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Laboratory studies of water ice in space : optical and photochemical properties

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Chapter 1

Introduction

Stars and planets find their origin in the interstellar medium, the highly dilute environment that bridges the space between stars. Astrochemistry studies the chemical processing in the ISM, and this holds the key to understanding the evolutionary track that starts with diffuse and dense interstellar clouds, and results in the formation of protoplanetary disks and planetary systems like our own Solar system. To study these cosmochemical stages, astronomical observations, astrochemical models and laboratory experiments are combined. This thesis focuses on laboratory experiments, performed under fully controlled conditions and simulating the conditions in ISM environments.

Particle densities in the diffuse ISM, with temperatures in the order of 100 K, are exceedingly low, estimated around 100 particles per cm^3 and comprising mostly of atomic species and small molecules, such as di- and tri-atoms. Denser regions in the ISM are dark or molecular clouds, which have much lower temperatures in the order of 15 K and densities up to 10^6 particles per cm^3 . Today more than 200 different molecules have been identified in the interstellar and circumstellar medium (McGuire, 2018) and the molecular composition exhibits a surprising diversity, ranging from H_2 to complex molecules with more than ten atoms, and includes both stable and reactive species. The molecular inventory in dark clouds also includes the so-called complex organic molecules, or COMs (Herbst and van Dishoeck, 2009). A number of these are considered to be of prebiotic relevance and as such play a role in our search for the origin of life (Ehrenfreund et al., 2002). Because of the low particle densities, both in the diffuse and dense ISM, collisions are far too rare for efficient gas-phase chemistry to take place. Exceptions exist, but the majority of the identified molecular abundances in the ISM cannot be explained with gas phase reactions only. Under these exotic conditions, another type of chemistry becomes relevant, based on reactions taking place in cryogenic solid-state

samples. In regions where densities are high enough, ice layers can form on cold (~ 20 K) carbonaceous and silicate nano to micrometer-sized dust particles through accretion (van de Hulst, 1946; Gillett and Forrest, 1973). These dust particles are left over from the previous generation of stars, which may produce these refractory elements when they explode (Tielens, 2013). The ice layers, containing predominantly H_2O , CO , and CO_2 , but also other species like CH_4 , CH_3OH and NH_3 offer a molecular reservoir. Here particles diffuse and can collide and react, with the solid phase acting as a third body absorbing excess reaction energy, facilitating the formation of species far more efficiently than in gas phase reactions. It is generally assumed that the chemical composition of icy dust layers exceeds the 10 to 12 different species identified so far in ices, but although a number of unidentified features are seen, no identification of the species responsible for these absorptions have been found (Boogert et al., 2015). In the laboratory, however, it has been shown that many different species can be formed from ice mixtures representative for the ISM upon ice processing with for instance UV-irradiation, bombardment with electrons or H-atoms and upon cosmic ray impacts or thermal processing. (Öberg et al., 2009a; Fuchs et al., 2009; de Barros et al., 2011; Theulé et al., 2013; van Dishoeck, 2014; Öberg, 2016)

Dark clouds are the regions in the ISM where stars and planets form. When a cloud starts to gravitationally collapse, a protoplanetary disk can form. This protoplanetary disk consists of the gas and dust originating from the molecular cloud material, with a young stellar object (YSO) in the center, that will eventually develop into a star. The material in the protoplanetary disk is what later forms the planets, moons, comets and other celestial bodies. The chemical evolution of the ice-covered particles in the ISM thus plays a role in the chemical enrichment of planets. Moreover, ice layers are relevant in the coagulation efficiency of dust particles (Ormel et al., 2009; Krijt et al., 2016). Different species condensate at different temperatures, and regions where these temperatures occur are referred to as snow lines. The position of these snow lines at specific distances from the YSO are considered essential for the chemical composition of the celestial bodies forming around it. During a later stage, after the planets are formed, they are bombarded by left-over debris – comets, asteroids, interplanetary dust particles – including all the material formed in the ISM, including water and COMs, effectively enriching the surface of planets with building blocks of life (Chyba and Sagan, 1992; Ehrenfreund et al., 2002; Herbst and van Dishoeck, 2009; Herbst, 2014). The chemistry evolves further during the protoplanetary phase, as matter is exposed to heat and radiation from the newly forming star, and the chemistry evolves for another few million years under the relatively dense conditions in the protoplanetary

