure 1.3: Schematic representation of the protostellar environment. The protostar attracts material from the cloud that moves into the protoplanetary disk and onto the star. Some of the material flowing into the young star is spewed out again via an outflow. Radiation and heat from the young star heats its surrounding and creates a hot core region.

1.3. Observing ice chemistry in the gas phase

1.3.1. Hot cores and corinos

While chemical and physical processes are ongoing on dust grains, the dark cloud as a whole also undergoes changes. Dense regions within the cloud start to gravitationally attract gas and matter, a process that will speed up as the density increases. Once a protostar has formed - a ball of hot gas in which nuclear fusion does not yet take place - it will heat and irradiate its surroundings. This protostar will eventually evolve into a (pre-) main sequence star.

Grains and gas move towards the protostar and leave the dark cloud environment into the envelope around the protostar. Through an accretion disk this material spins inward to the protostar and falls upon it. Depending on the evolutionary stage of the young stellar object, the disk has a high density and shields its midplane from the radiation and heat of the protostar. However, in the directions perpendicular to the disk, densities are lower and thus radiation and heat easily traverse this region and impinge on the envelope edge. Also, along the axis of the protostar it releases a jet and winds of hot gas at high velocities that sweep up material in the envelope in a so-called outflow. At the envelope-protostar interaction the dust grains are heated up and start to thermally release their ice mantles. What results is a bubble of warm gas, typically 100 K or warmer, where most of the molecular species from the grains have instantaneously desorbed together with water, the most abundant ice mantle component (see Fig. 1.3). This is called a hot core in case of high mass sources like Orion KL, Sgr B2, W33A or NGC6334I or a hot corino for its low mass counter part, such as IRAS 16293–2422 or NGC 1333-IRAS 2A. Because the complete ice mantle is rapidly desorbed to the gas phase, hot cores are thought to give a relatively good representation of the compositions of icy grains.

In many aspects high and low mass sources, and thus hot cores and corinos, are similar, however there are also fundamental differences. From an observational perspective it is easier to detect molecules toward high mass sources, due to their greater brightness. However, multiple high mass protostars are often found to contribute to the emission of this type of source. This makes it hard to understand the processing history of gas and grains. Also the fact that these sources are located at large distances, more than 1000 parsec (pc, 1 pc = 3.26 light year) is common, makes it hard to resolve their structure.

Low mass sources are quite the opposite. Their envelopes are less massive, making it harder to detect molecules. On the other hand low mass sources are often not as clustered as high mass sources are. Interferometers can for example easily resolve the two protostars, A and B, in the low mass binary source IRAS 16293–2422. The fact that this source (and many other low mass sources) is relatively nearby at $\sim$160 pc helps and mitigates its lower envelope mass. From these objects it is thus easier to get a clean snap shot of the chemistry that is going on. This leads to easier to interpret chemical pathways and physical structures.

Besides observational differences there are physical differences between high and low mass sources as well. High mass protostars are warmer, send out more UV radiation and evolve much more quickly than their low mass counterparts. This reflects in the chemistry. Different time scales for the hydrogenation processes in ice apply, varying levels of radiation or energetic processing are a possibility and the ice could be relatively warm, even in the pre-collapse stages.

1.3.2. Observations

The gases in hot cores and corinos are mainly studied with millimeter-wave telescopes such as *James Clerk Maxwell Telescope* (JCMT), *Atacama Pathfinder Experiment* (APEX), *SubmillimeterArray* (SMA), IRAM 30m and *Atacama Large Millimeter/submillimeter Array* (ALMA). Because the sensitivity of these techniques is higher than IR spectroscopy, often by a factor of 10^{2-3}, molecules at lower abundances can be detected. Whereas in the ice about 10 species have been detected, close to 200 molecules are now known in interstellar gas, the majority discovered by millimeter-wave telescopes.

