Organic chemistry around young high-mass stars
Allen, Veronica Amber

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2018

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Download date: 06-03-2020
Chapter 1

Introduction

Galaxies are made up of more than just stars, they also contain gas and dust in clouds with a variety of densities. The coldest, densest, and darkest of these clouds are composed mostly of molecular hydrogen ($\text{H}_2$). In these molecular clouds, the formation of new stars takes place. Depending on a number of factors, including gas temperature (typically 10-100 K), density ($> 10^4$ atoms/cm$^3$), interstellar radiation field (ISRF – from $G_0=1$ locally to $10^5$ in Orion), and extinction ($A_V > 2$), we find that the chemical composition of these clouds and their substructures can be considerably different. The interdisciplinary sciences of astrochemistry and astrobiology have experienced a surge of interest in recent years. This is due, in part, to the detection of a multitude of extrasolar planets (see the NASA Exoplanet archive – Akeson et al. (2013) which could harbor life and to the discovery of living organisms in unexpected parts of the Earth – such as the deep oceans (Gerringer et al. 2017) or extremely acidic (Johnson & Schippers 2017) or alkaline (Grant et al. 1990) environments. Studying the chemical processes involved in producing organic molecules in space, especially in star-forming regions where these raw materials can be delivered to young planets, will lead to a better understanding of how life itself can begin. The study of chemistry in space is also important to chemists as it probes conditions that are not possible on Earth. In this work, we treat astrochemistry and star formation both as tools and subjects – using astrochemical models to interpret star-formation observations, and using observations to address the chemistry near star-forming regions.
Figure 1.1: The cycle of gas in galaxies. Diffuse gas clouds become dense molecular clouds, which fragment and collapse into protostars. Protostars gather mass through their accretion disks and will eventually form a main-sequence star, possibly with a planetary system. At the end of the star’s life, it loses mass to the interstellar medium where diffuse clouds are formed from which the cycle begins again. Image by Bill Saxton (NRAO/AUI/NSF).

In Figure 1.1 we see how the gas in galaxies is recycled and is chemically enriched through the life cycles of stars. The cycle begins with a diffuse atomic gas cloud (typical hydrogen densities: $n_H \sim 100-500$ atoms cm$^{-3}$) becoming a dense molecular cloud ($n_H > 10^4$ atoms/cm$^3$), where stars begin to form. The protostar gathers mass facilitated by an
accretion disk of gas and dust until it reaches the main sequence and begins fusion. The circumstellar disk can become a planetary system. Throughout the star and planet formation process, molecular species are forming, which could lead to prebiotic molecules being delivered to a planet and kickstarting life. At the end of a star’s life, it sheds its outer layers, returning its chemical complexity to the interstellar medium and eventually to diffuse clouds from which new stars form. The cycle can then begin again, driving the evolution of galaxies.

1.1 Star formation

1.1.1 The first stages

The earliest stages of star formation begin within molecular clouds. These objects tend to be tens of parsecs in size with gas densities of \(10^3 - 10^6\) cm\(^{-3}\) and at cold temperatures (10-50 K). Most recently, Herschel Space Observatory observations showed that these tend to be composed of elongated structures, earning them the name “filaments” (André 2017 and references within). Filaments typically have many stars forming within them that have not had a chance to interact with their surroundings and are therefore good locations to find pre-stellar cores (PSCs), the phase during which the collapsing core is gravitationally bound but has not yet formed a central hydrostatic object.