disk (Visser et al., 2009; Eistrup et al., 2016). Molecules formed on icy grains in dense interstellar clouds thermally desorb (sublimate) and react in the gas phase. Other species may fragment or ionize upon UV irradiation from the light emitted by the star, a process that is strongly depending on the position of the icy dust particles in the disk. Subsequently the species may deposit again, resulting in large scale mixing of water throughout the protoplanetary disk.

The work described in this thesis focuses on radiation-induced chemical processes in inter- and circumstellar ices. Along the ice's journey from a dark cloud to protoplanetary disks and planetary systems, the icy dust grains are continuously exposed to energetic radiation of various kinds. Cosmic rays, energetic particles generated in supernovae, can penetrate deep into the ice and generate a plethora of secondary reactions. During the dark cloud ages, cosmic-rays can induce excitation of hydrogen, resulting in a steady flux of Lyman α (121 nm) and other vacuum ultraviolet (VUV) radiation. Later, in the protoplanetary and planetary phase, ice is exposed to radiation from the host star. The VUV photons can result in photo-desorption, a process well studied in the laboratory astrophysical context (Öberg et al., 2009b; Fayolle et al., 2011; Fayolle et al., 2013; Muñoz Caro et al., 2016; Bertin et al., 2016; Cruz-Diaz et al., 2018). Photons with wavelengths shorter than 250 nm, emitted by young stars, are energetic enough to break most chemical bonds, resulting in photo-dissociation or ionization within the ice, further inducing chemical reactions. In order to study these processes quantitatively on Earth, a special laboratory setup has been used, capable of simulating the physical conditions that the icy dust grains experience in the ISM. Water ice has been investigated as a host for different molecules of interest: polycyclic aromatic hydrocarbons (PAHs), which are estimated to carry approximately 10% of the cosmically available carbon Tielens (2013), and amino acids, fundamental in life as we know it. As water is one of the most abundant molecules in dark clouds, part of the work presented here also focuses on characterizing the optical properties of water ice in space. The results contribute to our understanding of the chemical role of ices in space and may help to interpret and to guide astronomical observations. The work described in this thesis focuses on radiation-induced chemical processes in inter- and circumstellar ices. Along the ice's journey from a dark cloud to protoplanetary disks and planetary systems, the icy dust grains are continuously exposed to energetic radiation of various kinds. Cosmic rays, energetic particles generated in supernovae, can penetrate deep into the ice and generate a plethora of secondary reactions. During the dark cloud ages, cosmic-rays can induce excitation of hydrogen, resulting in a steady flux of Lyman α (121 nm) and other vacuum ultraviolet (VUV) radiation. Later, in the protoplanetary and planetary phase, ice is exposed to radiation from the host

star. The VUV photons can result in photo-desorption, a process well studied in the laboratory astrophysical context (Öberg et al., 2009b; Fayolle et al., 2011; Fayolle et al., 2013; Muñoz Caro et al., 2016; Bertin et al., 2016; Cruz-Diaz et al., 2018). Photons with wavelengths shorter than 250 nm, emitted by young stars, are energetic enough to break most chemical bonds, resulting in photo-dissociation or ionization within the ice, further inducing chemical reactions. In order to study these processes quantitatively on Earth, a special laboratory setup has been used, capable of simulating the physical conditions that the icy dust grains experience in the ISM. Water ice has been investigated as a host for different molecules of interest: polycyclic aromatic hydrocarbons (PAHs), which are estimated to carry approximately 10% of the cosmically available carbon Tielens (2013), and amino acids, fundamental in life as we know it. As water is one of the most abundant molecules in dark clouds, part of the work presented here also focuses on characterizing the optical properties of water ice in space. The results contribute to our understanding of the chemical role of ices in space and may help to interpret and to guide astronomical observations.

