Inextricable ties between chemical complexity and dynamics of embedded protostellar regions

Drozdovskaya, M.N.

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Author: Drozdovskaya, Maria
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INTRODUCTION

1.1 ASTROCHEMICAL SPRING

The study of chemical species and reactions in space constitutes the astrochemical field of research. It is one of the most interdisciplinary topics in astronomy and chemistry based on work that is theoretical, experimental and observational in nature. The footing of the field relies on the initial cosmochemical nucleosynthesis of light elements (hydrogen, H, and helium, He; see Galli and Palla 2013 for a review) and the subsequent stellar nucleosynthesis of heavy elements (such as carbon, C, oxygen, O, and nitrogen, N; see Nomoto et al. 2013 for a review). All the subsequent chemical evolution of ions, atoms, radicals and molecules is studied by astrochemists. The research field blends with the field of astrobiology, which covers the largest biocompounds and habitability conditions for life. Although, the definition of life itself is an actively debated topic[1]. The main goal of this thesis is to start putting together our 'astrochemical ancestral tree', i.e., to go after the simplest building blocks to life at the earliest phases of star and planet formation.

Some of the first interstellar polyatomic molecules detected in space were inorganic ammonia (NH_3, towards Sgr A and B2; Cheung et al. 1968) and water (H_2O, towards Sgr B2, the Orion Nebula and W39; Cheung et al. 1969), and the first organic polyatomic - formaldehyde (H_2CO, in numerous sources including Sgr A and B2; Snyder et al. 1969). A molecule is defined as organic if it contains at least one carbon atom. These earliest detections were made in the microwave range (wavelengths, λ, of $\sim 1-1.5$ cm; or frequencies, ν, of $\sim 20-30$ GHz) of the radio regime of the electromagnetic spectrum and paved the way to modern astrochemistry. Soon thereafter, in the 1970s, when dedicated millimeter ($\lambda \sim 1$ cm -1 mm; $\nu \sim 30-300$ GHz) telescopes became available, the list of observed species quickly expanded with many being detected towards high-mass star forming regions (e.g., Blake et al. 1987; Lovas et al. 1979; see Herbst and van Dishoeck 2009 for the most recent review on interstellar chemical complexity). Now, almost 50 years later, ever more complex compounds are being detected under interstellar conditions. The most recent highlights include the detection of the simplest sugar towards the low-mass protostar IRAS 16293-2422, glycoladehyde ($HOCH_2CHO$; Jørgensen et al. 2012); the first detection of a branched alkyl molecule towards Sgr B2(N), *iso*-propyl cyanide (i-C_3H_7CN; Belloche et al. 2014); and the first chiral molecule, propylene oxide towards the same star-forming region (CH_3CHCH_2O; McGuire et al. 2016). These discoveries indicate the presence of biologically relevant molecules in systems analogous in mass to our primitive Solar System and the existence of side-chain structures under interstellar conditions, which are characteristic to amino acids - the building blocks of life.

Gaseous molecules are not the end of the story for astrochemistry. Cold interstellar regions are also rich in various ices. Water ice was first detected towards the Orion Nebula via its very strong absorption feature at 3.1 μm caused by the O-H vibration

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[1] ESA definition `http://sci.esa.int/home/30551-what-is-life/`; NASA definition `http://www.nasa.gov/vision/universe/starsgalaxies/life's_working_definition.html`; ROSCOSMOS definition `http://www.federalspace.ru/1305/` (all as seen on June 14, 2016).

band (Gillett and Forrest 1973; see Dishoeck et al. 2013 and Dishoeck et al. 2014 for detailed reviews on interstellar water). Other confirmed solid-phase molecules include carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4) and methanol (CH_3OH; Whittet et al. 1996). Ices more complex than methanol, specifically formic acid (HCOOH), ethanol (C_2H_5OH) and the formate ion ($HCOO^-$), have only been tentatively detected, because it has been difficult to identify a single carrier (Schutte et al. 1999; see Boogert et al. 2015 for the latest review on interstellar ices). These findings signify that solid-phase molecules from the earliest coldest stages of star formation could potentially be incorporated into the building blocks of comets and planets as the ice-covered dust grains assemble to form larger bodies.

Astrochemistry is also booming in our Solar System. Thanks to flyby missions, remote observations and in situ measurements, the chemical inventory of several comets has now been probed and shown to be complex (as reviewed in Mumma and Charnley 2011). Until recently, the most complex cometary molecule detected was ethylene glycol towards C/1995 O1 (Hale-Bopp; Crovisier et al. 2004). Since then, ethylene glycol has also been detected towards comets C/2012 F6 (Lemmon) and C/2013 R1 (Lovejoy; Biver et al. 2014). The picture has just changed even further, with the *Rosetta* mission detecting a whole zoo of molecules towards 67P/Churyumov–Gerasimenko (67P hereafter; Le Roy et al. 2015), including glycine (Altwegg et al., 2016). Glycine (NH_2CH_2COOH) is the simplest amino acid with a disputed interstellar detection (Kuan et al., 2003; Snyder et al., 2005), which remains to be confirmed with ALMA (Kuan and Chuang, 2014). Complex organic molecules have also been found in other Solar System bodies. Ethyl cyanide (C_2H_5CN; Cordiner et al. 2015) and vinyl cyanide (CH_2CHCN; Palmer et al. 2016 subm.) have been detected in Titan's atmosphere (also see the review of Cable et al. 2012). Diacetylene (C_4H_2) and methylacetylene (CH_3C_2H) have been measured in Saturn's atmosphere (Guerlet et al., 2010), as examples.

