Table of contents

Introduction

1

The chemistry and physics of the universe have been intertwined ever since molecules first appeared during the Dark Ages. Observations of molecules are therefore effective probes of physical processes in space, but astrochemistry is more than a means to a physics end. During star- and planet-formation the chemistry must evolve from atoms and ions to organic acids and sugars; astrochemistry sets the stage for the origin of life at the ever increasing number of exo-planets.

This chemical evolution depends on the presence of dust grains in the interstellar medium and on the icy layers that form around them. Ices form rapidly during the different stages of star formation through condensation of gas onto cold grains and through an active grain chemistry. In interstellar clouds, the birth places of stars, this results in an ice mixture with simple components: H_2O, CO_2, CO, CH_3OH, NH_3 and CH_4.

Ices around protostar do not remain simple for long. Heat and UV from the newborn star both evaporate ices back into the gas phase and open up reaction pathways towards a complex organic chemistry in the ice phase. The grain-gas interactions – freeze-out, quiescent ice reactions and the ice processing due to energy input from the new star – can be investigated in the laboratory in vacuum chambers that simulate the situation in space. This is a crucial compliment to astrophysical observations which under most circumstances only provide snapshots of the ongoing chemistry towards different objects.

The thesis aims to combine quantitative laboratory simulations with ice and gas observations to map out key gas-grain processes during star formation, and thus the chemical evolution from dark clouds to comets. The investigations rely on knowledge of the physics of low-mass star formation, which directs the chemistry, and on previous developments of observational and laboratory techniques to study ices. The following pages introduce these pre-requisites together with the current understanding of astrophysically important ice processes. The origin of chemistry goes further back than the first star formation event, however, and this dark age is the topic of the first section.

1.1 The first molecule

Fourteen billion years ago, the Big Bang created the universe hot, dense and filled with radiation – too hot for even the elements of atoms, such as protons, to exist at any length. As the universe expanded the energy spread out and the temperature decreased. After the first second of the Universe's existence, it had already cooled enough for protons (hydrogen nuclei), neutrons and electrons to form and remain intact. 200 seconds later the temperature was 'only' a billion degrees, cool enough for protons and neutrons to combine to form helium, deuterium, beryllium and lithium nuclei. With further expansion and cool-down the nucleosynthesis stopped. Still the radiation field was too intense for atoms; a capture by a nucleus of an electron was immediately followed by photoionization, i.e. the stripping of electrons following the absorption of a high-energy photon. This continued for another 400 000 years, while the universe expanded, grew colder and grew darker (Dalgarno 2006).

Around this time, at a redshift[1] $z < 10000$, the photons had become scarce enough for atom-electron recombination to become significant, though it would take until $z < 2000$ for the Universe to become predominantly neutral (Galli & Palla 1998; Seager et al. 2000). This recombination of nuclei and electrons proceeded sequentially dependent on the ionization energies of the species; Helium was the first neutral species. The lack of photons during the next period in the Universe's history has provided the name of the epoch, the Dark Ages; its hospitality to neutral species meant the dawn of chemistry.

At a redshift $z \sim 3000$, He and H^+ (or He^+) radiatively associated to form the Universe's first molecular compound HeH^+ (He_2^+) (Galli & Palla 1998; Lepp et al. 2002). It took another $z = 1000$ before the first neutral molecule, H_2, formed. H_2 is still the most common molecule today though its dominant formation path has changed radically over the ages. At $z > 100$ H_2 formed from H^++H radiative association, followed by H_2^+ charge transfer with H. Around $z = 100$ a new more efficient formation channel became available, associative detachment of H^- and H. Both these processes are very inefficient compared to the predominant formation mechanism today, which is H recombination on grain surfaces. Two H atoms cannot simply recombine in the gas phase. With no third body available, the energy released from the atoms binding together can only be irradiated away and this is extremely slow because H_2 has no dipole moment compared with the probability of the two atoms flying apart again.

Grain formation requires C, O and Si, however, and this only became available after the birth and death of the first stars at $z \sim 15$. The collapse of gas into these first, giant stars ended the Dark Ages and the Universe was re-ionized by the starlight. Nucleosynthesis inside the stars turned hydrogen into carbon and oxygen and other heavier species. Many stars in this era ended in violent explosions – the most distant discovered is at $z = 8.3$ (Tanvir et al. 2009) – and thus ejected the new elements into the interstellar medium, dramatically changing the chemical conditions. Observations of probable dust continuum emission towards quasars at $z = 6.4$ indicate that these novae were efficient producers of

---

[1] The redshift is produced by the Doppler effect from the expansion of the Universe. The higher the redshift of the observed light, the farther away and further back in time is its origin. For a matter dominated universe, $t = 14 \times 10^9/(1 + z)^{3/2}$ years, where z is the redshift and t the age of the Universe when the light was emitted.

small dust grains (Bertoldi et al. 2003). When protected from radiation, the grains are cold surfaces on which gas phase atoms and molecules condense to form icy layers and there is tentative evidence of ice formation already at this early epoch of the Universe (Dudley et al. 2008).

This enrichment of the interstellar medium with heavy atoms and dust grains continued for the next billions of years and is still continuing today. The organic chemistry observed here on Earth, on other bodies in our solar system, around new-born stars and in distant galaxies all has its origin in these blasts, which began when the Universe was only a little more than a billion years old.

1.2   Stellar birth, life and death

While the first stars are still somewhat of a mystery, the life cycle of stars such as our own is fairly well understood (Fig. 1.1). Except for dust particles and large molecules, most molecular compounds are easily destroyed when exposed to UV irradiation, which is universally present in the interstellar medium. Therefore the chemistry has to start over in each stellar cycle, which begins with the formation of an over-dense region, a cloud, consisting of gas and dust, both primordial H and He, and heavier elements produced in the previous stellar life cycles. These clouds contain enough matter to absorb some or all of the interstellar UV light and thus protect molecules from destruction.

The most tenuous clouds, so called diffuse ones, are still harsh environments where molecules are continuously destroyed by UV light. The rich molecular inventory of such clouds discovered first in the 30s came therefore as somewhat of a surprise (Snow & McCall 2006, for a review). CN, CH and CH^+ were the first molecules to be discovered. Now it is well established that molecules of all sizes are present in these clouds including H_2, CO, carbon chains and H_2CO. Their presence despite the strong UV field implies efficient formation mechanisms. For most molecules ion-neutral reactions in the gas phase are fast enough to explain the observed abundances. Other molecules, especially H_2, require a grain reaction pathway.

The tenuous clouds can be compacted through a range of events, including colliding diffuse cloud streams, and energy input from stellar winds and supernovae (Vázquez-Semadeni et al. 2003). The result is a dense, gravitationally bound cloud, whose interior is completely protected from external UV rays. The dense clouds are thus cold ($\sim$10 K) and molecules dominate the chemistry. The high densities and low temperatures result in rapid accretion of gas-phase molecules onto grain-surfaces, forming ices (van Dishoeck & Blake 1998, for a review). These grains are also active chemical sites, which is discussed further in §1.3.

Molecular clouds contain even denser core regions, which are the birth places of solar-type stars. The density of the cores is higher than 10^5 molecules cm^{-3}, which can be compared to molecular cloud densities of 10^3–10^4 molecules cm^{-3} and diffuse cloud densities of 1–10^2 molecules cm^{-3}, and to the atmosphere on earth with $> 10^{19}$ molecules cm^{-3}. If the core's density is high enough to induce a collapse under its own gravity it is termed pre-stellar, i.e., it will eventually form a star. This collapse releases a large amount of
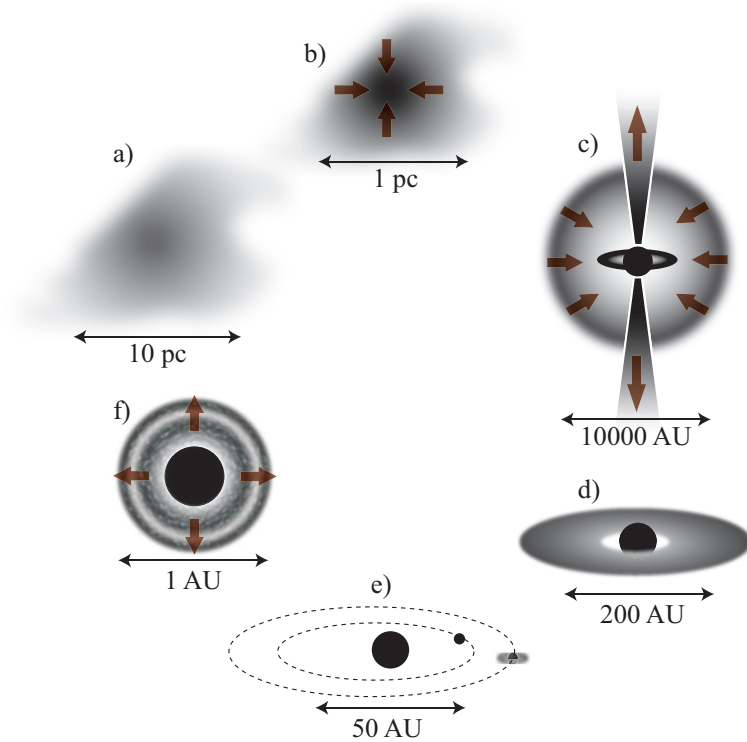
Figure 1.1 The stellar life cycle from a) diffuse clouds to f) star death. The dense cloud (b) contains cores which collapse under their own gravity to form a protostar (c), which is still embedded in cloud material. As the cloud disperses, the pre-main sequence star and an accompanying disk are exposed (d). With time the disk material is incorporated into planets or dispersed resulting in a main sequence star with a planetary system (e). When the star dies, stellar winds and novae drive newly formed elements and dust grains back into the diffuse interstellar medium (f). The length scales for each stage are order of magnitude estimates.