By far most molecules have been detected towards Orion KL and the galactic centre source Sagittarius B2. The brightness and large chemical complexity of these star forming regions have made them favourite targets for observations since the early days of millimeter-wave astronomy. Some of the abundant, commonly observed molecules such as acetonitrile (CH_3CN), formamide (NH_2CHO), dimethyl ether (CH_3OCH_3) and ethanol (CH_3CH_2OH) have been detected first in these sources (Solomon et al. 1971; Rubin et al. 1971; Snyder et al. 1974; Zuckerman et al. 1975). Other molecules, like the elusive methylamine (CH_3NH_2) have exclusively been observed towards these sources (Kaifu et al. 1974). More exotic molecules like the halogens HF and HCl, tracers of the hydrogen reservoir, have been found here as well (Zmuidzinas et al. 1995;

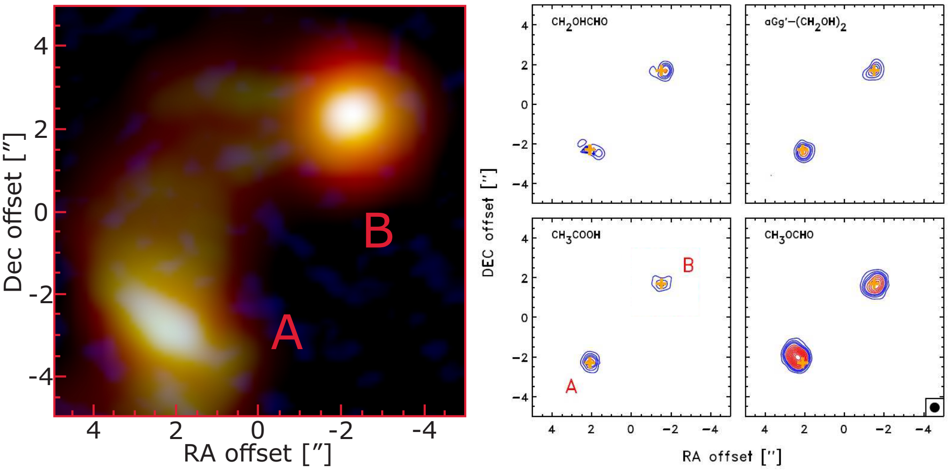

Figure 1.4: Left: the continuum emission map due to cold dust from 0.87 to 3.0 mm of IRAS 16293–2422 with the location of source B and A indicated. 1″ corresponds to 160 AU. Right: the contour maps of the species glycolaldehyde (362.406 GHz; upper left), ethylene glycol (348.550 GHz; upper right), acetic acid (352.872 GHz; lower left), and methyl formate (360.467 GHz; lower right). Images taken from Jørgensen et al. (2016).

Neufeld et al. 1997). On a yearly basis molecules keep being found in these sources, with some of the more recent finds being the amides acetamide and N-methyl formamide (CH_3CONH_2 & CH_3NHCHO), ethanimine (CH_3CHNH), methyl isocyanate (CH_3NCO) and the chiral molecule propylene oxide (C_3H_6O, Halfen et al. 2011; Loomis et al. 2013; Cernicharo et al. 2016; McGuire et al. 2016; Belloche et al. 2017). These latest results show that a large part of the interstellar chemistry is not yet explored, particularly of the nitrogen bearing species.

Many of the more abundant interstellar molecules have been observed toward other high mass and low mass sources as well. Methanimine (CH_2NH), an implied precursor of methylamine and glycine, has been found in several high mass sources (Dickens et al. 1997; Suzuki et al. 2016). Various observational results show that HNCO and NH_2CHO are related and hint that at least formamide is formed on dust grains and that hot corinos can be just as chemically complex as their high mass counterparts (van Dishoeck & Blake 1998; Bisschop et al. 2007a; López-Sepulcre et al. 2015; Taquet et al. 2015; Coutens et al. 2016). This is certainly the case for the sun-like protostars of IRAS 16293–2422 (see Fig. 1.4). Due to its relatively high brightness it has become one of the best studied low mass sources and gained a reputation as a low mass counterpart of Orion KL. Many studies have been dedicated to this source (e.g., van Dishoeck et al. 1995), including the including the *Protostellar Interferometric Line Survey* (PILS) with ALMA. An overview of the PILS survey and earlier studies on this young stellar object can be found in Jørgensen et al. (2016). Chapters 6 and 9 make use of the PILS data. Chapters 8 and 9 present the observational investigation of methylamine.