In the next sections, the astrochemical environment is discussed in more detail. In section 1.1 an overview is presented of what we know about ice in the ISM. The chemistry in and on the icy dust grain is described in section 1.2. Section 1.3 focuses on water ice in space, its formation, and its physical properties. Then the possible role of frozen PAHs is discussed in section 1.4. The laboratory aspects are discussed in section 1.5. This chapter concludes with summaries of the main results described in Chapters 2 to 5 of this thesis.

1.1 Ice in the interstellar medium

Icy dust grains are found in the dense and dark regions of the ISM known as dark or molecular clouds (Bergin and Tafalla, 2007). These patches in the sky were initially identified as “starless regions” when discovered in the 18th century (Herschel, 1785). Later it was hypothesized that the stars were not absent, but likely obscured in some way (Barnard, 1919; Bok and Reilly, 1947). Dark clouds are opaque when investigated in the optical regime, but in infrared and submillimeter wavelengths, observations showed that dust is blocking the optical view on the interiors of these clouds and that in fact these regions are very dynamic and active formation of stars is taking place here. Figure 1.1 shows a molecular cloud, NGC 6334, also known as the Cat’s Paw nebula, both in the visible/near infrared, where mostly stars are seen, and in the submillimeter, showing emission from cold dust particles. The dark patches in

the top picture appear void of stars, and correspond to the presence of most dust emission in the bottom picture. The contrast between what we see in the UV-vis and what is seen in submillimeter wavelengths is a good example of what one can learn from looking into space at different wavelengths: regions that may be dark in one wavelength range may be very bright and rich in information in other wavelength ranges.

Dark clouds are typically several light years in size. If one would take a cross-section, the density increases and the temperature decreases when going from the edge deeper into the cloud. The depth is often expressed in visual extinction: A_v . Visual extinction is determined from the amount of light absorbed and scattered by the cloud, ideally by looking at a well-characterized standard background star. As dust is found to predominantly attenuate light with shorter wavelengths, one can look at the amount of 'missing' light when comparing the star's spectrum with a black body emission curve. With increasing A_v more volatile species deposit on the cold dust grains, and column densities of ice are found to increase: H₂O ice is found from $A_v > 2$, CO₂ ice is present from $A_v > 3$, and CO ice is seen deeper when $A_v > 8$ (Boogert et al., 2015).

Our knowledge about the internal composition of dark clouds is largely based on observations performed in the infrared between (3 and 16 μm) using telescopes in space, as Earth's atmosphere makes observing the broad ice features from ground-based facilities nearly impossible. Particularly important were the infrared space observatory (ISO) and *Spitzer* space telescope (Gibb et al., 2004; Boogert et al., 2008; Pontoppidan et al., 2008; Öberg et al., 2011). Water is found to be the most abundant species in interstellar ice, and other confirmed species are: CO, CO₂, CH₄, NH₃, and larger species like CH₃OH (Grim et al., 1991; Boogert et al., 2008; Boogert et al., 2015), as well the ions OCN⁻ and NH₄⁺ (van Broekhuizen et al., 2005; Schutte and Khanna, 2003). An overview of the detected ice components is shown in Table 3.1. It is very likely that many more molecules reside as frozen species on dust grains, such as larger COMs formed in ongoing surface reactions (Schutte et al., 1996; Gibb and Whittet, 2002), as well as polycyclic aromatic hydrocarbons (Sellgren et al., 1994; Hardegree-Ullman et al., 2014). For the latter ones, no spectroscopic proof has been found yet, even though dozens of COMs and PAHs embedded in water matrices have been studied in the laboratory (see Schutte et al., 1999; Terwisscha van Scheltinga et al., 2018; Bouwman et al., 2011) or collected in the online databases summarized in Boogert et al. (2015). Figure 1.2 shows a spectrum of ice absorption in the light from an embedded YSO. The spectrum is dominated by water, shown separately at the top, and a number of