The *Rosetta* mission is a unique endeavor to study 67P, as it is capable of performing in situ measurements of the gas and dust in its coma. The orbiter has been following the comet from the 6th of August, 2014 and will still orbit it until September 30th, 2016. This also includes the period of highest activity at perihelium on the 13th of August, 2015. The Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) instrument aboard *Rosetta* is of particular interest to astrochemistry thanks to its high mass resolution. The orbiter was also paired with the lander *Philae*, which executed a historic landing on a comet on November 12th, 2014. Even if for a short while, Philae was able to obtain the only currently available data set from the surface of the comet. As more data are being processed, further discoveries about 67P and its role as a probe of the initial makeup of our Solar System are anticipated.

Two schemes towards interstellar chemical complexity have been postulated (see Tielens 2013 for a review). The first is that of 'bottom-up chemistry' when large complex organics form from small simple species via various reactions in the gas and in the solid phase (Charnley et al., 1992; Herbst and van Dishoeck, 2009; Tielens and Charnley, 1997; Tielens and Hagen, 1982). The second is that of 'top-down chemistry', which starts with polycyclic aromatic hydrocarbons (PAHs) - organic compounds composed of hydrogen and carbon and that include aromatic rings (see Tielens 2008 for a review). As a result of photodissociation by ultraviolet (UV) photos, PAHs undergo dehydrogenation and fragmentation giving rise to flat carbon sheets, rings, chains and fragments, which are then free to assemble and combine with various functional groups (Allamandola et al., 1989). In reality, it is likely both schemes are active in different interstellar environments.

Bottom-up chemistry is supported by observations of complex organics (such as ketene, CH_2CO, formic acid, HCOOH, methyl formate, $HCOOCH_3$, acetaldehyde, CH_3CHO, dimethyl ether, CH_3OCH_3) under dark cold conditions of prestellar cores (in L1689B, L183 and L1544; Bacmann et al. 2012; Requena-Torres et al. 2007; Vastel et al. 2014) and laboratory experiments showing the formation of similar species under analogous conditions (see, e.g., Linnartz et al. 2015 for a review). Meanwhile, top-down chemistry is reinforced by the detection of interstellar fullerenes (spherical carbon cages, e.g., C_{60} and C_{70}; Cami et al. 2010), which theoretical models and laboratory experiments have shown to be formed via isomerization of dehydrated PAHs (Berné and Tielens, 2012).

Currently several facilities with unprecedented capabilities are in operation, including the Atacama Large Millimeter/submillimeter Array (ALMA) and *Rosetta*. The list will be extended in 2018 with the *James Webb Space Telescope* (*JWST*) and the Square Kilometre Array (SKA) in 2025 (tentatively). The JWST will be capable of exposing interstellar ices and key gas-phase molecules (such as CO_2, acetylene (C_2H_2), CH_4), while the SKA has the capability of accessing low-excitation rotational transitions of prebiotic compounds, both at much higher sensitivities than previously possible. Furthermore, several spectral surveys have been attempting to assemble the complete chemical inventory of star-forming regions. Recent examples include the Herschel observations of EXtra-Ordinary Sources (HEXOS) of Orion KL (Phillips et al., 2010)[2]; Exploring Molecular Complexity with ALMA (EMoCA) in Sagittarius B2(N2) (Belloche et al., 2014); the Protostellar Interferometric Line Survey (PILS) with ALMA of IRAS 16293-2422 (Jørgensen and et al., 2016)[3]; and Seeds Of Life In Space (SOLIS) survey of multiple targets with the NOrthern Extended Millimeter Array (NOEMA)[4]. The stream of major astrochemical discoveries in the last 5 years alone, and the state-of-the-art observing facilities at the disposal of scientists now and in the near future, implies that this is just the astrochemical spring.

1.2 MAKINGS OF PLANETARY SYSTEMS

Galaxies are characterized by strongly varying amounts of gas by mass depending on their stage of evolution from those that are gas-rich with high rates of star formation (such as spirals and irregulars) to those devoid of gas and newly formed stars (ellipticals; see (Courteau et al., 2014) for a review). On smaller scales of the interstellar medium (ISM), the gas is organized into ionized (gas temperatures, T_{gas}, of several thousand K), atomic ($T_{gas} \sim 1000$ K) and molecular phases (T_{gas} on the order of several hundred K and colder). Upon cooling, the diffuse atomic medium gives rise to dense giant molecular clouds, which are home to ongoing star formation. On the scales of these giant molecular clouds (~ 100 pc), physical phenomena such as gravitational collapse, pressure confinement, magnetic fields, turbulence, galactic sheer motions and various forms of feedback (e.g., HII regions and supernova) shape the internal structure of the gas in these clouds (see Dobbs et al. 2014 for a review). Observations have shown that the internal structure is complex and filamentary in nature. The filaments are long, but typically have widths of ~ 0.1 pc. They tend to be structured into dominating 'ridges' and disorganized networks or 'nests'. Dense cores ($\sim 0.01 - 0.1$ pc or $\sim 2000 - 20\ 000$ AU) form primarily along filaments likely as a result of fragmentation through gravitational instability, and consequently, are clustered together. The cores are classified into 'starless', i.e., lacking

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[2] http://www.submm.caltech.edu/hexos/
[3] http://youngstars.nbi.dk/PILS/
[4] http://solis.osug.fr/

a central protostar, and 'prestellar', defined as gravitationally bound and starless, but likely to collapse in the future (see André et al. 2014a for a review). In prestellar cores, the initial physical and chemical conditions for individual star and planetary system formation are set.

