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A molecular journey : tales of sublimating ices from hot cores to comets

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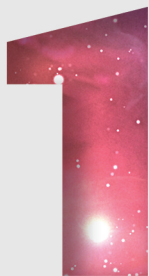
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1

Introduction

Throughout the Milky Way, stars are continuously being born, evolving and dying in a life cycle dictated by simple laws of physics. During this cycle, the material from which the stars form is processed in a number of different reactions under varying environmental conditions. The reservoir which holds this material is called the interstellar medium (ISM) and is found throughout the Galaxy. The ISM is generally a heterogeneous structure, however; small, cool and dense regions exist within it and it is in these regions that new stars are formed. As the stars evolve, their material is processed in the stellar interiors through a succession of nuclear fusion reactions which enrich the material with heavy elements. The enriched material is eventually returned to the ISM, either in a continuous manner via stellar winds or in an instantaneous manner via supernova explosions. This injection of stellar mass back into the ISM is accompanied by the release of large amounts of energy, generating turbulent motions and triggering new star formation in dense regions. With this last step, the loop of the ISM cycle is closed (see Fig. 1.1).

The subject of this thesis is the chemistry associated with the regions of the Galaxy in which new stars are being formed. Specifically, the thesis focuses on characterising the complex molecules found in these regions and compares the reservoirs of species found in sites of low- and high-mass star formation, respectively. The molecular compositions associated with the star-forming clouds are also compared with the chemical inventory of Solar System comets in an attempt to better understand the initial conditions of the Solar Nebula.

The subsequent sections will outline the primary physical and chemical processes associated with the formation of stars and planetary systems. Next, the main scientific questions investigated in the thesis will be summarised. The general conclusions drawn on the basis of the presented work will then be stated before the introduction is concluded by an outlook.

1.1 The formation of stars and planetary systems

Stars form from clouds of interstellar gas and dust that become so dense that they no longer are able to withstand the force of gravity, making them unstable, and bringing them to collapse. During this collapse, the material of the cloud is heated due to release of gravitational potential energy until the temperature and density in the centre of the forming star finally reaches such heights that nuclear fusion processes can take place. At this point the forming star has reached a state of hydro- and thermodynamical equilibrium and settles onto the main sequence; it has reached the end of its formation and has emerged from its natal cloud (see, e.g. Stahler & Palla, 2005).

The simple formation process outlined above is in reality a much more complicated affair, intrinsically linked to a number of physical mechanisms including gravity, magnetic field interactions, turbulence and gas- and radiation pressure. Despite each of these phenomena being fairly well understood by themselves, when combined, they still comprise a multitude of unanswered questions. These include speculations of whether stars form primarily from spontaneous gravitational insta-

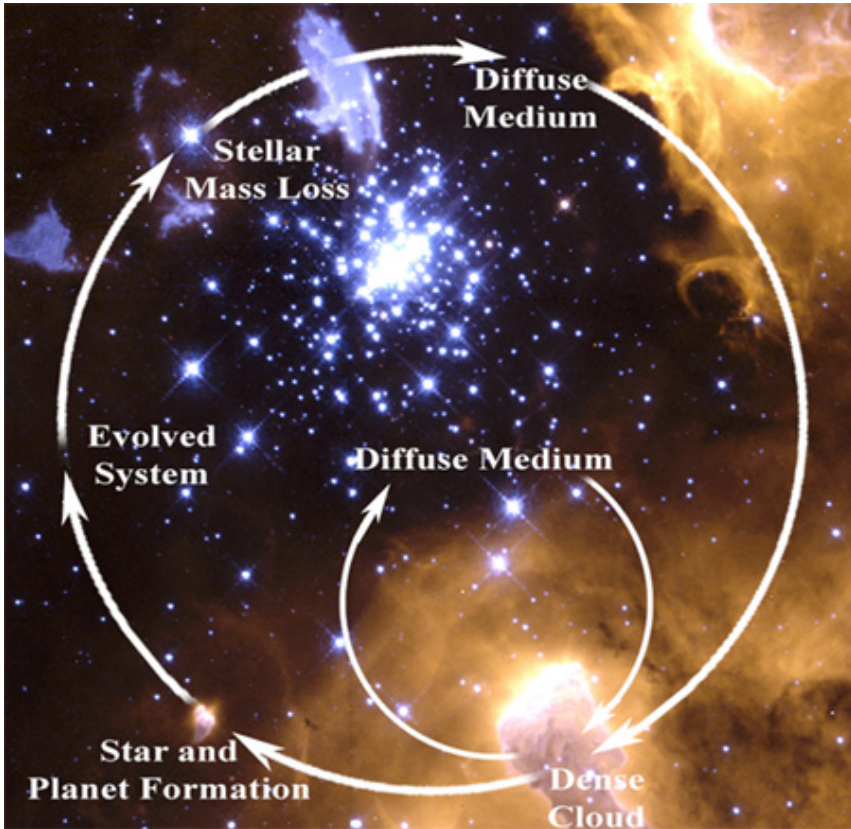


Figure 1.1: The life cycle of interstellar material. Main stages are as follows: (1) the formation of stars and planetary systems as dense and cold clouds collapse. (2) The processing of light elements into heavy elements by nuclear fusion as stars evolve. (3) The recycling of enriched materials into interstellar space by stellar mass loss as stars evolve and die. (4) New stars forming from the enriched material and the process beginning anew. Composite image adapted from the website of NASA/Goddard Space Flight Center/GCA. Background: NGC 3603 imaged by HTS. Credit: NASA/ESA/STScI-JPL/IPAC-UW-UI-UC.

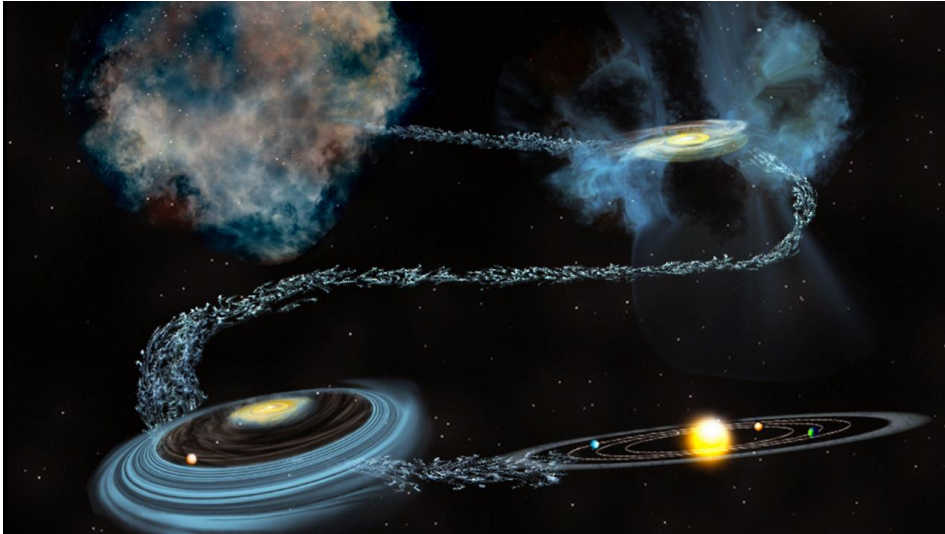


Figure 1.2: Artist impression of the evolutionary progression from the molecular cloud through the stages of a star-disk system embedded in a surrounding envelope, a star-disk system without an envelope and finally a mature star and planetary system. Image credit: B. Saxton/NSF/AUI/NRAO.

bilities or if their formation is externally triggered; if the formation of high-mass stars differs from that of low-mass stars; and whether accretion is continuous or episodic and how fast and efficient the formation process is. In summary, it remains a challenge to understand the wide variety of interlinked physical and chemical processes involved in star formation.