Important constituents of giant molecular clouds are Infrared Dark Clouds (IRDCs), discovered in the late 1990s (Perault et al. 1996). These are very cold (<25 K) filamentary structures that are optically thick at mid-IR wavelengths due to their high column densities \(N_{\text{col}}\) (gas density in a column along the line of sight) of \(10^{23} - 10^{25}\) cm\(^{-2}\). They are several parsecs in length and it is thought that these clumps (self-gravitating structures that will fragment into clusters Tan (2017)) house numerous pre-stellar cores. Figure 1.2 shows the Snake nebula G11.11-0.12, a commonly studied IRDC. Wang et al. (2014) found that in two bright regions (P1 and P6) there were multiple stars forming on small scales. Shipman et al. (2014) found there were several objects within the dark regions of the Snake nebula, including a more evolved protostar with signs of an outflow and a younger source that is possibly a high-mass pre-stellar core.
1.1.2 Low-mass star formation

Low-mass (M$< 2$ $M_\odot$) star formation has been fairly well understood for over 30 years based on the ideal isolated case presented by Shu et al. (1987). Figure 1.3 summarizes this process. A rotating stellar core is formed when part of a molecular cloud exceeds the mass where gravitational potential energy is balanced by the kinetic energy from the internal thermal pressure, magnetic fields, and turbulence. This is known as the
1.1 Star formation

Figure 1.3: **Top:** The stages of low-mass star formation. a) Dense cores form within dark molecular clouds. b) Large-scale gravitational collapse c) A protostar forms within an envelope of infalling material with an accretion disk and bipolar outflow. d) Mass accretion slows and the star becomes a T Tauri star – young low-mass pre-main sequence stars known for their variability (presumably due to accretion). e) Accretion stops and a pre-main-sequence star and circumstellar disk forming planets continues to evolve. f) The star reaches the main sequence and becomes a stellar system.

**Bottom:** Details of the accretion stage. Gas and dust fall from the envelope onto the circumstellar disk, which feeds the protostar. A bipolar outflow allows radiation to escape without halting accretion. (Images from Greene 2001)
Jeans Mass \( (M_J) \) and is given by \( M_J = \left( \frac{5kT}{Gm_H} \right)^{3/2} \left( \frac{3}{4\pi \rho_C} \right)^{1/2} \) where \( k \) is the Boltzmann constant, \( T \) is the temperature of the core, \( \mu \) is the mean molecular mass, \( m_H \) is the mass of hydrogen, and \( \rho_C \) is the density of the core. Observations show that, within filaments, collapse tends to begin with the shortest axis, then the longer axis, before finally becoming spherical. As the spinning core collapses, it develops a disk of infalling (accreting) material and a shock front, which generates most of the luminosity of these protostars, and bipolar outflows, which help to carry away excess angular momentum (see bottom panel of Figure 1.3). Eventually, the outflows become powerful enough that matter will fall preferentially onto the disk rather than onto the star, causing the protostar to cease accretion, though the surrounding circumstellar disk is still a source of excess infrared emission. The surrounding disk will likely develop planets that clear away much of the gas and dust until the star reaches the main sequence and its stellar wind blows the remaining material away, leaving a young stellar system possibly with planets.

### 1.1.3 High-mass star formation

While low-mass star formation can be studied relatively easily, studies of high-mass \( (M > 8 \, \text{M}_\odot) \) star formation have been troubled by physical and observational limitations (see review by Zinnecker & Yorke (2007), and more recently Tan et al. (2014) and Motte et al. (2017)). High-mass stars form deeply embedded in their molecular cloud and cannot be observed at optical wavelengths until well after they have reached the main sequence. This complicates the detection of new high-mass star-forming regions and the study of known ones. Additionally, high-mass stars are intrinsically rare (as seen from the long tail on the Initial Mass Function) and evolve quickly, making them even harder to detect. This is best illustrated by comparing the Kelvin-Helmholtz time \( (\tau_{\text{KH}} = GM^2/RL) \) with the free-fall timescale \( (t_{\text{ff}} = \left( \frac{3\pi}{32G\rho_0} \right)^{1/2}) \). The Kelvin-Helmholtz time is, effectively, the length of time before fusion begins (\( \sim 10^4 \) years for high-mass stars) and the free-fall timescale is the length of time a cloud takes to collapse to a point (\( \sim 10^5 \) years for \( n = 10^5 \, \text{cm}^{-3} \)). For high-mass stars, \( \tau_{\text{KH}} < t_{\text{ff}} \), so the star will reach the main sequence while still embedded in its natal cloud. Each stage in the low-mass star formation sequence has clear observational signposts, generalized using
Figure 1.4: Theoretical pre-main sequence life stages of a massive star: First, mass condensations form in a molecular cloud (top left) and collapse begins (top right). Hot molecular cores are formed (middle left) and radiation escapes from the poles in outflows. The radiation from the new stars forms hyper and ultra-compact HII regions (middle right). Finally, the new cluster of massive stars produces a photon-dominated region (bottom). (Figure from van der Wiel thesis 2011)
the shape and peak of the spectral energy distribution (SED), but this type of metric does not yet exist for high-mass star formation. This is because all of the pre-main sequence stages of high-mass star formation are embedded, therefore the SEDs look very similar whereas only the very earliest stage of low-mass star formation is embedded. There have been different attempts to classify young high-mass stars based on their near-, mid-, and far-infrared colors, as in the Red MSX Source (RMS) survey \cite{Lumsden2013}, or based on luminosity and clump mass \cite{Molinari2016}, among others.

