From Midplane to Planets
The Chemical Fingerprint of a Disk

Christian Eistrup

Promotor: Prof. dr. Ewine F. van Dishoeck
Co-promotor: Dr. Catherine Walsh

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Til mor, far og Astrid, for støtten til at tage springet!

The stars are for everyone to see, yet for no one to touch and control. So let go, sit back, relax, be fascinated, become curious, and wonder. The Universe can open and broaden your mind!

Contents

1 | Introduction

Since the dawn of time, two fundamental questions have caused amazement and wondering for humanity: Where do we come from? Are we alone? Although these questions are multifaceted, they are both addressed in the science of astronomy.

"Where do we come from?" seeks a coherent series of events, mechanisms and effects leading from the beginning of our Universe up until we ask the very question. And then asking the question "are we alone?" begs an understanding of our own "place" in the Universe, "why" we are able to philosophise and ask these questions, and ultimately, if someone or something else outside the Earth, or outside the Solar System, might be asking the same questions. In other words: is life unique to the Earth, or is there life outside it?

Addressing this requires input and expertise from several branches of science: physics, astronomy, chemistry, geology and biology, to mention some. The last two branches concern the evolution of a planet and of life on it, when the planet has already formed. The first three branches, on the other hand, can be used to predict to formation and evolution of planets.

1.1 Planets and exoplanets

A planet is, as currently defined by the International Astronomical Union (IAU), a celestial body that (1) is in orbit around the Sun, (2) has sufficient mass for its self-gravity to overcome rigid body forces so that it assumes a hydrostatic equilibrium (nearly round) shape, and (3) has cleared the neighbourhood around its orbit. Out of nine celestial bodies in our Solar System historically recognised as planets before the above IAU definition of 2006, eight of them satisfy these requirements, leaving out Pluto, which is now considered a dwarf planet.

Until quite recently (mid 1990s), the planets in the Solar System were the only ones known to orbit a main-sequence star. Since the first detection of a planet, a so-called exoplanet[1], in the 51 Pegasus system by Mayor & Queloz (1995),

[1] Extra-solar planet, orbiting another star than the Sun

an entire new field has erupted which is now flourishing in astronomy, namely exoplanet science. Given the basic challenge that planets and exoplanets are much smaller and much dimmer than their stellar hosts, thus intuitively very difficult to "see" through observations, a range of inventive and creative techniques have had to be developed for the detection of exoplanets. Only one of these, the direct imaging technique, can detect the signal from an exoplanet by simply observing the sky. This is due to advanced techniques, such as coronagraphy, whereby the observed starlight can be dimmed, so that the exoplanet signal does not drown in the stellar signal (see e.g. Marois et al. 2010). All other detection techniques used to this day, the radial velocity (RV) and transit methods, transit-timing variations, microlensing and astrometry, produce indirect detections of exoplanets, by observing the light from the host star and tracking changes in this light that are caused by the presence of a planet.

After more than 20 years of searching for exoplanets, almost 4000 have been confirmed to date. A "confirmed" exoplanet is one that has been detected using multiple detection techniques, thereby ruling out signals that may not come from planet interactions. The efforts going into searching for exoplanets have included the use of the world's most advanced telescopes, both on ground and in space, including such facilities as ESO's Very Large Telescope in Paranal, Chile, NASA's Hubble Space Telescope, as well as dedicated exoplanet hunting space missions such as NASA's Kepler, with more facilities planned for operation in the near future. However, smaller telescopes are also very effective, with the Lick Observatory, the Haute Provence Observatory, the Danish Telescope in La Silla, Chile, and the MEarth-project all having pioneered exoplanet discoveries.

The confirmed planets can be straightforwardly compared to the eight planets in the Solar System, in terms of sizes (planetary radii), masses and orbital distances from their host stars. This comparison shows that the exoplanets detected so far are mostly very different from the eight Solar System planets, rendering the Solar System architecture and planetary characteristics quite special. Predictions based on the sample of exoplanets so far point to planets being very common around stars in our galaxy, with Cassan et al. (2012) predicting 1.6 planets per star for the Milky Way. Dressing & Charbonneau (2013) suggest that exoplanets 0.5-4 times the radius of the Earth should be common around M dwarf stars.

The exoplanets vary greatly in size and orbital distance. Most exoplanets detected are small like the Earth, and they orbit close to their host stars (at fractions of an AU) See exoplanet.eu, but biases in the detection techniques play a crucial role here: the larger (for the transit and transit timing variations methods) and more massive (for the radial velocity, astrometry and microlensing methods) an exoplanet is, and the closer it orbits its host star (for the transit, transit timing variations and radial velocity methods), the easier the planet is to detect. Everything from sub-Earth sized planets (Barclay et al. 2013) to super Jupiter-sized exoplanets have been detected, and even multiple exoplanets orbiting the same star (see e.g. Gillon et al. 2017). All kinds of planets and planetary system architectures therefore seem possible.

Two goals of exoplanet science are 1) understanding the outcome scenarios of planet formation, and what exoplanets with certain characteristics tell us about how the exoplanets formed and evolved, and 2) finding habitable exoplanets, and ultimately the search for signatures of life on such planets, to be able to answer the fundamental question posed in the beginning of this text: Are we alone? An additional goal is also to construct an inventory of planets orbiting all types of stars, after all, the close to 4000 confirmed exoplanets are still few considering the predicted number of planets in the Milky Way galaxy: 1.6 exoplanets per star, with $\sim 10^{11}$ stars in the galaxy.

1.2 Making planets

Connecting detected exoplanets to how they were formed is an exciting and active field of astronomy. It links the hunt for, and study of exoplanets, to the field of star and planet formation. Planets form around stars, largely from the same type of material that the stars form from. The whole process starts when a large volume of space filled with gas and dust (a so-called molecular cloud) collapses under its own gravity, with material in the cloud compactifying on a smaller and smaller scale (see review by Li et al. 2014). In the centre of this collapse a protostar is formed and, because of the non-zero initial angular momentum of the material in the molecular cloud, gas and dust start rotating around the protostar in a protoplanetary disk. The material in this disk moves inwards towards the star, but this happens slower than the gravitational free-fall time, because the gas in the disk exerts an outwards pressure, and because the whole disk is rotating, thus adding an outwards pointing centrifugal force.

