Ice and gas in protostellar clouds and planet-forming disks: a combined laboratory and observational study

Terwisscha van Scheltinga, J.

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1 | INTRODUCTION

It is easy to forget in the rush of our daily lives that planet Earth is an extraordinary place. A small rocky planet at the right distance from our Sun that formed approximately 4.6 billion years ago, where everything aligned to eventually harbour us and every other living being. Throughout human existence, we have looked at the stars and wondered, are we alone? After the first confirmed detection of two exoplanets in 1992 by Wolszczan & Frail (1992), many others followed. As of writing, almost 5000 exoplanets have been discovered, and it is suggested that on average every star is accompanied by at least one planet. Although many of these planets may not harbour life as we know it, the population of stars and planets is unfathomable. It is rather unimaginable that there is no other place besides Earth in the vastness of the universe where physical and chemical evolution have also aligned to create life or will do so in the future.

In order for life, as we know it, to start on a planet certain organic building blocks have to be available. On Earth, organisms require different types of molecular structures to survive, thrive, and evolve. Be it an unicellular or multicellur organism, proteins, nucleic acids, carbohydrates, and lipids are a necessity. Each of these fulfill different functions, for instance, lipids are used to create cell membranes, and nucleic acids form DNA where genetic information is stored. This raises the question, were these building blocks of life formed on Earth, or are they formed in a universal way during star and planet formation filling the entire universe with the seeds of life?

In the last 100 years, our understanding of the physical and chemical processes that occur in the universe have greatly improved. It was once believed that under the harsh conditions in space, that is extremely low temperatures and strong radiation fields, no molecule could survive. However, the detection of CH by Swings & Rosenfeld (1937) and subsequent detections of many other molecules contradicted this, and showed that molecules can be formed and sustained in space. Today, over 240 different molecules have been detected (McGuire 2018). These molecules range from diatomics and small molecules, both stable and radicals, to fullerenes, such as C_{60} and C_{70}. A subgroup of these molecules are defined as complex organic molecules (COMs), where a COM is a molecule consisting of six or more atoms of which at least one is carbon and another is either nitrogen, oxygen, phosphorus, or sulfur. COMs are of particular interest as they are the smaller siblings of the previously mentioned building blocks of life. Whether and how these organic molecules are formed and incorporated in the different stages of star and planet formation is key in understanding the formation of life on Earth, and potentially in other planet-forming systems (see e.g., reviews by Herbst & van Dishoeck 2009; Öberg & Bergin 2021).

1.1 Star and planet formation

Our Solar system is a mature system in which no significant physical and chemical evolution takes place anymore, at least at Solar system size. However, at a "young" age, that is, below 10 million years, it went through different evolutionary stages in which conditions varied significantly. It started with a molecular cloud that initially contained only gas and small dust particles, and turned into the Sun and planets we know today. One way to look at the composition of the material available at these early stages, and if they contained COMs, is through comets. Comets are essentially large and dirty snowballs that are created from the same material and at the same time as planets, and contain large amounts of the most pristine material available in our Solar system.

On the 2nd of March 2004, the European Space Agency launched its *Rosetta* mission. Its goal was to intercept the comet 67P/Churyumov–Gerasimenko, henceforth 67P, and, among other science tasks, teach us about its molecular composition. As the comet approached perihelion, that is, the closest distance to the Sun, more and more of 67P's icy surface layer started to sublimate. Once arrived at 67P, the ROSINA instrument on board the *Rosetta* spacecraft allowed for *in situ* measurements of the coma surrounding 67P created by this release of ice. Molecules, such as water (H_2O), oxygen (O_2), nitrogen (N_2), and methanol (CH_3OH) were readily detected, but most intriguing was the detection of glycine (NH_2CH_2COOH; Altwegg et al. 2016, 2019). The significance of this detection is high, as glycine is the simplest amino acid, and is part in the creation of protein molecules. This suggests that prebiotic molecules are already available in the very early stages of our Solar system, and may have played a role in the development of life on Earth.

Another way to investigate the presence of organic molecules is through astronomical observations of distant objects in our skies that are still in their early stages. The stellar evolution starts in molecular clouds, where as the name suggests the first generation of molecules are formed, such as hydrogen (H_2), carbon monoxide (CO), and water. In the diffuse interstellar medium (ISM) these molecules have a high chance to get dissociated or ionized due to the harsh radiation field, but in a dark molecular cloud the densities are high enough to shield these molecules from the harsh external radiation field. Moreover, in these clouds temperatures are approximately 10–20 K, which is important for the formation of these molecules as will be discussed later.

Molecular clouds are also known as stellar nurseries, because in the dense cores of these clouds star formation starts through gravitational collapse. In this process denser regions become even denser as more and more material is pulled in through its own gravitational interaction, and starless cores are formed. If enough material accretes onto a starless core, enough to eventually form a star, it is called a prestellar core. The angular momentum at large molecular cloud scales (several pc) is conveyed into the scales of prestellar cores (~ 10000 au). This angular momentum in combination with the gravitational pull results in the rotation of the material toward the gravitational center. The material at this center forms a point source, and in this process the release of gravitational energy heats the surrounding material. It is at this stage that we consider that a protostar has formed, which is known as a Class 0 object. The evolution between a prestellar core and planetary system is divided into four stages, that is, Class 0, Class I, Class II, and Class III (Shu et al. 1987). This classification is based on the appearance of the object in the infrared, which informs us on the