The process of star formation is thought to be better understood for the case of low-mass than for high-mass stars. Under the influence of gravity, the prestellar core is expected to undergo uniform, spherically symmetric Larson-Penston collapse with a flat density distribution at the center (Larson, 1969; Penston, 1969). This gives rise to the first hydrostatic Larson core (Larson, 1969). Thereafter, inside-out collapse of an isothermal sphere in isolation with an associated expansion wave and an initial central singularity (Shu, 1977) gives rise to the protostar (see Dunham et al. 2014a for a review). Initially, the protostar is deeply embedded in the remnant material of its parent core - the so-called envelope. This corresponds to the Class 0/I phases of protostellar evolution. Prestellar cores have an inherent initial rotation rate, and the conservation of angular momentum gives rise to a disk around the central object. Depending on the scientific community, this disk can be called an accretion disk (for those studying the growth of the protostars via accretion of material from the envelope and the disk), a circumstellar disk, a protostellar disk or a protoplanetary disk (for those researching planet and comet formation). Although there is much debate about the timing and formation mechanisms of rotationally supported disks (see Li et al. 2014, Turner et al. 2014 and Williams and Cieza 2011 for reviews), observations show that such disks are common in the Class II phase. Detections of flattened disk-like structure in earlier phases have recently been increasing (e.g., Ohashi et al. 2014; Tobin et al. 2012, 2015). The system further powers bipolar outflows along the axis of its angular momentum with opening angles that increase with time and become less collimated (see Frank et al. 2014 for a review). Accretion of material onto the protostar and the disk, in combination with the widening of the outflows, clear out the surrounding envelope material. Eventually, the central protostar and its protoplanetary disk are fully revealed, which corresponds to the Class II phase. In reality, however, many stars form in clustered environments and as binaries (see Krumholz et al. 2014; Luhman 2012; Reipurth et al. 2014 for reviews), thus smearing the idyllic scenario. Furthermore, the accretion of material by the protostar may occur through episodic events rather than as a continuous process as suggested by outflow and FU Ori observations (e.g., Plunkett et al. 2015; as reviewed in Audard et al. 2014; Hartmann and Kenyon 1996).

As the star-disk system evolves, the protoplanetary disk disperses via processes such as accretion onto the protostar, photoevaporation, stellar and disk winds, leaving behind a transitional and, subsequently, a gas-poor debris disk (see Alexander et al. 2014; Espaillat et al. 2014; Matthews et al. 2014 for reviews). Such disks are classified as Class III. The final phase of the evolutionary sequence corresponds to a mature star with a planetary system. Initially, in prestellar cores and Class 0-II protoplanetary disks, the dust is thought to constitute a mere $\sim 1\%$ by mass ($\sim 99\%$ of mass as gas; Williams and Cieza 2011). However, the gas to dust mass ratio decreases with time, as the dust becomes the only remaining disk constituent. From the onset of collapse in the prestellar phase, the micron-sized dust particles undergo grain growth processing (see Testi et al. 2014 for a review), which results in km-sized planetesimals and several thousand km-sized rocky planets. The various mechanisms of planet formation have a few Myr to build a gaseous giant, which is the typical lifetime of a gas-rich protoplanetary disk (Alexander et al., 2014; Williams and Cieza, 2011). The formation of such large bodies in turn contributes to the dispersal of the disk and has been suggested to erode gaps as early as in the Class I phase, based on high spatial resolution ALMA data (e.g., ALMA Partnership et al. 2015). Along with the same processes that build protoplanets or planetary embryos, comets are also formed. The reasons behind certain bodies growing to planets, while others remain small, are most likely correlated with the availability of dust and pebbles for accretion, and the destruction processes. Comets are also thought to spend most of their lifetime in the most distant regions of planetary systems, and hence are considered the most pristine tracers of the parent protoplanetary disk (see A'Hearn 2011 for a review). However, at the very least, their surfaces are subject to continuous space-weathering (as reviewed in Bennett et al. 2013). It remains to be modeled where exactly they are assembled in protoplanetary disks, which are thought to be subject to various internal dynamic processes especially in the Class II phase (see Armitage 2011 for a review).

The constraints on high-mass star formation are weaker than those on low-mass star formation, which in part has to do with larger distances to these sources, making spatially resolved studies more difficult. Several formation theories have been postulated (as reviewed in Tan et al. 2014). One of them is that of scaled-up low-mass star formation. However, high-mass protostars are associated with a significantly stronger radiation field, which gives rise to a (hyper or ultra) compact HII region and to radiation pressure that is capable of preventing accretion. This sets them apart from the weaker low-mass counterparts. The existence and survival of disks around such high-mass objects is currently in the early stages of verification (as reviewed in Beltrán and de Wit 2016). Multiple intermediate-mass A-type stars and high-mass B-type stars have been shown to have Keplerian disks (e.g., Cesaroni et al. 1999; Ilee et al. 2013; Kraus et al. 2010), while AFGL 4176 is for now the sole high-mass O-type star displaying a 'Keplerian-like disk' (Johnston et al., 2015). Whether such disks are able to form planets is currently entirely unknown.

1.3 THE CHEMICAL CONNECTION

The highest known level of chemical complexity is found here, on Earth. It appears that within our Solar System, complex organic molecules are also readily available in numerous comets and some of the atmospheres of our planets and moons (e.g., Saturn and Titan). Beyond our Solar System, the highest degree of complexity is found towards young star-forming regions. They are most easily detectable as gases in the hot inner regions of such systems - the so-called hot cores or hot corinos in the case of high- and low-mass star formation, respectively. It is currently still unclear which zone gives rise to this emission, whether this is thermally desorbed envelope ices, or outflow cavity wall-related emission (e.g., Dishoeck et al. 1995a), or ring-shaped emission associated with the centrifugal barrier (e.g., Oya et al. 2016). However, this may also depend on the mass regime. Nevertheless, the chemical links between a mature planetary system, such as our own, and the younger phases of extrasolar systems are intriguing. Chemical processes are expected to be universal; however, the commonality of conditions for efficient pathways towards chemical complexity is yet unknown.