The dust in the disk will tend to settle gravitationally to the midplane of the disk, and will move closer towards the star than the gas. This is because the dust will dynamically decouple from the gas, when it has grown larger than a few microns. A dust grain will then no longer feel the outwards and upwards gas pressure, but will attempt to move in a Keplerian orbit around the protostar. However, since the dust is immersed in gas, it feels the gas as a head wind, and it thus moves slower in its orbit. This mean that the gas will slow down the dust grain, the dust grain will lose angular momentum, and will drift inwards. The efficiencies of these slowing mechanisms for dust grains depend on the size of the grains, with larger grains, around one centimeter in size, moving faster through the disk than smaller grains (see Lambrechts & Johansen 2012).

These grains consist of initially μm-sized silicates and carbonaceous material, and may have their surfaces covered with ice, depending on the temperature at their distance away from the protostar. The colder it is, the more different volatile molecules will be below their freezing point, and thus be frozen out onto the grain surfaces. In a typical protoplanetary disk, such volatile molecules are H_2O, which freezes out at temperatures below $\sim$180 K (dependent upon density and pressure), and CO_2, CH_4 and CO freezing out at decreasingly lower temperatures. The radial position in the disk midplane where the freeze-out rate of a given molecule onto a grain surface matches the thermal desorption rate of that same molecule off the grain surface is called the *iceline* for that molecular species. Icelines are important in the context of protoplanetary disks, as they largely define where in a disk,

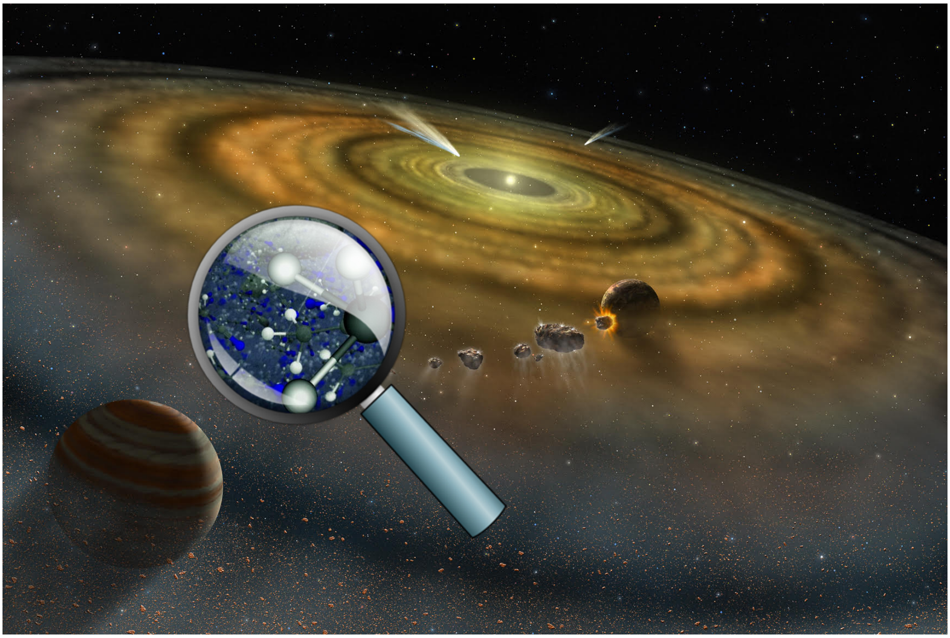

Figure 1.1: Artist's impression of planets forming in a protoplanetary disk of gas and dust. Solid impactors are seen hitting down on a planet. A zoom-in (under the magnifying glass) reveals that the gas and the dust are made up of molecules. *Composite image by Iris Nijman made from artist's impressions by NASA and by B. Saxton / NRAO / AUI / NSF.*

depending on the temperature and density structures, a molecular species is in the gas and ice phase.

The grains grow larger over time, mostly due to agglomeration at locations in the disk midplane that can facilitate a pile-up of grains. This can happen due to radial bumps in the gas-pressure profile (Pinilla et al. 2012), or due to streaming instabilities (Youdin & Goodman 2005), amongst other mechanisms. With a large enough concentration of solid bodies of different sizes, the larger bodies (planetesimals) above kilometer sizes can accrete smaller bodies called pebbles (Lambrechts & Johansen 2012) of centimeter to meters in size. This can lead to growing the planetesimals even larger, and when they reach tens-to-hundreds of kilometers in size they can start shaping themselves as spheres (see Fig. 1.1). Finally, when they reach several times the mass of the Earth, the bodies will be massive enough to have surrounding gas in the disk collapse down on their surfaces, in what is known as run-away gas accretion.

Upon accretion of the surrounding gas, a gas giant planet has been formed, of which the Solar System planets Jupiter and Saturn are examples. This is one theory for how planets are formed, the so-called core accretion theory, see Pollack et al. (1996). A planet forming through core accretion can experience a depletion in the material, solid and gas that it can form from. This happens if the planet forms late, after other planets have already used up material, or if it forms in a less massive disk, or in certain parts of the disk, with less material. In such situations some steps towards becoming a gas giant can be halted, and the results will be a less massive planet. Ice giants, like Uranus and Neptune, have icy cores and atmospheres made of hydrogen and helium, that are smaller than the atmospheres of Jupiter and Saturn. Lastly, giant planets can potentially also form by gravitational collapse of material locally in a protoplanetary disk, if the disk is massive enough. This scenario is called gravitational instability (Takahashi & Inutsuka 2014), and it is proposed as the explanation for giant exoplanets orbiting their host stars at large radii, from tens to hundreds of AU.