energy, which threatens to stop the collapse through the increased pressure building up from the heated gas. The presence of molecules prevents this from happening. Molecules are efficient coolants; they can be thermally excited through collisions at a range of temperatures, and then irradiate the energy at specific wavelengths. Some of the discrete radiation escapes from the core and thus carries away energy.

During the collapse, the protostar starts to release angular momentum through large outflows and through the formation of a dense disk, which continues to accrete material onto the protostar (Bachiller 1996; Jørgensen et al. 2005). Because of the high density of the disk ($< 10^6$ cm^{-3}), grains coagulate, forming larger and larger boulders, and eventually planets (Dullemond & Dominik 2005; Johansen et al. 2007). This process continues after the now pre-main sequence star has dispersed the last surrounding cloud material. The large number of discovered exo-planets (353 as this thesis goes into print) shows that the production of planets in such disks is quite efficient. The protoplanetary disk is less protected than the protostellar envelope and has a surface layer where the chemistry is dominated by UV radiation and heat from the protostar. Deeper in ices may still survive and continue to affect the chemistry actively (Chiang & Goldreich 1997). The composition of comets suggests that at least some of the ice is pre-stellar in origin (Bockelée-Morvan et al. 2000).

Eventually the disk is cleared of gas by irradiation and winds from the star and by the gravitational pull of the young star and of planets. For the next billions of years most of the interesting chemistry in the solar system will take place in comets, and on planets and moons. As the star closes in on its end, its outer atmosphere becomes a production factory of dust particles and other complex molecules and aggregates of molecules, just as it did in the earlier generations. These particles and macromolecules are fed back into the diffuse interstellar medium and the process starts over, though more enriched in heavy elements than last time around.

This is the life cycle for solar-type stars and for low-mass stars in general. High-mass star formation probably shares some of the same processes, but their exact evolution from giant molecular clouds to stars is still contested. All types of star formation are however accompanied by a rich chemistry which evolves with the physical environment, dependent on changes in the density structure, temperature, availability of surfaces, UV light flux and other energy fluxes. Molecular and atomic spectra are used routinely to probe the physical processes described in this section – it is often the most efficient means to investigate astrophysical processes, especially during the heavily obscured stages of star formation. Molecular and atomic abundances also affect its physical environment through for example cooling, as described above. This coupling between the chemistry and physics implies that understanding the chemical processes in space is important for most branches of astrophysics. The remainder of this introduction and this thesis both focus, however, on the understanding of astrochemistry for its own sake and how investigating gas-grain interactions provides crucial clues to how the chemistry evolved from dense molecular clouds to solar systems such as our own.

5

1.3 Ices in star forming regions

The presence of ices in general and water ice in particular in the interstellar medium was first proposed in the astrophysical literature by Eddington (1937), building on the argument that the obscuring clouds between stars had protected interiors, where water molecules could aggregate together to form small ice particles. This was 23 years after the discovery of the first interstellar absorption line (Hartmann 1904), and just prior to the first identification of an interstellar molecular species (Swings & Rosenfeld 1937). Eddington was right: ice is present in space. When progressing from diffuse regions to dense clouds, water (H_2O) ice is the first ice to form and it is the most common ice species throughout the molecular cloud in all but a few sources (Bergin et al. 2005; Sonnentrucker et al. 2008), closely followed by carbon dioxide (CO_2) and carbon monoxide (CO). Observations of ices and their implications for how the first ices form, how they are destroyed and how they react into more complex ones are the topics of this section and of Fig. 1.2.
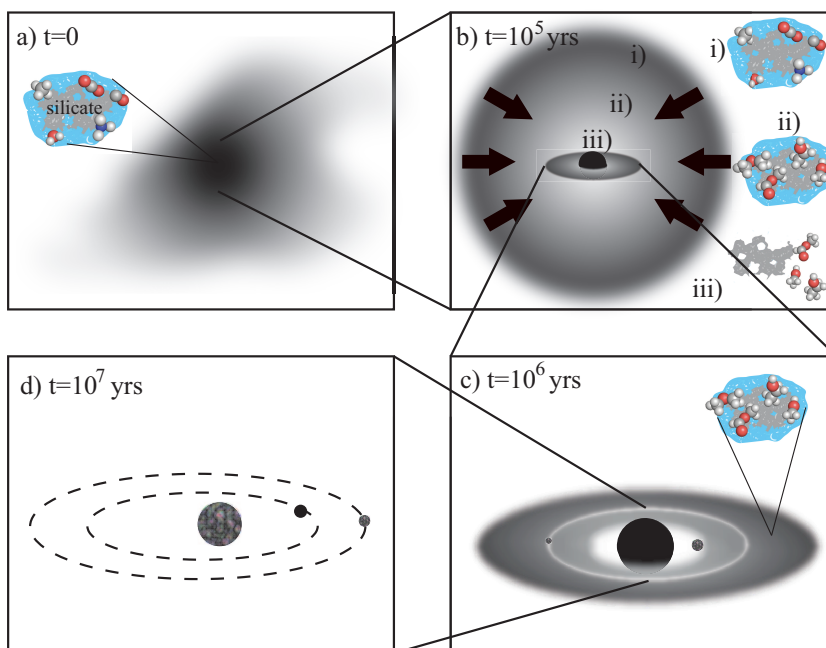

Figure 1.2 The proposed ice evolution during star and planet formation starting with simple ice formation in dark clouds and cloud cores (a). Heat and UV from the protostar may result in a more complex ice mixture (b.ii), which evaporates close to the protostar (b.iii). Some of this ice becomes incorporated in the protoplanetary disk instead (c), and further into comets and planets (d).

1.3.1 Ice observations and infrared spectroscopy

Water ice was first detected in the 1970s. Shortly afterwards ices of different kinds were determined to be a common constituent of molecular clouds. (Gillett & Forrest 1973; Merrill et al. 1976). Over the years H_2O, CO_2, CO, CH_3OH, NH_3 and CH_4 ice have all been observed, and some of their abundances have been established in a range of astrophysical environments, including the inner and outer regions of dense molecular clouds, protostellar envelopes and protoplanetary disks (Knez et al. 2005; Gibb et al. 2004; Boogert et al. 2008; Pontoppidan et al. 2005, and Chapter 2–3 of this thesis). These ices reside on the surfaces of (sub-)micron-sized dust particles, whose composition, origin and evolution are treated in detail by Whittet (1992).

Identification and abundance determinations of ices rely on infrared absorption spectroscopy, i.e., the different absorption patterns of different ice species superimposed on a background continuum light source, such as a protostar. The frequency of light that is absorbed by a certain molecule depends on the molecular motions that can be excited. When free-floating, molecules have degrees of freedom corresponding to translation, rotations and vibrations, and to electronic transitions. In an ice, the molecules are immobilized. Thus there is no translation nor any rotations. The molecule still vibrates, however, and these vibrations are excited by the absorption of infrared radiation.

In the gas phase these vibrationally excited states can be populated thermally as well, through collisions between molecules. This is not possible for ices, since the required temperatures exceed the evaporation temperatures of all common ices. Thus only infrared absorption spectroscopy of ices is possible – far-infrared transitions due to hindered rotational transitions can be populated thermally for the less volatile ices and H_2O ice has been observed in emission at these wavelengths (Molinari et al. 1999). In general, the investigation of ices in space is restricted to specific lines of sight, since background sources with strong infrared continua are rare, except for protostars. Therefore ices around protostars are among the most well studied, while less is known about ices in the densest cloud cores before the onset of star formation.