There are two leading theories about the formation of high-mass stars: core accretion and competitive accretion. In the core accretion (also turbulent core or monolithic collapse) theory \cite{McKee2003}, a massive near-virial-equilibrium starless core will collapse to form a single massive star or close binary system, forming an accretion disk as a low-mass star would. A disk allows material to fall onto the star shielded from radiation pressure, while providing an outlet for radiation in the polar directions \cite{Krumholz2009}. In this theory, the accretion rate would have to be high, so models favor a very dense (surface density $\sim 1 \text{ g cm}^{-2}$), turbulent core. In these massive starless cores, support against fragmentation would be provided by turbulence, radiative feedback, and magnetic fields. A high-mass prestellar core has not yet been unequivocally identified, though numerous candidates have been proposed \cite{Pillai2011, Beuther2013, Tan2013, Cyganowski2014, Ohashi2016, Sanhueza2017}.

In the competitive accretion theory \cite{Bonnell2004, Bonnell2011}, one clump in a molecular cloud will form many low-mass cores, which will funnel the previously unbound gas preferentially onto the most massive core, forming a cluster of many low-mass stars surrounding a few high-mass stars. This process was shown to require a very-low-turbulence environment to form a massive star in the required timescale \cite{Krumholz2005}.

A third theory – coalescence – where two or more low-mass protostars come together to form a very massive star, may be applicable to some of the most massive stars discovered. Its authors \cite{Bonnell2011} admit that it is not likely to be a common formation scenario due to the extremely dense stellar clusters needed.
1.1.4 Circumstellar disks

The circumstellar disk is necessary for star formation in order to allow angular momentum to be transferred from the collapsing cloud while facilitating mass accretion. In young low-mass stars, disks have been consistently detected with a velocity field that shows Keplerian rotation, even at the youngest stages (Tobin et al. 2012). These disks tend to have radii of 100-300 AU, but disks with radii as large as 800 AU have been detected (Piétu et al. 2007).

Circumstellar disks around young high-mass stars have been more elusive. There have been several young high-mass stars housing Keplerian-like disks detected in recent years (Sánchez-Monge et al. 2014; Beltrán et al. 2014; Johnston et al. 2015; Cesaroni et al. 2017), two of which are the focus of Chapters 2 and 4 (G35.20-0.74N and G35.03+0.35). These tend to have radii of thousands of AU, though some as small as 300 AU have been reported. Many of these show asymmetries or inhomogeneities, which could be a sign of clumps or spiral structure, or could arise from interactions with other nearby objects as high-mass stars tend to form in groups. For a recent review of observations of circumstellar disks see Beltrán & de Wit (2016). A definitive detection of a high-mass protostar with a Keplerian disk and outflows would be a huge step in the study of high-mass star formation.