Despite the open questions above, the current understanding of star formation is sufficient to provide a comprehensive theory. The following sections will give an overview of the main evolutionary stages. It should be noted, however, that the understanding of these stages is based primarily on studies of low-mass stars forming in relative isolation. At the end of the section a few notes will be given on the formation of high-mass stars ($> 8M_{\odot}$) which is not as well understood as that of their low-mass counterparts.

The next sections focus mainly on the physical changes which occur as the system develops while the chemical evolution accompanying these changes will be discussed in sect. 1.2. Figure 1.2 presents an overview of these formation stages: the molecular cloud from which the stars condense, a protostar and disk which are embedded in the remnant material of their parent cloud, the so-called envelope, and finally, a mature star and planetary system.

From molecular cloud to dense core

The clouds of gas that hold the raw material from which stars form, are found throughout the ISM and are known as *giant molecular clouds*. These structures are among the largest cohesive entities found in the Galaxy, with radii of ~ 5 to

200 pc (see, e.g., Table 1 of Murray, 2011) and masses ranging from $\sim 10^2 M_{\odot}$ for small clouds at high galactic latitudes and in the outer disk of the Milky Way, up to $\sim 10^7 M_{\odot}$ for giant clouds in the Galactic Center (see review by Dobbs et al., 2014). Typical densities are $\sim 100 \text{ cm}^{-3}$, though the clouds are highly inhomogeneous and density distributions have large contrasts. These inhomogeneities are observed throughout the clouds as complex patterns of long and narrow filaments, with typical widths of the order 0.1 pc ($\sim 20 \times 10^3 \text{ au}$), compact ridges and irregular clumps (see review by André et al., 2014). It is within these clumpy, filamentary structures that the new stars are forming.

The clouds are predominantly comprised of atomic (H) and molecular hydrogen (H_2), although atomic helium (He), traces of carbon (C), oxygen (O) and nitrogen (N), as well as small molecules such as CO and CN, are also present, albeit at much lower abundances (e.g., Herbst & van Dishoeck, 2009). Physical conditions vary throughout the cloud and processes which shape the cloud structure include effects of gravity, turbulence, magnetic fields, galactic sheer motions and various forms of feedback such as supernovae and H_{II} regions associated with massive, newborn stars (Heyer & Dame, 2015). Generally, the outer and more diffuse parts of the clouds, which are more transparent to radiation from neighbouring stars, tend to be warm (temperatures of $\sim 100 \text{ K}$ or higher), and are subjected to ultraviolet radiation, causing the H_2 molecules to dissociate (Mathis et al., 1983). In contrast, the H_2 molecules located in the inner parts of the cloud complex are shielded from UV radiation, both by the gas on the edges of the cloud, mainly H_2 itself, but also by the assortment of small solid particles that form the interstellar dust grains. These grains, which consist primarily of a mixture of carbonaceous material and silicates (and perhaps with traces of metals), have sizes ranging from nanometres to millimetres and efficiently absorb and scatter light with wavelengths smaller than their diameters ($\sim 0.1 \mu\text{m}$). Because of the obscuring effects of dust at short wavelengths, and the subsequent re-emission at longer wavelengths, these regions are best studied at infra-red through radio wavelengths using both emission from spectral lines and continuum emission from the dust (see review by Dunham et al., 2014).

Regions where the dust effectively blocks the light from background stars are traditionally known as *dark clouds* since they appear dark at optical wavelengths. As long as the dark cloud is not disrupted by external forces the system is relatively stable and will remain in hydrostatic equilibrium. The critical mass above which the gas pressure is insufficient to support the cloud, bringing it to collapse, is called the Jeans Mass (Jeans, 1902). The original work by Jeans (1902) assumes that the collapsing cloud is spherically symmetric, isothermal and includes only thermal and gravitational effects. A more realistic description of how and why the cloud collapses would have to include physical effects such as rotation, turbulence and magnetic field interactions. However, including these effects does not interfere with the general conclusion that stars form in dense, low temperature regions. Such regions are referred to as *dense cores* and are found as substructures throughout the molecular clouds, particularly along filament ridges or at locations where filaments intersect or merge. In particular, studies of molecular clouds in the Gould Belt have shown that approximately 70% of the dense cores from which stars will eventually

condense are associated with filaments (André et al., 2014). This implies that the high column densities accumulated in the filaments may provide the initial conditions necessary for new stars to form. Typical densities in the dense cores are $10^4\text{--}10^6\text{ cm}^{-3}$ and temperatures can be as low as 10 K. At such low temperatures, most gas-phase species freeze out onto the dust grains leaving only substantial amounts of H_2 , H and He in the gas-phase (Herbst & van Dishoeck, 2009).

A protostar and disk is formed

After the initial collapse of the dense core, a protostar is formed at its centre. As the system evolves, material from the cloud continues to fall towards the centre of the core, through the envelope, and the protostar enters its main accretion phase. Due to the conservation of angular momentum, a flattened disk is formed around the protostar. This disk is referred to as a circumstellar or protoplanetary disk. After the initial disk has formed, infalling material is accreted onto the disk before being transported further inwards and finally falls onto the protostar itself. Simultaneously, the disk continues to grow in mass and radius (Dunham et al., 2014, and references therein). Protostars in this stage are also associated with powerful, highly-collimated ejections in the form of jets and winds which sweep up surrounding material and form bipolar outflows extending along the axis of the system's angular momentum. These outflows help carry away mass and excess angular momentum from the forming system.

As the young protostar evolves, it starts to heat its surroundings, creating a region of warm ($>100\text{ K}$) gas, the so-called *hot core*. The increased temperature in this region, causes thermal desorption of icy grain mantles, enriching the gas with complex molecules and providing a snapshot of the chemical evolution which has taken place on the dust grains since the initial freeze-out of species in the dark cloud. The hot core stage is therefore essential when studying the chemical evolution of star-forming regions since it reflects the chemical processes which have occurred during earlier stages of formation which are challenging to probe directly.

The composition of the forming system initially reflects that of the ISM, with gas amounting to 99% of the total mass, while solids represent only 1%. However, as the system evolves and the disk is gradually dispersed, the gas-to-dust ratio decreases.

The formation of a planetary system

Ultimately, through the combined effects of incorporation of envelope material into the disk and central protostar and the dissipative role of outflows and jets, the cocoon of material surrounding the young system is disrupted and the star-disk system becomes optically visible.