Figure 1.3 shows the infrared spectrum towards a protostar with several of the identified ice species marked out. Spectra of molecular clouds and towards circum-stellar disks share most of the spectral features found towards protostars, with clear detections of H_2O, CO_2 and CO ice and a deep silicate feature at 10 μm from the grain cores themselves (Knez et al. 2005; Pontoppidan et al. 2005). The ice composition thus seems only marginally affected by the transition between these different evolutionary stages of low-mass star formation, suggesting that most of the ice forms already in the molecular cloud. This is supported by mapping of ice absorptions toward molecular clouds, which shows that once a certain distance threshold into the cloud is overcome, the water ice abundance is linearly correlated with the cloud material, i.e. it forms before the cloud core stage is reached. Some of the carbon dioxide ice is also observed towards the cloud edges. In contrast to water ice, it increases somewhat in abundance further into the cloud core. This second growth seems dependent on a catastrophic freeze-out of CO ice, which only happens in the cloud core itself (Pontoppidan 2006). These observations then imply a structured ice mantle with a layer of H_2O-rich ice directly on the grain core and a second
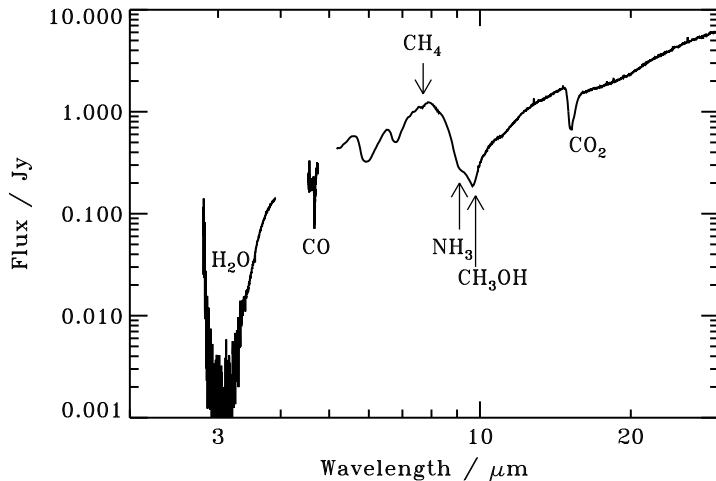
Figure 1.3 Ice spectrum towards the low-mass protostar HH 46, which has been published by Boogert et al. (2004), together with some peak assignments.

layer of CO-rich ice on top.

This scenario is consistent with the observed ice spectra. The CO_2 ice absorption features have been compared with laboratory spectra (§1.4.2) and are best explained by CO_2 present in two separate ice environments: a H_2O-rich and CO-rich one. CO ice is observed to be mostly pure except for a small part mixed with CO_2. Once the protostar turns on these original ice mixtures are modified through distillation and segregation and pure CO_2 ice becomes common as well (Pontoppidan et al. 2008). These processes are the topic of Chapters 5–6, while the formation conditions of different ices during star formation is investigated through statistical analysis of a large sample of protostars with ice observations in Chapter 2.

The observations in Chapter 2 and 3 were mainly acquired with the *Spitzer Space Telescope*. Some infrared observations are possible through spectral windows in the atmosphere of the earth. Only space-born telescopes gives access to the entire infrared spectral region and *Spitzer* was the first space-born telescope with high enough sensitivity to carry out ice observations towards low-mass protostars. This has dramatically increased the number of ice detections and thus our understanding of how the first ices form.

1.3.2 The first ices

From observations, ices thus first appear in dense molecular clouds. The observations described above have shown that even there ice formation is not possible up to the edges of the clouds where the irradiation field is strong. This is not to say that molecules do not form on surfaces in these harsher environments. They do. They also evaporate due to different non-thermal processes, such as UV photodesorption, before an ice layer can be built up (Fig. 1.4).
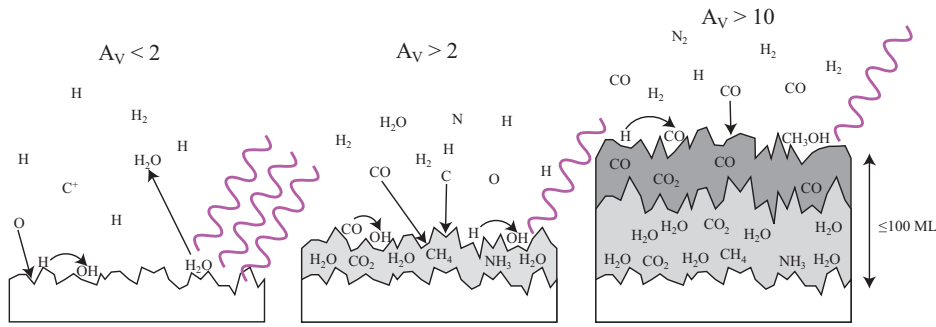
Figure 1.4 The proposed ice evolution in molecular clouds before the onset of star formation resulting in a layered ice structure.

The proposed formation paths of interstellar ices have changed through the decades as theory, observations and laboratory experiments have become more detailed. When Eddington first proposed the existence of ices in the interstellar medium, he assumed that they could form as in our atmosphere, where gas phase molecules freeze out on macromolecules or on soot particles. This may explain some of the observed ices in molecular clouds, especially CO ice, but for most ices, the gas phase production mechanisms are simply too inefficient to explain the observed abundances. This is especially true for H_2O, CH_3OH and CO_2.

A decade after Eddington, van de Hulst (1946) first proposed an active ice chemistry where C, O and N atoms condense on particles consisting of dust and ice aggregates and subsequently react with hydrogen to form an ice consisting of H_2O, CH_4 and NH_3. The hydrogenated atoms should dominate the ice composition since hydrogen is orders of magnitude more abundant than any of the heavier atoms and thus the probability for any specific atom to react with hydrogen far exceeds the probability of it reacting with another C or O atom. This framework of atom-radical reactions on ice or grain surfaces still holds, though the exact reaction schemes have evolved.

This ice formation framework reached a new level of sophistication when Tielens & Hagen (1982) proposed a combined gas and grain chemistry where atoms accrete onto grain surfaces, depending on their gas phase abundances and sticking probabilities. In their model the energy barrier for an atom, molecule or radical to hop around the surface is assumed to be lower than the desorption or evaporation barrier and thus a given atom will hop around the grain for a period of time, whose length depends on the grain temperature. If the atom encounters another atom or radical during its time on the grain, they react, since radical-radical reactions have no activation barriers. At typical molecular cloud temperatures of $\sim$ 10 K, hydrogen atoms will scan the grain surface orders of magnitude faster than the second smallest common atoms, C, N and O. Therefore the formed ice is still predicted to be abundant in hydrogenated atoms, i.e. H_2O, CH_4 and

NH_3. Because of the different transition conditions between the atomic and molecular form for hydrogen and the heavier species, hydrogenation of molecules and oxygenation are important processes as well. CO forms efficiently in the gas phase, and thus CO ice is explained by direct freeze-out of the molecular gas. Hydrogenation of CO produces methanol, while its oxygenation results in CO_2.

There are few laboratory studies of the proposed grain surface reactions. The hydrogenation of CO to form H_2CO and CH_3OH is an exception. A key experimental result is that in a molecular and atomic mixture of CO and C or N_2O and O, hydrogen atoms react preferentially with the atoms rather than the molecules (Hiraoka et al. 1998). Thus methanol is expected to form at a later stage than methane even if the carbon and carbon monoxide co-exist in the outer parts of molecular clouds. In pure CO ice, hydrogenation to form H_2CO and subsequently CH_3OH seems efficient though absolute rates are still lacking (Watanabe et al. 2003, Fuchs et al. A&A in press).

Combining the model, laboratory experiments and astrophysical observations, the ice chemistry is proposed to proceed as in Fig. 1.4. In the diffuse clouds and at the edges of denser clouds atoms accrete onto the surface for long enough to react with hydrogen. Efficient UV induced desorption (Chapter 7–9) prevents the formed molecule from remaining on the surface long enough to form more than a monolayer of ice (Hollenbach et al. 2009). As the cloud grows denser, or alternatively deeper into an existing cloud, atoms start to convert into molecules in the gas phase since they are now protected from most UV light. This also allows for the build-up of ices. O, C, N and CO accrete onto surfaces, and the atoms are preferentially hydrogenated as predicted by experiments. CO is thus not hydrogenated at this stage, but instead reacts with oxygen, probably in the form of OH, to form CO_2. As the gas is depleted of C and O atoms and the density increases, CO accretes rapidly onto the surface with only a small portion being turned into CO_2, while the remainder is either converted to CH_3OH or not reacting at all. Some non-thermal desorption is present deep into the cloud because of direct cosmic ray desorption, cosmic-ray induced UV desorption and desorption due to release of chemical energy (Shen et al. 2004; Garrod et al. 2007).

This figure is however a proposition, not a fact. Chapter 2–3 provides further observational evidence in its support, but the real lack is in laboratory data rather than in ice observations. Without laboratory tests, the relative and absolute efficiency of these different reactions remain speculative.