1.3 Protoplanetary disks, and the era of ALMA

Studying disks and planet formation has undergone a quantum leap in recent years, due to extraordinary new observational facilities, first and foremost ALMA (the Atacama Large Millimeter/submillimeter Array located in the Atacama Desert in Chile). ALMA, with its extraordinary spatial and spectral resolution power for radio frequencies from 84 to 950 GHz, has opened up opportunities for constraining structures of gas and dust, temperatures, densities, and molecular compositions of protoplanetary disks. All of these are vital for understanding how disks evolve, and, importantly, how planets may form inside them (see Williams & Cieza 2011, for a pre-ALMA summary).

ALMA has unveiled complex physical structures for both the gas and dust in disks, and also detected simple and complex chemical species in the gas. Some prominent findings of ALMA have been the detection of a dust trap (likely induced by a planet) in a transitional disk (in the object IRS 48 by van der Marel et al.

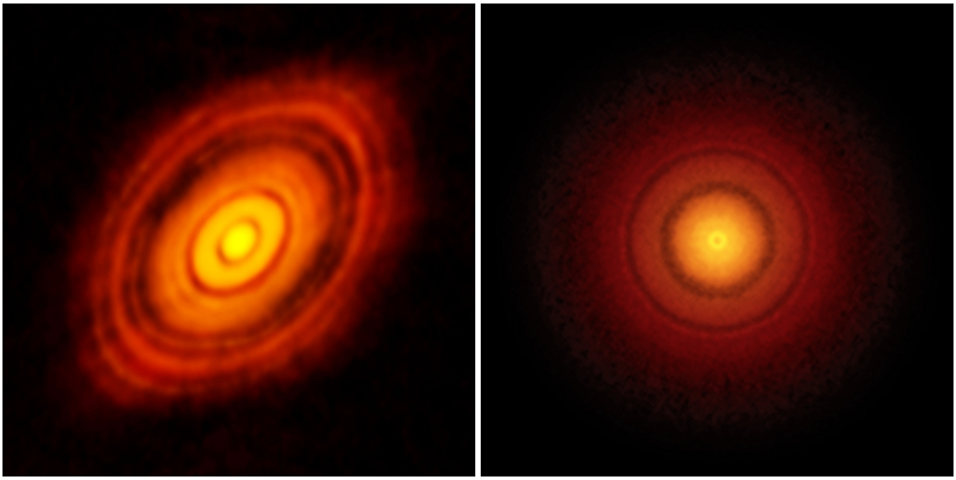

Figure 1.2: Images of millimeter dust emission from the disks around HL Tauri (left) and TW Hydrae (right). Rings are seen around both protostars. *Credit left: ALMA Partnership et al. (2015), credit right: Andrews et al. (2016)*

2013), the detections of dusty rings of millimeter sized dust around young stars (see e.g. ALMA Partnership et al. 2015; Andrews et al. 2016, and Fig. 1.2), and dust being concentrated closer to the star than the gas, which extends out to larger radii (see Facchini et al. 2017). The dust concentration close to the star points to dust evolution (although differences in optical depths of gas and dust also play roles): grains in the protoplanetary disk settle toward the disk midplane, and subsequently migrate radially towards the protostar, enhancing the dust concentration there. The rings of dust indicate that substructure exists in the dust concentration close to the protostar. The largely azimuthally symmetric nature of this substructure, as in the cases for the disks TW Hya and HL Tau, points to the millimeter-sized dust depleting in orbits of specific radii around the protostar: this could be a sign of protoplanets in the process of accreting, or already having accreted the surrounding dust in their orbits in order to grow larger, but there are also other explanations. However, the best evidence for ongoing planet formation, is in transitional disks because of the depth of the gas and dust cavities there (van der Marel et al. 2016).

The revelations of dust traps and ringed substructure in the dust emission from disks were therefore the first sparks in the field of observational planet formation. ALMA was also recently used to infer planets in formation around the protoplanetary disk HD 163296, this time not using dust emission, but instead the emission lines from carbon monoxide (CO), and specifically the subtle variations in the orbital speed of the CO gas, variations of order five to tens of percent, which only ALMA has the sensitivity to detect. These small orbital speed variations were linked to radial changes to the gas pressure induced by the presence of planets forming in the disk. Together, two teams of reseachers (Pinte et al. 2018; Teague et al. 2018) predicted three giant planets in formation around HD 163296.

Other examples of predictions of protoplanetary presence around protostars include the detection of spiral structures in the dust emission from a disk (e.g. Pérez et al. 2016; Hall et al. 2018), although thus far such spiral structures are rare. Hydrodynamical simulations have shown that a sufficiently massive planetary object orbiting at a large radius can stir up the dust structure inside the planet, and cause spiral structures in dust (Dong et al. 2015). The indications are thus plentiful, and the evidence growing, that ALMA is indeed able to detect signs of planets in formation, opening up an observational laboratory to test existing physical model predictions of how planet formation takes place.

Another aspect of protoplanetary disks and planet formation that ALMA has opened up is the mapping of the chemical (gas-phase) inventory of disks. With unrivalled spectral resolution, ALMA can detect spectral signatures of both simple molecules, like CO, HCN and HCO^+, and more complex ones, like H_2CO and CH_3OH, to mention a few. Other facilities, like the space missions *Spitzer* and *Herschel* have detected additional molecules emitting in the infra-red, and far-infra-red, respectively. Pontoppidan et al. (2014) gives an overview of detections by *Spitzer* such as CO_2, H_2O, C_2H_2 and HCN. Hogerheijde et al. (2011) detected cold H_2O and Salinas et al. (2016) detected NH_3, both using *Herschel*.

Observations of the disk around TW Hydrae (the left image in Fig. 1.2) have for one revealed much less CO gas than expected (see e.g. Nomura et al. 2016; Kama et al. 2016; Schwarz et al. 2016). Efforts with ALMA have also been put into tracing the CO iceline through observations of molecular species that can only exist in the gas-phase when CO is frozen out. N_2H^+ and DCO^+ are such molecules, and they have been successfully detected by Qi et al. (2013); Öberg et al. (2015). The detection of CN in disks has similarly been used to trace the exposure and penetration of UV radiation on disks, and hence their dust structure (Cazzoletti et al. 2018).