In this final stage of the formation process the disk which surrounds the young star disappears. During the dispersion, the gas in the disk is processed mainly through viscous accretion and photoevaporation due to UV and X-ray radiation, both from the central star and from external stars. This results in a disk which is composed of ionised and atomic gas at the disk surface and upper layers while the composition of the molecular gas in the interior of the disk is generally left

intact. Also the disk solids undergo dramatic changes. These occur as the grains, which initially are small ($\sim 0.1 \mu\text{m}$) and follow the motion of the gas, grow due to collisions and agglomeration. As the grains grow, they decouple from the gas and settle towards the disk midplane where the increased dust density accelerates the grain growth even further. In this way, the dust grains, which in the parent cloud are mostly micron-sized, grow in the disk to centimetre-sized pebbles and meter-sized rocks on their path to become first planetesimals and eventually full planets (see review of dust evolution in protoplanetary disks by Testi et al., 2014). Eventually, the remaining gas is removed from the disk completely. This happens rather rapidly via inside-out erosion as the accretion rate of gas drops below the photoevaporation rate of the newly formed star (see review by Williams & Cieza, 2011).

After the gas has been removed from the disk, the only remaining constituents are solid bodies which may eventually evolve into planets. Statistical studies of exoplanets, that is planets orbiting stars other than the Sun, suggest that most stars in the Milky Way host at least one planet (Tuomi et al., 2014). This indicates that the formation of planets is a natural by-product of star formation. Indeed, observations over the past few decades have revealed a wealth of exoplanetary systems, some even hosted by stars similar to the Sun (see review by Winn & Fabrycky, 2015). Although none of these are directly equivalent, in terms of its broad characteristics, the Solar System is not expected to be extremely rare (Martin & Livio, 2015). The fact that Solar System-like systems do not appear to be very infrequent implies that physical parameters, related to the architecture of planetary systems, are likely not the limiting factor for life.

Not all solids in the disk are incorporated into planets: some reside in smaller bodies such as asteroids and comets. Contrary to asteroids, comets are thought to have spent the majority of their lifetime in the outermost regions of the system, well away from the heat of the star, and the chaotic assembly of planets. These bodies are therefore considered the most pristine tracers of the protoplanetary disk. In a similar way, the frozen, fossil record preserved in Solar System comets, offers a unique view into the composition and chemical evolution undergone by the disk which eventually formed Earth.

To date, a number of cometary nuclei have been imaged and more than 20 molecular species have been detected in the comae of comets through various remote and in situ missions (see reviews by A'Hearn, 2011; Mumma & Charnley, 2011). The most recent, and most spectacular, of these is ESA's *Rosetta* mission which followed the comet 67P/Churyumov-Gerasimenko (hereafter 67P) for more than two years (August 2014 to September 2016) and succeeded in landing a module, *Philae*, on its surface. Throughout the mission, the *Rosetta* orbiter monitored the comet's evolution closely and provided the most detailed mapping of a cometary nucleus to date (Fig. 1.3). Data from the orbiter also confirmed the presence of many complex species such as CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, CH_3CHO , $(\text{CH}_2\text{OH})_2$ and CH_3NH_2 , which are also observed towards star-forming regions (Le Roy et al., 2015; Altwegg et al., 2017), proving that the chemical complexity which is known to evolve during the star-forming process is preserved in comets.

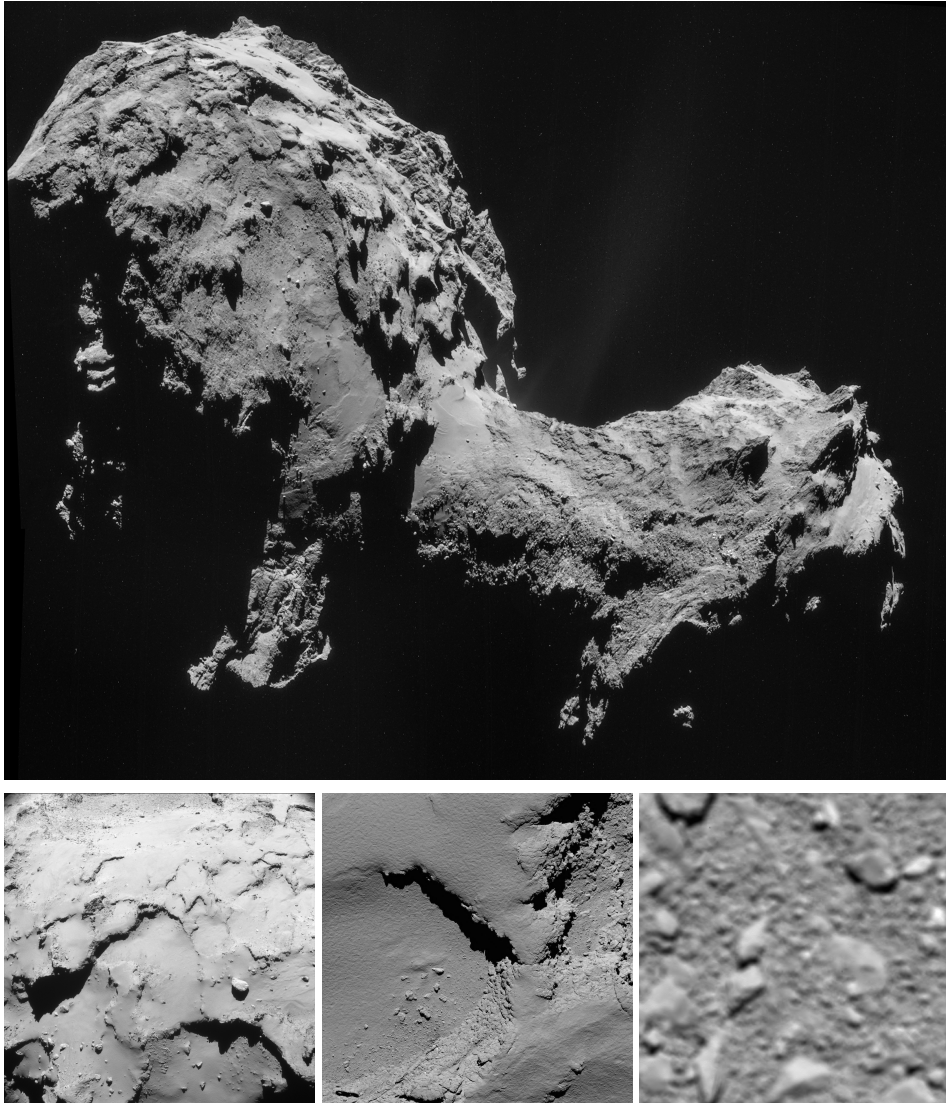


Figure 1.3: *Top:* Comet 67P/Churyumov-Gerasimenko as seen by Rosetta on 9 September 2014, at a distance of 28.6 km from the comet. *Bottom:* Sequence of images of comet 67P as seen by Rosetta on 30 September 2016, during the spacecraft's final descent. From left to right: Rosetta's last navigation camera image taken just after the collision manoeuvre sequence, when the probe was ~ 15.4 km above the comet's surface. Image of surface taken ~ 5.8 km above the surface. Rosetta's final image of comet 67P, taken shortly before impact, at an estimated distance to the surface of ~ 25 m. The images reveal the topography of the cometary surface which displays both sites of ridges and cliffs, as well as planes covered by smooth, fine-grained material and bulky rocks. Credit top: ESA/Rosetta/NAVCAM, credit bottom left: ESA/Rosetta/NAVCAM - CC BY-SA IGO 3.0, credit bottom middle, right: ESA/Rosetta/MPS for OSIRIS Team