The molecular inventory of protoplanetary disks can be probed via near-infrared (near-IR) in the inner 1 AU, mid-infrared (mid-IR) in the surface layers of the disk and millimeter/submillimeter in the outer disk (see e.g., fig. 1 of Dullemond and Monnier 2010). The midplane, where most of the dust and icy volatiles reside, is unfortunately obscured from direct observations. However, indirect chemical tracers can potentially be used to trace the major volatile reservoirs. For example, rings of gas-phase DCO^+ and N_2H^+ have revealed where gas-phase CO is enhanced in the midplane, i.e., where the temperature for its efficient thermal desorption is exceeded (also known as a 'snowline' or 'iceline'; Mathews et al. 2013; Öberg et al. 2015a; Qi et al. 2015a; Schwarz et al. 2016). The first complex organic molecule, gaseous methyl cyanide (CH_3CN), has been detected with ALMA in 2015 in a Class II disk around MWC480 (Öberg et al., 2015b). In 2016, ALMA revealed gas-phase methanol in the Class II disk around TW Hya (Walsh et al., 2016). These are the first observational signals that chemical complexity persists in protoplanetary disks, which has long been predicted by models (see Dutrey et al. 2014 and Henning and Semenov 2013 for reviews). These two detections pertain to molecules made available in the gas-phase in the cold outer disk regions via non-thermal desorption processes.

Although refractories (the silicates and carbonaceous compounds that make up interstellar dust particles) build up the rocky component of planets and comets, it is the volatiles (all the species that thermally desorb at temperatures below a few 100 K) that set the scene for prebiotically-relevant chemistry. In order to understand the chemical connection between the various phases of star and planet formation, it is necessary to piece together the transport and degree of processing from the initial prestellar core to the protoplanetary disk and into the protoplanetary and cometary bodies. For comets, this link can be studied via icy volatiles, since they do not retain any disk gases. For the case of gas giant planets, either the gases of the protoplanetary disk are needed to assemble their atmospheres or their atmospheres can be built up via accretion of icy pebbles. However, atmospheric physical conditions enable efficient two- and three-body gas-phase reactions due to high densities and temperatures. This implies that their composition is likely highly modified from the initially accreted gases, breaking the link with earlier phases of evolution.

The two extreme scenarios for the history of icy volatiles are that of *inheritance*, when the prestellar ices remain entirely unaltered and are incorporated into protoplanets and comets as such, and that of *reset*, when ices need to reform at some point between the prestellar phase and the incorporation into large bodies (Pontoppidan et al., 2014). Inheritance is tentatively supported by rough similarities in abundance ratios between prestellar cores and comets (Mumma and Charnley, 2011; Öberg et al., 2011c); while reset is founded on the presence of calcium-aluminium-rich inclusions (CAIs) in meteorites that require high-temperature processing. Since observations will always be snapshots of various stages of evolution of different systems due to the long astronomical timescales involved, models are the key to providing an answer to this question.

Some of the largest variations in terms of physical conditions are experienced by the volatiles during the initial collapse of the system. The typical dark, cold prestellar core conditions are replaced by a central irradiating and heating source, while densities range across many orders of magnitude. In the star formation community, it is thought that the temperatures are elevated from ~ 10 K to several tens of K closer to the central source, and to several hundred K in the inner ~ 1 AU for low-mass protostars (inner ~ 100 AU for high-mass protostars; Fig. 1.3; see Henning and Semenov 2013 for a review). Furthermore, simulations show the newly formed protoplanetary disk is to be warm ($20 - 80$ K; e.g., Visser et al. 2009a). This implies that during the transport from core to disk, icy volatiles are only selectively stripped from the grain surfaces via thermal (and non-thermal) desorption. This is considered the 'cold cloud start' perspective.

The Solar System community, on the contrary, typically favors the 'hot disk start' scenario. It is believed that the primitive Solar System formed from an initially hot (several hundred to several thousand K) Solar Nebula as evidenced by meteoritic samples and

Table 1.1: Summary of the assumptions made by the Solar System and star- and planet formation communities on the evolution of volatiles in the primitive Solar Nebula

Solar System	Star- and planet-formation
$T\,(\text{disk}) > 100$ K $\forall R$	$T\,(\text{disk}) \in [20, 80]$ K for $R > 1$ AU
inheritance of prestellar ices as gases and subsequent adsorption	transport of prestellar ices into the disk as ices during collapse
chemical equilibrium	non-equilibrium chemistry

the detections of crystalline sillicates out to tens of AU. However, this is not observed for extrasolar disks and likely does not imply these hot conditions for the entire innate protosolar disk. It is not excluded that certain regions may be hot enough for the production of CAIs and crystalline syllicates via shocks and viscous heating of the densest inner regions, for example. The unique cometary in situ measurements by the *Rosetta* mission promise to resolve these conflicting views (as summarized in Table 1.1) by providing one of the best data sets on cometary composition, which can then be compared and related to that of extrasolar analogues.

1.4 OBSERVING ASTROCHEMISTRY

Astrochemical questions can be targeted from three interconnected directions. The first approach is observational, which allows the determination of abundances, ratios and spatial distributions of various species under a range of different physical conditions. The second method involves laboratory studies, which are designed to mimic interstellar conditions under a controlled environment thereby permitting various processes to be disentangled. Alternatively, such studies are performed under conditions that can be extrapolated to those of the ISM, e.g., as done for the determination of rate coefficients for gas-phase reactions. The third technique is that of theoretical models, which incorporate experimental results and attempt to reproduce observations.

