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Physics and chemistry of interstellar ice

Guss, K.M.R.

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Author: Guss (née Isokoski), Karoliina Marja-Riita

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Chapter I

INTRODUCTION

The importance of ice in the interstellar medium (ISM) is indisputable. Gas phase reactions relying on three-body collisions are exceedingly rare in the sparse medium between the stars. On solid surfaces, atoms and molecules can reside and rove the surface until a reaction takes place. Upon reaction, the released energy is dissipated into the grain, allowing the new species to form. Solid surfaces thus act as sites for chemical processes, that would otherwise be very slow, or not take place at all.

Interstellar processes influence the structure, composition and evaporation of ices. Astronomical observations of ices and gas evaporated from them, are direct probes of the physical conditions in the interstellar medium. Ices can therefore trace the evolution of material and shed light on essential processes, such as the formation of solar systems like our own.

Owing to the strong hydrogen bonding in interstellar ices, sticking of small icy dust grains may be enhanced. Porous ice structures dissipate collision energy and hence facilitate the aggregation at high velocities. This can promote coagulation and the formation of larger solar system bodies and planetesimals.

Interstellar ices are important repositories of complex organic molecules and have a potential prebiotic bearing on the origin of life. Icy comets may have delivered volatiles and organic material relevant for the origin of life on the early Earth. Also water in our oceans may derive from this reservoir. With the growing number of detected exoplanets, this may be universally important.

Hence, the composition and physical structure of interstellar ice are of fundamental importance to our understanding of the formation of stars, planets and the origin of life. This thesis is devoted to the understanding of the physical and chemical properties of interstellar ice using a range of observational and experimental techniques.

1.1 Formation and evolution of interstellar ice

No discussion of interstellar ices would be meaningful without an understanding of the environment in which they are formed: dense molecular clouds. The interstellar medium – material between stars in the galaxy – is an inhomogenous distribution of gas (99 mass %) and dust (1 mass %). The most dense regions of the ISM are the protostellar cores, where the density is high enough to lead to a gravitational collapse resulting in the birth of new stars and planets (Shu et al. 1987, McKee & Ostriker 2007). The collapsing regions are fed from a larger molecular cloud, the density of which is high enough (10^3 – 10^5 cm⁻³) to provide shielding from the harsh external UV field. It is under these conditions that interstellar ices form on cold dust grains. At average molecular cloud densities of 10^4 cm⁻³ atoms and molecules land on the surface of a sub-micron sized dust grain in average once per day (e.g., Tielens & Allamandola 1987). The low temperatures allow particles to accrete, rove the surface and form new molecules. Sheltered from the strong UV field, molecules are able to accumulate on the grain to form a mantle of interstellar ice (Fig. 1.1).

The composition of interstellar ice is determined by the physical conditions in the ambient gas. Most carbon arrives on the dust grain in the form of carbon monoxide (CO). Hydrogen (H), nitrogen (N) and oxygen (O) may be in atomic or molecular form. Even at

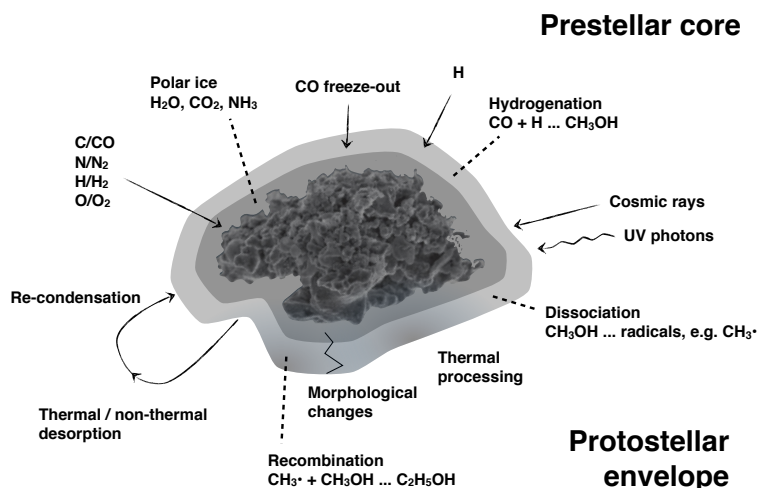


Figure 1.1 – Processes in interstellar ices.

the low temperatures of the cloud ~ 10 K, atoms are able to scan the grain surface and find other atoms and molecules to react with. Hydrogen atoms do so by quantum tunneling (Manicò et al. 2001), while heavier atoms such as C and O through thermal hopping (Tielens & Allamandola 1987). The resulting ice layer is a result of simple atom addition reactions. The molecular composition of these pristine interstellar ices is expected to be dominated by water (H_2O), with significant amounts of H_2CO , N_2 , CO_2 , H_2O_2 , NH_3 , and CO (Tielens & Hagen 1982).