Formation of high-mass stars

While the formation of high-mass stars, that is stars with masses exceeding $8 M_{\odot}$, likely follows more or less the same sequence of formation steps as their low-mass sibling, the physical processes related to these are not as well understood. Nevertheless, it is important to understand the formation of these sources since massive stars play dominant roles in terms of their feedback and synthesis and dispersal of heavy elements. The weaker constraints on the formation of high-mass stars as compared to those of low-mass sources, are due in part to the larger distances to these sources. Sites of high-mass star formation are generally located more than 1 kpc away from the Sun, making spatially resolved studies difficult. Another reason is the much shorter time-scales on which these massive objects form, reaching the main sequence even before accretion has subsided (see review by Tan et al., 2014, and references therein). High-mass protostars are also associated with strong radiation fields, potentially capable of halting accretion. In order to overcome this radiation pressure, significantly enhanced accretion rates compared to those of low-mass sources are likely required for the massive stars to form. Another puzzle is the fact that a core large enough to form a massive star is likely to fragment before the massive star has had time to assemble. Finally, since high-mass stars are often found in clusters, forming simultaneously with other stars, studying their formation implies dissecting their parental dense cores from those of their companions. High angular resolution imaging at far-IR and (sub)millimetre wavelengths are therefore essential for resolving these deeply embedded sources (Motte et al., 2018).

1.2 Chemistry in star-forming regions

Accompanying the many physical changes to the star-forming environment, is a dramatic increase in the degree of chemical complexity. The chemical processes governing this increased complexity can be roughly divided into two types, namely those occurring in the gas-phase and those occurring on the surfaces of dust grains. Generally put, these reactions account for the formation, destruction or re-arrangement of chemical bonds between atoms or molecules. That is, they link atoms into molecules, break down molecules into smaller constituents or transfer parts of one reactant to another.

Due to the low density of gas in the ISM, even in molecular clouds, atoms and molecules do not often meet and therefore the opportunity for species to react is limited. For example, a neutral molecule in a dense core with a H_2 density of 10^4 cm^{-3} , will collide with a H_2 molecule only once every month, while the time scale for collisions with neutral molecules other than H_2 is a few hundred years (Sakai & Yamamoto, 2013). In addition, the low temperatures characterising the dense cores ($T_{\text{gas}} \approx T_{\text{dust}} \approx 10 \text{ K}$) mean that only exothermic reactions (i.e., reactions which release energy), and reactions which have no activation barrier between reactants and products, can occur. These constraints mean that reactions have to be efficient, if a rich gas-phase chemistry is to be achieved. This chemistry therefore mainly proceeds via barrierless ion-neutral reactions (i.e., a neutral molecule

reacting with a positive ionised atom or molecule), followed by ion-electron interactions to generate neutral molecules (see review by Herbst & van Dishoeck, 2009, and references therein). On the other hand, cold dust grains provide a surface onto which atoms and molecules can accrete, creating a high density environment and enhancing the probability for these to meet and react. Also, the dust grain acts as a third-body, absorbing excess energy released in chemical reactions, thereby stabilising the reaction product. In gas-phase reactions, this excess energy is often stored as internal energy in the newly formed molecule and may result in the subsequent dissociation of the species. The dust grain therefore acts both as a reservoir of molecules and as a solid-state catalyst (although the surface itself does not participate in reactions).

On the grain, reactions occur primarily between radicals, that is atoms or molecules with unpaired electrons, resulting in high reactivity. These reactions mainly involve hydrogen atoms, which are abundantly present on the grain surface at low temperatures, and which, for example, form water (H_2O) by reactions with atomic oxygen (see van Dishoeck et al., 2013, and references therein). Overall, the efficiency of grain-surface chemistry is determined by the accretion rate of species onto the grain, which in turn is determined by a species' sticking efficiency and binding energy, the diffusion of species on the grain surface and the availability of additional energy, delivered by, for example, cosmic rays and photons.

While each of these processes, that is gas-phase and grain surface reactions, respectively, dominate the formation of a subset of molecular species as well as different physical regions and stages of the star-forming process, there is also a strong level of interplay between the mechanisms. Molecules which are originally formed in the gas-phase may subsequently freeze out onto the dust grains and here participate in new reactions. Likewise, species formed on the surface of grains may be released into the gas-phase and undergo further processing there. A key example is H_2 which is formed on the grain surface but forms the base for the formation of other species in the gas-phase (see review by Caselli & Ceccarelli, 2012, and references therein).

The following sections will summarise the chemical evolution of molecules in various astronomical environments. The first section will focus on the chemistry occurring in the ISM, specifically the buildup of simple molecules in molecular clouds, while the second section will describe the chemical processes associated with the hot core and protoplanetary disk.

Chemistry of the interstellar medium and molecular clouds

The gas which constitutes 99% of the total mass of the ISM is primarily composed of H and He, 90% and 8% by number, respectively, with heavier elements making up the remainder. The heavy elements are predominately O, C and N, which have abundances of 4.9, 2.7 and 0.7×10^{-4} that of H, respectively. Refractory species such as magnesium (Mg), silicon (Si) and iron (Fe) are present at lower abundances of $\sim 3 \times 10^{-5}$ (van Dishoeck, 2014, and references therein). The remaining 1% of the ISM total mass is made up of dust grains.

The gas of the ISM can be divided into different components depending on local

temperatures and densities. The main phases of these components are an ionised phase (gas temperatures, $T_{\text{gas}}, \sim 10^4 - 10^6$ K, density of H-nuclei, $n, \sim 10^{-3} \text{ cm}^{-3}$) an atomic phase ($T_{\text{gas}} \sim 1000$ K, $n \sim 0.1 - 10 \text{ cm}^{-3}$) and a molecular phase ($T_{\text{gas}} \sim 100$ K or colder, $n \geq 10^2 \text{ cm}^{-3}$; e.g. Table 1 of Ferrière, 2001). It is the latter of these phases which is of interest for the formation of molecular complexity. Going from diffuse to dense interstellar clouds, densities gradually increase, resulting in a higher degree of shielding from the InterStellar Radiation Field (ISRF, Mathis et al., 1983) and subsequently a drop in temperature. Even on the outer, more diffuse, edges of the molecular clouds, self-shielding against the ISRF, primarily by H and H₂, will prevent molecules produced in the gas-phase from being photodissociated. A notable example of this is carbon monoxide (CO), the most abundant interstellar molecule after H₂ (van Dishoeck & Black, 1988).

The next step in the formation process is the freeze-out of gas-phase species onto the surface of dust grains. This freeze-out is a natural consequence of the quiescent nature of the molecular cloud, as the low temperatures characterising these regions prevent species which have landed on the surface of grains from thermally sublimating.

Atomic species such as H, C, O and N will first accrete onto the grain and thereafter diffuse on its surface. In particular, the abundant and light hydrogen atoms will diffuse quickly and engage often in so-called hydrogenation reactions. These reactions result in the build-up of large amounts of water, followed by smaller amounts of methane (CH₄) and ammonia (NH₃) (e.g., reviews by Tielens & Hagen, 1982; van Dishoeck et al., 2013; Linnartz et al., 2015). Diffusion reactions will also form carbon dioxide (CO₂) after CO molecules, which are formed in the gas-phase, start to freeze out on the dust grains at sufficiently low temperatures. Together, these simple molecules coat the grains in a layer of molecular ice whose dominate component is water.