Gaseous molecules can be observed via electronic transitions in the UV and visible part of the electromagnetic spectrum, vibrational transitions in the IR, rotational transitions in the microwave or combinations thereof (rovibrational, vibronic and rovibronic transitions). Many astrochemical studies today are carried out in the millimeter/submillimeter regime, pushing from the radio into the far-infrared (FIR) range. Furthermore, smaller dishes are being incorporated into interferometric arrays, leading to a much larger synthesized antenna and very high angular resolution. Unfortunately, observations at mid- and far-IR wavelengths are difficult from the ground, since the atmosphere is strongly opaque in that range. Ground-based millimeter/submillimeter facilities such as the 100-m Robert C. Byrd Green Bank Telescope (GBT), the 15-m single-dish James Clerk Maxwell Telescope (JCMT), the single-dish Institute for Radio Astronomy in the Millimeter Range (IRAM) 30-m telescope, the single-dish 12-m telescope on Kitt Peak (as of 2013 operating with the European ALMA prototype antenna), the Nobeyama 45-m Radio Telescope and the recently upgraded eight 15-m antenna NOEMA (previously known as the Plateau de Bure Interferometer, PdBI) have consequently carried out much of the astrochemical observations. Additional progress has been made with the *Herschel Space Observatory* with a top spectral resolution, $R = \Delta\lambda/\lambda$, of $\sim 10^7$ for $\lambda \sim 150 - 600$ μm.

Currently in operation is the Stratospheric Observatory for Infrared Astronomy (SOFIA), which is an airborne observatory. At its cruising altitudes of $12-14$ km, only $\sim 1\%$ of the Earth's atmospheric water vapor remains, hence a larger fraction of the IR window is open for observations, albeit at a much lower sensitivity than *Herschel*[4]. SOFIA carries several instruments onboard, covering the $\sim 1-240$ μm range.

In 2016, ALMA is the most state-of-the-art interferometer in operation with fifty 12-m antennas in the main array (the 12-m Array), twelve 7-m antennas in the Atacama Compact Array (ACA or the 7-m Array) and four 12-m antennas in the Total Power Array (TP Array; ALMA Partnership et al. 2016). ALMA covers the $\lambda \sim 0.4-3$ mm ($\nu \sim 84-950$ GHz) range with resolutions ranging from $0.7''$ at 675 GHz to $4.8''$ at 110 GHz in the most compact configuration (~ 150 m) and from $0''.006$ at 675 GHz to $0''.037$ at 110 GHz in the most extended configuration (~ 16 km). ALMA Science Verification (SV) data with baselines of ~ 15 km reached unprecedented angular resolutions of $0''.075$ (10 AU) to $0''.025$ (3.5 AU) for continuum images at wavelengths of 2.9, 1.3 and 0.87 mm for the low-mass HL Tau star-forming region at a distance of 140 pc and revealed detailed ring structures (ALMA Partnership et al., 2015), which are currently a topic of heated debates (e.g., Dipierro et al. 2015; Okuzumi et al. 2016; Zhang et al. 2015). Thereby ALMA is zooming in on the dust evolution in the planet-forming region of disks and signaling that the processes of planetesimal formation are initiated very early on in the embedded phase.

Observations of solid phase molecules are more challenging from the ground. Only the strongest transitions of the most abundant solids can be studied, since solely vibrational transitions are possible in this phase, which correspond to the low atmospheric transmission region in the IR. However, the first ice detection was made with a 152-cm ground-based Mount Lemmon Observing Facility of the University of Minnesota with $R \approx 100$ at $\lambda \sim 2.8-5.6$ μm. The Very Large Telescope (VLT) consists of four 8-m telescopes that are used individually and cover the visible and IR ranges with subarcsecond capability and $R \approx 10^4$. It has been used, for example, to map the distribution of methanol ice and to study solid CO and OCN^- towards low-mass protostars (Broekhuizen et al. 2005; Pontoppidan et al. 2003a,b). Much progress has been made with spaceborne facilities, which included the *Infrared Space Observatory* (*ISO*) with peak $R \sim 1\,000$ (for ices) for λ in the $\sim 10-40$ μm range and the *Spitzer Space Telescope* with a maximum of $R \sim 600$ for a similar λ range (e.g., Boogert et al. 2013; Öberg et al. 2011). The difficulty with such space missions is not only the cost of construction and launch, but also the limited lifespan of infrared operations. Such instruments must be cryogenically cooled to just a few K in order to limit their own thermal radiation and become sensitive to IR emission from targeted sources; thus, once the coolant runs out, IR observations are no longer possible. The much anticipated JWST will once again open up the IR regime in the $0.6-28.5$ μm range for ice observations.

1.5 MODELING ASTROCHEMISTRY

Many different types of chemical and physical models are currently available. The choice of an appropriate model depends on the goal that one wishes to attain. Fig. 1.1 organizes the types of chemical models based on their microchemical accuracy and the feasibility of simulating the largest complex organic molecules. Quantum chemical calculations are used to precisely describe the state of a small system, for example that of a potential

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[4] SOFIA technical brochure, `https://www.sofia.usra.edu/sites/default/files/SOFIAtech2016.pdf`