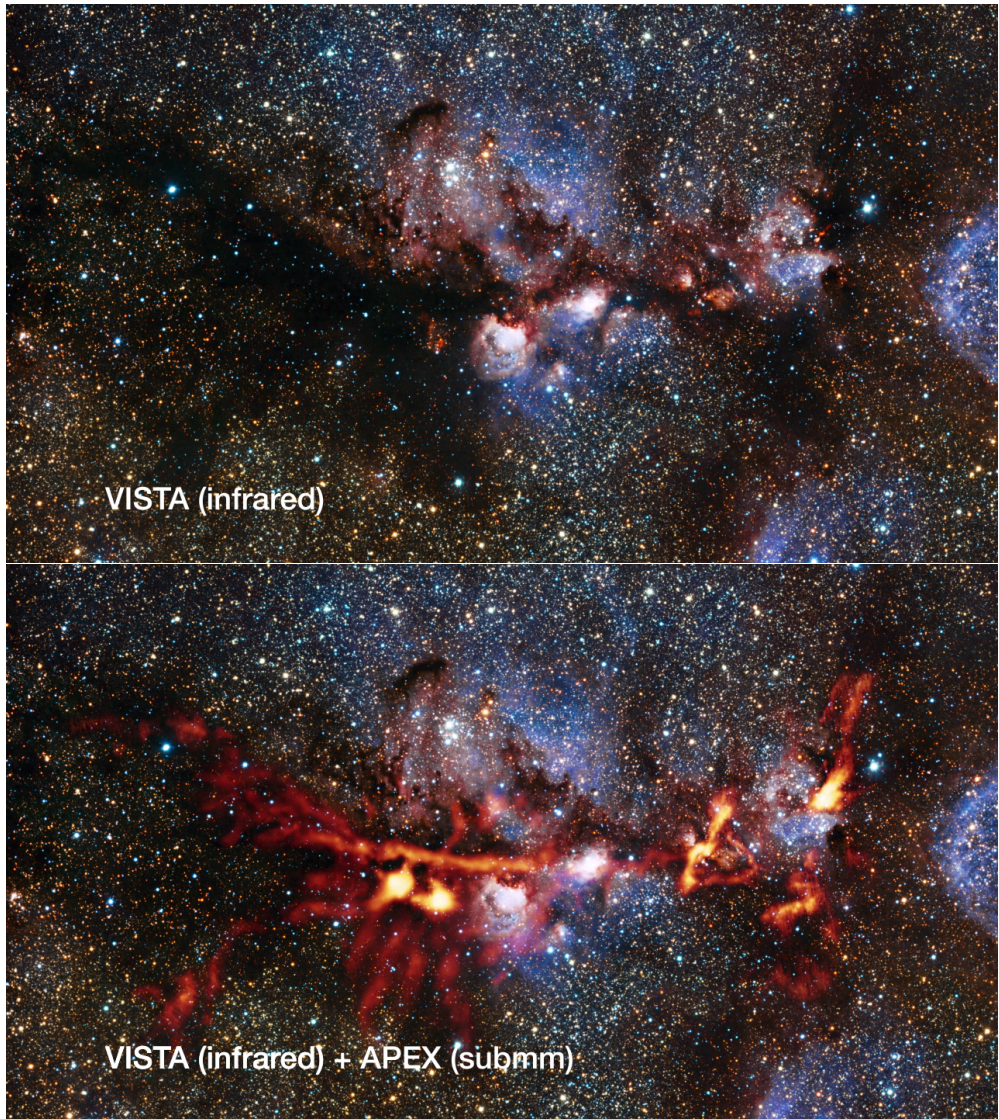


FIGURE 1.1: Two images showing the NGC 6334 molecular cloud at two different wavelength regimes. The top image shows areas where stars appear to be sparse, but in fact, stars are obscured by dust particles, as shown in the bottom panel by the submillimeter emission. These very same dust particles can carry the interstellar ice studied in this thesis. Credits:

ArTeMiS/ESO

other prominent molecules are highlighted. The full list of species detected in interstellar ices is shown in Table 3.1.