Due to its volatile nature, the bulk of the gas-phase CO will freeze out only at the coldest temperatures of the dense core stage (the sublimation temperature for pure CO is ~ 20 K compared with ~ 45 K for CO₂ and ~ 90 K for H₂O, Boogert et al., 2015). Once these are reached, a catastrophic freeze-out of CO will follow, creating a distinct CO layer on top of the water-dominated layer. Further hydrogenation reactions of CO then result in the formation of formaldehyde (H₂CO) and methanol (CH₃OH). This basic, layered structure of the ice mantle on grains has been observed with various infra-red space observatories (see Boogert et al., 2015, for a review).

Further chemical complexity in the ice mantels can occur as a result of successive addition of C- and H-atoms to CO, forming for example both acetaldehyde (CH₃CHO) and ethanol (C₂H₅OH; Tielens & Charnley, 1997). In addition, laboratory experiments, which simulate the CO freeze-out stage, have shown that even molecules as large as glycolaldehyde (CH₂(OH)CHO) and ethylene glycol ((CH₂OH)₂) may also be formed in the ice (Fedoseev et al., 2015).

Due to the low temperatures which characterise the centres of dense molecular clouds, the majority of molecules are expected to be frozen-out in these regions. However, some molecules have been detected in the gas-phase towards cold dense cores (e.g., Bacmann et al., 2012; Cernicharo et al., 2012). These observations can

be partly explained by gas-phase reactions but also by a fraction of the species, which reside in the icy grain mantle, being returned to the gas-phase via non-thermal desorption mechanisms such as photodesorption and reactive or chemical desorption (Öberg et al., 2007; Minissale et al., 2016; Oba et al., 2018; Chuang et al., 2018). These desorption processes are driven mainly by cosmic rays and include energetic processing of the grain mantle by cosmic-ray bombardment as well as dissociation by cosmic ray-induced UV photons (see review by Caselli & Ceccarelli, 2012).

Chemistry in hot cores and protoplanetary disks

As the forming star starts to heat up its surroundings, the molecules which were formed in the ice on the surface of grains in the dense clouds become increasingly mobile and react to form new, more complex species on the grain surface. In particular, biologically relevant molecules such as glycine, the smallest amino acid, may be formed at this stage of the star-forming process (e.g., Garrod et al., 2008; Garrod, 2013).

When sufficiently high temperatures are reached ($T_{\text{gas}} \sim 100$ K), the ice mantles which have build up during the dense core stage, will sublime completely and enrich the inner envelope with a considerable amount of gas-phase complex molecules. As mentioned in sect. 1.1, this stage in the star-forming process is referred to as a hot core. The spectroscopic fingerprint of the species which are released into the gas-phase during the hot core stage can be observed through their rotational transitions, which are accessible in the millimetre wavelength regime. These transitions are more easily excited compared with vibrational or electronic transitions and therefore even species with low abundances may be detected. In particular, the Atacama Large Millimeter/submillimeter Array (ALMA) has in recent years provided a wealth of information on the chemical composition of star-forming regions (e.g., Jørgensen et al., 2016; Belloche et al., 2016; Pagani et al., 2017).

At the same time, molecules released from the grains also set the stage for warm gas-phase chemistry, resulting in the formation of additional molecular species (see review by Sakai & Yamamoto, 2013). These processes may proceed either via pure gas-phase reactions or via gaseous species interacting with species still residing on the grain surfaces. Molecular species can also be destroyed as a consequence of the increasingly powerful radiation field associated with the forming star. Also, outflowing material, transported away from the forming system in the form of jets, will create shocks when encountering the quiescent gas of the envelope and surrounding molecular cloud. These shocks sputter the icy grain mantles and in some cases even vaporise refractory grains completely (Caselli & Ceccarelli, 2012). Both of these processes result in a partial reset of chemistry.

Contrary to the material in the hot core, the gas and dust residing in the protoplanetary disk stays largely shielded from radiation and temperatures remain low. As material flows from the envelope towards the centrally forming star, the chemistry which evolved in the icy grain mantles during the dense core stages, is fed into the disk, where it can continue to evolve in a similar fashion. The

chemical and physical structure of the disk may be traced through observations of simple molecules such as DCO^+ and DCN and it has become apparent that in particular the disk midplane is cold enough to maintain grain surface chemistry (e.g., Drozdovskaya et al., 2016; Salinas et al., 2017; Carney et al., 2018). As a consequence, the pristine composition which formed in the ice in the dense core stage may be preserved on the dust grains residing here. On the other hand, the inner regions of the disk, closest to the forming star, as well as the upper layers of the disk, are warmer and significantly more irradiated compared to the midplane. These regions are therefore dominated by molecules produced by gas-phase chemistry and species released from grains (see review by Bergin et al., 2007). Observations of these molecules therefore provide a glimpse of the chemical inventory of the dust grains in the disk midplane which are otherwise very difficult to probe (Öberg et al., 2015; Walsh et al., 2016).

Finally, as dust in the disk midplane coagulates, a fraction of the icy grains are likely preserved and consequently end up in planetesimals, the seeds of comets, asteroids and planets. Subsequent processing of the planetesimals as the planetary system evolves may alter this pristine material significantly. However, because comets predominantly reside in the outer parts of the disk, well away from the heat of the forming star, these objects are believed to preserve a nearly pristine record of the disk (A’Hearn et al., 2012). Characterising the composition of comets is therefore key when studying the final phase of chemical evolution during star formation. In addition to storing a record of this evolution, comets in the Solar System likely also acted as ‘polluters’ of the young Earth, potentially providing the planet with the essential prebiotic building block from which life evolved (Mumma & Charnley, 2011).

1.3 Star formation in the era of ALMA

When studying sites of star formation, the main observational challenges relate to achieving high spatial and spectral resolutions as well as high sensitivity. High spatial resolution observations are essential in order to probe individual objects so that confusion of material associated with different regions or averaging over environments which are different, either in terms of chemical composition or in terms of physical characteristics, may be avoided. Similarly, high spectral resolutions are needed in order to dissect the very line rich spectra associated with star-forming regions. Finally, because the column densities associated with sites of star formation are high, the transitional lines of the most abundant species are often optically thick. These species are therefore best probed through their less abundant, rarer isotopologues. Because the transitions of these isotopologues are often weak, high sensitivity observations are necessary for their detection.

Whereas single dish observations often suffer from at least one of these limitations, to greater or lesser extent, ALMA has been a true game changer. Constructed on the Chajnantor plateau in the Atacama Desert located in the northern part of Chile, ALMA is currently the world’s largest radio telescope. The facility is composed of 66 high-precision antennas, operating as an interferometer with

baselines of up to 16 km, making it possible to resolve spatial scales down to a few milliarcsecond. To date, antennas are equipped with 8 receivers (Band 3 – Band 10) covering the frequency range from 84 to 950 GHz (0.3 mm up to 3.6 mm), with the Band 1 receivers, operating in the range 35 to 50 GHz (6 – 8.5 mm), currently under construction. Both the sensitivity and resolving power offered by ALMA are unprecedented. Therefore, it is not surprising that since the start of operation in 2011, observations carried out with ALMA have revealed structures in star-forming clouds (e.g., Plunkett et al., 2015; Brogan et al., 2016; Tobin et al., 2016; Pagani et al., 2017) and protoplanetary disks (e.g., van der Marel et al., 2013; Andrews et al., 2016; Cieza et al., 2016; Pérez et al., 2016) which were never seen before. Examples of these structures are shown in Fig. 1.4. Specifically, the high angular resolution offered by ALMA has allowed star-forming regions and protoplanetary disks to be studied on solar system scales. In contrast, the much larger beam sizes associated with single dish studies, frequently result in insufficient spatial resolution and consequently may cover multiple sites of star-formation in a single beam making the characterisation of a region much less accurate. Furthermore, ALMA observations do not suffer from effects of beam dilution which may result in large uncertainties on derived molecular column densities if not accounted for correctly in single dish studies. In addition, the high spectral resolution and high sensitivity of ALMA observations has also resulted in numerous detections of new molecular species in various environments (e.g., Jørgensen et al., 2016; McGuire et al., 2018, and Fig. 1.5).