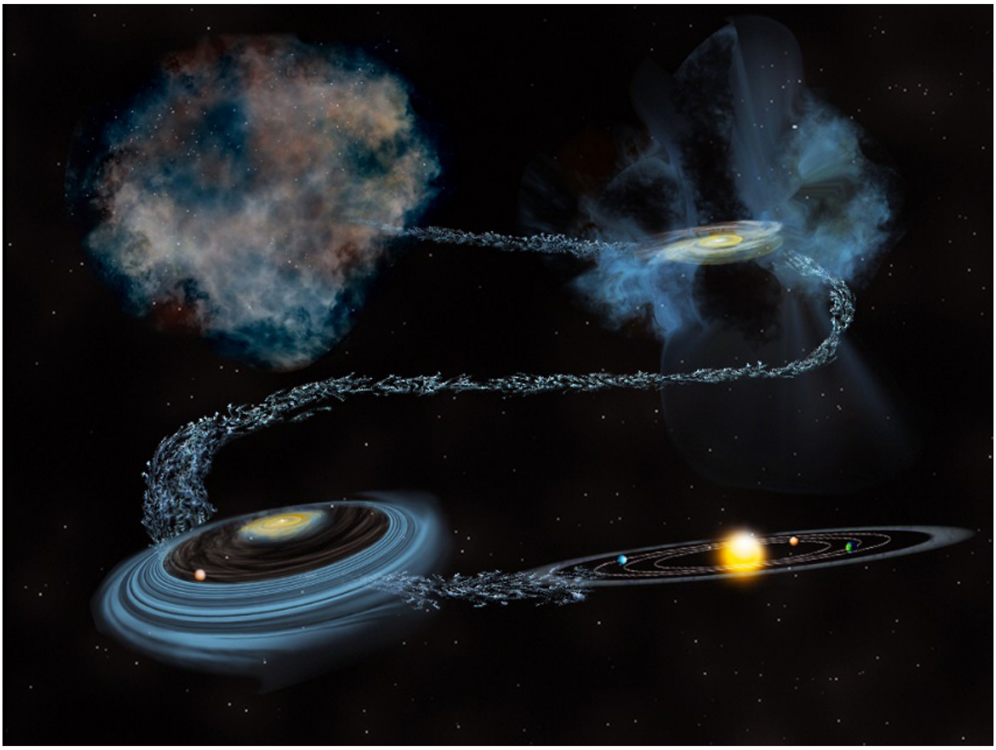

Figure 1.1: Artist impression of the evolution of stars and planets. It starts in a molecular cloud (top left), which through its own gravity collapses and starts forming protostars with envelopes (top right, only one is shown). The star enters the pre-main sequence once the majority of the envelope has accreted and only a disk is left, a so-called protoplanetary disk (bottom left). This protoplanetary disk eventually evolves into a planetary system (bottom right; Credit: Bill Saxton, NSF/AUI/NRAO).

protostar and the surrounding material. Figure 1.1 shows a visual representation of these different stages of star and planet formation.

The angular momentum of the infalling rotating material has to be preserved, and results in the formation of an embedded disk in the envelope. Another result of the preservation of angular momentum is the appearance of outflows and jets, perpendicular to the rotational plane, which partially opens the envelope (see e.g., review by Larson 2003). In the Class 0 stage, the majority of the mass is still in the envelope surrounding the protostar. However, as time progresses more of the envelope material accretes onto the protostar. Eventually, the envelope mass is significantly smaller than the mass of the protostar. The system is now classified as a Class I object. After this, the protostar starts contracting and turns into a pre-main-sequence star. The temperature of the star has increased significantly. However, it is not yet enough to start the fusion process of hydrogen in its core, but its radiation is strong enough to blow away the remainder of the envelope. With the envelope dissipated, a protoplanetary disk is left rotating around the pre-main-sequence star, classified as a Class II object. The dust in the protoplanetary disk keeps evolving into larger bodies, and the protoplanetary disk itself evolves into a debris disk, which is classified as a

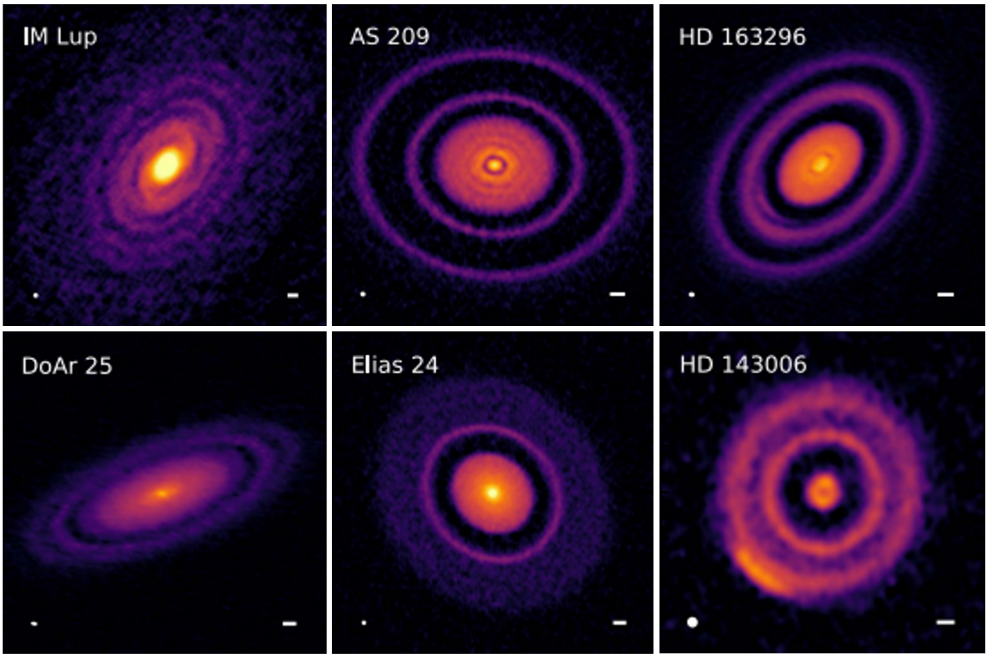

Figure 1.2: Six sources taken from the large ALMA program DSHARP observed at 240 GHz, that is, 1.25 millimeter-dust continuum emission. Beam sizes are shown in the bottom left and the width of the bar in the bottom right depicts 10 au (Adopted from Andrews et al. 2018).

Class III object. Once the star starts burning its hydrogen through fusion it enters the main sequence, and any of the residual dust and gas is blown away leaving a planetary system such as our Solar system.

The embedded disks around protostars set the scene for planet formation. As the system evolves on large scales, there is also significant evolution on the small scales. In the molecular cloud, the cold dust particles have sizes ranging from a few nm to 0.1 micron. However, by the time they reach the protoplanetary disk stage, the majority of the dust population has aggregated and grown to mm-sized dust grains. Although there are still gaps in our knowledge on the formation of large bodies, exoplanets are readily detected. An example is the meter-size barrier, which is a long-standing issue in planet formation (Weidenschilling 1977). It seems that bodies of approximately a meter quickly drift into the young star or are destroyed due to collisions instead of growing into larger bodies. In the last decade, observations with the Atacama Large Millimeter/submillimeter Array (ALMA) and Very Large Array (VLA) suggest that planet formation starts in the Class 0/I stage, as dust masses in protoplanetary disks (Class II) are not sufficient to form planetary systems (e.g., Tychoniec et al. 2020).

The amount of substructure seen in dust disks of Class II objects seems to suggest that indeed large bodies are present. The ALMA DSHARP program looked at the millimeter-dust distribution of 20 nearby protoplanetary disks at a spatial resolution of 5 au, roughly the distance from the Sun to Jupiter (Andrews et al. 2018). Figure 1.2 shows a select few of the protoplanetary disks observed in this program. Dust rings and gaps are seen from a few au away from the pre-main-sequence star, to all the way to the edge of the dust disk. Hydrodynamical simulations of both the gas and dust show excellent agreement with the observed substructures in AS 209 with a planet in the 100 au gap (Zhang et al. 2018). However, other scenarios, such as snow lines, dead zone transition, and secular gravitational instability, can produce substructures in disks (e.g., review by Andrews 2020, and references therein).