A number of interstellar ice surveys have been carried out (Gibb et al. 2000, 2004, Knez et al. 2005, Boogert et al. 2008, Pontoppidan et al. 2008, Öberg et al. 2011a, Bottinelli et al. 2010). Fig. 1.2 shows the ice composition towards a dust-embedded high mass young stellar object (YSO) W33A obtained with *Infrared Space Observatory* (ISO) (Gibb et al. 2000). This typical spectrum of interstellar ice shows silicate features from the dust as well as small molecules frozen as interstellar ice. Ices are dominated by water (H_2O), with significant amounts of CO, CO_2 and CH_3OH , as well as smaller abundances of NH_3 , CH_4 , H_2CO , HCOOH , OCS and several ionic species (van Dishoeck 2004). Methanol (CH_3OH) is one of the more common ice components with abundances varying from 2 to 15 % relative to H_2O (Bottinelli et al. 2010, Boogert et al. 2008). CH_3OH forms on the cold dust grains through successive hydrogenation of CO (Tielens & Hagen 1982, Tielens & Allamandola 1987, Hiraoka et al. 2002, Watanabe & Kouchi 2002, Fuchs et al. 2009) and is considered an important intermediate in the production of complex organic molecules in the star-forming regions (Charnley 1997, Garrod & Herbst 2006, Garrod et al. 2008, Öberg et al. 2009b).

Ice mantles covering the interstellar dust are inhomogeneous in their composition. Species with relatively low volatility accumulate more readily on the grain surface than

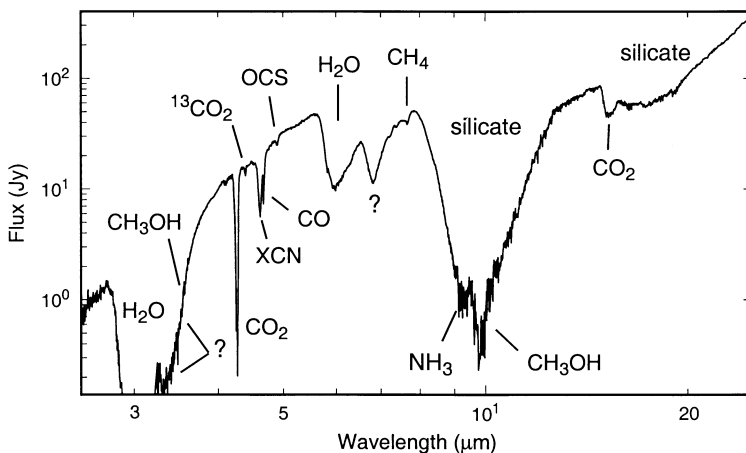


Figure 1.2 – 2.4–25 μm SWS flux spectrum of W33A from [Gibb et al. \(2000\)](#).

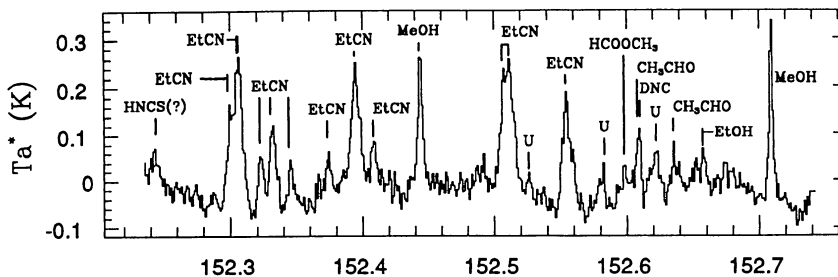


Figure 1.3 – Spectrum of Orion-KL from [Ziurys & McGonagle \(1993\)](#).

those with high volatility. As the cloud collapses and the density and shielding gradually increase, the dust will first acquire a polar layer dominated by H_2O , followed by CO freeze-out into a separate apolar layer ([Bergin et al. 2005](#), [Knez et al. 2005](#), [Pontoppidan 2006](#)). Furthermore, temperature changes in the cloud can cause distillation and segregation of mixed ice components ([Öberg et al. 2009a](#), [Fayolle et al. 2011](#)). As the majority of the CO_2 forms simultaneously with H_2O on the grain ([Bergin et al. 2005](#)), this process is considered responsible for the presence of pure CO_2 in interstellar ices ([Gerakines et al. 1999](#), [Pontoppidan et al. 2008](#), [Kim et al. 2012](#)). Various mechanisms are suggested to return ice molecules into the gas phase, including grain heating by cosmic rays, mantle explosions, ejection upon chemical reaction, sputtering through low-velocity shock waves and grain-grain collisions ([Willacy et al. 1998](#), [Bergin et al. 1998](#), [Charnley et al. 2001](#), [Markwick et al. 2000](#), [Dickens et al. 2001](#)).