1.1.5 Hot Cores

After the earliest stages of high-mass star formation, there is a chemically-rich phase during which molecular species are released from the icy mantles covering dust grains that have been warmed by the protostar. Alternatively, molecular species could form in the warm gas surrounding the protostar. In high-mass stars, this is called a hot molecular core (HMC; Figure 1.4 – middle left) and the low-mass equivalent is a hot corino. It is during this stage that we observe complex organic molecules, molecules with at least 6 atoms containing both carbon and hydrogen (Herbst & van Dishoeck 2009). The detection of these species marks an important age milestone for high-mass protostars, as they are quickly (within 100 kyr) destroyed by the radiation from the star. It is expected that some of these complex organic molecules will remain in ice in the outer reaches of a star-forming region or freeze out within the mid-plane
of a protoplanetary disk at a later stage of stellar evolution and end up in comets or other planetary system bodies. This ice is important in an astrobiological sense, given that the delivery of organic compounds to a primitive Earth is likely to have been key in the origin of life.

At this stage, the envelope surrounding the protostar is heated by the collapse and much of this extra energy is radiated away through molecular transitions. These objects also have powerful outflows where high energy molecular and atomic transitions can be seen (upper energy levels of >500 K). As hot cores are empirically identified (as warm, dense, compact regions containing young high-mass stars showing complex organic chemistry), it is unknown whether this emission arises in the inner envelope, a circumstellar disk, or outflow cavity walls. The hot-core stage ends when the star begins ionizing its surroundings and becomes a hyper-compact HII region (Figure 1.4 – middle right), signposted by the detection of hydrogen recombination lines and free-free radio continuum emission.

The main focus of this thesis is the chemistry associated with hot cores. The current major questions about this stage of high-mass star formation concern the physical nature of HMCs and whether the young star also hosts an accretion disk during this stage.

1.2 Astrochemistry

1.2.1 A multidisciplinary field

Astrochemistry is the study of reactions and interactions between atoms and molecules in space. In the field of astrochemistry, observers, theorists, and experimentalists are tightly bound to each other (Figure 1.5) and communication between the three groups is necessary but can be difficult. Experimentalists test the effects of different astronomical phenomena (such as high energy radiation) on chemical reactions in a vacuum (or as close to a vacuum as we can achieve on Earth). These results are used by theorists to create chemical models that can show how the abundances of molecular species change with changing parameters (like gas temperature and density) and/or over time. Observers study spectra from different astronomical phenomena and rely on laboratory-tested or theoretically calculated frequencies to determine which spectral lines
1.2 Astrochemistry

Figure 1.5: Astrochemistry requires observers, theoreticians, and experimentalists to work together in concert. This thesis include both observational and theoretical results. (Adapted from the Widicus Weaver group website http://chemistry.emory.edu/faculty/widicusweaver/overview.html)

arise from which species and determine the chemical composition of their object. Theorists and observers work together using models to understand how the observed sources got their chemical composition, which at the same time tests if the models can reproduce reality. Often, spectral lines are observed for which there is no clear identity, and it may then be the case that the database is incomplete for some species and the experimentalists must seek to discover which species may be associated
with a particular transition using spectroscopy. The work in this thesis strives to bring these communities together.

1.2.2 Complex organic molecules

In chemistry, the term “organic” refers to species containing carbon and hydrogen atoms. Historically, this is because the chemists of the eighteenth century believed that organic matter from living things had chemical properties to differentiate it from inorganic matter. This turned out to be the presence of carbon and hydrogen and we continue to call molecules containing C and H organic molecules. Complex organic molecules, those consisting of 6 atoms or more (Herbst & van Dishoeck 2009), are a signpost of the hot-core stage, especially methyl formate (CH$_3$OCHO) and ethylene glycol [(CH$_2$OH)$_2$].

Around young high-mass stars, there are three phases that are important to the formation of complex organic molecules: a cold phase ($T \sim 10$ K), a warm-up phase ($T=10$-100 K), and a hot core phase ($T > 100$ K – high enough for gas-phase chemistry only).