Besides the dust, there is also a substantial amount of gas in the regions where stars and planets are formed. On average the gas-to-dust ratio is found to be 100 in the ISM. It is generally assumed that this value is preserved throughout the different stages of star and planet formation. This gas and dust interacts with each other in both physical processes, such as viscous evolution, and chemical processes, such as formation of organic molecules. Given the amount of substructure seen in protoplanetary disks it is very likely that the organic content and its evolution are linked to these changes in physical structure. Preliminary results from the ALMA large program Molecules with ALMA at Planet-forming Scales (MAPS) does indeed show that this is the case.

An example of a crucial interaction between gas and dust is the formation of H_2O, one of the most important molecules to sustain life on Earth. The formation of water occurs in the molecular cloud on the surface of dust grains. Specifically, the increasing density results in shielding of the material which in turn lowers the temperature of the dust grains. An effect of this lower temperature, that is, 10–20 K, is that species from the gas phase, such as atomic hydrogen and oxygen, can adsorb on the surface and diffuse across it. When these diffusing atoms find each other they can react and form H_2O. Besides the formation of water, many other molecules are formed on the dust grains, also those that fall under the category potential building blocks of life (see e.g., Linnartz et al. 2011, 2015, and references therein). The processes that result in the formation of molecules on the dust grains are discussed later in more detail.

1.2 Organics through the eyes of telescopes

Probing the full organic inventory in star- and planet-forming regions is challenging. Low abundant organics are hidden in the noise, while line opacities can result in underestimated column densities and dust opacities hide molecules in plain sight. Telescopes such as the Infrared Space Observatory (ISO) and the *Spitzer* telescope have shown that simple species, such as H_2O, CO, CO_2, and NH_3, but also CH_3OH are present in the icy layers on top of dust grains in star- and planet-forming regions (e.g., review by Boogert et al. 2015). An example of such an observation is given in Figure 1.3, where absorption features toward AFGL 7009 S, as observed by ISO, are assigned to solid-state molecules. With the exception of methanol, no other COMs have been securely identified. Two other COMs have been tentatively detected, namely acetaldehyde (CH_3CHO) and ethanol (CH_3CH_2OH), in the massive protostar W33A (Schutte et al. 1999; Öberg et al. 2011). This is because space-based telescopes, such as the infrared space observatory (ISO) and the *Spitzer* telescope, lacked spectral resolution and sensitivity to detect larger COMs. Ground-based infrared telescopes suffer from telluric contamination and have so far only detected methanol in the solid state (e.g., Boogert et al. 2011, PhD thesis D. Qasim).

There is, however, an upcoming infrared space telescope, namely the *James Webb* Space Telescope (JWST), which will bring new impetus to the investigation of solid-state species that cover dust grains. In preparation to observations with JWST, this thesis contains two chapters, that is, Chapters 3 and 4, in which infrared spectra of

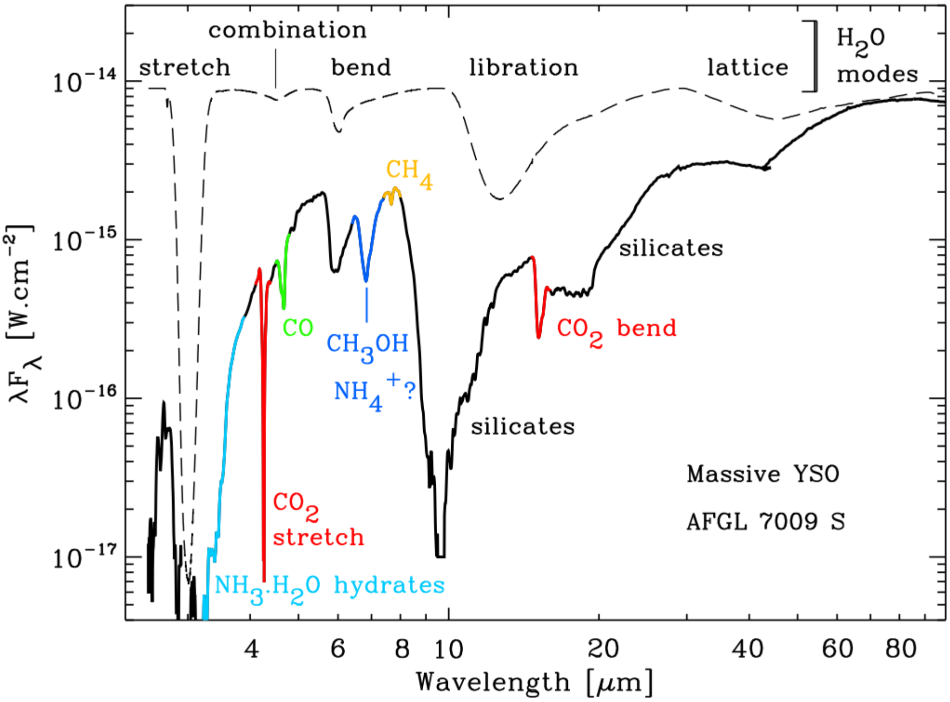

Figure 1.3: Infrared spectrum of the massive young stellar object AFGL 7009 S in black, where the colored parts are assigned to accompanied species in the solid state. The dashed line represents pure H_2O ice (Credit: Boogert et al. 2015).

astronomically relevant COMs are characterized to help identification of these COMs in JWST spectra of star- and planet-forming regions.

In contrast to the solid state, COMs are readily detected in the gas phase, especially in the early Class 0 stages of star and planet formation. As accretion of material onto the protostar continues, the star's temperature and that of its surrounding material increases and this creates a so-called hot core. In these hot cores, the temperature increases enough to thermally desorb ice constituents on dust grains into the gas phase. ALMA observations of gas-phase species of such hot cores have revealed that they are rich in both O- and N-bearing COMs (see e.g., Bøgelund et al. 2018, 2019b; van Gelder et al. 2020; Nazari et al. 2021).

In the following stage, that is, Class I, the detection of gas-phase COMs is already slightly more challenging. In general these sources do not show COM emission, but there are exceptions. For example, the Class I outbursting protostar V883 Ori has episodes of highly increased luminosity, which temporarily increases the temperature profile in the embedded disk surrounding the young star. This sudden increase in temperature pushes the snowlines, that is, the location in the disk midplane where significant amounts of a species start freezing out, outward and sublimates molecules that otherwise would not have been released. ALMA observations of V883 Ori have shown COMs, such as methanol, acetone (CH_3COCH_3), acetonitrile (CH_3CN), acetaldehyde (CH_3CHO), and methyl formate ($HCOOCH_3$) in the gas phase (van 't Hoff et al. 2018b; Lee et al. 2019).