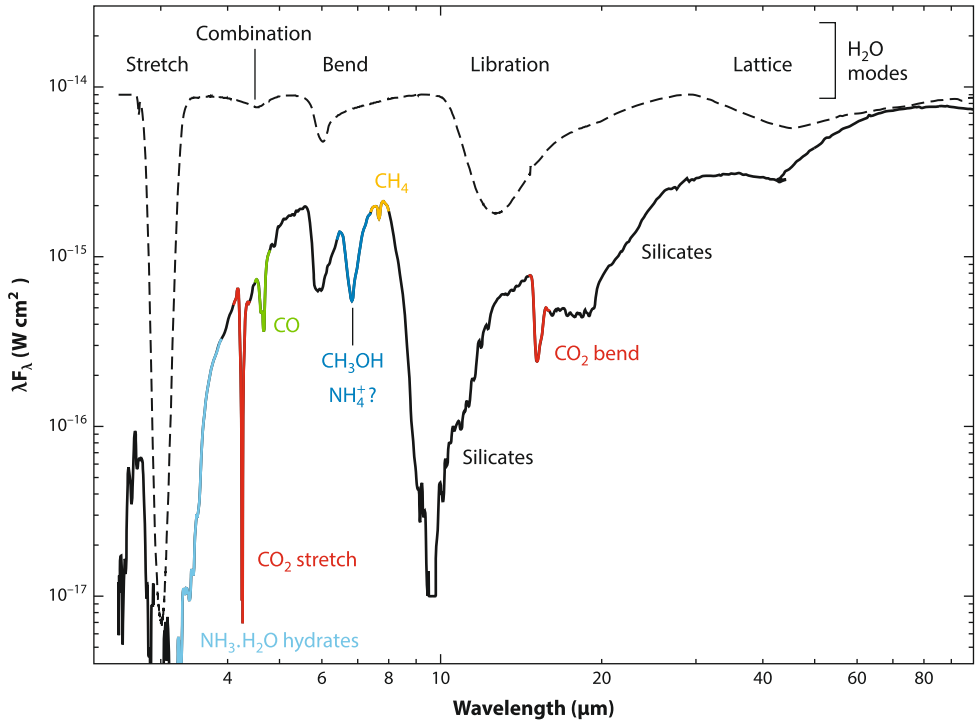


FIGURE 1.2: Infrared spectrum of ice-covered dust grains towards massive young stellar object AFGL 7009 S. Modified from Dartois et al. (1998) and Boogert et al. (2015).

Returning to the ice's journey from the embedded YSO phase; as the YSO continues to evolve, more material falls into the center, the YSO growing more massive, and increasing in temperature and pressure until fusion conditions are met (e.g. see the classification by Lada and Wilking, 1984 or Evans et al., 2009). With the increasing amounts of radiation, the surrounding natal cloud will eventually be stripped away. A fraction of the icy dust grains will be heated above the sublimation temperature of the ice, revealing its composition in the gas phase. As the dust and gas are blasted away, the presence of a disk is revealed (Evans et al., 2009; Williams and Cieza, 2011). This protoplanetary disk consists of a relatively flat, dense region in mid-plane, rotating perpendicularly to the star's rotation with a large amount of gas and dust suspended around it. Part of the ice-covered dust particles survive the transition into the protoplanetary disk, but mainly in the denser mid-planes

closer to the star and further away where temperatures are low enough to maintain the low temperatures (e.g. Markwick et al., 2002 or Visser et al., 2009). Protoplanetary disks are highly dynamic, and modeling studies suggest they have lifetimes in the order of around 10 Myr. The active photo-processing of the disk results in a release of once-frozen species, and allows us to observe the physical conditions and the chemical abundances in these regions. Ice has been detected in edge-on disks, and is expected to be a major reservoir of species in the midplane (Visser et al., 2009; Boogert et al., 2015). It is expected that the upcoming James Webb Space Telescope, which has significantly more resolving power and sensitivity than ISO or *Spitzer*, will provide much insight into ice in disks, and possibly reveal the presence of larger molecules embedded within these ices.