In the cold phase, once gravitational collapse has begun but the temperature is still low, synthesis of complex organic molecules can begin in the icy mantles of dust grains as modeled by Charnley (2001) where a host of organic species are created by hydrogen addition reactions starting from CO in the ices (see Figure 1.6).

In the warm-up phase, more energetic transitions are seen as the radiation from the young star heats the dust and sublimes some of the ice mantle (Viti & Williams 1999; Viti et al. 2004; Garrod & Herbst 2006; Garrod et al. 2008). At these higher temperatures, the more complex molecules released from the dust grains drive a new, richer gas-phase hot core chemistry where many complex organic species can be formed. Chapters 3 features chemical models of the warm-up phase.

1.2.3 Gas and grain chemistry

In the laboratory, molecular species are investigated to determine the energies and frequencies associated with various rotational, vibrational, or electronic transitions for spectroscopy. Two major databases for these results are the JPL molecular spectroscopy database\(^1\) (Pickett et al. 1998)

\(^1\)http://spec.jpl.nasa.gov/
Figure 1.6: Organic molecules synthesized on grain surfaces. Broken arrows indicate activation energy barriers and the addition of 2H implies a barrier penetration reaction followed by an exothermic addition. Blue species have been detected in star-forming regions. (From Herbst & van Dishoeck 2009 based on Tielens & Charnley 1997)

and the CDMS (Cologne Database for Molecular Spectroscopy) (Müller)

http://astro.uni-koeln.de/cdms
et al. [2001]). Data concerning the collisional rates between molecules and \( \text{H}_2 \) or electrons are necessary for radiative transfer calculations but these are difficult to determine. Experimentalists determine collisional rates under laboratory conditions, but these must be scaled to lower pressure environments. Important databases where these data can be found are LAMDA (Leiden Atomic and Molecular DAtabase\(^3\)) (Schöier et al. [2005]) and BASECOI\(^4\) (Dubernet et al. [2013]). Theoreticians create chemical networks by determining the formation and destruction pathways of a large number set of molecules and their corresponding reaction rates. Such models estimate the abundances of each species based on the density and temperature of the gas, the UV field to which it is exposed, cosmic-ray ionization rate, and other physical conditions. Two databases for chemical reactions are KIDA (KInetic Database for Astrochemistry\(^5\)) (Wakelam et al. [2012]) and the UMIST database for astrochemistry\(^6\) (McElroy et al. [2013]). All of these databases are needed to get a complete picture of the chemistry in star-forming regions linking observations (transition frequencies) with models (abundances from chemical networks) and radiative transfer (excitation and collisional cross-sections).

In a pre-stellar core (the stage before gravitational collapse takes over to form a central object), atoms and molecules freeze onto dust grains. Here grain-surface chemistry proceeds and more complex molecules are built and occasionally released back into the surrounding gas. At mid-infrared wavelengths we can study the vibrational transitions of the ices frozen onto the surfaces of dust grains (Boogert et al. [2015]). Common species found in the ice mantles of dust grains are carbon monoxide (CO), methanol (\( \text{CH}_3\text{OH} \)) and water (\( \text{H}_2\text{O} \)). During this stage, areas with lower gas-phase CO abundance can be seen as a consequence of CO molecules freezing out of the gas onto the grain surfaces. CO is one of the main destructive partners of \( \text{H}_2\text{D}^+ \) so as a result, the deuterium fraction of the surrounding gas can increase significantly (Caselli & Ceccarelli [2012]).

Most gas-phase reactions in dark clouds and hot cores are two-body reactions between atoms, molecules, ions, and electrons where two of

\(^3\)http://home.strw.leidenuniv.nl/~moldata/
\(^4\)http://basecol.obspm.fr/
\(^5\)http://kida.obs.u-bordeaux1.fr/
\(^6\)http://udfa.ajmarkwick.net/index.php
these reactants combine to form one or more products. There are several types of two-body reactions based on the reactants and the products like neutral-neutral \((A + BC \rightarrow AB + C)\), ion-neutral \((A^+ + B \rightarrow AB^+)\), and dissociative recombination \((AB^+ + e^- \rightarrow A + B)\), among others. Photo-processes are also important with processes like photo-dissociation \((AB + h\nu \rightarrow A + B)\) and photo-ionization \((AB + h\nu \rightarrow AB^+ + e^-)\). Cosmic-rays become an important ingredient to the chemistry of dark regions where UV photons cannot penetrate. Cosmic-rays can directly ionize atoms and molecules but can also induce photo-processes.