While the majority of the features observed in ices (Fig. 1.2) can be explained by non-

energetic surface reactions, there is evidence that interstellar ices are subject to energetic processing. One of such is the XCN feature around $4.62 \mu\text{m}$ (Gibb et al. 2000), which is attributed to OCN^- formed by UV photolysis, ion bombardment and/or thermal reactions (e.g., Grim & Greenberg 1987, Bernstein et al. 1995, Schutte & Greenberg 1997, Demyk et al. 1998, Bernstein et al. 2000, Palumbo et al. 2000). Indeed, interstellar ices are not shielded from cosmic rays which can penetrate deep into the cloud. In addition to direct interaction with the ice, cosmic rays generate an internal UV field in the cloud through secondary electron excitation of H_2 (Prasad & Tarafdar 1983, Gredel et al. 1989). The resulting flux of $10^3 \text{ photons cm}^{-2} \text{ s}^{-1}$, while much smaller than in the unshielded regions outside of the cloud, is strong enough to drive photochemistry in the ice. Both UV photons and cosmic rays break bonds in ice molecules producing highly reactive radicals. The radicals may directly recombine to reform the parent species or be left with enough energy to relocate and react with another molecule. Radicals can also become trapped in the ice, immobilized until further changes in the ice conditions.

In the early phase of cloud collapse, atoms and molecules radiatively cool the cloud (Bergin & Tafalla 2007). As the cloud opacity increases with density, energy can no longer escape, which inevitably leads to heating of the ices in the surrounding envelope. One of the consequences of increasing temperature for ices is the mobilization of larger species in the ice, and consequent recombination of radicals into larger, complex organic molecules (Garrod et al. 2008). It is difficult to find observational evidence for molecular complexation in interstellar ices (Schutte et al. 1999, Gibb et al. 2004). Fundamental vibrational transitions of ice species are located in a relatively narrow spectral window. Line broadening caused by the solid environment leads to overlapping features, that are dominated by the most abundant ice components. The abundance of species decreases with complexity, making IR spectroscopy of ices a futile method to study complex molecules in the interstellar medium.

Large number of complex molecules are observed in the gas phase around high- and low-mass protostars (Herbst & van Dishoeck 2009) (Fig. 1.3). The temperature in these regions has increased beyond 100 K, leading to the evaporation of ices. The origin of these complex molecules was initially thought to be the rich gas phase chemistry of evaporated species (e.g., Herbst et al. 1977, Millar et al. 1991, Charnley et al. 1992, 1995). However, recent experimental work shows the inefficiency of gas phase reactions (Horn et al. 2004, Geppert et al. 2006) and that according to models many of the observed molecules must be primarily produced in ices prior to evaporation (Garrod & Herbst 2006, Garrod et al. 2008, Wakelam et al. 2010).

1.2 Complex molecules in the laboratory

A large portion of experimental astrochemistry is dedicated to the simulation of interstellar ices in the laboratory. These interstellar ice analogs are grown and processed under space-like conditions; high- or ultra-high vacuum (10^8 – $10^5 \text{ particles cm}^{-3}$) and low temperatures (10–300 K). Under controlled laboratory settings, astronomical processes can be isolated and characterized, and their astronomical relevance assessed, e.g., though as-

trochemical models.