With the advances of ALMA, the chemical composition of star-forming regions may be probed on smaller scales and through weaker transitional lines, for example belonging to rare isotopologues, than were accessible through single dish observations. In addition, the high spectral resolution of ALMA observations also allows spectral features which are blended at lower resolution, to be resolved into contributions from individual species. By modelling the emission of these species and comparing the modelled spectra with the observations of ALMA, the molecular inventory of star-forming regions may be characterised in great detail.

1.4 This thesis

The overarching question addressed in this thesis is how interstellar chemistry evolves as a function of time and changing physical architectures during the formation of stars. This question is motivated by the insights in the complex nature of star-forming regions which have been gained over the last few years, thanks to the high sensitivity offered by ALMA, and an aspiration to better understand how the Solar System came to be, which processes led to its chemical composition and ultimately, what enabled life to evolve on Earth. To answer these questions, the ideal target to study would be a system which will eventually evolve into a star similar to the Sun, and potentially the planetary system that orbits it, but that is currently under formation. Despite such systems being very numerous in the Galaxy, detailed analysis of their chemical composition and physical structure is extremely challenging because these systems are faint, obscured by the clouds

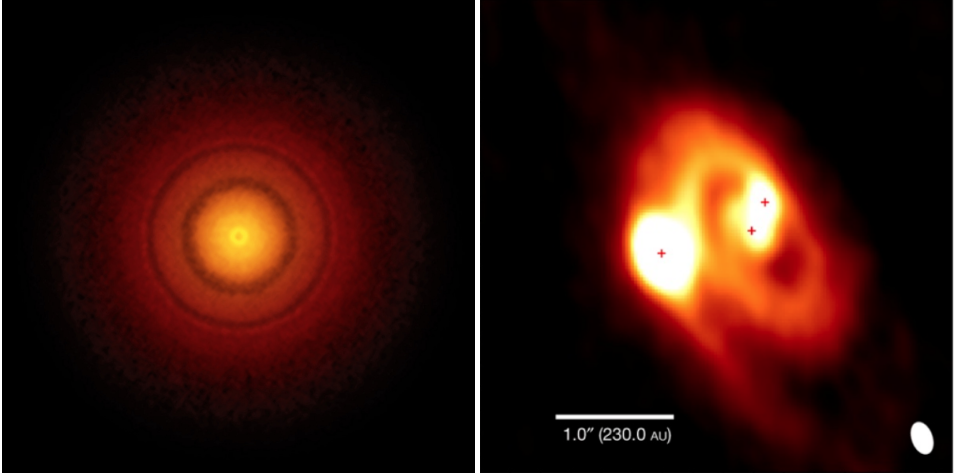


Figure 1.4: *Left:* Millimetre dust emission from the disk around the young star TW Hydrae observed by ALMA. Substructures in the disk in the form of rings and gaps in the distribution of the dust hint at dynamical processes associated with planet formation. *Right:* Millimetre dust emission from the extended disk around the triple system L1448 IRS3B revealed by ALMA. The positions of the three protostars are indicated by red crosses. Gravitational interactions between the forming stars leave clear imprints on the distribution of the surrounding material which appears to form a spiral arm emerging from the close pair (IRS3B-a and b) and extending to IRS3B-c. Credit left: Andrews et al. (2016), credit right: Tobin et al. (2016).

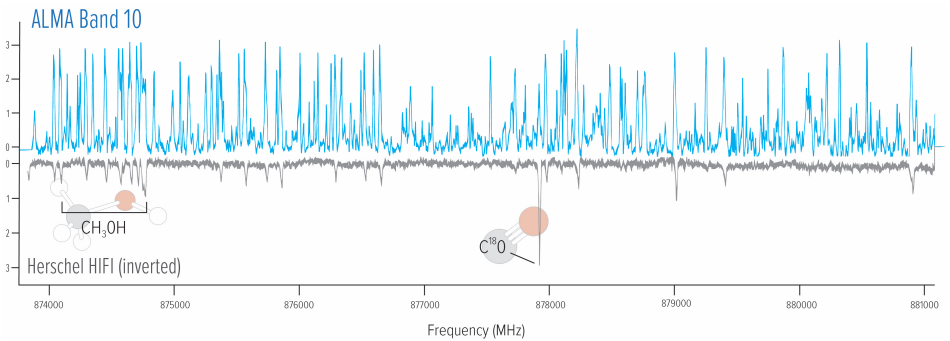


Figure 1.5: Comparison of ALMA data (top) to observations by ESA's *Herschel* Space Observatory (bottom) towards the high-mass star-forming region NGC 6334I. The line density of the ALMA spectrum is higher than that of the *Herschel* spectrum by more than a factor of ten (note that the *Herschel* data have been inverted for comparison). Lines of CH_3OH and C^{18}O are labelled. Credit: NRAO/AUI/NSF, McGuire et al. (2018).

from which they are forming and occupy a small spatial scale. In contrast, systems evolving into massive stars are much brighter and more easily resolved. In particular the high-mass star-forming regions located near the Galactic Center and in the Orion Nebula have been favoured targets for studies of chemical complexity. This is due to the high activity of star-formation in these regions, resulting in the sublimation of many ice species, making them more easily accessible for studies of molecular inventories. Also, the proximity of the Orion Nebula (~ 400 pc), making it visible to the naked eye and the closest region of massive star-formation to the Sun, has resulted in this region being a preferred target. However, in this thesis, the molecular composition of additional sites of high-mass star-formation, located away from the Galactic central region, are analysed. Studying these sites is important in order to better understand how star formation proceeds under less extreme conditions than those found in the Galactic Center and will eventually provide a link to the formation of low-mass, Solar-type, stars. In order to achieve this link, the thesis investigates the chemical composition found in high-mass star-forming regions located away from the Galactic Center and compares their composition to the composition of the few low-mass sources which have been extensively studied as well as to the composition derived for Solar System comets. Specifically, the chapters of the thesis investigate the following questions:

- How does the chemical composition of high-mass hot cores compare to the composition of their low-mass counterparts?
- How does the chemical composition of a star-forming region reflect its physical properties?
- Which molecules are available in hot cores for the formation of larger, more complex species?
- Does the inventory of Solar System comets reflect the composition of the hot cores?

The results presented in the following chapters are based on observations carried out with ALMA which, for the first time, has allowed sites of massive star-formation to be probed on solar system scales. In addition, the high sensitivity offered by ALMA ensures a more complete and more accurate characterisation of the chemical inventory of these sites compared with those derived based on single dish observations.