Only in a handful of the protoplanetary disks methanol has been detected. The most likely reason for this is that the envelope has completely dissipated at this stage and the remaining ice reservoirs are shielded in the disk midplane. Even methanol itself is challenging to detect at this stage. Physical-chemical models of the disk around TW Hya predicted up to a 100 times more methanol than eventually was detected (Walsh et al. 2016). Surprisingly, the protoplanetary disk around HD 100546 does show significant amounts of gas-phase methanol. In fact, the HD 100546 disk shows so much methanol, that physical chemical models suggest that this methanol must have been inherited from the molecular cloud (Booth et al. 2021). The gas-phase abundance of methanol in HD 100546 is explained by thermal desorption of large ice resevoirs. This is possible in HD 100546 as it has a large inner cavity (13 au) in its dust structure, which allows heating of a large solid-state reservoir. In contrast to HD 100546, a stringent upper limit was derived for methanol in a similar source, namely HD 163296. Deep ALMA observations of this source showed that there is at least one order of magnitude less gas-phase methanol compared to HD 100546. HD 163296 has a substantially colder disk as it does not have a large inner cavity (< 5 au) and thus shielding the methanol ice reservoir (Carney et al. 2019).

The formation of methanol through reactions in the gas phase is extremely inefficient at the temperatures and densities of these regions. However, formation of methanol on the dust grains is found to be efficient at low temperatures and is deemed the origin of most observed gas-phase methanol in these regions (e.g., review by Linnartz et al. 2015). In order to better understand the formation of methanol one can look at its chemical precursor formaldehyde (H_2CO). The ratio of methanol to formaldehyde is said to trace how chemically evolved the ice is. However, opposite to methanol, formaldehyde also has an efficient gas-phase formation pathway. It is thus important to verify if the observed formaldehyde originates from the solid state or from the gas phase in order to link it to methanol. In Chapter 5 of this thesis, observations of TW Hya with ALMA are used to constrain the formation pathway of formaldehyde.

A lot of the organics, especially COMs, are present in the solid state or when detected in the gas phase seem to originate from the solid state. In the next section, the different processes that occur on and in the icy layers on dust grains are described. This is important as it holds the key to understanding how the potential building blocks of life are formed.

1.3 Grain processes

In a similar way as the formation of water, molecular hydrogen (H_2) is formed on the surface of dust grains when two diffusing hydrogen atoms meet and react with each other. However, the H_2 is released into the gas phase after formation, as the temperature of the dust grain is higher than the desorption temperature. This processes is know as thermal desorption. The temperature at which a species desorbs is dependent on its binding energy to the surface and can even vary with different surfaces. These binding energies determine under which physical conditions molecules are either in the gas phase or in the solid state. At the time that H_2O is formed, carbon monoxide (CO) is present in the gas phase, and since its binding energy is low compared to the dust grain temperature at this stage the majority of CO remains in gas phase above temperatures of ~ 20 K.

However, as the dark cloud contracts under its own gravity, the density increases and subsequently the temperature drops, allowing gas-phase CO to freeze out on top of the water-rich ice layer. This freeze out of gas-phase CO is an important step in creating the building blocks of life. Once CO is in the solid state, it can interact with atomic hydrogen and proceed through tunneling into the formyl (HCO) radical. This process is called hydrogenation and occurs sequentially, after HCO the molecule formaldehyde is formed, one of the simplest organic molecules. The hydrogenation process does not stop at formaldehyde, after two more hydrogen are added one of the simplest COMs is formed, namely methanol (Watanabe & Kouchi 2002a; Fuchs et al. 2009). The intermediate radicals created through hydrogenation, that is, formyl, methoxy (OCH_3), and hydroxymethyl (CH_2OH), are able to react with each other and form COMs, such as methyl formate ($HCOOCH_3$), glycolaldehyde ($HOCH_2CHO$), and ethylene glycol ($HOCH_2CH_2OH$; Fedoseev et al. 2015a; Chuang et al. 2016). Atoms additions and radical recombination reactions are considered as non-energetic processes, as they do not require external energy (e.g., UV photons or cosmic rays) to proceed. Recent laboratory results showed that through these types of non-energetic processes glycine can be formed in the molecular cloud stage (Ioppolo et al. 2021). This could explain the origin of glycine detected in 67P, as mentioned earlier.

The densities of the dark cloud do not allow the external radiation field to penetrate and induce photoprocessing of the ice. Cosmic rays, however, induce an internal UV field through the excitation of H_2, which subsequently emits UV photons upon relaxation. Additionally, in the Class I stage the external radiation field is able to penetrate again, and as the star enters the pre-main-sequence stage the SED contains significant amounts of high energy photons to break bonds and induce chemical reactions. Processes induced by UV, shorter-wavelength photons, and other energetic particles (e.g., electrons or cosmic rays) are considered as energetic processes. An example of such energetic processing is the interaction of UV photons with ices on dust grains. A molecule absorbs an UV photon and is raised into an excited state. This results in the nonthermal desorption (of itself or neighboring molecule), or dissociation of the molecule. The desorption of molecules through photons, that is, photodesorption, is a nonthermal desorption process, which explains the presence of, for example, gas-phase CO in regions where freeze-out timescales are short.

Dissociation of molecules through energetic processes is another way to increase the molecular complexity in star- and planet-forming regions. The dissociation products diffuse across and through the ice to form larger molecules. Laboratory experiments where pure methanol and methanol mixed with CO or CH_4 were irradiated with UV photons show formation of COMs, such as acetaldehyde, ethanol, dimethyl ether, methyl formate, glycolaldehyde, and ethylene glycol (Öberg et al. 2009b). Another example is the work by Ligterink et al. (2017) who looked at the formation of methyl isocyanate (CH_3NCO) from an ice mixture of isocyanic acid (HNCO) and methane (CH_4). The formation of methyl isocyanate is of particular interest as it has a similar chemical structure as a peptide bond, which connect amino acids, such as glycine, in long protein chains. In a follow-up study other amides were detected in the solid state after UV irradiation, such as formamide, carbamide, acetamide, and N-Methyl formamide (Ligterink et al. 2018a). Similar experiments, but with electrons or other high energy particles produce similar COMs (see e.g., Modica & Palumbo 2010; de Barros et al. 2011; Boamah et al. 2014; Maity et al. 2015; Inostroza-Pino et al. 2020).