Energetic processing of simple interstellar ice analogs drives the formation of complex molecules in the ice (*e.g.*, Hagen et al. 1979, Allamandola et al. 1988, Schutte et al. 1993b, Bernstein et al. 1995, 2002, Muñoz Caro et al. 2002, Muñoz Caro & Schutte 2003, Bennett & Kaiser 2007, Elsila et al. 2007). The products depend primarily on the available reactants and the ice temperature. In UV irradiated pure CH₃OH ice, the photo-fragments: CH₃, CH₂OH, HCO and CH₃O, recombine to produce complex organic species such as C₂H₅OH, HCOOCH₃ and CH₃OCH₃ (Gerakines et al. 1996, Öberg et al. 2009b), all of which have been observed in the ISM. In general the production of complex molecules sets off at elevated temperatures (≥ 50 K) as the radical fragments become mobile. While CH₃OH is able to provide the fragments for many of the observed gas phase molecules, the presence of NH₃ opens new reaction pathways to nitrogen containing, biologically interesting molecules. NH₃ catalyzes the thermal polymerization of H₂CO to polyoxymethylene (POM) $-(CH_2-O)_n-$ (Schutte et al. 1993b,a, Bernstein et al. 1995). In mixed ices, the hydrogen atoms tend to be replaced by active functional groups $-OH$ and $-NH_2$. In UV photoprocessed interstellar ice analogs, a large portion of NH₃ is converted into a cyclic hexamethylenetetramine (HMT) – a precursor of amino acids (Bernstein et al. 1995).

Correlation of results obtained from interstellar ice analogs with ices in the interstellar medium requires critical evaluation of the applicability of those results. One of the main concerns for the solid state production of complex molecules is the reliability of the analysis techniques; are the produced molecules formed under interstellar conditions or during the sample analysis? In order to avoid the latter, non-intrusiveness of the analysis methods is important. IR spectroscopy reveals the composition of ice remotely through excitation of vibrational modes of the molecules. As is the case for astronomical ice observations, the main problem for H₂O dominated interstellar ices is the large width of the solid state absorption features, caused by the broad energy range of the trapping sites. Line widths of trapped species that do not participate in the hydrogen bonding network, such as CO (ν_3) stretch ($4.6 \mu\text{m}$), are around 10 cm^{-1} compared to the 2.2 cm^{-1} in pure form (Bouwman et al. 2007). IR spectra of complex organic species are characterized by their functional groups (*e.g.*, ketones C=O) which coincide for different molecules belonging to the same group. Due to these factors, the applicability of IR spectroscopy is limited to relatively simple ices.

Mass spectrometry is a sensitive technique in which molecules are transported from the ice to the sensor where the identification is based on their mass. Mass spectrometry requires relocation of the sample, which poses a challenge to maintain the chemical composition during sample analysis. Relocation of volatile ice components is currently done by slowly warming the ice until species evaporate. This temperature-programmed desorption (TPD) provides an inventory of molecules produced in the ice, but is blind to the low temperature chemistry and the transient species in the ice. For the understanding of complex ice chemistry, the large involatile species are of particular interest. UV photoprocessed interstellar ice analogs leave behind a significant residue at room temperature. The chromatographic analysis of the material reveals the presence of a number of complex species including amino-acids (Fig. 1.4). Again, only a final inventory can be obtained.

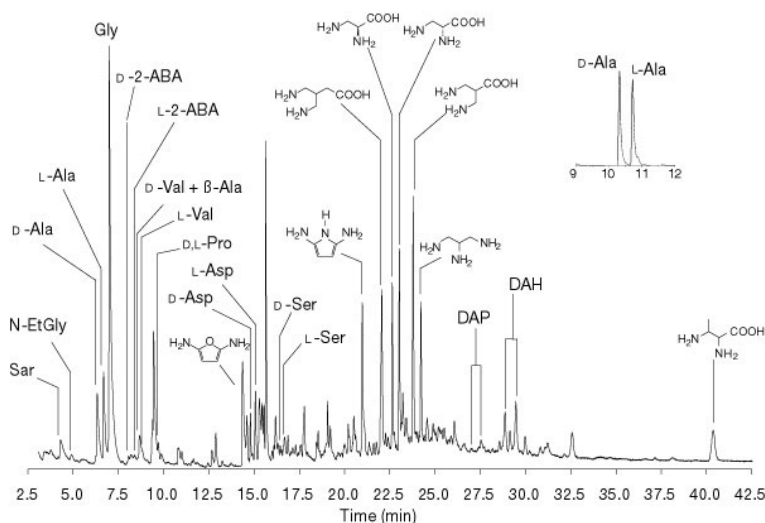


Figure 1.4 – Gas chromatography mass spectrum (GC-MS) of a room-temperature residue of UV photoprocessed interstellar ice analogue from [Muñoz Caro et al. \(2002\)](#).

Moreover, the analysis requires chemical alteration which may generate molecules, that are not present in the ices prior to analysis. For the characterization of the processes and evaluation of their importance in an astronomical environment, the experimental challenges described above remain to be dealt with.