On grain surfaces there are four important processes: adsorption (an
atom or molecule “freezing out” onto the surface), desorption (an atom or molecule sublimating off the surface), diffusion (an atom/molecule moving around on the surface), and reaction (Figure 1.7). Various types of neutral-neutral reactions take place between atoms, molecules, and radicals (atoms or molecules containing at least one unpaired electron). The simplest of these reactions is hydrogenation: adding a hydrogen atom to another atom or molecule. Radical-radical reactions generally proceed easily, as they have no activation barrier. Irradiation of ices by photons or cosmic rays opens up new avenues for chemistry to proceed. The two most important mechanisms for chemical reactions on grain surfaces are the Langmuir-Hinshelwood mechanism and the Eley-Rideal mechanism. The Langmuir-Hinshelwood mechanism is where both species in the reaction are moving over the surface and react upon meeting. The Eley-Rideal mechanism is when one stationary reactant on the grain surface is hit by another species from the gas-phase.

Some complex organic molecules are formed predominantly on grain surfaces and others in the gas phase, but generally there are contributions from both phases to the final gas abundances. The main formation route for the eight complex organic molecules studied in Chapter 3 is via grain surfaces.

### 1.2.4 Chemical modeling

Theoretical astrochemists use computer-based chemical models to better understand how different species form in different astronomical environments. Cuppen et al. (2017) give a recent review of gas-grain models which are summarized here. The two most common approaches are Monte Carlo models and rate-equation-based models. Microscopic Monte Carlo models typically follow the formation of molecules on the surface of a dust grain and show the physical distribution and composition of each layer of ice on a dust grain. The chemical networks in Monte Carlo models are very limited (100-200 species and a few hundred surface reactions). Rate-equation-based models use a series of ordinary differential equations describing the rates of two-body, photon-induced, and cosmic-ray induced reactions (as well as rates for desorption and adsorption) to show the overall gas- and (sometimes) ice-phase abundances of all species included in the model. This type of model does not indicate on which layer of ice molecules form, but gives the concentration over
1.2 Astrochemistry

time. Recent examples of rate-equation based studies are by Walsh et al. (2014, 2015); Drozdovskaya et al. (2014, 2015); Quénard et al. (2018) and Monte Carlo based studies are Vasyunin et al. (2009); Vasyunin & Herbst (2013).

Typically, rate-equation-based models are favored in large-scale models for their computational convenience. Single-point two-phase (gas and grain surface) models with thousands of reactions can take less than one minute to run. Adding physical structure requires a couple of weeks of computing time, but including bulk ice chemistry (a third phase with deep layers of ice where diffusion is inhibited) can increase this time to months. Monte Carlo models are computationally expensive with simple models taking days to weeks, but are useful for understanding the physical conditions on dust grains and interpreting both laboratory and astrophysical results.

The rate-equation based models in this work are used to determine differences in age between different high-mass hot cores by attempting to reproduce the observed molecular abundances with the model. Using this sort of model it is possible to test the effect of the physical environment on the chemistry. For example, changing the UV field, gas temperature, or gas density could change the abundances of various molecular species at a particular modeled time.