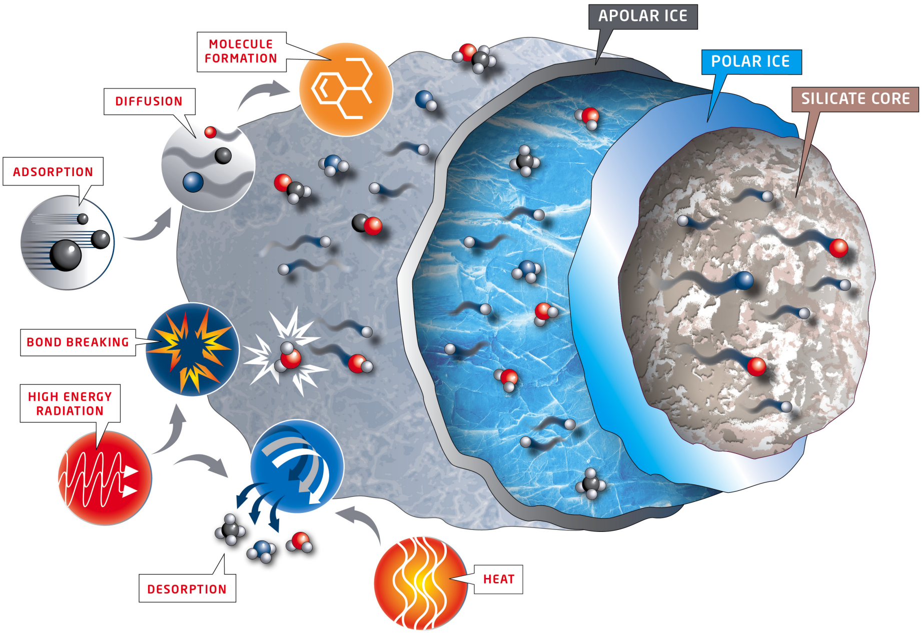

Figure 1.4: Artist impression of a dust grain covered with ice. Through adsorption, diffusion, and high energy radiation species are formed on top of the silicate core, forming a polar and an apolar ice layer (Credit: Leibundgut Design & Center for Space and Habitability).

To summarize, due to the decreasing temperature atoms are able to diffuse across the surface of the dust grains and form simple species, such as H_2O, NH_3, and CH_4. These species have significant dipole moments and the layer they form on top of the dust grain is called polar ice. A further decrease of the temperature allows CO to freeze out on top of the polar layer. This layer is called apolar ice, because it mainly consists out of CO, which does not have a significant dipole moment. The hydrogenation of CO results in H_2CO, CH_3OH, and larger COMs. Additionally, irradiation of these ices, with for example, UV photons or electrons, induces chemical reactions further increasing the molecular complexity. All the above described processes are visualized in Figure 1.4.

1.4 Laboratory astrochemistry

In order to gain better understanding of the molecular complexity in astronomical environments it is key to investigate in the laboratory, quantitatively, their characteristic properties, such as spectroscopic features, and the processes that result in their formation and/or destruction. Such information is needed to interpret astronomical observations and as input for astrochemical models. Laboratory experiments allow careful control of the parameters, while only looking at one or a few processes at the time. These experiments are performed on setups that mimic the conditions in which the icy grains reside. In general, space is associated with extreme conditions where it either extremely hot or cold, extremely dense or and highly dilute. In this thesis the focus is on the cold and dilute regions. The number density in the interstellar medium is many orders of magnitude lower than in the Earth's atmosphere. For example, in molecular clouds the number density is roughly 10^6 molecules per cm^3, whereas on Earth at sea level, this is approximately 10^{19} molecules per cm^3. The temperatures in the laboratory range from a few K up to a couple of hundred K when investigating the processes in the solid state. This is representative of the temperature in which the majority of the icy dust grains reside in star- and planet-forming regions. In contrast, processes at these low temperatures on Earth are considered ineffective.

In astrophysical and astrochemical laboratories around the world highly specialized setups are used that exploit different techniques to learn more about the processes that determine star and planet formation, either directly by providing spectra that can be compared with astronomical data or with insight in the underlying processes. For this thesis, two experimental setups are used in the Laboratory for Astrophysics at Leiden Observatory to investigate ice processes on dust grains. These setups are the high-vacuum setup (HV setup) and the Cryogenic Photoproduct Analysis Device 2 (CryoPAD2). A short introduction to the setups and techniques is given here, while in Chapter 2 a more detailed description will be given. The main chambers of the HV setup and CryoPAD2 are pumped down to high vacuum and ultra-high vacuum, respectively. The pressure on CryoPAD2 is the lowest pressure commercially available and approaches the pressure in a molecular cloud. However, the pressure in the diffuse ISM is still many orders of magnitude lower. At the center of these chambers a substrate is placed as an analogue for a dust grain surface. These substrates are cryogenically cooled to mimic the temperatures in star- and planet-forming regions. Growing ices on these cold substrate allows for characterization of icy analogues and studying irradiation processes under astrophysical conditions. In the following two sections the diagnostic techniques used by these setups are described, namely vibrational spectroscopy and mass spectrometry.

1.4.1 Vibrational spectroscopy

The molecules adsorbed onto the dust grains in star- and planet-forming regions or those on the substrate of laboratory setups cannot rotate. This makes it impossible to observe them through rotational spectroscopy, as with gas-phase species, with telescopes such as ALMA or microwave spectroscopy in the lab. Although the molecules are rotationally hindered, they are still able to vibrate in the solid state. The vibrational transitions of molecules can be excited by absorption of infrared photons, and thus provides a tool to investigate solid-state molecules. In the laboratory this is generally realized through the use of Fourier transform infrared spectroscopy (FTIRS).

In this thesis two types of FTIR spectroscopy are applied, namely transmission spectroscopy and reflection adsorption infrared spectroscopy (RAIRS). In transmission spectroscopy the infrared light passes, under normal incidence, through an infrared transmissive window on which species are deposited, while in RAIRS the infrared is incident under a grazing angle, and reflected of the surface on which species are deposited. The latter has increased sensitivity over the former as the optical path length through the adsorbed ice is increased, but spectra could look slightly different and thus should not be used for comparison to infrared observations. This is because in transmission spectroscopy, under normal incidence, only transverse optical (TO) phonon modes are recorded, while in RAIRS longitudinal optical (LO) phonon modes can appear (see e.g., Palumbo et al. 2006).

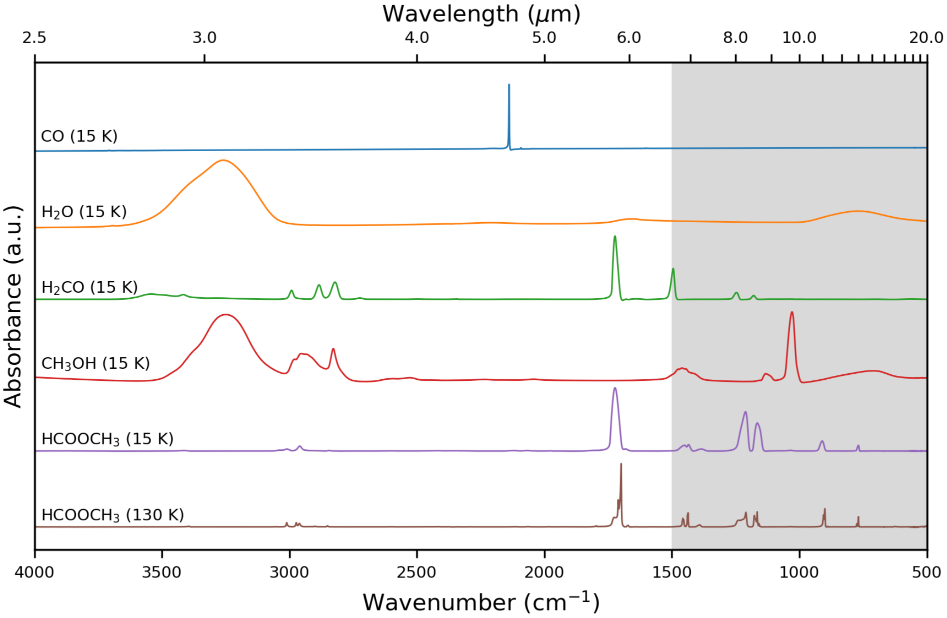

Figure 1.5: Normalized transmission infrared spectra of carbon monoxide (CO), H_2O, formaldehyde (H_2CO), methanol (CH_3OH), and methyl formate ($HCOOCH_3$) at 15 K. The spectrum of methyl formate ($HCOOCH_3$) at 130 K is added to show the effects of crystallinity on the infrared absorption bands. The shaded area indicates the fingerprint region in which identification of species is most likely.