1.3.3 A complex ice chemistry?

The ice chemistry does not necessarily stop with methanol. While there is only a handful of ice observations towards high-mass protostars with evidence of more complex species forming in the ice, the detection limits in such observations are high because of the intrinsic overlap of many organic ice features (Gibb et al. 2004, Chapter 2). Still, as discussed further in Section 1.3.4, the gas phase observations of complex molecules around protostars and in shocked regions seem to provide indirect evidence of the evaporation of complex ice species.

Two different kinds of models in the literature result in complex ice formation. One

possible formation route is atomic accretion and recombination on grain surfaces, similarly to how smaller species form (Brown et al. 1988; Tielens & Charnley 1997). Building on this idea, Charnley (2004) suggested that complex ices form either through hydrogenation of molecules and radicals, such as CO and HCCO, or through a combination of hydrogenation and oxidation starting with C_2H_2. Similar reaction schemes are suggested to explain observations of complex gas phase species by e.g. Bisschop et al. (2007) and Requena-Torres et al. (2008). Whether such a formation route is efficient for complex molecules under astrophysically relevant conditions remains to be shown. Experimental studies indicate that dissociative reactions may be the favored outcome of hydrogenating larger molecules and fragments (e.g. Bisschop et al. 2007), hampering the build-up of large quantities of complex molecules. Quantitative experiments are however still lacking for most reactions.

Figure 1.5 A proposed reactions scheme to form complex ices from CH_3OH ice, through UV-photodissociation followed by radical diffusion and radical recombination (Chapter 10).

A competing scenario is formation of complex molecules through energetic processing of simpler ices, such as CH_3OH, NH_3 and CH_4. In this scenario cosmic rays and UV photons break apart the existing ices into smaller fragments which subsequently diffuse and recombine into more complex species (Fig. 1.5). Cosmic rays can penetrate deep into cloud cores and protostellar envelopes, while externally produced UV rays are rapidly extinguished. The cosmic rays produce an internal UV field, however, through interactions with molecular hydrogen. Thus energetic processing of ices through both direct cosmic ray bombardment and the secondary UV field are possible also during the cold, protected stages of star formation.

A few theoretical studies have investigated this route during star formation. Most recently Garrod & Herbst (2006) and Garrod et al. (2008) modeled the formation of complex molecules in ice through radical diffusion and recombination during the slow warm-up of ices in an in-falling protostellar envelope. The increasing temperature towards the protostar (20–100 K) allows for the diffusion of heavier and heavier radicals such as CH_3 and CH_2OH, which recombine to form larger and larger molecules. The model continues until all the ice is evaporated and the resulting gas phase abundances reproduce some of the abundance ratios and temperature structures seen in hot cores around protostars. Improvement of these model predictions is mainly limited by lack of quantitative experimental data on photodissociation branching ratios of simple ices, diffusion barriers of the formed radicals and binding energies of most complex molecules. The experimental quantification of this complex molecule formation route is the goal of Chapters 10 and 11.

1.3.4 Observations of evaporated ices in the gas phase

Ice evaporation is required to explain gas phase observations in cloud cores, at cloud edges and in protostellar envelopes. Thermal evaporation is possible once the protostar has turned on and started to heat up the cloud remnant. It explains the excess gas phase abundances of water and methanol in the inner regions of protostellar envelopes as well as the presence of more complex molecules; the high abundances of these complex species require either an efficient gas phase formation route from thermally desorbed CH_3OH ice or an efficient ice formation pathway followed by evaporation. In general, models predict that thermal evaporation of ices sets the stage for the gas phase chemistry during the warmer stages of star formation because of the large amounts of molecules bound up in ices during the preceding colder stages (e.g. Aikawa et al. 2008).

The evaporation temperatures for a number of ices have been investigated experimentally and the determined desorption energies range from the volatile N_2 and CO, desorbing ~30 K at laboratory time scales, to H_2O and larger organic molecules, which desorb above 150 K (e.g. Sandford & Allamandola 1988; Fraser et al. 2001; Collings et al. 2004; Öberg et al. 2005) – at astrophysical timescales the desorption temperatures are lower. Because of the large range in evaporation energies, thermal evaporation is expected to proceed sequentially during star formation starting with the most volatile species. Mixed ices may however not segregate completely prior to desorption, resulting in efficient trapping of volatile molecules in the water ice, which is further discussed in §1.4.3 and in Chapters 5–6.

Ices can also desorb non-thermally, through sputtering by particles in shocks, through cosmic ray spot-heating of the ice, through release of chemical energy during bond formation and through UV photodesorption (Shen et al. 2004). The relative importance of these different mechanisms in different astrophysical environments has so far been difficult to assess because of a lack of quantitative experimental data. Observations of excess gas phase water at cloud edges and carbon monoxide and methanol in cloud cores can only be explained by a high efficiency for at least one of the latter three mechanisms (Melnick & Bergin 2005; Garrod et al. 2007; Hollenbach et al. 2009), while dramatic enhancements of

e.g. methanol in outflows are explained by grain sputtering, since methanol does not form efficiently through gas phase reactions (Blake et al. 1995; Garrod et al. 2006). Chapters 7–9 are dedicated to the quantification of one of these mechanisms, UV photodesorption of ices.

Thus ice chemistry and ice desorption are crucial to explain several kinds of gas phase observations. The inverse is also true; gas phase observations are crucial to understand the ice evolution inaccessible by infrared ice spectroscopy. While gas phase spectroscopy is possible at a range of frequencies, all of the above observations were carried out at millimeter and sub-millimeter wavelengths to probe pure rotational transitions. Such radio observations allow for investigations of orders of magnitude lower abundances of molecules compared to the infrared. Added to that, peak overlaps are significantly reduced in radio observations compared to infrared ice spectroscopy, facilitating molecular identifications. Thus while CH_3OH is the most complex ice molecule to be securely identified, the three times larger CH_3CH_2CHO has been identified around protostars from its rotational spectra (Belloche et al. 2009). If the grain-gas interaction becomes well understood, rotational spectroscopy of gas phase molecules may provide powerful constraints on the ice evolution during the warm protostellar and disk stages and thus provide the stepping stone between the simple ice chemistry observed directly around protostars and the complex molecules found in comets and meteorites in our own solar system. The observations of non-thermally evaporated ice provides additional information, since it probes the chemical evolution before the onset of thermal evaporation. This is the topic of Chapter 12.

1.4 Ices in the laboratory

Laboratory solid-state astrophysics has two main objectives: identifications of ice spectral features and simulations of astrophysically relevant ice processes. Most chapters in this thesis fall in the second category, while it was with spectroscopy that this field of study began half a century ago.

1.4.1 The need for laboratory experiments

Astrophysical observations directly provide spectra of interactions between light and matter towards specific objects at specific times. Laboratory studies are thus first required to identify what species produce the observed spectra. Laboratory spectroscopy is also needed to extract information about the physical conditions from the spectra, such as the density and temperature.

The second challenge of astrophysical observations, which laboratory studies address, is the fact that astrophysical time scales are typically orders of magnitude longer than human life spans – even the relatively fast collapse of cloud cores to form protostars takes a minimum of 1000 years. Thus it is seldom possible to observe either the chemical or the physical evolution of a specific object. Rather observations aim to provide 'snapshots' of the evolution towards a large set of objects at different evolutionary stages and then put

them into an evolutionary sequence. This is not trivial and laboratory studies of different astrophysical processes are key to solve the puzzles. In the laboratory, the chemical evolution is sped up by increasing the UV flux or the heating rate or any other parameter of interest. It is therefore possible to investigate each step in the ice evolution on time scales of hours instead of thousands of years and then use the laboratory predictions of how the ice will change with time, temperature or flux to interpret the astrophysical observations.

1.4.2 Spectroscopy of astrophysical ice equivalents

The development of spectrographs and astrophysical spectroscopy are historically inseparable. When Joseph von Fraunhofer invented the spectrograph in 1817, he also discovered the Sun's atomic absorption lines, though not identified as such until 1859 by Kirchhoff and Bunsen. It was also credit to visible spectroscopy that the presence of external galaxies was first established in the early 20th century; spectroscopy of the closest spiral galaxy, M31, (M for Charles Messier who cataloged it in 1734) revealed a stellar spectrum and a higher Doppler shift than had been observed anywhere in the Galaxy, both which separated it from local nebulae such as M42 and the Orion Nebula.

Infrared spectroscopy, the preferred tool for ice identification, was developed during the same period, though it did not reach the accuracy of visible spectroscopy until much later – one William Herschel's many discoveries was the presence of infrared light, which he first detected around 1800. Draper first managed to photograph infrared absorption bands in 1842 (Lewis 1895), while infrared *ice* spectroscopy only dates back to the early 20th century.