The protoplanetary disk from which our planets formed is called the solar nebula. The clear distinction between inner rocky planets and the outer gas giants reveals some of the history of the protoplanetary disk, and reflects what the disk temperature was at the time of planet formation. The presence of the so-called snow lines provides an inner limit on the solid phase of volatile species, resulting in the current layout of our planets: rocky in the inner solar system and gas-rich further away from the sun (the terrestrial planets being too light to retain H₂ and He). It should be noted though, that recent discoveries of exo-planets have put a side note to this theory, as gas giants are seen too close to their host stars to be consistent with how much material is expected to be present in the protoplanetary disk (e.g. see Dawson and Johnson, 2018). It is thought that planet migration plays an important role here, resulting in planetary composition beyond the restrictions of the snow lines in protoplanetary disks. Nevertheless, the rocky planets in our solar system are thought to be formed from the bare dust grains (Morbidelli et al., 2012). At a later stage, water, other volatiles and more complex molecules were likely delivered to planets by comets, asteroids, meteorites, and interplanetary dust particles (IDPs) (Morbidelli et al., 2012; Alexander et al., 2018). The implications of this are that the dust grains, ice-covered or not, do not only play an important role in planet formation, but also contribute significantly to the composition of planets like our own, and possibly even to our current biosphere, if delivered by comets or interplanetary dust particles.

Interestingly, significant overlap exists between interstellar ice species and molecules detected in the coma of comets (Mumma and Charnley, 2011). Comets are considered as the most pristine material left over from the solar nebula, and thus provide insight into its composition at that time. This applies particularly dynamically new comets, which are comets which are thought to

have been in the Oort since the formation of the Solar System (Mumma and Charnley, 2011). Cometary and interstellar ice shows overlap in their molecular composition, even though the methods used to study them are vastly different; interstellar ice constituents are detected by their solid-state infrared absorption features, but comets can be studied in emission from the vacuum UV to the radio regime. As the material in the coma is sublimated, and subsequently studied in the gas phase, the species present in the gas phase are an indirect probe of the cometary nucleus. This leaves relatively large uncertainties on the constraints of the original ices. Moreover, strong compositional variations are seen on diurnal and seasonal time scales, indicating that the nuclei itself is all but homogeneous (Dello Russo et al., 2016; Bockelée-Morvan et al., 2016). Here, visits to comets by space craft provide especially valuable information. The Rosetta mission to 67P/Churyomov-Gerasimenko, for instance, has provided much information about 67P that could not be obtained from Earth. One particularly relevant example for this thesis is the detection of the simplest amino acid, glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) in the coma of 67P/C-G (Goesmann et al., 2015; Altwegg et al., 2016), but also the detection of a relatively large reservoir of molecular oxygen (Bieler et al., 2015) and the abundance of noble gases and their isotopes (Balsiger et al., 2015; Marty et al., 2017) have provided surprising insights into molecular cloud and protoplanetary disk processing. The abundance of noble gasses in 67P is directly linked to the abundance of Xe and its isotopes in the Earth's atmosphere (Marty et al., 2017). It is important to keep the limits of the remote-observation techniques in mind when considering our knowledge about cometary and interstellar ices.