In laboratory astrochemistry, vibrational spectroscopy is used to trace the chemical and physical evolution of the ice during processing and to supply reference spectra to compare with observational spectra. Since each molecule has its own distinct vibrational spectrum, it is possible to determine which molecules have formed during an experiment or are present in the early stages of star and planet formation. Especially, the fingerprint region, that is, 1500–500 cm^{-1} (6.6–20 μm), is well suited for identification of molecules in the solid state. Figure 1.5 shows the vibrational spectra of carbon monoxide, H_2O, formaldehyde, methanol, and methyl formate. As molecular complexity increases, so does the number of absorption modes for each spectrum. This is because the amount of atoms in a molecule determines the number of vibrational modes a molecule has. The number of vibrational modes equals $3N - 5$ for linear molecules and $3N - 6$ for nonlinear molecules, where N equals the amount of atoms in the molecule. For example, CO is a linear molecule and consists of two atoms and thus has one vibrational mode. Methyl formate is a nonlinear molecule and consists of eight atoms. Through the above rule, this gives 18 vibrational modes for methyl formate. However, at 15 K we see at most 11 vibrational modes, while at 130 K the number of absorption features is above 18. The former is because vibrational modes can be inactive or degenerate with each other, that is, adsorb photons of similar frequencies. The latter is either because not all the molecules are in a similar crystalline structure and/or because molecules interact with each other and have combined vibrational modes. A way to eliminate this is to heavily dilute the molecule in an infrared inactive species, such as argon. However, this is of course not representative of the conditions in which molecules reside on dust grains.

The measured spectra of ices are not only dependent on the composition, but also on the orientation of the molecules. When molecules adsorb onto a cold substrate they do so in a random orientation, forming an amorphous ice. As the temperature of the ice increases, molecules gain mobility and move themselves in a more energetically favourable configuration. The change in orientation slightly changes the resonant frequency of the molecules and results in spectral features with distinct shapes and at subtly different wavelengths. When the molecules have oriented themselves in their most favourable configuration, it is called a crystalline ice. Different ice constituents reach crystallinity at different temperatures. Once an ice has become crystalline, it normally does not turn amorphous anymore. The difference between amorphous and crystalline methyl formate ice is shown in Figure 1.5 (see also Chapter 4).

So far only pure ices have been discussed, but in the star- and planet-forming regions different molecules are formed at the same time. This means they are intimately mixed with each other in the ice layers on top of the dust grains. The presence of different molecules also changes the vibrational properties of a molecule. One can expect shifts in peak position, change in peak profile, increase or decrease of amplitude, or even peak splitting. At first this seems to complicate the identification of species, but once these changes are properly characterized they allow for an additional tool to investigate the ice environment in which the molecules reside.

1.4.2 Mass spectrometry

Another commonly used analysis technique in laboratory astrochemistry is mass spectrometry. This technique exploits that different molecules are composed of different atoms, and thus have different weights. The weight of a molecule is commonly expressed in the dalton standard, where one Da is defined as 1/12 of the mass of a carbon atom. For instance H_2O consists out of two hydrogen atoms and one oxygen atom, and thus a total mass of 18 Da. Another example is carbon monoxide (CO), which consists out of one carbon and one oxygen atom, and thus a total mass of 28 Da. By measuring the mass of a molecule, one can deduct from the mass what atoms build up that molecule. However, there are molecules that have a similar mass. For example carbon monoxide (CO) and molecular N_2 both weigh 28 Da, because atomic nitrogen equals 14 Da. A more general example are isomers, isomers are molecules that consist out of the same atoms, and thus have the same weight, but have different chemical structures. An example of an isomer is C_2H_6O, which can be either ethanol (CH_3CH_2OH) or dimethyl ether (CH_3OCH_3).

Instead of actually weighing the molecules, a mass spectrometer relies on a mass filter. Without such filter, the spectrometer would measures every particles that arrives at the detector at once. There are several ways to make a mass spectrometer mass selective, for example, with a quadrupole mass filter, time of flight system, or an ion trap. In this thesis the focus is on quadrupole mass spectrometry (QMS) as this is the technique used on CryoPAD2. A QMS works on the principle that ionized species can be manipulated by an electric field. Before molecules enter the mass filter, the molecules are ionized with electrons at 70 eV. After ionization they are “pushed” by ion optics into the mass filter. Here, four rods, in pairs of two, are placed in such a way that once an oscillating electric field is applied to those rods only ions with

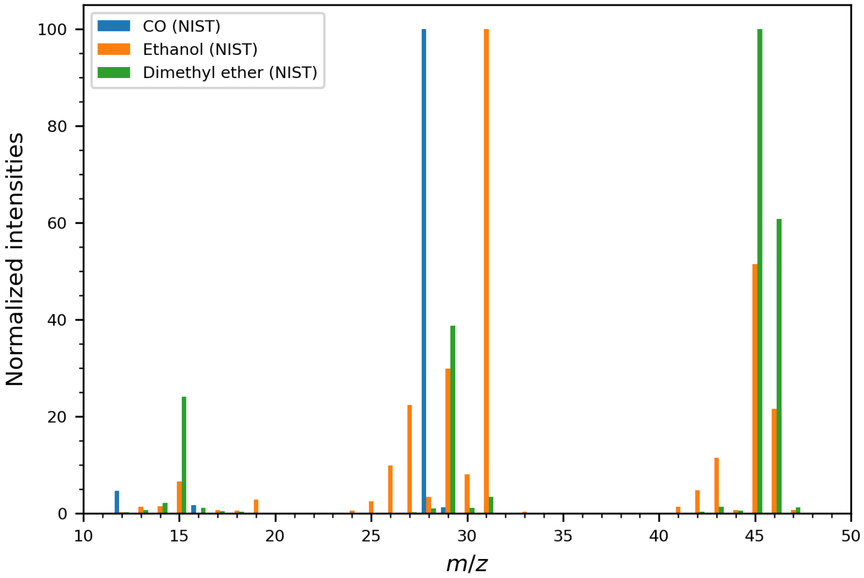

Figure 1.6: Normalized fragmentation patterns of carbon monoxide (CO) and the two isomers of C_2H_6O, namely ethanol (CH_3CH_2OH) and dimethyl ether (CH_3OCH_3). Values are retrieved from the NIST database.

the correct mass-to-charge ratio (m/z) pass through and others are deflected. By scanning through a range of different electric fields applied to those rods different m/z are measured as a function of time, that is, a mass spectrum.