Molecular vibrations are excited by infrared radiation dependent on the derivative of dipole moment function $d\mu/dR$. Most molecules have a permanent dipole moment, since all different atoms attract electrons differently, producing a charge imbalance in the molecule. Exceptions include both homo-nuclear diatomic molecules, such as molecular oxygen (O_2), and larger molecules that are symmetric, e.g. carbon dioxide or O-C-O. The latter kind still have dipole-allowed infrared absorption features, since $d\mu/dR \neq 0$ during some vibrations, while homo-nuclear di-atomics to a first order do not have any detectable infrared transitions – the quadrupole-allowed H_2 transitions are exceptions because hydrogen is so abundant.

In isolation, molecular vibrations have specific frequencies, dependent on the strength on the vibrating bond. In solids, interactions with the molecules around it modify these bond strengths, which often results in a range of overlapping frequencies for one type of molecular vibration. For example the symmetric H_2O stretch vibrates at a frequency of $3657\,\text{cm}^{-1}$ ($2.7\,\mu\text{m}$) in a dilute gas, but at $3000\text{-}3600\,\text{cm}^{-1}$ ($2.8\text{–}3.3\,\mu\text{m}$) in an amorphous, i.e. disordered, ice. The feature changes again when the H_2O ice is in a mixture.

The discoveries of ices in space prompted targeted spectroscopy of ices and ice mixtures to pursue the identifications of different infrared bands observed towards star forming regions, starting in the 1970s in Leiden. This spectroscopy began before the discovery of the $3.1\,\mu\text{m}$ band, associated with H_2O ice, towards several astrophysical sources (Gillett & Forrest 1973; Merrill et al. 1976), and was further driven by the observation that the $3.1\,\mu\text{m}$ profile does not match pure H_2O ice perfectly. Hagen et al. (1980) investigated the
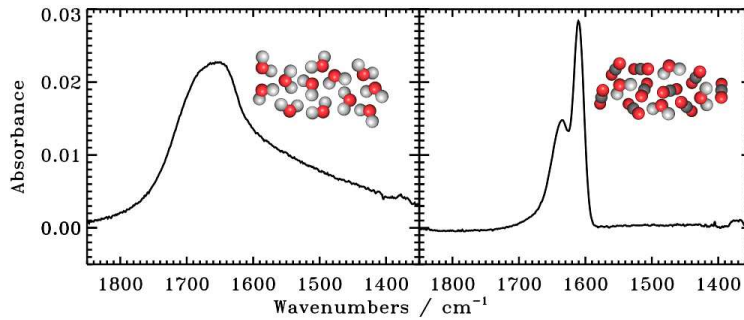
Figure 1.6 The water infrared bending feature in a pure water ice (left panel) and in a carbon dioxide ice mixture (right panel).

impact on the 3.1 μm feature when adding different molecules to the H_2O ice. They noted that in addition to profile changes due to overlap between features of different species, the ice mixture spectra also contained distorted isolated bands compared to the pure ice spectra. Figure 1.6 shows qualitatively the dramatic change of the water bending feature at 6 μm between pure H_2O ice and H_2O mixed with CO_2 ice (from Chapter 4). This both adds confusion and extra information when interpreting astrophysical observations; changes in shapes can easily be mistaken for spectral features of new species, but if correctly assigned the spectral shapes add information on the structure of the ice in addition to its composition. These distortions are almost impossible to calculate in amorphous ices though recent attempts exist (Mate et al. 2008). Therefore spectroscopy of different ice mixtures is an ongoing work of which Chapter 4 is part.

The set-up used for transmission infrared spectroscopy of ices in this thesis is shown in Fig. 1.7 and also discussed in detail by Gerakines et al. (1995). A gas mixture is prepared separately and then attached to the set-up, which consists of a high-vacuum chamber with infrared-transmitting windows, one or more inlet tubes for the gas mixture, an outlet for the pump and an infrared-transmitting window in the center of the chamber which is cooled by a helium cryostat down to 15 K. The ice mixture is built up diffusively by letting gas into the chamber and where it freezes out onto the cold window. The spectra of the ice can then be monitored with a Fourier transform infrared spectrometer ranging between 4000-400 cm^{-1} at 15–200 K.

1.4.3 Ice dynamics – mixing, segregation and desorption

Amorphous ices may be best thought about as very viscous fluids, where the viscosity depends steeply on ice temperature. Below 20 K most ices are immobile on laboratory time scales. H_2 and H can still scan the surface and also penetrate somewhat into the ice (Ioppolo et al. 2008). CO and N_2 become mobile around 25 K (Öberg et al. 2005; Bisschop et al. 2006, Chapter 5). Other potentially important molecules and radicals sequentially start to diffuse in the ice, dependent on their binding energies. At higher
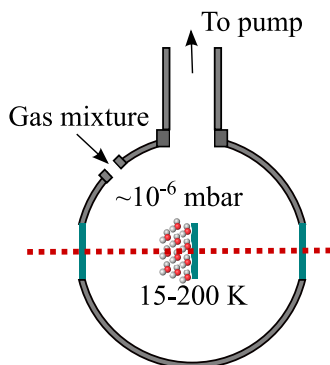
Figure 1.7 A drawing of the key features of the HV set-up for transmission ice spectroscopy.

temperature the ices start to evaporate, again dependent mainly on the binding energies, though the ice structure plays a role as well (Collings et al. 2004).

In the literature, ice dynamics are studied using a range of tools including infrared spectroscopy of the ice, quadrupole mass spectrometry of the desorbing molecules and quartz-balance measurements of the mass of the ice on the surface. Infrared spectroscopy can be used both to determine the amount of ice on a surface and to probe the ice structure. The latter is based on the dependence of infrared ice-band shapes on its bonding structure and the nature of its nearest neighbors as discussed above (Fig. 1.6). Thus ice spectroscopy can be employed to measure ice desorption, through continuous measurements of the ice amount as a function of temperature, as well as ice mixing and segregation through analysis of changes in the spectral band shapes.

Mass spectrometry is used to probe desorption at a higher time resolution and at a higher sensitivity than is possible with infrared spectroscopy of the ice. It is also the only molecule-specific tool available to probe species without dipole-allowed infrared transitions and complex ice species whose infrared bands are impossible to separate from the absorption bands of other species. Finally quartz balances provide the most sensitive measurements of total ice desorption, both thermal and non-thermal, but cannot be used to determine which ice species desorb from an ice mixture.

Figure 1.8 illustrates the use of spectroscopy and mass spectrometry during segregation and desorption studies of $H_2O:CO_2$ ice mixtures when a particular ice mixture is heated with a linear heating ramp between 20 and 200 K (taken from Chapters 4–6). Before the onset of CO_2 desorption the spectral profile of CO_2 changes, indicating an ice restructuring. At higher temperatures the mass spectrometer starts to detect CO_2 molecules in the gas phase, indicative of ice desorption. Simultaneously the infrared spectroscopy reveals a loss in CO_2 absorbance. By combining the heating rate and the temperature at which the dynamical process occurs it is possible to derive an energy barrier for the dynamical process in question. This can subsequently be incorporated into an astrophysical model, predicting when and where ices segregate and desorb in space.

The simplest dynamical process in ices is thermal desorption of pure ices and this has been studied quantitatively by a number of groups. Desorption of binary mixtures is
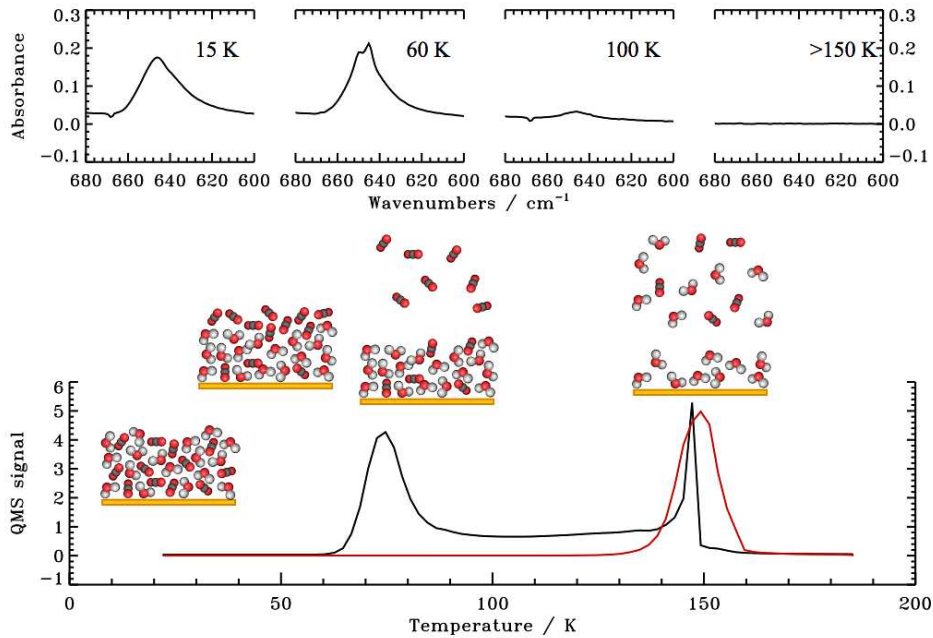
Figure 1.8 The changes in a H_2O:CO_2 ice mixture with temperature and the recorded output by the mass spectrometer and the infrared spectrometer in response to the dynamical processes in the ice. The top panel shows the CO_2 bending mode at 15 μm at 15 K when mixed with H_2O, at 50 K when the ice is partly segregated ice, at 100 K when most CO_2 has desorbed and above 150 K following desorption of the H_2O ice and the CO_2 molecules trapped in the H_2O matrix. The bottom panel shows the CO_2 (black) and H_2O (red) ice desorption rates as a function of temperature. In this mixture most CO_2 desorbs around 70 K, but some is trapped in the H_2O ice and desorbs with H_2O at 150 K.