In addition to ALMA observations, optical and near-infrared facilities have also contributed with new insights on planet formation. Recently, Keppler et al. (2018) revealed images of a planet in formation around the young star PDS 70, which was detected using observations from the VLT/SPHERE, the VLT/NaCo and the Gemini/NICI telescopes and instruments. This discovery was the first-ever direct image of a forming planet, and it highlights the value of multi-wavelength observations (e.g. millimeter/submillimeter and optical/near-infrared) of protoplanetary disks, for a more detailed understanding of planet formation.

Because planets are forming in these disks, they will form from material containing these molecules, and by knowing how much of each molecule there is in the disks, and where it is located, predictions can be made as to the molecular composition of the planets. This can be predicting the relative amounts of CO_2 and H_2O, but more importantly the relative amounts of elemental carbon, oxygen, and nitrogen that goes into forming the planets.

1.4 Astrochemistry: laboratory, simulations and observations

Understanding the chemical composition in planet-forming regions is essential for predicting the compositions of the planets that form therein. In turn, given the growing chemical characterisations of exoplanet atmospheres, astrochemistry is essential for tracing the formation histories of these planets.

So what is the chemical composition of planet-forming material, i.e. the gas and ice-covered dust residing in the disk midplane? The answer to this is a link between observational exoplanet science, which has already detected CO, H_2O and CH_4 (Swain et al. 2008; Barman et al. 2015) in the atmospheres of exoplanets, and the science of protoplanetary disks and planet formation. The chemical composition of the latter must be what sets the chemical content of the former. There are at least two challenges to answering the questions.

First challenge. It is difficult to determine the chemical composition in the protoplanetary disk midplanes, even with ALMA. This is due to the upper layers of the disks obstructing the emission coming from the midplane, meaning it is mostly emission from the upper layers of the disk that can be observed. Since these upper layers have different physical conditions than the midplane, in that they are more diffuse, warmer, and experience more UV radiation from the protostar, the chemistry in these layers is different from the chemistry in the midplane, and the chemical compositions of the upper layers can thus not be used as probe for the midplane composition (see e.g. Walsh et al. 2015). However, successful efforts have been made by Zhang et al. (2017) to probe the CO in the midplane through detections of CO isotopologues, but it remains difficult to probe other gas species in the region (although for less volatile molecules this is due to them being frozen out in the outer regions, rather than intermediate layer obscuration).

Second challenge. Should it be assumed that the chemical composition in the midplane is directly inherited from the parent molecular cloud, such that the molecules in the cloud survived the trip to the midplane (Madhusudhan et al. 2014; Mordasini et al. 2016), and subsequently the incorporation into a planet? Or will chemical reactions happen along the way, thereby changing the chemical composition of the material? The molecules in the inner, hotter part of the disk could also be assumed completely reset (dissociated into atoms, see Visser et al. 2009; Pontoppidan et al. 2014) upon arrival in the disk midplane, followed by either LTE condensation when the disk cools, or chemical kinetics dictating the reactions between the atoms (Willacy et al. 1998; Aikawa & Herbst 1999; Vasyunin et al. 2008).

With the currently available data from astrochemical laboratories there is now a good basis both for binding energies for molecules to surfaces, and reaction rate coefficients for chemical kinetics in both gas phase and in the ice (see review by Cuppen et al. 2017). These coefficients can be used to construct chemical models that can simulate the kinetics of chemical reactions in space, based on balancing reaction rates that are forming versus destroying a given molecule. The rates of different reactions depend on physical conditions such as temperature and density, as well as the assumed timescale (more chemical changes can take place over longer time), and the abundances of ions and radicals, which are in turn products of ionisation by e.g. galactic cosmic rays. Given high enough temperatures and densities, local thermodynamic equilibrium (LTE) can be attained, at which point the equilibrium abundances of molecules can be computed via Gibbs' Free Energy minimisation.

LTE conditions may be present close to the star, or in a Hot Jupiter atmosphere, but in the colder disk midplane such conditions are not achieved. Therefore chemical kinetics is a more appropriate approach in these environments. Chemical kinetics are computationally slower and more complicated to handle than Gibbs' Free Energy minimisation, because of the larger amount of chemical species and reactions to account for, with a need to solve up to 1000 differential equations, and choosing appropriate numerical solvers and parameters to achieve a stable solution. Added complications are the uncertainties associated with the reaction rate coefficients, the need to treat gas-phase chemistry, gas-grain interactions and grain-surface chemistry simultaneously, and the question on how to parameterise grain-surface ice chemistry.

Several disk chemistry codes are available, codes that couple chemistry with disk physics (temperature, density, radiation field etc.). These are codes like the ProDiMo code (Woitke et al. 2009) and the DALI code (Bruderer et al. 2014). Other codes treat the chemistry independently of the physics, such as the BADASS code (Walsh et al. 2015). The different codes employ various degrees of complexity with regards to the different types of chemistry that they are focusing on: gas-phase, gas-grain interaction, or grain-surface chemistry, as well as assumptions for the physical conditions and feedback effects between physical and chemical evolution. Due to computational limitations, the codes are usually either treating the physical-chemical feedback effects self-consistently (the DALI code), but with limitations regarding chemical complexity (especially grain-surface chemistry), or treating especially said grain-surface chemistry extensively, but with no feedback effects from chemical to physical evolution (the BADASS code). The codes take their reaction rate coefficients from publicly available databases such as KIDA/OSU[2] or UDfA[3].