1.3 Morphology of interstellar ice

H_2O dominates the composition of interstellar ice (*e.g.*, [Whittet et al. 1998](#), [Gibb et al. 2004](#), [Pontoppidan et al. 2004](#), [Boogert et al. 2008](#)). In the gas phase H_2O has abundances varying from 10^{-8} (with respect to H_2) in cold dense regions where most of it resides in ices on interstellar dust grains, to 10^{-4} in warm gas and shocked regions where it evaporates or is sputtered from the ice ([van Dishoeck & Helmich 1996](#), [Melnick & Bergin 2005](#), [Bjerkeli et al. 2009](#)). Gas-phase chemistry cannot reproduce the H_2O abundances observed in the interstellar medium ([d’Hendecourt et al. 1985](#), [Hasegawa et al. 1992](#)). Formation of H_2O through several different grain-surface routes was suggested by [Tielens & Hagen \(1982\)](#), and in recent years has been subject to a number of studies, both theoretical ([Cuppen & Herbst 2007](#), [Goumans et al. 2009](#), [Cazaux et al. 2010](#)) and experimental ([Miyachi et al. 2008](#), [Ioppolo et al. 2008](#), [Matar et al. 2008](#), [Oba et al. 2009](#), [Mokrane et al. 2009](#), [Ioppolo et al. 2010](#), [Cuppen et al. 2010](#), [Dulieu et al. 2010](#), [Ennis et al. 2011](#), [Romanzin et al. 2011](#), [Jing et al. 2011](#)). While the importance of different routes remains to be confirmed, the origin of H_2O in surface-catalyzed reactions is now recognized.

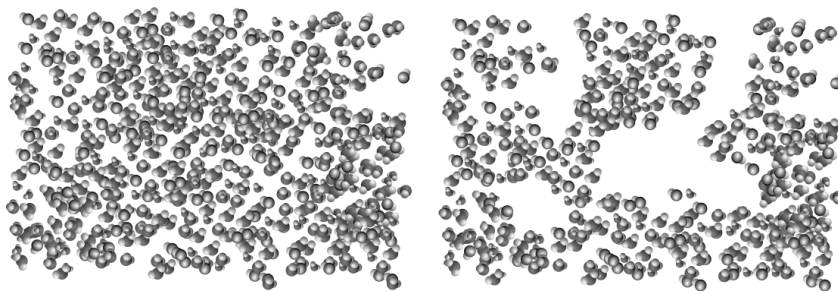


Figure 1.5 – Illustration of compact (left) and porous (right) amorphous solid water.

The morphology of H_2O is dominated by its hydrogen-bonding character. Depending on the pressure and temperature, H_2O can exist in 15 different forms, differentiated by the degree of crystalline structure, ordering and density. In the biosphere, practically all water is in crystalline I_h form, with hexagonal symmetry and near tetrahedral bonding angles. In astronomical environments, most observed H_2O is in amorphous form, deduced from the broad absorption feature around $3.07 \mu\text{m}$, corresponding to the bulk asymmetric OH stretching (ν_3) mode. Amorphous solid water (ASW) exhibits tetrahedral H-bonding network, but lacks long range crystalline order. The unordered structure provides a broad range of trapping sites, making the absorption features broad (Hagen 1981). ASW can be subdivided into three distinct structures, defined by the distance between adjacent O atoms: low-density ASW (I_{lda}) with a density of 0.94 g cm^{-3} (Narten et al. 1976), high-density ASW (I_{hda}) with a density of 1.17 g cm^{-3} (Mishima et al. 1984), and very high-density ASW (I_{vhda}) with a density of 1.26 g cm^{-3} (Mishima 1996, Loerting et al. 2001). The structure of vapor deposited H_2O , relevant for some interstellar ices, depends on the temperature. In the laboratory, deposition onto a surface below 30 K results in I_{hda} , while $\geq 30 \text{ K}$ I_{lda} is produced (Jenniskens et al. 1995). I_{vhda} has not been shown to form through vapor deposition. Upon increase in temperature, I_{hda} restructures to I_{lda} at 38–68 K (Jenniskens & Blake 1994) owing to defects in the ice structure. At 148 K, the ice structure changes into cubic crystalline I_c until its evaporation between 180 and 188 K.