1.4. Snowlines and non-thermal ice desorption

The dust grains can also follow an infall path taking them into the protoplanetary disk. The densities in this disk can be high ($n \sim 10^{6-15}$ cm^{-3}), but vary greatly from the lower density outer edge and upper layers to the dense midplane region. In the midplane, temperatures are similar to that of a dark cloud, whereas the top layer of the disk is heavily irradiated and heated by the protostar. It is possible that molecular complexity survives in the midplane, but chemical processes also continue into the protoplanetary disk and add to further complexity (Bergin et al. 2007; Walsh et al. 2014; Drozdovskaya et al. 2014, 2016).

In the upper warmer regions of the disk the grain mantles desorb, enriching the gas phase with molecules. Because of the temperature gradient throughout the disk toward the protostar, these species release at distinct locations which are dependent on their specific binding energy. For example water has a high binding energy and thus will desorb closer to the star than CO, which has a low binding energy. The resulting ring-like structures around the protostar are called snowlines and indicate the border between freeze-out and sublimation. In the age of ALMA it has become possible to image these snowlines in protoplanetary disk, for example, the snowline of CO has been imaged via DCO^+ and N_2H^+ in various sources (Qi et al. 2013; Mathews et al. 2013; Qi et al. 2015; Öberg et al. 2015). It is important to note that the concept of snowlines is not unique to protoplanetary disks, but they can also be present in protostellar envelopes (Jørgensen 2004; Anderl et al. 2016).

Interestingly, snowlines have been observed that are spatially located in disk regions where the dust temperature is too low for thermal desorption to occur. For example, around the young star IM Lup a double CO ring is imaged (Öberg et al. 2015, Fig. 1.5 left). The inner ring belongs to thermally desorbing CO, but the outer ring cannot be explained by this mechanism. Similar is the case for water, ammonia and methanol observed in the TW Hya disk, where they are located in regions that are too cold for thermal desorption to occur (Hogerheijde et al. 2011; Walsh et al. 2016; Salinas et al. 2016). Both these examples hint to non-thermal desorption mechanisms being at play.

One such mechanism is photodesorption, the VUV induced release of a molecule from the solid state to the gas phase. Many laboratory studies have investigated this effect, mainly for CO (Öberg et al. 2007; Muñoz Caro et al. 2010; Fayolle et al. 2011; Chen et al. 2014; Muñoz Caro et al. 2016; Paardekooper et al. 2016, Chapter 3), but also for water, methane and CO_2 (Öberg et al. 2009c,b; Fayolle et al. 2013; Fillion et al. 2014; Dupuy et al. 2017). In many cases photodesorption rates are found to be high (10^{-2}-10^{-3} molecules photon^{-1}) and are for the case of CO sufficient to explain the observation of a second ring in IM Lup. However, the opposite is true for methanol for which recent laboratory experiments show that it does not photodesorb intact (Bertin et al. 2016). Its upper limit ($\leq 3\times10^{-6}$ molecules photon^{-1}) is deep enough to show that it can not explain the methanol observation in the TW Hya disk. Clearly other non-thermal desorption mechanisms need to be invoked.

A number of alternative options do exist; reactive desorption, cosmic ray spot heating and co-desorption. With reactive desorption two species, for example radicals, react to form a product and the residual energy of the reaction is