The BADASS code has a more extensive treatment of ice chemistry than the other codes. This code includes not only atom-addition (hydrogenation), but also radical-radical or radical-molecule reactions involving ice species that thermally diffuse from one surface site to another (e.g. $\mathrm{iCO} + \mathrm{iOH} \longrightarrow \mathrm{iCO_2} + \mathrm{iH}$, where "i" denotes ice species). Because the gas and dust in the dense disk midplane can be assumed to be thermally balanced, the gas-phase chemistry can be treated simultaneously with these chemical effects on the grains. This also means that the code can treat adsorbed molecules (molecules that bind to the grain surface from the gas-phase) as a part of the grain-surface chemistry, even if the temperature is higher than the freeze-out temperature prescribed by the binding energy of the molecule, because diffusion across the ice surface is faster than desorption due to the lower barrier for the former. This effect is a consequence of the treatment of

[2] http://kida.obs.u-bordeaux1.fr/networks.html
[3] http://udfa.ajmarkwick.net

freeze-out in the chemical kinetics framework: a chemical species does not simply exist as gas inside its iceline, and as ice outside it. The freeze-out and desorption terms for a given molecule in the rate coefficients framework are always both at play, and the iceline is simply the radial location where temperature and density lead to the two terms matching each other. But a molecule can still freeze out inside the iceline, and still thermally desorb from the grain surface outside of it, thus allowing for interesting chemical effects in the vicinity of icelines.

Chemical kinetics, including complex grain-surface chemistry, allows for a comprehensive treatment of chemistry for volatile molecules (molecules with a low binding energy) in the midplanes of disk. Chemical kinetics codes are thus important for predicting how the chemical composition in the midplane evolves over time, and what the composition of the material will be when it is being incorporated into planets and other celestial bodies.

1.5 Combining astrochemistry and planet formation

Planet formation models have thus far mostly assumed that the chemical composition of the planet-forming material was inherited from the parent molecular cloud, and remained chemically inert until incorporation into planets (see e.g. Ali-Dib 2017; Alibert et al. 2013; Mordasini et al. 2016). Because a certain set of molecular abundances has then been assumed for the planet-forming disk midplane, this simplification has meant that at any radial point in the disk (with a given temperature) it was known which molecular species were in gas-phase and which were ices on grains. This would only depend on the binding energies of the molecules.

Depending on where a planet is then assumed to be formed, and which stage of formation it is in (only growing from solid material, or also accreting gas), its final composition could be estimated, from the molecules at that location in the disk. Especially the relative amounts of elemental carbon and oxygen at the location (see Fig. 1.3) would then set the chemical basis for bulk and atmospheric chemistry in the planet, where chemistry is likely closer to equilibrium conditions (see e.g. Mollière et al. 2015) than was the case in the protoplanetary disk midplane. Planet formation modelling efforts that have included treatment of chemical evolution in the disk midplane before forming planets include Cridland et al. (2016, 2017). However, they focused on the final chemical composition of the formed planetary atmospheres, rather than the chemical changes to the gas and ice in the disk midplane occurring before initiation of planet formation.

Another key question in modelling especially giant planet formation is if their atmospheres are built mostly from gas accretion, or from impacting icy solids. Cridland et al. (2016, 2017) assumed only gas accretion at play for building a planet atmosphere, whereas Mordasini et al. (2016) found that by accreting gas and icy pebbles onto the giant planets, their atmospheric compositions ended up dominated by that of the pebbles, rather than that of the accreted gas. However, it is still debated to which extent, and for which impactor sizes and velocities, the solid bodies will be gravitationally scattered by the planets, rather than accreted

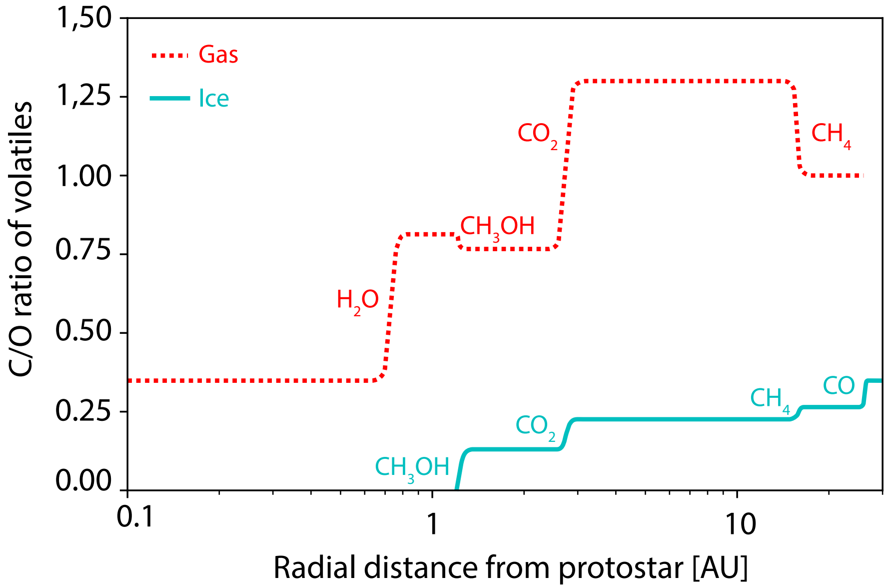

Figure 1.3: Carbon-to-oxygen (C/O) ratios of gas and ice in the disk midplane as a function of distance from the protostar. Each vertical transition marks the iceline region of the molecule noted next to the transition. Overall C/O ratio is 0.34, therefore the gas has this value close to the star where all volatile molecules are in the gas, and the ice has the value in the colder, outer disk where all volatile molecules are ices on grains. No chemical reactions are included besides freeze-out of molecules onto grain surfaces, and desorption of molecules off the surfaces of grains. *Image credit: Iris Nijman and Christian Eistrup*

(see e.g. Birnstiel et al. 2016; Johansen et al. 2014; Bitsch et al. 2015). Because the answer to this question remains unclear, the evolution of the chemical composition of both the gas and ice in the midplane of a disk are of interest in the context of formation of giant planet atmospheres.