In the interstellar medium, particles land on the dust grain in random trajectories. On the cold $< 130 \text{ K}$ surfaces, where diffusion is limited, larger particles become incorporated in the ice near their landing site. For H_2O , this "hit and stick" film growth results in porous ice structure (Buch 1992, Barabási & Stanley 1995, Cuppen & Herbst 2007). Porous ASW, as opposed to compact ASW (Fig. 1.5) has mm-sized cavities with internal surface area from hundreds to thousands of m^2/g (Mayer & Pletzer 1986, Bar-Nun et al. 1987, Manca 2000, Martin 2002, Ayotte et al. 2001). The porosity of ASW depends on the ice growth conditions such as temperature, growth rate and directionality of H_2O molecules landing on the ice surface (Berland et al. 1995, Westley et al. 1998, Stevenson et al. 1999, Kimmel et al. 2001b,a, Dohnálek et al. 2003). Energetic processing in the ISM is expected to reduce the porosity of ASW. The compaction of porous ASW has been experimentally

demonstrated to be driven by cosmic rays and UV photons (Palumbo 2006, Palumbo et al. 2010, Raut et al. 2008), as well as by thermal processing (Bar-Nun & Owen 1998, Bossa et al. 2012).

In the interstellar medium, porosity can have an important impact on chemical processes relying on surface accessibility. Porous ice provides large effective surface areas for adsorption of atoms and molecules, catalysis of chemical reactions, and further retention of these species. Large quantities of molecules are stored inside pores and later thermally released (Collings et al. 2003, Raut et al. 2007a). Structural changes in interstellar ices (intrinsic phase transitions and reduction of porosity) can have interesting consequences for the chemistry. Pore collapse at low temperatures may drive diffusion limited recombination of radicals trapped in interstellar ices (Schutte 1988, Jenniskens & Blake 1994).

1.4 Composition of interstellar ice

The band profiles of molecules trapped in interstellar ices provide a wealth of information about the ice composition. The lattice environment influences the strength of molecular bonds, and the vibrational frequencies become shifted from the corresponding gas-phase values. The presence of multiple trapping sites manifests itself as an overall broadening of absorption features. The lattice environment is primarily determined by the molecular composition of the ice. The composition of interstellar ice can therefore be inferred from the shape of the observed absorption features. Moreover, certain ice features may be influenced by the shape of the grain. While this complicates the interpretation of the ice composition, it can also be used as an indication of how the ice layer has been formed.

A number of laboratory studies have focussed on the characterization of the band profiles of abundant ice species, particularly that of CO₂ and CO (Sandford et al. 1988, Sandford & Allamandola 1990, Tielens et al. 1991, Palumbo & Strazzulla 1993, Ehrenfreund et al. 1996, 1997, 1998, 1999, van Broekhuizen et al. 2006, Bouwman et al. 2007, White et al. 2009). Observations of these features towards icy sources, and comparison to laboratory spectra, has revealed the presence of CO in multiple solid environments, namely pure CO, CO₂-containing or crystalline CO and CO in polar, possibly H₂O-rich environment (Pontoppidan et al. 2003b). For CO₂, comparison of laboratory spectra with observations imply co-existence with both H₂O-rich and H₂O-poor, as well as in pure form (*e.g.*, Gerakines et al. 1999, Keane et al. 2001, Pontoppidan et al. 2008).

The molecular environment can constrain the chemical correlations between different molecules, as well as the formation processes of the ices. The presence of abundant pure CO component, supports its freeze-out separate from other components, while intimate mixing with CO₂ supports the chemical correlation between the two. For CO₂, the presence of pure component is taken as an evidence for thermal processing, which segregates it from its native H₂O-rich environment (Ehrenfreund et al. 1998, Öberg et al. 2009a, Fayolle et al. 2011). The lattice structure of a particular ice composition changes with ice morphology, and can give further insight into the thermal history of the ice. The absorption features in crystalline (ordered) structure are typically more narrow than those

in amorphous (unordered) structure (*e.g.*, [Hagen 1981](#)).

Porosity of H₂O-dominated ice influences the absorption spectra by *e.g.*, an emergence of an additional features corresponding to interaction with a dangling OH bond of H₂O in the surfaces of the pores ([Tielens et al. 1991](#), [Al-Halabi et al. 2004](#)). The H₂O-rich CO component has not been able to reproduce in the laboratory, and it has been suggested that the discrepancy results from different ice morphologies ([Palumbo 2005](#)).

Interpretation of the astronomical ice features is complicated by not only the simultaneous influence of all above, but also the fact that an observational spectrum along a given line of sight typically contains several ice compositions at different evolutionary stages. Not all band profiles have been assigned to a specific molecule in a specific molecular and morphological environment. Therefore the interpretation of the observed features varying in ice composition and morphology presents a great challenge to experimentalists aiming to reproduce interstellar ices in the laboratory.