less understood, though a few composition specific models of e.g. $H_2O:CO$, $CO:N_2$ and $CO:O_2$ mixtures exist (Collings et al. 2003; Bisschop et al. 2006; Acharyya et al. 2007). Segregation and mixing of binary ices have not been treated quantitatively, except for in the desorption studies, and the underlying mechanisms are still unknown. These two problems are treated by a combination of experiments and modeling in Chapters 5–6.

Desorption and ice structure changes can also be induced by cosmic ray/ion bombardment (Baratta et al. 1991) and UV photons (Westley et al. 1995; Leto & Baratta 2003). UV photodesorption is potentially the life line between gas and ices in quiescent regions and thus three of the chapters here aim to quantify the rates and mechanisms of ice photodesorption. Previous photodesorption experiments showed a high desorption yield per incident UV photon for water ice (Westley et al. 1995), while the yields for other astrophysically relevant ices have not been previously measured and often assumed to be negligibly small (e.g. Ruffle & Herbst 2001). Even in the water experiments an observed fluence dependence seems to limit the astrophysical applicability of the previous experimental results. To address this, photodesorption yields of pure and mixed ices containing CO, N_2, CO_2 and H_2O are presented in Chapters 7–9.

1.4.4   Ice chemistry

The formation of the first ices, such as CH_3OH and H_2O, is investigated in atomic bombardment experiments where the reactions of atoms or atoms and molecules are observed on ice surfaces (Hiraoka et al. 1998; Watanabe et al. 2003; Ioppolo et al. 2008). Qualitatively, hydrogenation of both molecules and atoms seems highly efficient even at low temperatures, confirming the previous hypothesis that the observed simple ices, CH_3OH and smaller, form through this route.

Experiments on complex ice formation have investigated the effect of energetic bombardment of simpler ices with ions or UV photons (e.g. Stief et al. 1965; Hagen et al. 1979; Allamandola et al. 1988; Gerakines et al. 1995; Hudson & Moore 2000; Bennett et al. 2007). With a few exceptions, most studies have focused on the qualitative assignment of final products, following irradiation or bombardment of ice mixtures that are proposed to mimic ice compositions in star forming regions. The investigated ice mixtures are usually converted into a mixture of more complex species upon irradiation. Photolysis of ices is thus a potential pathway of complex molecule formation in space. The traditional approach with high-vacuum set-ups and irradiation during deposition followed by warm-up and analysis of the complex residue has provided valuable insights into the possible outcomes of UV- and ion-chemistry, but little quantitative data that can be tested against astrophysical observations.

The approach to UV induced ice chemistry in this thesis is different. The studies do not propose to perfectly imitate either the conditions or the ice compositions in space. Therefore the results are not meant to be directly translated into astrophysical predictions. Rather the aim is to run experiments from which physical properties can be extracted, such as photo-production cross sections and branching ratios, and radical diffusion barriers in the ice. These physical properties, to a first approximation, do not depend on the time scale of the process and are thus equally valid in a laboratory setting and in space. Thus,

astrochemical models including these barriers and cross sections can provide direct tests of the likelihood of snap-shot observations being due to a proposed chemical scenario.

This affects the design of the experiments. The experimental set-up used for the UV-experiments is described in detail below. The general philosophy has been to focus on pure ices or other well-constrained ice systems rather than ice mixtures with all components present in interstellar ices. The chemistry in these simpler ices are then investigated during the full range of laboratory conditions available including different radiation fluxes, ice temperatures, ice structures and so forth to provide the maximum amount of constraints on the underlying physical quantities, i.e. the diffusion and reaction barriers and dissociation cross-sections. The experimental results are presented in Chapter 10 and 11, while the quantitative modeling of these processes to extract the physical quantities will be presented in a series of papers by Garrod & Öberg (in preparation).
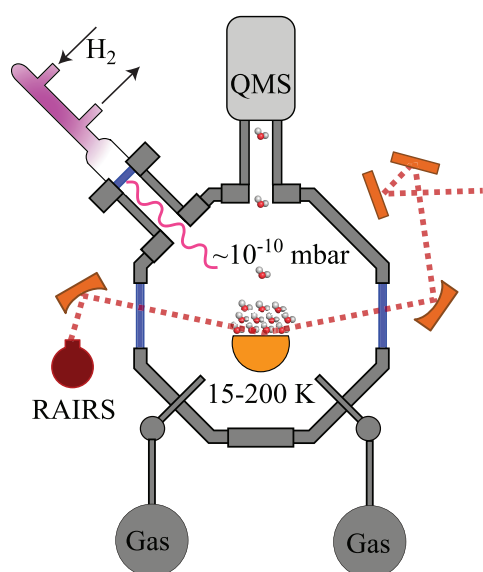
1.4.5 CRYOPAD

Figure 1.9 A drawing of the key features of the experimental set-up CRYOPAD including the hydrogen discharge UV lamp. The temperature refers to the gold substrate on which the ices are deposited.

The ice dynamics, ice photodesorption and ice photochemistry experiments are all carried out under ultra-high vacuum conditions ($\sim 10^{-10}$ mbar) in the CRYOPAD set-up, which is described in detail in Öberg et al. (2005) and Fuchs et al. (2006). The set-up was built as part of the Ph.D. thesis project of van Broekhuizen (2005) and has been further modified during the present thesis to achieve its current form (Fig. 1.9). CRYOPAD was built with for the specific purpose of studying photochemistry, but as this thesis shows, it is a versatile instrument suitable for a range of dynamics and chemistry experiments.

In the beginning of each experiment, pure ices and ice mixtures are grown *in situ* with monolayer (ML) precision at thicknesses between 1 and 100 ML, by exposing a

cold substrate at the center of the vacuum chamber to a steady flow of gas, directed along the surface normal. The ultra-high vacuum allows for the study of thin ices, similar in thickness to those found in space, since the contamination level is low. The substrate is temperature controlled between 15 and 200 K.

The set-up is equipped with a Fourier transform infrared (FTIR) spectrometer in reflection-absorption mode (Reflection-Absorption InfraRed Spectroscopy or RAIRS) and a quadrupole mass spectrometer (QMS) to investigate ice evolution and ice desorption. In the photo-experiments the ice films are irradiated at normal or 45° incidence with UV light from a broadband hydrogen microwave-discharge lamp, which peaks around Ly α at 121 nm and covers 115–170 nm or 7–10.5 eV (Muñoz Caro & Schutte 2003).

Compared to the interstellar environment CRYOPAD reproduces the ice temperature well. The vacuum consists mainly of H_2, as in space, and is comparable to the conditions of disk midplanes and pre-stellar cores. The UV irradiation is however several orders of magnitude higher compared to most astrophysical regions. This will certainly affect the relative time scales of photodissociation and radical diffusion in the laboratory ice compared to astrophysical settings; hence the need of extracting underlying physical quantities from the experiments rather than applying laboratory ice product compositions and formation rates directly to the chemistry around protostars. Another major difference is the choice of substrate. Gold is inert and should thus not affect the chemistry observed in the lab, but additional effects of silicate grains on the chemistry in space can at this point not be excluded. In most regimes of interest the ice bulk or ice surface chemistry will dominate over the silicate grain surface chemistry, however, and then the difference between chemical path ways on the laboratory surface and astrophysical grains should be minimal.

1.5 This thesis

The first ices that form in dark clouds may be simple, but their evolution is complex. During star- and planet formation the original ices are exposed to atom-, UV- and ion-bombardment, and to heat, which interact to produce large organic molecules. The same bombardments and heat also evaporate ices into the gas-phase, further complicating the gas-grain interactions.