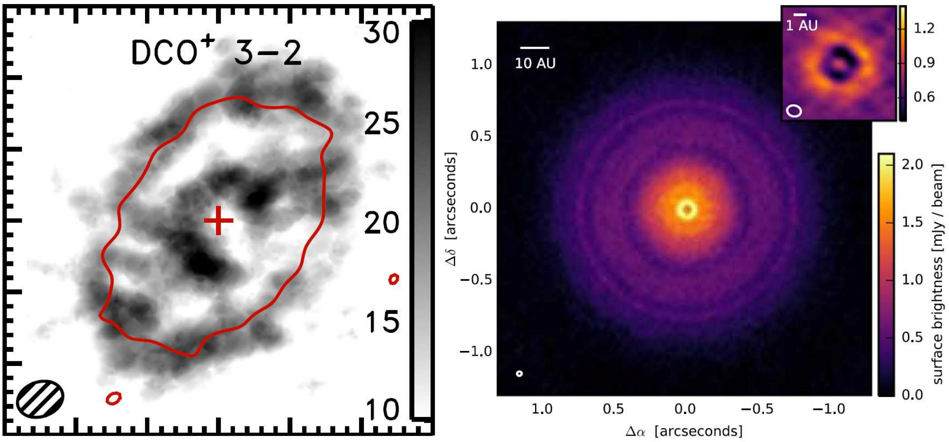

Figure 1.5: Left: the double ring structure of DCO^+ found in IM Lup attributed to the thermal CO snowline and an outward CO photodesorption ring. Image reproduced from Öberg et al. (2015). Right: the dust ring structure found in TW Hydrae, which in the inner 1 AU (inset) is potentially caused by a planetary object cleaning out its orbit. Image reproduced from Andrews et al. (2016)

used to break the physisorbed bond to the surface and release the product to the gas phase (Garrod et al. 2007; Minissale et al. 2016). Cosmic ray spot heating is the localized heating of the ice mantle and thermal desorption of its contents after it is hit by a cosmic ray (Shen et al. 2004; Ivlev et al. 2015). Co-desorption is a mechanism whereby a thermally desorbing species drags another molecular species with it to the gas phase. In this way it is possible that volatile species with a low desorption temperature carry species with a high desorption temperature, such as methanol, with them to the gas phase. For the case of methanol, these non-thermal desorption mechanisms are not well studied and more laboratory investigations are needed to study the relevance of these effects. The co-desorption case is studied in **Chapter 4**.

1.5. Icy rocks

ALMA also opened up the possibility to investigate the mechanisms that lead to planet formation in protoplanetary disks. Dust traps, i.e. regions where mm-sized dust grains can pile up and coagulate together, have been found (van der Marel et al. 2013). Also gaps in disks, cleared of a substantial part of their grains, have been imaged and attributed to a young planet emptying its orbit (Bruderer et al. 2014; Pérez et al. 2014; van der Marel et al. 2016; Andrews et al. 2016, Fig. 1.5 right). These observations hint to a general mechanism where submicron-size dust grains enter the protoplanetary disk and at some point efficiently coagulate together and grow to large rocky bodies up to comet size. The kilometer-size large rocks gravitationally attract each other and form a larger body that cleans out its orbit of all material and eventually forms a planet. Not all rocks are incorporated into planets, however. These rocks, or comets, are the left overs of planet formation. Since they are formed from icy dust grains there is the possibility that the chemical complexity reached in a dark cloud is transferred all the way to comets.

This idea was the basis for the *ROSETTA* mission to the comet 67P/Churyumov-Gerasimenko (67P/C-G). Since comets spend most of their lifetime in the cold outer part of the solar system, they should be the "cleanest" remnants of star and planet formation, they are well suited to study the chemistry in the earliest times of our solar system. Mass spectrometers on the orbiter and the Philae lander were used to study the coma and icy surface of the comet. On the surface a large number of complex molecules were found, although identification is limited due to low mass resolution of the mass spectrometer and limitations of IR spectroscopic techniques (Goesmann et al. 2015; Capaccioni et al. 2015). Data from the orbiter confirmed the presence of many complex molecules, especially the ROSINA mass spectrometer instrument with its high mass resolution, including the amino acid glycine (Le Roy et al. 2015; Altwegg et al. 2016). Also many sulphur bearing molecules, such as OCS, SO_2 are found to be present in 67P/C-G's coma (Calmonte et al. 2016). More exotic species such as HF, HCl, HBr, organo-halogens and phosphorus are detected as well (Dhooghe et al. 2016; Altwegg et al. 2016). These results not only show that the known chemical complexity observed towards protostars is preserved in comets, but also that the ingredients are available in the ice to make other life-bearing molecules. In Chapter 10 the ROSINA data on halogens is used to compare archive *Herschell* observations on HBr.