1.5 Complex organic molecules

More than 150 different gas phase molecules have been observed in the interstellar medium, mainly through rotational emission spectra ([Woon 2008](#)). Many of them are considered complex molecules having more than 6 carbon atoms and are found in circumstellar envelopes around evolved stars, cold interstellar cores, hot cores and corinos, lukewarm corinos and outflows ([Herbst & van Dishoeck 2009](#)). Millimeter lines from complex organic molecules are widely associated with high-mass star forming regions and indeed form one of the signposts of the deeply embedded phase of star formation (*e.g.*, [Blake et al. 1987](#), [Hatchell et al. 1998](#), [Gibb et al. 2000](#), [Fontani et al. 2007](#), [Requena-Torres et al. 2008](#), [Belloche et al. 2009](#), [Zernickel et al. 2012](#)). The richest molecular source in the galaxy is the hot core Sgr B2 (N), located in the Galactic Center giant cloud Sgr B2 ([Snyder 2006](#)). Among the observed species are acetone (CH₃COCH₃), ethylene glycol [(CH₂OH)₂], glycolaldehyde (HOCH₂CHO).

Most chemical models invoke grain surface chemistry to create different generations of complex organic molecules ([Tielens & Charnley 1997](#)). Hydrogenation of solid O, C, N and CO during the cold (< 20 K) pre-stellar phase leads to ample production of CH₃OH and other hydrogenated species ([Tielens & Hagen 1982](#)). Exposure to UV radiation results in photodissociation of these simple ices, with the fragments becoming mobile as the cloud core heats up during the protostellar phase. First generation complex molecules result from the subsequent recombination of the photofragments, and will eventually evaporate once the grain temperature rises above the ice sublimation temperature of ~100 K ([Garrod & Herbst 2006](#), [Garrod et al. 2008](#)). Recent studies suggest that the production of molecules, such as C₂H₅OH, HCOOCH₃ and CH₃OCH₃, relies on UV irradiation of interstellar ices ([Öberg et al. 2009b](#)). Subsequent to ice evaporation, hot core gas phase chemistry between evaporated molecules can drive further complexity in second generation species (*e.g.*, [Millar et al. 1991](#), [Charnley et al. 1992](#), 1995).

Observation of complex molecules evaporated from interstellar ices can be used to constrain the ice processes prior to evaporation. One of the most widely used method of

analyzing spectra of complex organic molecules is the rotation diagram method (Goldsmith & Langer 1999). The observed intensities from rotational emission lines may be translated to physical parameters, such as temperature and column density. Under local thermodynamic equilibrium (LTE) the rotational states are populated by excitation through molecular collisions, producing a Boltzmann distribution. The temperature of the gas can be derived from the relative intensity of the emission lines from the states with different energy. The column density of the gas is determined from the overall intensity of the emission lines.

1.6 This thesis

This thesis is dedicated to the study of the composition and physical characteristics of ices using a variety of experimental techniques and combined this with the analysis and interpretation of astronomical observations. The overall goal is to shed light on the processes that chemically enrich planet-forming regions. The specific objectives are to characterize morphological changes (Chapters 2 and 3) and molecular composition (Chapters 4 and 5) in interstellar ices, to explore new experimental techniques to study solid state reactions (Chapter 6), and to use complex molecules to probe large scale astronomical phenomena (Chapter 7).

Ice morphology

Chapter 2 and 3 focus on the morphology of interstellar ice. In the interstellar medium ice is expected to form with different morphologies. These chapters deal with thermally induced changes in porous, vapor deposited ice.

In Chapter 2, the thermally induced collapse of porous H₂O ice is studied using thin-film interference – a method conventionally used to monitor ice growth. This chapter shows that the decrease in internal surface area is accompanied by a 12 % decrease in ice thickness. Ice collapses gradually over the entire temperature range between 20 and 120 K.

Chapter 3 extends the work in chapter 2. The accuracy of the thickness measurement is increased by using sample specific optical properties and through instrumental improvements. The intrinsic phase transition from high-density to low-density amorphous H₂O triggers enhanced collapse of the porous structure. The structural collapse is found to be incomplete. The initial ice morphology influences the behavior of the ice until evaporation of the ice. The persistence of cavities may influence the surface chemistry and trapping of species at elevated temperatures. The study is extended to include CO₂, the dominant impurity of interstellar H₂O ice. CO₂ is found to have a profound impact on the H₂O morphology, particularly grown at low temperatures where porosity of the ice dominates the morphology.