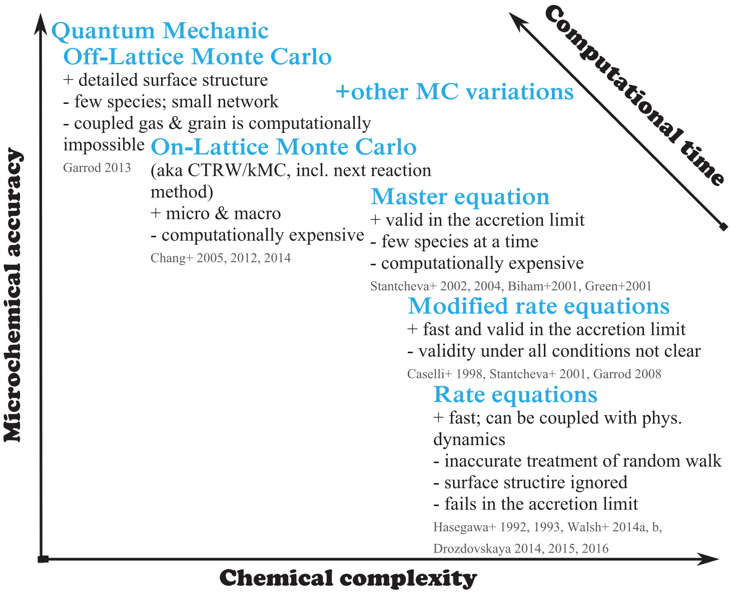

Figure 1.1: A summary of the types of chemical models available and their organization in terms of chemical complexity and microchemical accuracy.

well associated with a single binding site on the surface of a grain. The various types of Monte Carlo simulations can describe a larger section of a surface, but can only be coupled with a small set of species (see Cuppen et al. 2013 for a review). The rate equations method (Hasegawa and Herbst 1993; Hasegawa et al. 1992; see Herbst 1995 and Garrod and Widicus Weaver 2013 for reviews) is the computationally quickest approach available, thereby making it possible to compute the chemistry of complex organics, which require a large chemical network of several hundred species and several thousand reactions. Unfortunately, the speed comes at a price of chemical accuracy, because the detailed structure of the surface is completely neglected, for example. The modified rate equations and the master equation methods have the advantage of accounting for the case of single-monolayer chemistry; however, are also computationally slower.

In order to model the chemistry under interstellar conditions or for a certain source, the chemical model needs to be coupled with a physical framework (see Wakelam et al. 2013 for a review of the workflow). Fig. 1.2 thus adds two additional axis to the model space, in which the available physical models are organized in terms of complexity of physics that they account for and their computationally feasible run time, which corresponds to the age of the simulated target. The highest degree of detail is accounted for in hydrodynamic and magnetohydrodynamic models; however, they are also the most computationally expensive and not necessary more realistic than other types of models available. This implies that, in the context of star forming systems, they can typically be run only for the protoplanetary disk (e.g., Evans et al. 2015; Ilee et al. 2011) or the initial collapsing core (e.g., Aikawa et al. 2001, 2008; Furuya et al. 2012; Hincelin et al. 2013, 2016; Lee and Bergin 2015) separately. The simplest and quickest models are static and at most 2D in nature, i.e., no time-dependent physics (e.g., Aikawa et al. 1997, 2002). In such simulations the chemistry can be run for any desired amount of time, but are also an oversimplification of the physics involved. Semi-analytic models, in which physics change in time, have the advantage of accounting for macroscopic physical processes, while remaining computationally feasible in combination with chemical networks. Such are the models of Harsono et al., (2013), Visser and Dullemond, (2010), and Visser et al., (2009a, 2011), which compute the Shu collapse of an initial spherically symmetric core to an embedded star-disk system. The evolutionary nature of these simulations allows the reconstruction of the dynamic transport of the material into the protoplanetary disk and the computation of the physical conditions encountered en route.

Chemistry of prestellar cores is typically simulated within the simplest physical frameworks - single point models, since the physical conditions do not vary significantly within the cores (such efforts are reviewed in Agúndez and Wakelam 2013). Chemical networks are compiled based on the number of phases they account for and the types of chemical reactions included. For example, two-phase models account for the gas and solid phases, while three-phase models treat the surface and bulk of the ice separately. Gas-phase chemistry includes ion-neutral, neutral-neutral, photodissociation and ionization reactions (as reviewed in Smith 2011). In the context of complex organic chemistry, it has been demonstrated that most gas-phase reactions are not sufficiently efficient at producing observable abundances of such molecules (see the review of Geppert and Larsson 2013 on ionic reactions). Although, some neutral-neutral reactions and ion-neutral reactions with NH_3 may produce appreciable abundances of some complex organics under certain conditions (Balucani et al., 2015; Taquet et al., 2016). Typically, grain-surface chemistry that occurs directly in the solid phase has been invoked to reproduce the complex organic budget. This realm comes with many more processes and free parameters than gas-phase chemistry. Additionally, much depends on the detailed structure of the surface, and efficiencies of processes are typically species-dependent. The processes of adsorption, surface diffusion, quantum tunneling through diffusion barriers and nuclear spin conversion are reviewed in Hama and Watanabe, (2013) on the surface of amorphous water ice. It is thought that complex organics can form via radical-radical reactions and hydrogenations on the grain. Such chemistry can be UV-induced (see Öberg 2016 for a review), but can also occur under dark (in the absence of UV) conditions (Chuang et al., 2016; Fedoseev et al., 2015).

The solid and gaseous phases are coupled through the processes of thermal and non-thermal desorption. Non-thermal processes such as photodesorption due to UV irradiation (of internal protostellar, external or cosmic-ray induced origins) and reactive desorption are responsible for the gaseous abundances of volatiles at conditions cooler than the respective desorption temperatures (e.g., Vasyunin and Herbst 2013b). Quantum chemistry and molecular dynamics have helped to understand exactly how photodissociation and subsequent reactions lead to the expulsion of a gaseous molecule from different layers of the icy mantle (e.g., Andersson and van Dishoeck 2008; Andersson et al. 2006; Arasa et al. 2011) and how photodesorption of CO occurs ().