There are several known limitations to chemical models. For gas-phase processes, initial conditions can have an effect on the outcome of time-dependent models, chemical networks are not complete (and reduced networks are often used), and the range of model parameters (input temperature, density, UV field, etc.) can vary widely (Agúndez & Wakelam 2013). On grain surfaces, uncertainties are introduced simply by the fact that the processes involved are not well understood. Additionally, binding energies of molecules, the number density of grains and distribution of grain sizes, and diffusion rates all have inherent uncertainties.
1.3 Observational astrochemistry

1.3.1 Observing with sub-millimeter telescopes

Sub-millimeter (sub-mm) astronomy (wavelengths from 0.2-1 mm) has developed significantly in the past 30 years. Spectra from this wavelength range showcase molecular rotational-vibrational transitions, which can be used to determine the chemistry and physical conditions in cooler regions (up to a few 100 K) in the universe. Observing at these wavelengths requires precisely designed dishes with few imperfections (the irregularities in the dish must be less than 1/10th the observing wavelength – i.e. to observe at 0.8 mm the dish must be smooth to 0.08 mm scales) and a location with little atmospheric water vapor.

The first ground-based sub-mm observatories were opened in the late 1980s, as the technology for more sensitive receivers and dishes with higher surface accuracy improved. One of the first sub-mm telescopes was the James Clerk Maxwell Telescope (JCMT) on Mauna Kea, Hawaii.
This was connected to the Caltech Sub-millimeter Observatory to form the first sub-mm interferometer. The first major Hawaiian sub-mm interferometer was SubMillimeter Array (SMA), which opened in 2003. The Plateau de Bure interferometer (now NOEMA-NOrthern Extended Millimeter Array) began with three antennae in 1988 and has recently expanded to nine with the goal of a 12-dish interferometer by 2020. As technology continued to improve, the widely anticipated Atacama Large (sub)Millimeter Array (ALMA – Figure [1.8]), located in the Atacama desert in Northern Chile, was inaugurated in March 2013, and receivers continue to be added. ALMA’s large number of antennae with highly sensitive receivers (currently 66) and long baselines allow for spatial resolution down to 10 milli-arcseconds and velocity resolution as low as 50 m/s. Observational astrochemistry has experienced a boom in recent years with the advent of ALMA and the ability to detect very weak signals from rare molecular species and many lines from common species including their optically thin isotopologs. This gives observers the ability to characterize astronomical environments better than before with better accuracy and potentially greater chemical complexity. In chapters 2 and 5, we use ALMA for high spatial resolution and highly sensitive observations that allow us to resolve the structure of our young high-mass sources and detect weak signals from isotopologs and less abundant species.

There are several advantages of interferometric observations over single dish observations. First, additional antennae mean a larger collecting area and higher sensitivity. This allows the observer to detect very weak signals from rarefied gas. Second, the angular resolution is given by the distance between dishes so smaller structures can be resolved with more antennae at larger distances. Finally, several antennae linked together give two-dimensional maps with spectra at each pixel: a data-cube. Data-cubes are extremely useful in determining the small-scale structure in a star-forming region and observing the motion of the gas. Data-cubes can also be obtained with single-dish observatories using “on-the-fly” mapping, but these lack the sensitivity and angular resolution of interferometers. Very large dishes can be more sensitive than interferometers, but there is a limit to the size of dish that can be constructed. Even a dish with a diameter of 100s of meters will have an observable angular resolution limited by its size, whereas interferometers can have baselines of several kilometers giving a much higher angular resolution.
The main disadvantage to observing with an interferometer is that the observation will have a maximum recoverable scale (MRS) – that is, the largest feature that the observations are sensitive to. The MRS is related to the shortest baseline used in the observations and any emission that is more extended than the MRS will be filtered out. This was a minor problem with the observations in Chapter 2, which showed areas of absorption (“holes”) that did not originate with a physical structure, but from extended emission being filtered out. For this reason, when observing the outflows associated with these sources (Chapter 4), we used additional single-dish observations to ensure that extended emission would not be filtered.

1.3.2 Moment maps

One method that observers use to understand the distribution and movement of different molecular species within a gas is the moment map. The three most common are integrated intensity (moment zero), velocity (moment one), and line width or velocity dispersion (moment two). The moment zero map gives the total intensity of a particular spectral line at each pixel of the map, thereby showing the spatial distribution of the gas. The moment one map can be used to understand the motion of the gas and is particularly important when determining whether gas is rotating in an ordered way. The moment two map is important in understanding whether the distribution of gas velocities that are being observed is being affected by a temperature gradient or turbulence.