Though complex, these ice processes can be quantified through a combination of ice and gas observations, and laboratory spectroscopy and simulations. Chapters 2–3 set the stage for the thesis by presenting an inventory of simple ices in low-mass star forming regions and the constraints observations put on simple ice formation. This is used in Chapter 4–6 to experimentally investigate dynamics of astrophysically relevant ice mixtures. Chapter 7–11 continues with laboratory experiments on UV induced desorption and chemistry in pure and mixed ices. Chapter 12 concludes the thesis with a proposed approach to study these ice processes in space when it cannot be done directly through ice spectroscopy. The principal conclusions of this thesis, organized by chapter, are:

The Spitzer c2d ice survey towards low-mass protostars

Based on *Spitzer* data, with complimentary VLT and *ISO* observations, Chapters 2–3 investigate ice compositions and formation in the pre- and proto-stellar stages. The large sample size allows for a more statistical treatment than previously possible, which is fully exploited through variability plots, correlations studies, ice maps and principal component analysis. The results set the stage for the remainder of the thesis, which comprises laboratory experiments on how these first ices are affected by energetic processing.

Chapter 2 Ices towards low- and high-mass protostars form through a range of processes resulting in that ices vary between a factor of two and orders of magnitude between different protostars. All identified variable ices either depend on protostellar heating, e.g. CO and pure CO_2, or the pre-stellar CO freeze-out fractions, which traces the lifetime and density of the cloud core before the onset of collapse to form a protostar. The results suggest that the ice chemistry generally proceed in four steps, starting with hydrogenation of atoms, followed by hydrogenation of molecules, UV and ion processing of pre-existing simple ices and finally ice and radical diffusion due to protostellar heating

Chapter 3 Statistics on the abundance and variance of the smallest organic molecules CH_4 towards a large sample of protostars shows that it is a more common ice constituent than previously assumed. Its strong correlation with H_2O and CO_2 confirms its proposed formation path from hydrogenation of carbon atoms during the early stages of cloud formation.

Spectroscopy and dynamics of ice mixtures

Amorphous ices are disordered and thus difficult to model. Yet, the macroscopic dynamics, revealed by spectroscopy and desorption patterns, can be quantified by combining understanding of bond strengths and diffusion barriers with empirical models on the effects of different environmental parameters. Once quantified, ice spectroscopy and ice dynamics can be used to trace the thermal history, such as the occurrence of transient heating events, in protostars and disks.

Chapter 4 Water ice in $H_2O:CO_2$ ice mixtures has significantly different spectral profiles and band strengths compared to pure ice, which can be understood from the caging of H_2O molecules by CO_2, preventing resonance vibrations between hydrogen-bonded H_2O molecules. This must be taken into account both to correctly identify minor ice species with overlapping absorption bands with H_2O and to derive accurate column densities of water ice in space.

Chapter 5 Segregation of ices proceeds through fast surface diffusion, followed by slower bulk segregation in both $H_2O:CO_2$ and $H_2O:CO$ ices. This is reproduced in simulations where molecules diffuse through surface hopping and surface and bulk swapping. Ice segregation in thin ices can be characterized quantitatively, dependent only on the mixture composition and the relative binding energies of the involved

21

molecules. For H_2O:CO_2, surface segregation becomes important already at 30 K during protostellar collapse.

Chapter 6 Desorption from mixed ices depends on ice thickness, mixture ratios, heating rates and mixture constituents. Despite these numerous dependencies, the main attributes of desorption from mixed ices can be modeled with surprisingly few free parameters, when using a three-phase model where the ice bulk and ice surface are treated separately. The simplicity of the model allows for its use in large astrochemical networks and thus using observations of thermal desorption as an efficient probe during star formation.

UV induced desorption and chemistry in ices

UV photons are always present due to cosmic-ray induced radiation fields. Hence, photoprocesses are possible and potentially important at all stages of star formation and UV interactions with ice mantles have been proposed to explain excess gas in cold regions through photodesorption as well as the presence of complex molecules towards protostars through ice photochemistry.

Chapter 7 UV photodesorption of CO is orders of magnitude more efficient than previously assumed, but it is only possible from the surface layers of ices. CO has no dissociative transitions within the UV lamp spectral range and the photodesorption must thus occur through non-dissociative excitation followed by desorption. Pure N_2 ice, which does not have an allowed electronic transition in the UV lamp spectral range, has a much lower desorption efficiency. The high CO photodesorption yield per incident UV photon means that photodesorption may be the major link between the gas and the grain in quiescent regions.

Chapter 8 UV photodesorption of N_2 and CO_2 is also possible but through different mechanisms compared to CO: co-desorption following excitation of a neighboring molecule and desorption following photodissociation, respectively. The different mechanisms are apparent in the opposite ice thickness and temperature dependences of CO and CO_2. Despite the different mechanisms both CO and CO_2 have photodesorption yields of $\sim 10^{-3}$, while N_2 co-desorption is an order of magnitude less efficient.

Chapter 9 UV photodesorption of H_2O ice is confirmed to be efficient ($1 - 4 \times 10^{-3}$ per incident UV photon), with an increasing efficiency with temperature for thick ices, similarly to CO_2; at higher temperatures the ice is more mobile and thus desorption is possible from deeper within the ice. The high yield especially affects the chemistry in regions with excess UV photons such as protoplanetary disks, where photodesorption will maintain molecules in the gas phase significantly further towards the mid-plane, compared to thermal desorption.

Chapter 10 UV photons drive a rich chemistry in ices, which has for the first time been quantified for CH_3OH dominated ices. The detected photoproducts reproduce

the gas phase compositions around low-mass protostars and in comets, strengthening the theory that both have a protostellar ice origin. The large amounts of HCOOCH$_3$ and other CHO-bearing molecules towards some protostellar regions are explained by the experiments as originating from photochemistry of CH$_3$OH in CO-rich ices, while pure CH$_3$OH photochemistry produces more CH$_3$CH$_2$OH and related species. The quantified results are used to derived CH$_3$OH photodissociation branching ratios for the first time in either gas or ice, while absolute diffusion barriers requires more detailed modeling. The experiments predict certain molecules to co-vary and other ratios to depend on the local environment, which should provide observational tests on the importance of this formation pathway for observed complex molecules in astrophysical environments.

Chapter 11 The photochemistry of NH$_3$-containing ices provides a pathway to forming amino acids and other prebiotically interesting molecules during star formation. The study confirms that amino acids and amino acid-like molecules form during photolysis of ices with CH$_4$, NH$_3$ and CO$_2$, including ice mixtures that are more representative of astrophysical situations that previous experiments. It is however the quantification of the simpler chemistry in binary mixtures with H$_2$O, CO$_2$, NH$_3$ and CH$_4$ that provides data from which diffusion barriers and branching ratios can be derived. Their analysis reveals that while diffusion is fast at 20 K in H$_2$O-poor mixtures and the relative production of radicals governs the chemistry, in H$_2$O-rich mixtures the relative diffusion barriers of radicals instead decides the chemical evolution. This once again demonstrates the importance of constraining the underlying physics of ice processes rather than directly extrapolating results from the laboratory to the inter- and circum-stellar medium.

Observations of non-thermal ice desorption

Ices can only be observed in specific lines of sight because of the background light source requirement. In addition more complex ices cannot be observed directly by infrared spectroscopy because of overlapping features with simpler, more abundant ice species. Thus there is a need for complimentary methods to study the ice evolution.

Chapter 12 Photodesorption and other non-thermal desorption pathways provide means to observe ice compositions indirectly where direct ice spectroscopy is not feasible. This is tested in a pilot study of quiescent gas and ice towards a small sample of low-mass protostars. The observations are consistent with a representative fraction of the ice being constantly maintained in the gas phase due to non-thermal desorption. This opens up a door to studying the complex chemistry investigated in the previous chapters as it happens in the protostellar envelope and not just the evaporating end product.

23

1.6 Summary of main discoveries

Taken together, the results described in Section 1.5 can be summarized as follows.

1. Simple ices – from H_2O and CH_4 to CH_3OH – form sequentially during the dark cloud, cloud core and prestellar stages because of hydrogenation of atoms, direct freeze-out, hydrogenation of CO, O and N additions to CO and finally ice diffusion close to the protostar. The later an ice forms in this sequence, the more its abundance tends to vary between different sources. (Chapters 2, 3)

2. Thermal ice processes, such as segregation and desorption, depend on ice composition, mixture ratios, ice thicknesses and ice temperature. The dependences can be quantified and extrapolated to astrophysical conditions only by combining comprehensive sets of experiments with microscopic modeling, as illustrated by two test cases on desorption from, and segregation in, $H_2O:CO_2/CO$ ice mixtures. (Chapters 5, 6)

3. Photodesorption of pure ices is found to be much more efficient than previously assumed and photodesorption alone may be sufficient to explain puzzling observations of cold gas at the edges of clouds, in cloud cores and in protoplanetary disks. Furthermore, the photodesorption yield is constant, within a factor of three, for all common ice constituents, except for N_2 (Chapters 7–11). This suggests that photodesorption of ices results in an ice 'fingerprint' in the gas phase, which is found to be consistent with a proof-of-principle study on ice and gas phase abundances towards a few cold protostellar envelopes (Chapter 12).