Ice spectroscopy

Chapters 4 and 5 deal with the interpretation of astronomical ice observations using laboratory spectra of known composition and temperature.

Chapter 4 focuses on the observed CO ice feature at $4.65 \mu\text{m}$, and in particular on the red component which is characterized as CO in a polar ice environment. As laboratory mixtures of CO and H₂O have not been able to reproduce the observed feature, the possibility of a three-component polar mixture is examined, in which CO₂ blocks the dangling OH bond, responsible for the discrepancy between the observed and laboratory spectrum. It is shown that this scenario is not feasible, and that the observed feature can be solely explained by CO mixed with CH₃OH. The resulting CO line profile is consistent with a wide range of observations. The presented results are consistent with the chemical correlation between CO and CH₃OH (through hydrogenation). It also constrains the formation mechanism of CO₂, which according to this result has no parent in the H₂O matrix.

Chapter 5 focuses on the spectral properties of pure CO₂ ice. The interpretation of the CO₂ (ν_2) bending mode at $15.2 \mu\text{m}$ towards an exceptional young stellar object HOPS-68 requires high-resolution spectra, which are here made available. This CO₂ feature exhibits a particularly prominent fine structure, and cannot be reproduced in the same way as in most other sources. It is shown that the reason for the difference is an high thermal processing of the ices. The heating is manifested as a large amount of pure CO₂, as well as spherical shape of the grains, which results from fast re-condensation of the icy mantle.

Complex organic molecules

Chapter 6 introduces a new experimental technique to study the formation of complex organic molecules in interstellar ices. The experiment employs laser desorption time-of-flight mass spectrometry to increase the sampling sensitivity of interstellar ices while maintaining the conditions relevant to interstellar ices. This chapter demonstrates that laser desorption is a promising technique for vaporization of interstellar ices prior to mass spectroscopic analysis, and shows preliminary results on vacuum UV photo-processed interstellar ices.

Chapter 7 employs complex molecules as probes of massive star formation process, which to date remains poorly understood ([Zinnecker & Yorke 2007](#)). Formation similar to low-mass stars leads to a flattening of the accretion disk and opening of an outflow cavity. These structures have been observed for only few massive YSOs. The presence of an outflow cavity allows more UV light to escape from the central object, and to illuminate the walls of the outflow cavity where ices reside. The goal of this chapter is to compare the relative abundances of complex organic molecules in sources where disks have been observed and with those where this is not the case. It is found that there is no substantial difference in the abundance of complex molecules between the two source types. It is argued that this may be either because all massive stars form in similar geometry. An alternative possibility for the lack of difference is that the additional UV light from the central object is insignificant in the production of complex molecules, and that

their formation is dominated in the quiescent cold phase of the molecular cloud.

1.7 Main conclusions

- Thermal collapse of vapor deposited ice is a significant process which influences the solid-state chemistry in interstellar ices. The large ice surface area provided by porous ice at low temperatures decreases at elevated temperatures. While the mobility of ice components increases at higher temperatures, the available catalytic surface area decreases. Thermal collapse of the solid ice structure at low temperature can trigger chemistry before the mobilization of fragments.
- The initial morphology of the ice determines the ice structure until crystallization and beyond. Cavities remain in the ice throughout the solid phase. This enables trapping of other species until H₂O evaporation.
- IR spectroscopy of the dangling OH bond is not an adequate measure of ice morphology for thermally processed ices. Large cavities remain in the ice when dangling OH bonds have disappeared. The non-detection of the dangling OH bond is therefore not a valid argument for compactness of interstellar H₂O ice.
- The observed CO ice feature can be explained by a combination of three ice compositions: pure CO, CO in CO₂ or crystalline CO and CO in CH₃OH ice. CO:CH₃OH ice solves the mystery of the astronomically missing 2152 cm⁻¹ feature present in the laboratory spectra of CO:H₂O ice. The polar CO component is therefore due to CH₃OH, which supports the chemical link between CO and CH₃OH. The lack of a CO:H₂O component constrains the formation mechanism of CO₂, which has been suggested to form by UV irradiation of CO:H₂O ice.
- The abundance of complex organic molecules in hot cores of massive YSOs does not correlate with the detection of a disk geometry. Either the chemical complexity is already fully established in the ices in the cold pre-stellar phase or the material experiences similar physical conditions and UV exposure through outflow cavities during the short embedded lifetime.