1.6. This thesis

The journey that icy dust grains follow takes them through many different environments. Formation of ice layers start in the dark cloud when gas phase atoms and molecules stick long enough on grain to be hydrogenated to a number of simple species. The chemical complexity is enhanced by energetic processes, for example VUV irradiation. As the grains move toward the protostar they can enter the hot core around the young star, where the ice mantles thermally desorb and it becomes possible to study the chemical complexity of the dust grain in the gas phase. Another fraction of the dust grains will end up in the disk midplane. Here ice grain chemistry can continue, but also non-thermal desorption processes are evident. Finally, the grains in the midplane start to coagulate and form large rocky bodies, ranging from comets to planets. The ice coating of grains is locked up in comets and allows us to study the earliest stages of star formation. The chapters in this thesis touch upon all of these aspects of the icy dust grain. A number of key questions are addressed:

- What is the mechanism that drives low-temperature, non-thermal desorption of COMs, specifically methanol?
- Can COMs be directly observed in interstellar ice with *JWST*?
- What are the formation pathways to form nitrogen-bearing species with amine or amide functional groups?

- Which nitrogen-bearing COMs are observed in the interstellar medium, under which specific conditions, and what can we learn about their formation from these observations?
- Can we link the abundances of nitrogen-bearing COMs to comets?

The results of the chapters of this thesis are summarized as follows:

- **Chapter 2** details the construction and functioning of the Cryogenic Photoproduct Analysis Device 2 (CryoPAD2), a newly constructed set-up based on the original CryoPAD. This set-up is capable of performing VUV irradiation experiments on interstellar ice analogues under ultra-high vacuum (UHV) conditions. Compared to the previous set-up, capabilities to accurately determine photon fluxes and VUV spectra have been added and the implementation of a high sensitivity Quadrupole Mass Spectrometer (QMS) gives the possibility to measure low abundance photo-products.
- **Chapter 3** presents a full characterization of the Microwave Discharge Hydrogen-flow Lamp (MDHL), the source of VUV radiation in laboratory experiments. Using a calibrated VUV spectrometer, the effects of hydrogen flow and pressure, input power, add-mixing of noble gasses, microwave cavity position, pumping efficiency and lamp types are investigated. VUV spectra and fluxes are shown to be dependent on all these parameters, with the add-mixing of helium being the most significant to obtain a Lyman-α dominated spectrum (up to 80% of the flux of the full spectrum). Finally, a comparison of the CO desorption rate of an ice irradiated with a MDHL running on H_2 and a H_2:He mixture shows that this rate differs by a factor of 2, which is significant, but cannot explain order of magnitude differences seen in CO photodesorption experiments reported in the literature.
- **Chapter 4** revolves around the unexplained ALMA observation of rotationally cold methanol in the protoplanetary disk TW Hya. Non-thermal desorption mechanisms like photodesorption and reactive desorption have been unable to explain this observation. A combined laboratory and modelling investigation into a third mechanism, low temperature co-desorption of methanol with thermally desorbing CO molecules, is conducted. The laboratory work does not show any methanol releasing at the thermal release peak of CO, resulting in an co-desorption upper limit of $\leq 7.3\times10^{-7}$ methanol molecules CO^{-1}. Using this stringent upper limit co-desorption ratio in a chemical model does show that significant abundances of methanol can still be released to the gas phase.
- **Chapter 5** presents medium resolution infrared spectra of acetaldehyde, ethanol and dimethyl ether in pure form or mixed in astronomically relevant water, CO, methanol and CO:methanol ice matrices, to be used to guide future *JWST* interstellar ice observations. A number of spectral peaks are identified to be the most likely to be observed and a full peak position and *FWHM* characterization of these lines is presented. These results are used to re-analyse the 7.41 μm feature in *ISO* spectra of W33A. In agreement with previous results this feature can be explained by

acetaldehyde mixed in water, but acetaldehyde mixed in CO:methanol at cold (15 K) temperatures can explain this feature as well. Higher sensitivity and resolution *JWST* measurements are needed to securely determine in which layer acetaldehyde resides in interstellar ice.