1.2 The catalytic role of icy dust grains in the formation of molecules

Icy dust grains are not only a molecular reservoir but also facilitate surface reactions. It was in Leiden that the first ice mixtures of CO, H_2O , NH_3 , and CH_4 were irradiated with VUV radiation, simulating ISM conditions. The subsequently recorded infrared spectra hinted to a wealth of newly formed molecules (Hagen et al., 1979). The authors interpreted their experiment as the solid state equivalent of the Urey-Miller experiment (Miller, 1953). Years later similar experiments were conducted, and the *ex situ* mass spectrometric analysis of the resulting residues showed the presence of amino acids (Muñoz-Caro et al., 2002; Bernstein et al., 2002). With technical advances, more and more species have been detected in these "Greenberg" experiments by a number of groups, including urea (Nuevo et al., 2010) and sugars (de Marcellus

TABLE 1.1: Composition of interstellar ices and cometary ices relative to water. Where significant, a range is shown. The interstellar ice compositions cover those reported in the different environments by (Boogert et al., 2015). Values for comets are taken from (Mumma and Charnley, 2011), except for the values for CO_2 , CH_4 , and OCS , which are the averages as measured by VIRTIS on board the Rosetta spacecraft around 67P/C-G (Bockelée-Morvan et al., 2016).

Species	Interstellar Ice	Comets
H_2O	100	100
CO	3-85	0.4-25
CO_2	11-50	2-23
CH_3OH	3-31	0.1-5
NH_3	3-10	0.6
CH_4	1-11	0.35
H_2CO	2-7	0.4
OCN^-	0.1-1.9	-
OCS	0.01	0.15
HCOOH	4	0.09
HCOO^-	0.85	-
NH_4^+	10	-
SO_2	0.2	0.2

et al., 2015b; Meinert et al., 2016). High-resolution mass spectrometry studies revealed the presence of molecules with masses up to 4000 atomic mass units (Danger et al., 2016), indicating how vastly diverse and complex the composition molecules in these residues become. It should be noted though, that as these studies are *ex situ*, residues are heated to room temperature, and chemically treated prior to analysis, there still remains some ambiguity as to at which stage in the experiments the compounds are formed. The challenge of this work lies in understanding which processes take place and whether (all) these are astrophysically relevant. The molecular diversity found in the “Greenberg-experiments” was compared to the diversity in organic compounds found in the Murchison meteorite, which is one of the most studied carbon-rich meteorites (Danger et al., 2016). Carbon-rich meteorites of this type are amongst the earliest material formed in the solar system, (Cody and Alexander, 2005; Schmitt-Kopplin et al., 2010; Elsila et al., 2016). Similarly, the molecular diversity in comets is of comparable complexity, as was demonstrated from the analysis of interplanetary dust particles originating from comets, as well as from grains captured in the Stardust mission (Cody et al., 2011; Starkey et al., 2013; Brownlee, 2014). What the distribution of organic molecules in cometary grains, meteorites and the Greenberg experiments have in common is an extreme diversity in the molecular composition, resulting from excessive energetic processing.

Starting some 15-20 years ago, with the introduction of ultra-high vacuum technology in laboratory astrophysics, new types of experiments were conducted. Studying the reactions *in situ* and under well-controlled conditions, it became possible to reveal entire reaction mechanisms for individual molecules. VUV irradiation of methanol ice, for example, was shown to result in the formation of a substantial number of COMs, including ethers CH_3OCH_3 , aldehydes (H_2CO), esters (HCOOCH_3) and acids (CH_3COOH), aside from a number of smaller molecules such as CO and CH_4 and several radical species (Öberg et al., 2009a; Paardekooper et al., 2016). Some of these molecules were already identified in the gas phase in the ISM. Similar results were obtained when CH_3OH was exposed to energetic electrons (Bennett et al., 2007), and cosmic-ray-like particles (de Barros et al., 2011). Studies where simple ice mixtures consisting of $\text{CH}_4:\text{HNCO}$, both identified in interstellar ices (Lacy et al., 1984; Gibb et al., 2004; van Broekhuizen et al., 2005), were exposed to VUV radiation have shown to result in a plethora of amine ($-\text{NH}_2$) and amide ($-\text{C}(\text{O})\text{NH}_2$) containing compounds, opening the pathway for the formation of amino acids and peptide bonds (Ligterink et al., 2017; Ligterink et al., 2018). The formation of simple molecules, including H_2O , CO_2 , and CH_3OH was shown from the hydrogenation of O_2 and CO ice (Ioppolo et al., 2008; Ioppolo