Öberg et al. (2011) realized that the C/O ratios of gas and ice changes with disk radius due to the sequential, temperature-dependent freeze-out of the main volatiles, such as H_2O, CO_2 and CO. In Fig. 1.3 an estimate of carbon and oxygen content in the gas and ice as a function of radius can be seen, assuming the overall carbon-to-oxygen ratio (C/O ratio) to be 1/3, with abundances taken from Table 2 of Marboeuf et al. (2014). Changes to the gas and ice content of carbon and oxygen, respectively are seen at five distinct locations, namely (from inside to out) at the icelines of H_2O, CH_3OH, CO_2, CH_4 and CO (as marked in the figure). The icelines are not sharp. This is because the temperature and density-dependent balance between freeze-out and desorption makes for a radial range of change from gas to ice (outward), rather than sharp steps. This is thus slightly different from Fig. 2 in Öberg et al. (2011), which assumed sharp transitions from gas to ice. However, the big question remains: is it a good assumption that the planet-forming gas and ice in the disk midplane do not change chemically over time? And in case it does change, under which circumstances (temperature, density, ionisation level, and time frame) do changes occur?

In case the material does change (chemical evolution) it could have far-reaching consequences for the understanding of planet formation. First and foremost, changing chemistry for pre-Solar conditions could be compared to the current chemistry of the Solar System (e.g. planets and comets), to constrain which conditions the Solar System may have been subject to during its formation and evolution. Second, a treatment of disk midplane chemical kinetics incorporated into planet formation models may provide a more complete picture of the chemical makeup of exoplanets and their atmospheres.

1.6 Comets as fossils of planet-forming material

Planets are not the sole outcome of disk evolution: in the icy outer parts of disks, there are also left-over planetesimals made from the solid material that was not incorporated into larger bodies (see reviews by Mumma & Charnley 2011; A'Hearn 2011). These planetesimals are called comets, and consist mostly of volatile ices. Comets have been monitored and observed for decades, with comet 1P/Halley being one of the most famous comets. It is a short-period comet visible with the naked eye on the night sky every ∼75 years, and its appearance has been reported through millennia. It has a perihelion of 0.6 AU, thus inside the orbit of the Earth, making it an easy comet to study while on its close encounters with the Sun. The last encounter was in 1986, at which point the *Giotto* spacecraft came within close vicinity to it, enabling the detection of several molecular species in comet 1P's coma (Eberhardt 1999).

Besides *Giotto*, ESA's *Rosetta* mission recently accomplished landing a module (*Philae*) on comet 67P/Churyumov-Gerasimenko, as well as providing images of a comet with unprecedented detail (see Fig. 1.4). One of many interesting results from the *Rosetta* mission was the detection of abundant molecular oxygen at O_2 (moxy) at a level $\sim 4\%$ with respect to H_2O ice in the coma of 67P (Bieler et al. 2015). This was a surprising discovery, since O_2 ice is not thought to be abundant in molecular clouds. This result led to a re-analysis of data from the *Giotto* mission revealing similar levels of O_2 ice in comet 1P. O_2 ice may thus be a common ice species on comets in the Solar System.

Comets are considered relatively pristine composition-wise. Because they have likely formed from icy grains colliding and sticking, the ice composition on comets could possibly trace the icy volatile chemical history of our Solar System. Thousands of comets are known nowadays, and even the detections of exocomets orbiting other stars than the Sun have been claimed (Matrà et al. 2017a,b). In the Solar System many molecular species have been detected in comets, as seen in the cometary volatile inventory compiled by Le Roy et al. (2015). More is thus known about cometary composition than about exoplanet atmospheric compositions, and because comets likely play a role in planet formation (as planetesimals forming planetary cores, and as impactors "polluting" exoplanet atmospheres), it is important to understand the chemical evolution and composition of the comets

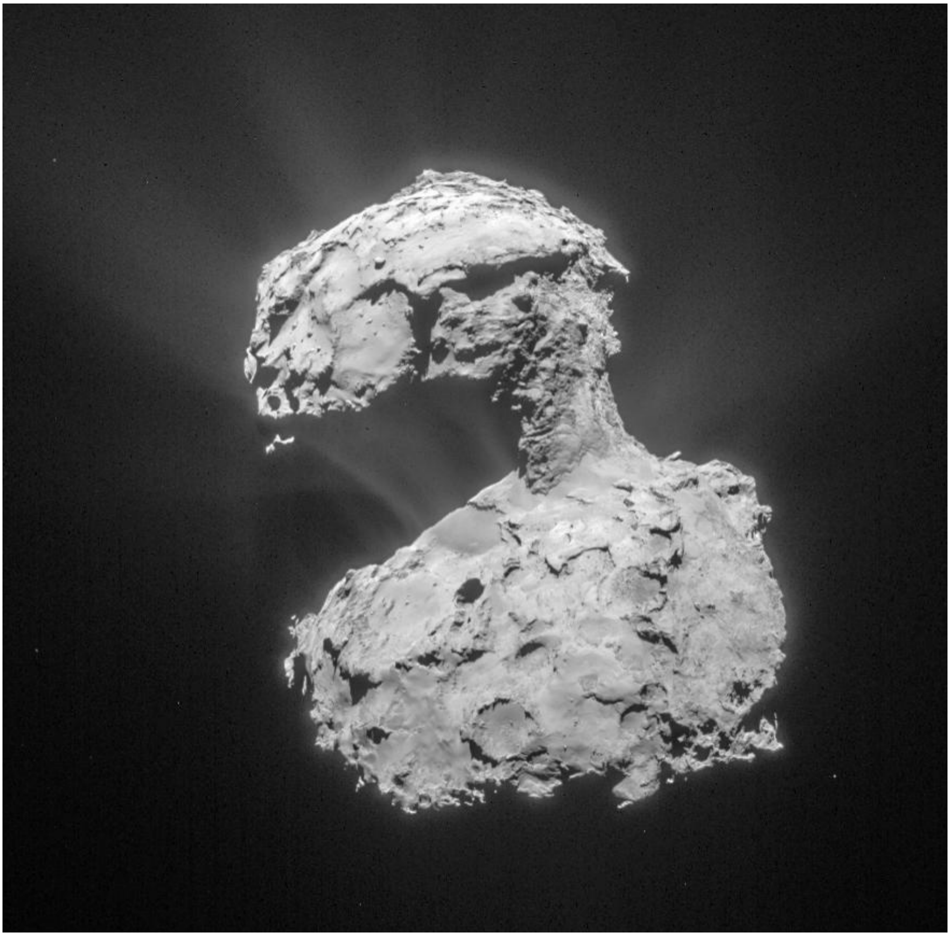

Figure 1.4: Image of comet 67P taken by the ESA *Rosetta* mission *Image credit: ESA/Rosetta/NAVCAM*

as a fossil of protoplanetary disk chemistry.