1.4.1 Analysis tools used in the thesis

For the analysis presented in the thesis, two main modelling tools have been used: Chapters 2 through 4 make use of the CASSIS¹ software for generating synthetic spectra while the analysis in Chapter 5 has been carried out using the LIME (Line Modeling Engine) radiative transfer code (see Brinch & Hogerheijde, 2010, for details). This section will shortly introduce each of these tools.

¹Centre d'Analyse Scientifique de Spectres Instrumentaux et Synthétiques:
<http://cassis.irap.omp.eu>

CASSIS

The CASSIS software has been developed by CESR/IRAP and can be used to identify and analyse spectral lines. The software reads spectroscopic data from common databases such as JPL (Jet Propulsion Laboratory², Pickett et al., 1998) and CDMS (Cologne Database for Molecular Spectroscopy³, Müller et al., 2001, 2005) and use these to generate synthetic spectra according to the inputs provided by the user. These inputs include excitation temperatures, column densities of the studied species, the source velocity of the studied object, the full width at half maximum of the lines as well as the angular size of the emitting region. By comparing an observed spectrum with the synthetic spectra generated by CASSIS, the molecular inventory of the region of interest may be characterised and excitation conditions determined. Within the CASSIS framework, model parameters may be optimised to fit an observed spectrum using a minimal χ^2 approach. CASSIS can be run assuming either local thermodynamical equilibrium (LTE) or non-LTE excitation conditions and can handle multiple temperature components as well as effects of optical depth.

LIME

LIME is a non-LTE radiative transfer code for modelling continuum and spectral line radiation, optimised for ALMA data. The code works in arbitrary, three dimensional geometries and may be used to model a variety of environments including giant molecular clouds, the disks and envelopes associated with forming stars, and in the case of this thesis, the coma surrounding a cometary nucleus. The code can solve the radiation transfer for an unlimited set of molecular species simultaneously and can handle overlapping lines. In addition to a physical model, the LIME code takes as input molecular collision rates, which may be adopted from, for example, the Leiden Atomic and Molecular Database (LAMDA; Schöier et al., 2005). This database holds collisional rates between H_2 and a number of the most abundant astronomical species. The output of LIME is a modelled sky brightness distribution that can easily be compared to observations.

1.4.2 Overview of chapters and general conclusions

In this section the main results presented in the individual chapters are summarised and the general concessions of the thesis presented.

Chapter 2 – Low levels of methanol deuteration in the high-mass star-forming region NGC 6334I

In this chapter, the methanol (CH_3OH) content of the high-mass star-forming region NGC 6334I is investigated. Since methanol is one of the most abundant organic species in star-forming regions it is often used as a reference when comparing chemical composition across sources. The characterisation of this species is

²<http://spec.jpl.nasa.gov>

³<http://www.ph1.uni-koeln.de/cdms/>

therefore essential. Utilising the high sensitivity and spatial resolution offered by ALMA, transitions of the less abundant, optically thin, methanol-isotopologues $^{13}\text{CH}_3\text{OH}$, $\text{CH}_3^{18}\text{OH}$, CH_2DOH and CH_3OD are identified in spectra extracted at nine locations across the NGC 6334I region. Based on these, the excitation temperature and molecular column density of each isotopologue is derived and the methanol deuteration fraction is compared between the different regions. The chapter concludes that both the $\text{CH}_2\text{DOH}/\text{CH}_3\text{OH}$ and $\text{CH}_3\text{OD}/\text{CH}_3\text{OH}$ values derived towards the hot cores in NGC 6334I are considerably lower than those derived towards low-mass star-forming regions, but only slightly lower than those derived for the high-mass star-forming regions in Orion and near the Galactic Center. Chemical modelling of the low methanol deuteration ratios indicate a grain surface temperature during the time of the systems formation of ~ 30 K, at which the efficiency of the formation of deuterated species is significantly reduced. This temperature is higher than what is predicted for low-mass star-forming regions where the levels of deuterium in simple molecular species indicate a dust temperature at the time of formation below 20 K.

Chapter 3 – Methylamine and other simple N-bearing species in the hot cores NGC 6334I MM1 – 3

This chapter continues the exploration of the chemical composition of the hot cores in NGC 6334I, with a focus on the simple nitrogen-bearing species methanimine (CH_2NH), methylamine (CH_3NH_2), formamide (NH_2CHO) and the ^{13}C - and ^{15}N -methyl cyanide (CH_3CN) isotopologues. These species are of particular interest when searching for the building blocks of life since nitrogen-containing bonds are essential for the formation of various biological structures, such as nucleobases and the linking of amino acids. In particular CH_3NH_2 is thought to be a key prebiotic species, but so far has only been securely detected in the giant molecular cloud Sagittarius B2, located near the Galactic Center. Using the same set of observations as in Chapter 2, a number of transitions of each of the N-bearing species are identified in spectra extracted at three locations across NGC 6334I. For each species and location, column densities and excitation temperatures are derived in order to investigate the relevance of the individual species as precursors of biogenic molecules. The chapter reports the first detection of CH_3NH_2 towards the hot cores in NGC 6334I. Taking methanol as a reference, the abundance of CH_3NH_2 derived towards NGC 6334I is slightly lower than towards Sagittarius B2 but higher by an order of magnitude as compared with the upper limit value derived for the low-mass protostar IRAS 16293–2422B. Based on the good agreement between model predictions of CH_3NH_2 ratios and the observations towards NGC 6334I, the chapter concludes that the formation of CH_3NH_2 is more likely to proceed via radical recombination reactions on grain surfaces than via gas-phase reactions. This process may be stimulated further by high grain temperatures allowing a larger degree of radical mobility, consistent with the relatively high dust temperature derived in Chapter 2.

Chapter 4 – Molecular complexity on disk-scales uncovered by ALMA: The chemical composition of the high-mass protostar AFGL 4176

This chapter presents an extensive analysis of the molecular inventory of the high-mass protostar AFGL 4176. By studying this inventory, the link between the chemical composition and evolutionary stage of the star-forming system is investigated and the source is placed in the broader context of star-formation. The AFGL 4176 system is of particular interest because it is one of the few known examples of a high-mass protostar for which signatures of a Keplerian-like disk have been detected. The analysis presented in this chapter is based on high sensitivity, high angular and spectral resolution observations obtained with ALMA, allowing many weak transitions to be identified. Across a total bandwidth of ~ 4.7 GHz, 354 lines are identified towards AFGL 4176 with a signal-to-noise of three or higher. Of these lines, 324 are assigned to 23 different molecular species and their isotopologues. For each detected species, the column density is derived and the abundance with respect to methanol is compared with abundances derived towards other high- and low-mass sources. The chapter concludes that AFGL 4176 comprises a rich chemical inventory including fourteen complex species, that is, species consisting of six or more atoms. The majority of the detected species are oxygen-bearing while fewer contain nitrogen, sulphur or a combination thereof. Taking methanol as a reference, the O-bearing species are three times more abundant than the N-bearing species. Overall, the chapter concludes that the chemical composition of AFGL 4176 is more similar to that of the low-mass protostar IRAS 16293–2422B than to that of the high-mass star-forming region Sagittarius B2(N). This similarity indicates that the production of complex species does not depend strongly on the luminosity of sources, but may be universal despite differences in physical conditions, or that the composition of species is set already in the ice during the cold cloud stage.