However, upon ionization many molecules fragment as bonds are broken. This complicates the mass spectrum of molecules, as multiple masses now represent a molecule. For instance, carbon monoxide (CO) has small fragmentation channels into C^+ and O^+ besides CO^+ as is shown in Figure 1.6. However, the fragmentation of a molecule upon ionization is unique and once properly characterized it can be used to distinguish between species. The ionization of N_2, which has a similar mass as CO, results in a fragmentation channel at $m/z = 14$. Because N_2 and CO have a different fragmentation pattern they are distinguishable from each other, which would not be possible if measuring at $m/z = 28$ only. Similarly, this can be use to distinguish isomers. Figure 1.6 also shows the fragmentation pattern of the two isomers of C_2H_6O, ethanol and dimethyl ether.

Since each molecule has its own distinct binding energy to a surface, different molecules can be distinguished from each other by looking at their desorption temperature. This is exploited in a so-called temperature programmed desorption (TPD) experiment in which the temperature of the sample is linearly increased and species desorb at their characteristic desorption temperature. During this temperature increase, the QMS continuously probes the gas phase for desorbing species from the solid state. In a sense, the ice is distilled and in order to assign molecules to the measured signals both the desorption temperature and fragmentation pattern should match. This technique is complementary to vibrational spectroscopy and allows for unambiguous assignment of species formed during experiments in Chapter 6.

1.5 This thesis

This thesis aims to take steps toward understanding the interaction between gas phase and solid state (organic) molecules in star- and planet-forming regions. Observations of hot cores show many different COMs in the gas phase. It is generally accepted that the majority of these COMs originate from the solid state. Providing astronomers with reference spectra of solid-state COMs mixed in astronomically relevant matrices will allow them to look for these COMs inside the ices where they are formed and bridge the gap between gas-phase and solid-state COMs.

Another way of tracing the chemical evolution is looking at the ratio between two closely related species: methanol and formaldehyde. Formaldehyde is the intermediate product in CO hydrogenation to methanol, and thus a high CH_3OH/H_2CO would suggest that the ice is significantly chemically evolved. However, this ratio is predominantly measured in the gas phase, and requires good understanding of the release into the gas phase and if gas phase chemistry is contributing to the observed abundances of these species. Formaldehyde has both efficient gas-phase and solid-state formation pathways. Understanding which chemical pathway is active under which physical conditions is crucial to link gas-phase formaldehyde to methanol formed in the solid state.

The interaction between gas and dust is not only important for the building blocks of life, but also for the material available for formation of planets themselves. Observations of protoplanetary disks suggest that they are generally either poor in gas or depleted in gas-phase CO. The general lack of gas in protoplanetary disks would hinder formation of gas giants as there is not sufficient gas to accrete. Since the gas mass is traced through CO and its isotopologues, it is proposed that CO may be chemically depleted. One of the pathways to chemical depletion would be through interaction of gas-phase CO with radicals on the surface of the icy dust grains.

The three aspects introduced above, that is, the spectroscopic identification of solid-state COM features, the gas or grain origin of gas-phase H_2CO, and the chemical conversion of gas-phase CO, are investigated in the remaining chapters of this thesis. Below a summary is given of the findings of each chapter, and afterward some overarching conclusions.

Chapter 2 describes the different tools and methods used in the subsequent chapters. Laboratory: the HV setup is a high-vacuum experimental system in which solid-state COMs are spectroscopically investigated through transmission FTIR. CryoPAD2 is an ultra-high-vacuum system in which chemical and physical processes through vacuum-UV irradiation can be investigated in the solid state. Temperatures can be as low as 15 K, and the probing techniques are RAIRS and QMS. Observational: ALMA is a millimeter/submillimeter interferometer, which allows to measure gas-phase species with high sensitivity and high spatial and spectral resolution in star- and planet-forming regions.

Chapter 3 presents the characterization of infrared spectra of three solid-state COMs, that is, acetaldehyde (CH_3CHO), ethanol (CH_3CH_2OH), and dimethyl ether (CH_3OCH_3), in pure form and mixed with astronomically relevant matrices. Infrared spectra are continuously acquired on the HV setup through FTIR with increasing temperature from 15 K until desorption occurs. Select vibrational modes, that is, those deemed most suited for detection with JWST, are characterized in peak position, full width half maximum (FWHM), and relative band intensities. Additionally, the recorded spectra are used to reanalyze the ISO spectrum of the massive protostar W33A.

Chapter 4 continues the work of Chapter 3, but now for the COM methyl formate ($HCOOCH_3$) in pure form and mixed with astronomically relevant matrices. Once again the HV setup is used to measure the infrared spectra as a function of temperature between 15 K and thermal desorption of the adsorbed species. The most promising features for detection with JWST are characterized in peak position, FWHM, and relative band intensities. A tentative assignment of methyl formate is made to the *Spitzer* observation of HH 46. The idea of looking for vibrational modes of molecules with similar functional groups is introduced.

Chapter 5 contains the observations and analysis of gas-phase formaldehyde (H_2CO) in the protoplanetary disk of TW Hya with ALMA. Specifically, this chapter presents seven transitions of H_2CO of which four are of the ortho-spin isomer and three of the para-spin isomer. Rotational diagram analysis of each separate spin isomer allows investigation of the excitation temperature, column density, and ortho-to-para ratio as a function of radius. It is found that the ortho-to-para ratio hints at formation above the CO freeze-out temperature, and thus suggests that the majority of the observed H_2CO is formed in the gas phase.

Chapter 6 investigates the interaction of gas-phase CO above its canonical desorption temperature with vacuum-UV irradiated water ice. It is found that gas-phase CO spends sufficient time on the water ice to react with OH radicals to form CO_2. This conversion of gas-phase CO into CO_2 at temperatures above the desorption temperature of CO can help explain the low observed CO abundances in protoplanetary disk. Additionally, it may explain how CO_2 embedded in the water-rich ice layer on top of dust grains in the cloud stage is formed.

The main conclusions of this thesis research project are:

1) Detection of COMs in the solid state is the next step in understanding the formation and incorporation of the building blocks of life in planet formation. Chapter 3 and 4 prepare for the observations of the COMs: acetaldehyde, dimethyl ether, ethanol, and methyl formate. The most likely candidates for identification of these frozen COMs are the following features:

- the 7.427 and 5.803 μm bands are recommended for acetaldehyde,
- the 9.141 and 8.011 μm bands should be used for dimethyl ether,
- the 11.36 and 7.240 μm bands are good candidates for ethanol, and
- the 13.02 and 10.98 μm bands are most suited for methyl formate.