1.3.3 Spectral modeling

Spectral analysis of star-forming regions has given insight into the molecular species found in space and the composition and abundances thereof gives insight into the chemical history of the cloud. Spectral line strengths can be used to determine abundances of species while line profiles reveal the kinematics in a cloud. The intensity ratios between different transitions of the same molecule can be used to determine the temperature and density of that species using local thermal equilibrium (LTE) radiative transfer calculations like that in the software packages Cassis\(^7\) and

\(^7\)available from http://cassis.irap.omp.eu/
1.4 Goals of this thesis

The focus of this thesis is understanding the chemistry surrounding young high-mass stars within the context of star formation. The major science questions that are answered are:

- How does the chemical composition of a source relate to its evolutionary stage in the process of star formation? (Chapters 2, 3)
- Do high-mass stars form via Keplerian disks and outflows? (Chapters 2, 4)
- How does the prebiotic molecule formamide (NH$_2$CHO) form? (Chapter 5)

1.5 Outline

This section briefly addresses the outline of the thesis and the topics of the chapters.

---

XCLASS (Möller et al. 2017) or non-LTE software like RADEX (van der Tak et al. 2007).

The XCLASS software package models all transitions of a species at the same time while taking into account opacity and beam-filling factor (source size) to determine the excitation temperature and column density. It is especially useful in analyzing hot cores as multiple molecular species can be modeled at the same time, aiding in disentangling blended lines. In Chapters 2 and 5, I use XCLASS to determine the chemical composition of several different hot cores based on single pixels. XCLASS can also be used on data-cubes to analyze every pixel in a map and show variation in temperature and density.

RADEX is a radiative transfer code that assumes an isothermal and homogeneous medium, treats optical depth with a local escape probability, and uses collisional rate coefficients from the LAMDA database (Schöier et al. 2005). In this thesis, we use this software to calculate line intensity ratios for methyl cyanide (CH$_3$CN) across a range of kinetic temperatures and densities.
In Chapter 2, we use Cycle 0 ALMA observations to determine the full chemical composition (using XCLASS and Cassis) of two high-mass star forming regions which have been proposed to contain Keplerian disks: G35.20-0.74N (G35.20) and G35.03+0.35 (G35.03). The disk candidate within G35.20 shows an intriguing chemical separation between nitrogen-bearing species and oxygen- or sulfur-bearing species. We determine that either the disk was fragmenting on an unresolved scale into separate sources, or that the chemical timescale for change must be very short.

In Chapter 3, we use time-dependent rate-equation-based gas-grain chemical models to understand the chemical segregation in G35.20. We model a single embedded \((A_V=10)\) point, warming up the gas and chemically enriched ice from 10-500 K over different time periods (related to mass). We test the effect of changing different input parameters on the final chemical composition with the goal of reproducing the observed abundances across the disk candidate in G35.20.

In Chapter 4, we search for the outflows expected to be associated with G35.20 and G35.03 using NOEMA observations with complementary IRAM 30m observations. We image SiO and HCO\(^+\), as these are tracers of outflow activity, and compare the results with other observations of large-scale outflow tracers, infrared \(H_2\) emission from shocks and radio emission showing knots of material.

In Chapter 5, we study the chemical origin of formamide (\(NH_2CHO\)), a prebiotic molecule whose main precursor is thought to be either HNCO or \(H_2CO\). We analyze Cycle 2 ALMA data of three high-mass star-forming regions, with six total sub-sources, expected to contain young O-stars. We use XCLASS to determine whether the three species have any correlation between their observed abundances, and compare the integrated emission peaks (moment zero), velocity structure (moment one), and line width (moment two) trends between our three focus species for each subsource.

Chapter 6 contains our conclusion and an outlook into future studies.