4. Ice photochemistry efficiently converts simple ices into more complex species, which can explain the observed abundances of complex molecules around protostars and in comets and explain the chemical differences between different sources. The results were acquired through *in situ* quantification of photochemistry, which provides an unprecedented understanding of complex ice chemistry at the level of elementary processes, sufficiently detailed to model complex ice chemistry during star formation and to predict the formation of yet undetected, larger complex molecules. (Chapters 10, 11)

References

Acharyya, K., Fuchs, G. W., Fraser, H. J., van Dishoeck, E. F., & Linnartz, H. 2007, A&A, 466, 1005

Aikawa, Y., Wakelam, V., Garrod, R. T., & Herbst, E. 2008, ApJ, 674, 984

Allamandola, L. J., Sandford, S. A., & Valero, G. J. 1988, Icarus, 76, 225

Bachiller, R. 1996, ARA&A, 34, 111

Baratta, G. A., Spinella, F., Leto, G., Strazzulla, G., & Foti, G. 1991, A&A, 252, 421

Belloche, A., Garrod, R. T., Müller, H. S. P., et al. 2009, A&A, 499, 215

Bennett, C. J., Chen, S.-H., Sun, B.-J., Chang, A. H. H., & Kaiser, R. I. 2007, ApJ, 660, 1588

Bergin, E. A., Melnick, G. J., Gerakines, P. A., Neufeld, D. A., & Whittet, D. C. B. 2005, ApJ, 627, L33

Bertoldi, F., Carilli, C. L., Cox, P., et al. 2003, A&A, 406, L55

Bisschop, S. E., Fraser, H. J., Öberg, K. I., van Dishoeck, E. F., & Schlemmer, S. 2006, A&A, 449, 1297

Bisschop, S. E., Fuchs, G. W., van Dishoeck, E. F., & Linnartz, H. 2007, A&A, 474, 1061

Blake, G. A., Sandell, G., van Dishoeck, E. F., et al. 1995, ApJ, 441, 689

Bockelée-Morvan, D., Lis, D. C., Wink, J. E., et al. 2000, A&A, 353, 1101

Boogert, A. C. A., Pontoppidan, K. M., Knez, C., et al. 2008, ApJ, 678, 985

Boogert, A. C. A., Pontoppidan, K. M., Lahuis, F., et al. 2004, ApJS, 154, 359

Brown, P. D., Charnley, S. B., & Millar, T. J. 1988, MNRAS, 231, 409

Charnley, S. B. 2004, Advances in Space Research, 33, 23

Chiang, E. I. & Goldreich, P. 1997, ApJ, 490, 368

Collings, M. P., Anderson, M. A., Chen, R., et al. 2004, MNRAS, 354, 1133

Collings, M. P., Dever, J. W., Fraser, H. J., & McCoustra, M. R. S. 2003, Ap&SS, 285, 633

Dalgarno, A. 2006, Faraday Discussions, 133, 9

Dudley, C. C., Imanishi, M., & Maloney, P. R. 2008, ApJ, 686, 251

Dullemond, C. P. & Dominik, C. 2005, A&A, 434, 971

Eddington, A. S. 1937, The Observatory, 60, 99

Fraser, H. J., Collings, M. P., McCoustra, M. R. S., & Williams, D. A. 2001, MNRAS, 327, 1165

Fuchs, G. W., Acharyya, K., Bisschop, S. E., et al. 2006, Faraday Discussions, 133, 331

Galli, D. & Palla, F. 1998, A&A, 335, 403

Garrod, R. T. & Herbst, E. 2006, A&A, 457, 927

Garrod, R. T., Park, I. H., P., C., & Herbst, E. 2006, Faraday Discussions, 133, 51

Garrod, R. T., Wakelam, V., & Herbst, E. 2007, A&A, 467, 1103

Garrod, R. T., Weaver, S. L. W., & Herbst, E. 2008, ApJ, 682, 283

Gerakines, P. A., Schutte, W. A., Greenberg, J. M., & van Dishoeck, E. F. 1995, A&A, 296, 810

Gibb, E. L., Whittet, D. C. B., Boogert, A. C. A., & Tielens, A. G. G. M. 2004, ApJS, 151, 35

Gillett, F. C. & Forrest, W. J. 1973, ApJ, 179, 483

Hagen, W., Allamandola, L. J., & Greenberg, J. M. 1979, Ap&SS, 65, 215

Hagen, W., Allamandola, L. J., & Greenberg, J. M. 1980, A&A, 86, L3

Hartmann, J. 1904, ApJ, 19, 268

Hiraoka, K., Miyagoshi, T., Takayama, T., Yamamoto, K., & Kihara, Y. 1998, ApJ, 498, 710

Hollenbach, D., Kaufman, M. J., Bergin, E. A., & Melnick, G. J. 2009, ApJ, 690, 1497

Hudson, R. L. & Moore, M. H. 2000, Icarus, 145, 661

Ioppolo, S., Cuppen, H. M., Romanzin, C., van Dishoeck, E. F., & Linnartz, H. 2008, ApJ, 686, 1474

Johansen, A., Oishi, J. S., Low, M.-M. M., et al. 2007, Nature, 448, 1022

Jørgensen, J. K., Bourke, T. L., Myers, P. C., et al. 2005, ApJ, 632, 973

Knez, C., Boogert, A. C. A., Pontoppidan, K. M., et al. 2005, ApJ, 635, L145

Lepp, S., Stancil, P. C., & Dalgarno, A. 2002, Journal of Physics B Atomic Molecular Physics, 35, 57

Leto, G. & Baratta, G. A. 2003, A&A, 397, 7

Lewis, E. P. 1895, ApJ, 2, 1

Mate, B., Galvez, O., Martin-Llorente, B., et al. 2008, J. Phys. Chem. A, 112, 457

Melnick, G. J. & Bergin, E. A. 2005, Advances in Space Research, 36, 1027

Merrill, K. M., Russell, R. W., & Soifer, B. T. 1976, ApJ, 207, 763

Molinari, S., Ceccarelli, C., White, G. J., et al. 1999, ApJ, 521, L71

Muñoz Caro, G. M. & Schutte, W. A. 2003, A&A, 412, 121

Öberg, K. I., van Broekhuizen, F., Fraser, H. J., et al. 2005, ApJL, 621, L33

Pontoppidan, K. M. 2006, A&A, 453, L47

Pontoppidan, K. M., Boogert, A. C. A., Fraser, H. J., et al. 2008, ApJ, 678, 1005

Pontoppidan, K. M., Dullemond, C. P., van Dishoeck, E. F., et al. 2005, ApJ, 622, 463

Requena-Torres, M. A., Martín-Pintado, J., Martín, S., & Morris, M. R. 2008, ApJ, 672, 352

Ruffle, D. P. & Herbst, E. 2001, MNRAS, 322, 770

Sandford, S. A. & Allamandola, L. J. 1988, Icarus, 76, 201

Seager, S., Sasselov, D. D., & Scott, D. 2000, ApJS, 128, 407

Shen, C. J., Greenberg, J. M., Schutte, W. A., & van Dishoeck, E. F. 2004, A&A, 415, 203

Snow, T. P. & McCall, B. J. 2006, ARA&A, 44, 367

Sonnentrucker, P., Neufeld, D. A., Gerakines, P. A., et al. 2008, ApJ, 672, 361

Stief, L. J., Decarlo, V. J., & Hillman, J. J. 1965, Canadian Journal of Chemistry, 43, 2490

Swings, P. & Rosenfeld, L. 1937, ApJ, 86, 483

Tanvir, N. R., Fox, D. B., Levan, A. J., et al. 2009, ArXiv e-prints

Tielens, A. G. G. M. & Charnley, S. B. 1997, Origins of Life and Evolution of the Bio-

sphere, 27, 23

Tielens, A. G. G. M. & Hagen, W. 1982, A&A, 114, 245

van Broekhuizen, F. A. 2005, PhD thesis, Leiden Observatory, Leiden University, P.O. Box 9513, 2300 RA Leiden, The Netherlands

van de Hulst, H. C. 1946, Recherches Astronomiques de l'Observatoire d'Utrecht, 11, 2

van Dishoeck, E. F. & Blake, G. A. 1998, ARA&A, 36, 317

Vázquez-Semadeni, E., Ballesteros-Paredes, J., & Klessen, R. S. 2003, ApJ, 585, L131

Watanabe, N., Shiraki, T., & Kouchi, A. 2003, ApJ, 588, L121

Westley, M. S., Baragiola, R. A., Johnson, R. E., & Baratta, G. A. 1995, Nature, 373, 405

Whittet, D. C. B. 1992, Dust in the galactic environment