However, even with JWST the detection of COMs in the solid state will be challenging. The MIRI instrument is expected to have a continuum signal-to-noise ratio of at most 300. This translates into a 3σ detection at 1% of the continuum flux, which would require significant column densities of COMs to reach. In addition to this, multiple features of a single COM will have to be detected, preferably also with the correct intensity ratio, to ensure it is a robust detection. Besides looking at individual molecules, it will be worthwhile to investigate column densities of similarly structured molecules through common vibrational modes of functional groups.

2) One should be careful using the gas-phase CH_3OH/H_2CO ratio as a tracer of the chemical evolution of the CO hydrogenated ice on dust grains. The results in Chapter 5 suggest that the observed gas-phase H_2CO in TW Hya is formed in the gas phase in an elevated layer. This would mean that it holds little information about the solid-state H_2CO in the midplane. Detection of H_2CO closer to the disk midplane outside of the snowline is prohibited due to dust opacities at (sub)millimeter wavelengths. Detections with current facilities at longer wavelengths are not possible due to unfavourable Einstein A coefficients. Observing H_2CO inside its snowline, however, is more likely, especially in the case that dust opacities are lowered because of substructures. The temperature at which H_2CO thermally desorbs is ~ 50 K, which would require high spatial resolution and long integration times with ALMA to probe this region. For example, the derived temperature structure for TW Hya puts a midplane temperature of 50 K at approximately 10 AU. This would require spatial resolution of at least $0\farcs15$ to spatially resolve the thermal desorption of the solid-state H_2CO reservoir in TW Hya, one of the closest protoplanetary disks.

3) In order to understand planet formation and the material incorporated into those forming planets it is important to not only look at the interaction between gas and dust in a physical way, but also in a chemical way. The laboratory experiments in Chapter 6 show the conversion of gas-phase CO above its canonical desorption temperature into CO_2 with OH radicals on the surface of water ice. This specific interaction between gas and dust holds the potential to explain embedded solid-state CO_2 in water-rich environments and low gas-phase CO abundances in protoplanetary disks. Besides this reaction between CO and OH radicals, other ice and gas interactions might also take place and be able to explain observations. For example, one of the postulated pathways in Chapter 5 is to form the observed gas-phase H_2CO through a combined ice and gas reaction.

4) The results in Chapter 6 suggest a conversion factor of 0.06 for the conversion of CO into CO_2 per adsorbed UV photon. The limiting step in this conversion factor is the production of OH radicals. This suggests that either the dissociation of H_2O is not unity upon UV absorption or there is significant more recombination back into H_2O, more than suggested by molecular dynamics calculations. It is important to understand if this is due to laboratory conditions, that is, high UV fluxes, or if the dissociation efficiency upon absorption of UV photons of solid-state H_2O is not unity. More in-depth investigation is required to understand how water dissociates under laboratory conditions and to translate this into physical-chemical models that represent star- and planet-forming regions.

1.6 Future Outlook

The launch date of the *James Webb* Space Telescope should be shortly after the defence date of this thesis. JWST will open a whole new avenue of research that was previously not possible. It is equiped with four instruments, namely NIRSpec, MIRI, NIRCam, and FGS/NIRISS. NIRSpec and MIRI are most valuable for detections of solid-state molecules, as they cover the 0.6–5.3 μm and 5–28 μm wavelength range, respectively. Especially MIRI is well suited for detection of organic molecules as it covers the entire molecular fingerprint region, that is, 6.6–20 μm. Even though molecules with similar molecular structures have similar vibrational modes, the combination of different vibrational modes is unique in the fingerprint region. This emphasizes the need for the spectral characterizations performed in Chapter 3 and 4 for vibrational modes of COMs in pure form, but also mixed with astronomically relevant precursor molecules. Besides COMs, JWST will supply us with a wealth of knowledge on the main ice constituents, such as H_2O, CO, CO_2, NH_3, and CH_4. The high sensitivity and spectral resolution will allow for accurate determination of solid-state column densities, while the high spatial resolution of JWST will allow to spatially probe ice constituents as a function of distance from young stars. Combining our knowledge from ALMA with for instance the ERS program Ice Age will greatly improve our knowledge on star- and planet-forming regions, which can be used to make physical-chemical models more accurate.

CryoPAD2 is a state-of-the-art experimental setup, which allows to investigate vacuum-UV photon induced chemical and physical processes. The extremely sensitive QMS, which is able to detected partial pressures of at least 10^{-15} mbar, and recently improved RAIRS sensitivity will allow for further investigation of ices under UV light. For example, it is possible that organic species such as formic acid (HCOOH) and carbonic acid (H_2CO_3) form from the interaction between gas-phase CO and solid-state OH radicals in Chapter 6. The improved sensitivity will allow for them to be detected or put stringent upper limits on their formation if not detected. The calibration of the QMS will allow to look at potential chemical- and photodesorption of organics during UV irradiation and get better insight on the processes that occur in star- and planet-forming regions. Installation of a different light source, for instance one that simulates stellar radiation, can be used to investigate processes in our own Solar system on ice moons, such as Enceladus.

ALMA has been fully operational since March 2013, and many plans exist to improve even further its capabilities over the upcoming years. One of such upgrades is the implementation of the Band 1 receivers. These receivers cover a frequency range between 35 and 50 GHz, and will allow ALMA to observe deeper into the protoplanetary disks as there is less dust opacity at these wavelengths. Additionally, at these frequencies lower energy rotational transitions are probed, which inherently allows probing of gas at colder temperatures, that is, closer to the disk midplane. This will allow for probing of organics in the gas-phase closer to the midplane. Another proposed upgrade is to add additional antennas at longer baselines, which would increase the spatial resolution at which ALMA can observe. This would allow for observations of gas and dust in the terrestrial planet zone of young planet-forming systems, but also investigate at higher spatial resulution the interaction between gas and dust. These and other upgrades will significantly increase our understanding of the incorporation of organic molecules in star- and planet-forming regions.

The Square Kilometre Array (SKA, currently being build) and proposed next generation Very Large Array (ngVLA), will operate in the 50 MHz to 20 GHz and 1.2–116 GHz frequency range, respectively. In this centimeter wavelength regime protoplanetary disks do not suffer from dust opacities. The SKA and ngVLA will be able to observe gas and dust all the way to the midplane of protoplanetary disks, where planets are formed from accreting dust and gas onto larger bodies. Many organic molecules, such as formaldehyde, have transitions with low upper energies in this frequency range, which will allow probing the organic inventory in the midplane. This will be complementary to what ALMA observes in the elevated layers, and will allow for a complete picture of the organic gas-phase inventory in star- and planet-forming regions. Now combine this with the solid-state species observed with JWST and our knowledge of the total budget of organic molecules, and its potential to feed life throughout the universe, will drastically improve.