From that perspective, the chemistry of hot cores is anticipated to be simpler, since all volatiles are thermally desorbed. In hot cores is also where gaseous complex organics are most abundant and they have been modeled with some of the largest chemical networks (see Garrod and Widicus Weaver 2013 for a review). However, other work suggests that this later phase of star formation is not decoupled from the chemistry that occurs earlier. The duration of the prestellar phase is thought to play a role. If it is short, then warm carbon chain chemistry occurs and complex organic formation is impeded, resulting

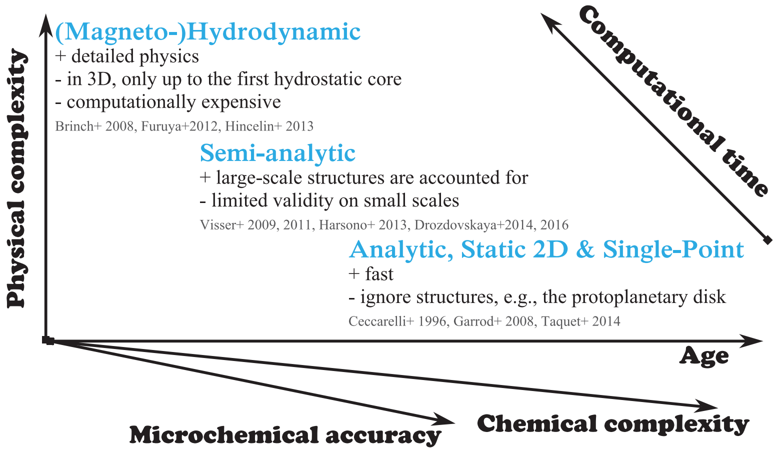

Figure 1.2: A summary of the types of physical models available and their organization in terms of physical complexity and the simulated age of the system.

predominantly in carbon chain molecules in the hot core (see Sakai and Yamamoto 2013 for a review).

Extensive astrochemical modeling effort has gone into protoplanetary disk models, which include static set ups, those that follow accretion flows within the disks and disks with turbulent mixing (e.g., Furuya and Aikawa 2014; Furuya et al. 2013; Semenov et al. 2006, 2010; Walsh et al. 2010, 2012, 2014a,b, 2015; Woitke et al. 2016). Such models have been successful at reproducing the observed molecules in the surface layers of disks and have raised questions on the chemical effects of mixing, turbulence and dust settling (e.g., Akimkin et al. 2013; Lee et al. 2010). Furthermore, dynamic processes may result in additional chemical modification (e.g., Aikawa et al. 1998; as reviewed in Aikawa 2013). Those can be accounted for in either the Lagrangian of the Eulerian specification of the flow field. In this thesis, the role of the earlier prestellar phase and the subsequent collapse to build a Class 0/I protoplanetary disk in the embedded phase is investigated. Thus, the output of the disk models discussed in subsequent chapters may be used as initial conditions for subsequent Class II disk models.

1.6 experimenting astrochemistry

The idea of getting a handle on interstellar chemistry under controlled experimental conditions came about just as soon as the flood of molecules started to be detected and dates back to 1937 (see, e.g., Hagen et al. 1979). In a laboratory setup, it is possible to regulate the availability of reactants and the physical conditions that they are exposed to, such as the temperature and UV flux. The methodology then allows the study of individual processes in a species-dependent fashion (see Linnartz et al. 2015 for a review). The most challenging aspect of experimental work is the detection of the products, in particular for solid phase experiments. It used to be necessary to transfer the more complex refractory products into a detector, such as a mass spectrometer, without inducing any additional chemical processing. Furthermore, the question of the extrapolation of experimental results to astronomical timescales remains to be tested with models.

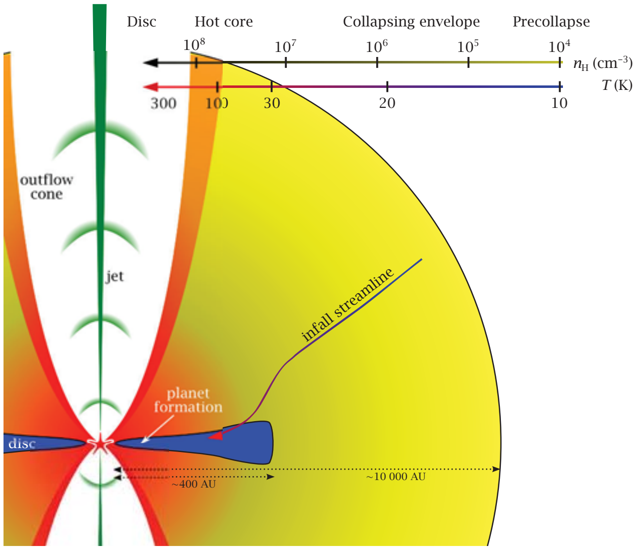

Figure 1.3: A schematic of the trail of collapsing material from the prestellar phase to their incorporation into planetesimals in the planet- and comet-forming region of the protoplanetary disk midplane in the embedded phase of star formation. Chemistry en route is pivotal for the main volatile species and the trace complex organics as a result of elevated temperatures and enhanced UV irradiation in the envelope. (Adapted from Drozdovskaya et al. 2014.)

On the other hand, laboratory experiments are the only way to disentangle on a reaction by reaction basis the intertwined reaction networks that operate under interstellar conditions. They are also key at providing crucial reaction rates and process efficiencies for use in chemical models. For example, the highly unconstrained processes of reactive desorption has been shown to be quite efficient on bare grain-like surface, but less so beyond a single monolayer coverage (Minissale et al., 2016b). Also, surface diffusion appears to be atom-dependent (Minissale et al., 2016a). Laboratory experiments are also capable of investigating the competition of a small network of reactions, such as that of the sequence of hydrogenation reactions of CO leading to CH_3OH. The most recent results are indicating that the various intermediate reactions are competitive and back reactions may also be important (Chuang et al., 2016; Minissale et al., 2016c). These results are yet to be incorporated into astrochemical models and are critical parameters for some of the model results presented in this thesis.