Chapter 5 – Exploring the volatile composition of comets C/2012 F6 (Lemmon) and C/2012 S1 (ISON) with ALMA

This chapter explores the volatile composition of the comae of comets C/2012 F6 (Lemmon) and C/2012 (ISON). These comets likely formed in the outer and cold parts of the disk which eventually evolved into the Solar System. Assuming that the comets have undergone no major processing since their formation, studying their composition can provide insight in the pristine composition of the Solar Nebula. Thereby, the comets provide a link between the chemical composition of the low-mass hot core equivalent from which the Sun formed and the planetary system which orbits the Sun today. As in the previous chapters, the analysis presented in this chapter is based on observations carried out with ALMA, making it possible to resolve the comae on spatial scales of ~ 300 km. The chapter presents the first ALMA detection of carbon sulphide (CS) in the coma of comet ISON as well as several newly detected transitions of methanol and one new transition of hydrogen cyanide (HCN) towards comet Lemmon. In addition, the previously reported transitions of HCN, hydrogen isocyanide (HNC) and formaldehyde (H_2CO) are confirmed towards both comets. Based on their spatial distribution, the chapter

concludes that HCN and CH₃OH are parent species, that is, species sublimated directly from the cometary nucleus, while CS, HNC and H₂CO are either daughter species, resulting from gas-phase chemistry in the coma, or parent species transported away from the nucleus by some refractory compound before being evaporated. For each detected transition, the line intensity is modelled and molecular production rates with respect to water are derived. These are consistent with ratios reported in the literature for other comets. The chapter concludes that the challenges faced when deriving molecular production rate ratios with respect to water due to the unknown collisional cross sections between water and other species, can be circumvented when only the innermost part of cometary comae is sampled. In this region of the coma, the densities are high and excitations therefore close to local thermodynamic equilibrium (LTE) meaning that the exact value of the collisional cross sections becomes less important. To achieve this sampling, the spatial resolution offered by ALMA is crucial.

In addition to the conclusions drawn on basis of the individual chapters the following lessons can be learned from the thesis as a whole:

- For the chemical characterisation of a star-forming region to be accurate and complete, high-quality observations, both in terms of sensitivity and in terms of resolution, are essential. As illustrated in Chapter 2, the high sensitivity of ALMA allows rare isotopologues, including deuterated species, to be detected. In turn, these detections provide a means by which the abundance of the corresponding main isotopologue, which is often optically thick in star-forming regions, can be estimated. In this way, a solid basis for comparisons of molecular species, both within a single sources and across different objects, is achieved. Similarly, the spectral resolution of observations is a critical factor for the secure detection of species in star-forming regions since spectra extracted from these are often very crowded and have many blended lines. Finally, as illustrated in Chapters 4 and 5, the high spatial resolution offered by ALMA makes it possible to sample cometary comae and star-forming regions on scales small enough to avoid confusion with surrounding material or averaging over environments that are different, thereby providing a purer picture of the molecular inventory of these objects. However, since opacities (of dust as well as gas) in regions of high-mass star formation can be high on these small scales, the necessity of high sensitivity observations, allowing isotopologue lines to be detected, as stated above, is even more crucial.
- The low deuteration of methanol observed towards the high-mass star-forming regions in NGC 6334I, similar to the levels of deuteration derived for regions near the Galactic Center, suggests that on cloud scales, the material of the star-forming region is "warm". In contrast, the higher relative abundance of O-bearing species compared with N-bearing species detected in the disk around the forming high-mass star AFGL 4176, similar to the ratios derived for the low-mass system IRAS 16293–2422, suggests that the material in this disk (and star) is cold, and may have been inherited from the densest, coldest, part of the parent cloud. If that is the case, the material which comprises

the disks around high- and low-mass stars, respectively, may have originated in environments which were equally cold. This implies that the disks in either region may be more similar than the conditions on cloud-scale suggest. Alternatively, AFGL 4176 may have formed in a relatively isolated environment rather than a cluster, which is otherwise typical for high-mass stars. In addition, many of the complex organic molecules detected towards high-mass stars (both in the NGC 6334I clouds and the disk around AFGL 4176), are also present in Solar System comets but have so far proven elusive in disks around low-mass stars, where they likely remain frozen. Disks around high-mass stars, where such organics are more easily detected, may therefore be very useful when making the connection between the composition of comets and the composition of disks around low-mass stars.

1.5 A look to the future

The search for complex molecular species in star-forming region is a highly active field of research and will continue to be so in many years to come. Historically, sites of high-mass star formation have been favoured in these searches since high-mass sites are generally brighter and have higher abundances of molecular species compared with low-mass regions, making them observationally more easily accessible. As telescopes have gained in sensitivity, many of the species known to exist in high-mass regions are now also being detected towards low-mass star-forming sites and in particular the high sensitivity offered by ALMA has played a crucial role in expanding the database of molecular inventories towards both high- and low-mass sources.

With the database growing, both in terms of the number of investigated sources and in the range of detected species, it becomes possible to test and refine the star-formation paradigm. In this respect, the statistical basis provided by the ever-growing database is essential, in order to ensure that the conclusions drawn regarding the processes occurring during the star-forming epoch may be free from observational biases due to a limited sample of sources. Detections of new species as well as revised abundances of known molecules in a wide variety of different sources will also help constrain their chemical formation pathways which can in turn be incorporated or updated in models of chemical reaction networks.

While the high spatial resolution offered by ALMA allows star-forming regions to be dissected and investigated on scales small enough to limit confusion from surrounding material, its high sensitivity enables the detection of many rare isotopologues, including deuterated species. A lot can be gained by studying these as the primary isotope of many of the most common and abundant species found in star-forming regions are optically thick and therefore cannot be used to derive column densities and excitation temperatures. In addition, the isotopologues likely trace different regions of the star-forming sites compared to those traced by the primary isotopes and may therefore provide a window through which regions that have so far not been accessible can be viewed. It is important to keep in mind, that if the search for rare isotopologues and deuterated species is to be a success, it

is of the utmost importance that the spectroscopic data of these species are available. To this end, laboratory investigations and theoretical calculations of the spectra of the species are essential. Finally, as the detection of rare isotopologues become routine in ALMA surveys, and the spectroscopic databases continue to be expanded with new species and transitions, the prospects for future studies of star-forming regions are bright.

In addition to the advances of ALMA, the future also brings exciting new possibilities for infra-red observations with the planned launch of the James Webb Space Telescope (JWST) in 2021. JWST will observe in the visible through mid-infrared ($0.6 - 27 \mu\text{m}$) wavelength regime, making it possible to probe the icy content of star-forming regions and study the molecular species found there. Also, the angular resolution of the JWST will allow the observations to zoom in on the innermost regions around forming stars as well as the ice in the dark clouds. In this way, a direct link between the complex species observed in hot cores and the species found in ices in dark clouds can be made.

Lastly, continued monitoring of Solar System comets is important and will provide tighter constraints on the composition of the Solar Nebula as well as an indication of the degree of molecular complexity present already at the planet-forming stage. In this respect, it will be important to characterise both the composition of comets but also the evolution and time variation observed in their comae as they are heated by the Sun. This will allow for a better separation of the chemistry induced in comets at later stages, such as thermal processing of the cometary surface near the Sun, from that which has been preserved from the protoplanetary disk stage. However, the short-term (less than an hour) time variability of comets also comprise a challenge for future observations since deep integrations will provide only a time-averaged view of the coma.