1.7 This thesis

Rapid advances have been made in recent years in fields relating to planets and planet formation. The theoretical understanding of protoplanetary disk physics and evolution has come far, likewise for planet formation. From an observational point-of-view, the dust and gas inventory of an increasing amount of diverse disks are being mapped out by ALMA (with new detections also made possible with *Spitzer* and *Herschel* space missions), and chemical compositions of disks, primarily in the upper layers, are being determined. Alongside, with the use of state-of-the-art facilities like ESO's VLT, the *Hubble* Space Telescope, and NASA's *Kepler* mission, a zoo of exoplanets of all sizes are being discovered, and pushing the current technology to the limit has revealed signs of several molecules in the atmospheres of some exoplanets (Snellen et al. 2010; Birkby et al. 2013; Kreidberg et al. 2014; Sing et al. 2016) .

A remaining challenge is understanding the chemical histories of the end-products: the planets, planetesimals and comets. What sets the molecular composition of planet atmospheres? How does the planet formation process affect the chemical make-up of the planets? While astronomers and planet formation experts have assumed the disk midplane composition to be chemically inert, thereby simplifying the incorporation of "chemistry" into their physical planet formation models, results from astrochemistry show a rich chemistry in disks, with chemical reactions under different physical conditions likely causing chemical changes to the material over time. The disk midplane, being the region of the disk relevant to planet formation, remains difficult to probe observationally, and is also too cold to be assumed to be in chemical equilibrium.

This thesis contributes a necessary step forward by simulating the composition and chemical evolution of the volatile midplane material using one of the powerful tools for understanding of interstellar chemistry that astrochemistry has to offer: chemical kinetics models. This thesis aims to test what effects chemical kinetics may have on the composition of the midplane material under the different conditions that a protoplanetary disk midplane may be subjected to. This, in turn, may lead to new insights into the chemical composition and formation histories of planets, exoplanets and comets.

Chapter 2: This chapter, employing the BADASS code, explores the effects of a static physical protoplanetary disk midplane with varied chemical conditions and ionisation levels on the chemical evolution over an assumed timescale of 1 Myr. The initial chemical composition, either fully molecular or fully atomic, is tested for effects on the chemical composition by 1 Myr. Likewise is the ionisation level, which assumes two non-zero levels, to test the dependence of ionisation on the chemistry. Lastly, the difference between gas-phase chemistry-only (including freeze-out and desorption) and grain-surface chemistry is explored. Despite this multidimensional approach, there are general trends in the results which constrain the effects of the different assumptions.

Amongst other results, it is found that no significant chemical evolution occurs only when chemical starting conditions are saturated molecules, and the ionisation level is low. The results also reveal that, in addition to gas-phase chemistry, grain-surface chemistry has a unique impact on the chemical evolution, pointing to a need to treat ice chemistry comprehensively in chemical kinetics codes.

Chapter 3: This chapter expands on Chapter 2. A physically evolving midplane structure is assumed (rather than a static one), which is cooling and losing material over a timescale of 7 Myr, thus considering a longer disk lifetime than in Chapter 2. Different chemical starting conditions and ionisation levels are considered here as well. Special attention is given to the evolution of the elemental carbon-to-oxygen ratios in the gas and in the ice, and how these ratios change along with changing chemical composition. This chapter opens up a new paradigm of disk midplane chemistry, in that it makes time-dependent predictions on the long-term chemical composition of the material in the midplane, and these results serve as more realistic chemical inputs to planet formation models than previous "chemically inert" assumptions.

The results show that the chemical composition of protoplanetary disk midplanes is continuously evolving over a timescale of 7 Myr, resulting in the radial C/O ratio profile for gas decreasing with time, and the C/O ratio profile for ice increasing with time (away from the initial conditions seen in Fig. 1.3). It is also found that an evolving physical disk structure only affects chemical evolution by shifting icelines inwards as a consequence of decreasing temperatures. Chemical evolution between icelines is largely the same for physically static and evolving disks. In the outer icy disk, a chemical steady state is reached by 7 Myr, suggesting that a certain (temperature dependent) set of icy disk midplane abundances are reached independent of initial assumptions about chemical composition, given a proper timescale to evolve. Also, the simultaneous treatment of gas-phase, gas-grains and grain-surface chemistry leads to a depletion of CO from the gas-phase inside its thermal iceline, due to the chemical conversion of CO into less volatile forms, such as CO_2 ice, on the grain surfaces. This effect creates a "fake" CO iceline, in agreement with reported observations of the CO iceline in TW Hydrae at a higher temperature than prescribed by the CO binding energy (Zhang et al. 2017).

Chapter 4: This chapter digs into a finding in Chapter 2: O_2 ice is being chemically produced to within 1-10% of H_2O ice for a specific subset of physical and chemical conditions. Because this abundance matches with the surprising observations of O_2 ice on Comet 67P by the ESA *Rosetta* mission, the production of icy O_2 in the colder, comet-forming region of the pre-Solar nebula is investigated in Chapter 4. The BADASS model is expanded to include the available laboratory and modelling results for O_3 ice chemistry, and two parameters controlling the efficiency of grain-surface reactions are varied to constrain under which conditions O_2 ice may have been synthesised in-situ on a grain or cometary surface in the pre-Solar nebula.