- **Chapter 6** presents the first detection of methyl isocyanate (CH_3NCO) toward a low-mass protostar, IRAS 16293–2422, and the first laboratory investigation into its formation. A total of 43 spectral lines of CH_3NCO are unambiguously identified, but its isomers, CH_3OCN and CH_3CNO, are not. Column density ratios of $N(HNCO)/N(CH_3NCO) = 12$ and 4 are found toward source B and A, respectively. Abundance ratios compare well with those found in high-mass sources. The laboratory results show that CH_3NCO is likely formed in the VUV irradiation of interstellar ice analogue mixtures of CH_4:HNCO at 20 K, where the VUV is used to produce CH_3 radicals. A proposed reaction mechanism is by CH_3 radical addition to (H)NCO.

- **Chapter 7** aims to expand the work of Chapter 6 into a larger network of peptide bonded molecules in VUV irradiated CH_4:HNCO mixed ices at 20 K. Specifically the H-atom addition reaction to CH_3NCO to form CH_3NHCHO is tested and the formation of other amides from reactions with intermediates and products resulting from HNCO. Processing of these ices shows the formation of acetamide (CH_3CONH_2), but not N-methylformamide (CH_3NHCHO). The non-detection of the latter species means the H-atom addition reaction has a barrier that can not be overcome or intermediates are efficiently destroyed in the ice. Formamide (NH_2CHO), urea (NH_2CONH_2) and methylamine (CH_3NH_2) are identified as well. Overall the work indicates that the NH_2CO radical is an important intermediate in the formation of amide bearing molecules. Indications of the formation of more complex molecules, likely amides as well, are found. Experimentally derived CH_3CONH_2 / NH_2CHO ratios are compared with interstellar observed ratios of the same two molecules toward Sgr B2 and show good agreement. This gives a strong indication that formamide and acetamide have a common formational origin, which is found in interstellar ices.

- **Chapter 8** presents the results of a JMCT survey toward several high-mass sources in order to detect methylamine (CH_3NH_2). This molecule is important to astrochemistry due to its implied link to amino acid formation, specifically glycine. No spectral features of methylamine are detected. A comparison of (upper limit) abundance ratios with methylamine detections in the high-mass source Sgr B2, shows that the upper limits are not deep enough to claim a difference between Sgr B2 and other sources, but hint that methylamine is overproduced in hot core models. The upper limits of this chapter can be used to guide future deeper searches for methylamine with ALMA.

- **Chapter 9** investigates the relation between the molecules NO, N_2O and NH_2OH and between CH_2NH and CH_3NH_2 with ALMA observations toward IRAS 16293–2422B to elucidate the formation mechanisms of

NH_2OH and CH_3NH_2, two species thought to be of importance to the formation of amino acids. We detected NO and, for the first time toward a low-mass source, CH_2NH, tentatively identify N_2O and do not detect NH_2OH and CH_3NH_2. The presence of CH_2NH around IRAS 16293–2422B shows that this suggested parent molecule to the formation of the amino acid glycine could already have been present at the earliest formational stages of our own solar system. However, the non-detection of NH_2OH and CH_3NH_2 makes amino acid formation routes involving these two species less relevant. Furthermore, upper limit abundance ratios determined for CH_3NH_2 show that these are at least 1-2 orders of magnitude deeper compared to detections of this molecules toward Sgr B2, showing that significantly less methylamine is present in this low-mass source and different physical conditions in these two sources play a role in the formation of CH_3NH_2.

- **Chapter 10** constrains the interstellar abundances of HBr with archive *Herschel* data on Orion KL, Sgr B2 and NGC6334, finding upper limits for this molecule in all three sources. Upper limit abundance ratios are compared with detections of HBr in the coma gas of the comet 67P/C-G and show that the upper limits are at a similar level as the comet detections. A chemical network for the formation of HBr is constructed, which suggests that HBr could be depleted from the gas phase, potentially locked up in interstellar ice.

The future is bright with ALMA, JWST and Rosetta data to follow the journey of icy grains from formation to incorporation in solar systems.