1.7 THIS THESIS: INFANT CHEMICAL COMPLEXITY

Astrochemistry has been a fundamental research topic at Leiden Observatory within Leiden University for several decades and is facilitated by several staff members from the observational, theoretical and laboratory perspectives under one roof. This thesis is centered around the embedded phase of star formation and the chemical links between the various stages of evolution. The primary goal of this work is to pinpoint the origins of cometary complex organic molecules in the proceeding protoplanetary disk and prestellar stages, both in the gas and solid phases. The grand motivation is to identify our interstellar roots. This work is unique in comparison to earlier publications due to the dynamic nature of the models used in combination with the large comprehensive chemical network. Three subsequent chapters pertain to physicochemical models and another is of observational nature. Main results of this thesis are given as bullet points below.

Chapter 2 The chemistry of methanol, a key precursor to complex organics, is studied as material undergoes dynamic transport from the prestellar phase to the protoplanetary disk. A 2D, semi-analytical collapse model by Visser et al., (2009a, 2011) is combined with a two-phase chemical network of Walsh et al., (2014a,b) and abundances are computed along trajectories that trace the assembly of a Class I protoplanetary disk around a low-mass protostar. Two disks on scales of several hundred AU are studied, which differ in the dominant large-scale motions that assemble them.

- *The results show that additional methanol ice is formed in the envelope en route to the disk; however, the net effect is that of reduction relative to the initial prestellar abundance due to destruction prior to disk entry.*

Chapter 3 The same two-phase chemical network is combined with a static, 2D physical framework mimicking the Class I phase of low-mass star formation on scales of several thousand AU. The chemistry of a set of oxygen-bearing complex organic species and their spatial distribution is modeled in the envelope, including the outflow cavity wall region. Outflow cavities enhance the FUV flux penetrating the envelope and thereby trigger frequent photodissociation within the ices, leading to active radical-radical chemistry.

- *Complex organic molecules are found to be abundant in the gas phase along cavity walls, if reactive desorption is efficient at a level of* 1%*, and in the solid phase at lukewarm dust temperatures in a toroidal region around the protostar.*

Chapter 4 The midplanes of the two disks studied in Chapter 2 are analyzed with high sampling in combination with an updated version of the same two-phase chemical network (Walsh et al., 2015) with the aim of obtaining detailed information on the comet- and planet-forming zone. This time, all the main volatile carriers and a set of complex organics are studied in order to obtain the dominant volatile and minor prebiotically-significant composition of the protoplanetary and cometary building blocks in Class I disks. The results support the 'cold cloud start' perspective based cometary correlations rather than the 'hot disk start' stance of the Solar System community. Additionally, the C/O and C/N ratios in gaseous and solid phases are derived based upon a full chemical network.

- *Model results indicate that volatiles are not simply inherited from the prestellar phase: the abundance of carbon dioxide ice can increase at the expensive of water ice, and complex organic ices form at the cost of methanol ice. The overall C/O and C/N ratios in the solid phase do not vary significantly in the planet- and comet-forming zone and models reproduce solar values within the assumed framework.*

Chapter 5 Sulfur-bearing species towards IRAS 16293-2422, the most chemically rich Solar System analogue, are analyzed based on ALMA data from the Protostellar Interferometric Line Survey (PILS). Abundances and upper limits are derived for molecules such as SO_2, OCS, CS, H_2CS and H_2S via multiple isotopologues. The results include a firm first-time detection of $OC^{33}S$ towards this source and a tentative first-time detection of $C^{36}S$ towards a low-mass protostar.

- A comparison of the PILS and ROSINA data on 67P/C-G in terms of ratios in sulfur-bearing molecules reveals that the comet is much richer in H_2S rather than OCS, which is the case of the protostellar Solar analogue. This potentially suggests that our Solar System formed in a warmer, CO ice-poor environment that inhibits efficient OCS formation via grain-surface chemistry.

Altogether, this thesis is an attempt to piece together the chemical connection between the prestellar core, the protoplanetary disk and the protoplanetary- and cometary materials, as illustrated in Fig. 1.3. The main take-home message is that the seeding of infant Solar System building blocks with complex organic molecules is unavoidable as a result of chemistry during protoplanetary disk assembly.

1.8 OUTLOOK: MATURE CHEMICAL COMPLEXITY

The suggested links between interstellar molecules and cometary chemical inventories are intriguing and require the extension of the work presented in this thesis. This connection must be thoroughly quantified, which is finally possible in light of the data from the *Rosetta* mission on 67P, which has the unique ability to probe the coma in situ. Future work will include the extension of the current chemical network with newly detected species in the coma of 67P. The physical model will be tailored to represent the innate Solar protoplanetary disk more closely, for example, by accounting for the Solar System environment (as reviewed in Adams 2010). In order to further extrapolate the connection, it is also necessary to accurately simulate the incorporation of ice volatiles into large bodies (e.g., Ciesla et al. 2015). Additionally, isotopic ratios acqross varies stages of evolution as measured in various species will be studied, as they could be an important tracer of the temperature during evolution. Potentially the first steps towards bridging the gap with astrobiology can also be made.

This research will be continued at the Center for Space and Habitability (CSH) at the University of Bern. The topic is timely with the current stream of astrochemical and cometary discoveries. The strong cometary and (exo-)planetary expertise at the CSH should yield fruitful interactions and depend our understanding of the chemical links from infancy to maturity of star- and planet-forming systems.