The results do show a sweet spot in the parameter space where O_2 ice, as well as the related H_2O_2 and O_3 ice all match the observed abundances in comet 67P. However, this sweet spot assumes somewhat extreme values for some reactions involving O_3, and for some grain-surface parameters, that are currently not fully supported by laboratory results. Thus, while more laboratory results on grain-surface reactions would be welcomed to improve the treatment of O_3 in chemical kinetics codes, a primordial origin (i.e. formed in the parental cloud from which our Solar System originated) remains the best explanation for the abundance of O_2 ice in comets 67P and 1P.

Chapter 5: This chapter continues in the path of understanding cometary origins by constraining their formation via chemistry. Comets exhibit a wide diversity of compositions that may be explained by disk chemistry in radius and time. In turn, the diversity in comets may help to understand the diversity in exoplanet atmospheric compositions, if these atmospheres are indeed fed by icy, solid impactors. The evolving chemical abundances over 7 Myr from Chapter 3 are compared to measured abundances of volatiles and simple organics from 15 well studied comets, in order to highlight where in this pre-Solar nebula, and when during disk evolution, the comets are most likely to have formed, given the compositional differences in the disk from Chapter 3. A χ^2 method comparing observed and modelled abundances is used to compute maximum likelihood surfaces, and estimate where and when each comet is most likely to have formed, given by the best overall match between observed and modelled molecular abundances.

The results are used to propose a taxonomy for comet families based on chemical similarity to the chemical composition of the disk midplane in which they once formed.

1.8 Main conclusions

- (Chapter 2 and 3) Disk midplane chemistry matters! Chemistry will always alter the molecular abundances and the elemental composition of gas and ice in a protoplanetary disk midplane, unless the disk inherits stable ice species from the parent cloud, and the ionisation is low.

- (Chapter 2 and 3) Ionisation, in particular from cosmic rays, is essential for chemical evolution. Ionisation initiates chemical evolution in the disk midplane, and the higher the ionisation level, the shorter the timescale for chemical evolution.

- (Chapter 2) At an early stage of chemical evolution ($\sim$0.1 Myr at high ionisation), beginning from atomic chemistry, O_2 ice is produced at an abundance with respect to water similar to the abundances measured in the comae of comets 1P and 67P.

- (Chapter 3) Chemical evolution taking place in a disk midplane will generally act to lower the elemental carbon-to-oxygen ratio of the gas, and increase the ratio for the ice. Chemical evolution also leads to the generation of a "fake" CO iceline that lies at a higher-than-expected temperature.

- (Chapter 4) Modelling of chemical evolution of ices in the pre-Solar nebula with the inclusion of O_3 chemistry, does not show the same abundance of O_2

ice as was found in Chapter 2 (without O_3). Therefore, a primordial origin remains the most likely explanation for the detections of O_2 ice in comets 1P and 67P.

- (Chapter 5) Chemical evolution models of disk midplanes can be used to constrain the formation histories of comets in the Solar System, when compared to abundances of molecular species in the comets.

- (This thesis) Modelling chemical kinetics in protoplanetary disk midplanes is an important tool for predicting the compositions of planets, as well as for tracing the formation histories of observed planets, exoplanets, planetesimals and comets.

1.9 Future outlook

In just a few years, the James Webb Space Telescope will be launched, which will provide exciting new insights into the contents of exoplanet atmospheres and ice species on grains in protoplanetary disks as well as the molecular reservoir in the disk atmosphere within the planet-forming region. In addition, the ESO Extremely Large Telescope will be able to dig even deeper into the compositions of atmospheres of not only Hot Jupiters, but also smaller and colder exoplanets, and disks. It is thus in the near future that further observational constraints will be put on planet formation theories and exoplanet atmospheres, and it is thus timely to incorporate more comprehensive treatments of chemistry into the already highly developed planet formation models on the market today.

The next step is to incorporate an understanding of disk midplane chemical evolution into planet formation models. It is key that planet formation modellers and astrochemists get together to properly combine the physical and chemical tools that are available today. It is also key that multiple combinations of physical and chemical codes and inputs are tested, to check for general trends, but also because there likely is no size fits all. The zoo of observed exoplanets speaks its own language. The Solar System is likely not the standard outcome of planetary system architecture and design. And in order to understand planetary systems in general, a range of physical and chemical scenarios are needed to simulate it and draw insights.

The planet formation and disks community and the exoplanet community also have important upcoming discussions: what do we know about exoplanets and their compositions, are they actually forming in rings around protostars depleted from millimeter-sized dust, and from which mechanisms, gas accretion or impacting solids, did they gain their atmospheres with a given C/O ratio?

Let chemistry meet planet formation, let chemistry meet exoplanets, and let that constitute a next important step in understanding the diversity of planets and exoplanets, and let it add a piece in the puzzling path for human kind to better understand its origins, and drive the ambition to discover life in space.

Finding extraterrestrial life is the ultimate motivation for me to learn, progress, reach dead-ends, discover, fail (it happens, and it is ok!), and ultimately achieve new insights. I am convinced that the detection of biosignatures on a rocky planet in the temperate zone around its host star will constitute a paradigm shift in human kind's understanding of itself, and its place and importance in the Universe. I think that the discovery will eventually humble human kind, and make us realise that we are not that special, but that we are fortunate enough to inhabit a small place in the vast cosmos, a pale blue dot[4], that we should care well for.

One thing that all humans on the Earth have in common is that we share occasional dark nights with beautiful bright dots spread across the tapestry above us. The universal tale that we are all together on our little Earth, here, somewhere in the cosmos, is a tale of peace, a tale of unison, a tale that should make us realise commonalities, rather than differences. It is my hope (and something I will actively contribute to) that astronomy can continue spreading a universal sense of fascination, of awe, of excitement and of peace for everyone on our planet, and that that can help human kind for generations to come in the future.

[4]Quote: Carl Sagan

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