et al., 2010; Cuppen et al., 2010). More recently, it was shown that radical recombination reactions can result in the formation of carbon-carbon bonds through successive addition/abstraction reactions, eventually yielding glycolaldehyde and glycerol (Chuang et al., 2016; Fedoseev et al., 2017). Thermally induced reactions also have been shown to result in the formation of larger complex species (Theulé et al., 2013). In parallel, the resulting parameters – reaction rates, reaction barriers, diffusion constants, and absorption energies – are used as input in astrochemical models (see e.g. Wakelam et al., 2010; Herbst, 2014 and references therein), allowing for simulation of the chemical evolution of dark clouds and protoplanetary disks.

From this, it is clear that many different processes, characteristic for specific evolutionary stages of ices in space, can result in the formation of new molecules in the solid state. In a reverse way, the detection of such species, when found in the gas phase will tell more about the processes at play. Molecules can be used as diagnostic tools as their spectral fingerprints do not only reveal their presence, but also reflect the physical conditions they are in.

Equally important is to understand how stable newly formed molecules will be. For example, once a solid-state reaction network has resulted in the formation of an amino acid, like glycine, how big is the chance that such a molecule survives inside the ice in the harsh conditions typical for the ISM? That is, besides pure spectroscopic studies of ices required to identify such species in the ISM, dynamical laboratory studies are also needed to simulate the processes taking place in the ice.

1.3 Water ice in space

As water is arguably the most important molecule in astronomical ices, constraining how water can be formed is of critical importance for our understanding of the ISM. In hot interstellar environments, water can be formed in the gas phase, resulting in a few 10^{-7} molecules of water per H_2 (Smith et al., 2004; van Dishoeck et al., 2013). For lower temperatures, such as those in dense clouds, gas phase routes towards water formation are relatively inefficient. As the observed abundance of water is $\sim 10^{-4}$ with respect to H_2 , other mechanisms must be involved (van Dishoeck et al., 2013). The solid-state formation of water was first described in detail from a theoretical perspective (mostly based on gas phase reaction rates) by Tielens and Hagen (1982). These authors used constants from the physical-chemistry literature to study the evolution of ices,

describing the concentration of each species as a function of time. A number of different formation mechanisms for water were proposed, for which the underlying reaction networks and temperature dependent reaction rates were experimentally determined much later (Miyachi et al., 2008; Ioppolo et al., 2008). Later computational studies constrained the relative importance of the different reactions, confirming that water forms in solid-state in hydrogenation schemes involving O, O₂ and O₃ (Cuppen et al., 2010; Lamberts et al., 2013; van Dishoeck et al., 2013; Linnartz et al., 2015).

Water ice in space is most often found in its amorphous form: ASW – amorphous solid water (Gillett and Forrest, 1973; Smith et al., 1989; Boogert et al., 2008). Laboratory studies have shown that ASW grown by deposition can contain varying amounts of void space, or porosity, as a function of the growth conditions (Dohnálek et al., 2003; Clements et al., 2018). It is still not fully clear how porous interstellar ASW is, but lacking signatures for unbound OH groups – an indication of porosity – suggests ASW may be compact, although this diagnostic is not fully conclusive (Keane et al., 2001; Bossa et al., 2015b). Crystalline water ice exists in space, but only when it has been radiatively processed or heated above 130 K (Palumbo, 2006; Raut et al., 2007). Crystalline water ice has been detected in protoplanetary disks (McClure et al., 2012; Terada and Tokunaga, 2012; Min et al., 2016). The transition from amorphous to crystalline is exothermic and non-reversible. Both amorphous and crystalline ice are known to trap volatile species such as N₂, CO and the noble gasses. The release of these gases coincides with the phase change from amorphous to crystalline and with the sublimation of the H₂O, i.e. at temperatures far above the sublimation temperatures of the trapped species (Bar-Nun et al., 1985; Bartels-Rausch et al., 2012; Rubin et al., 2015)

1.4 Polycyclic aromatic hydrocarbons in ices

Polycyclic aromatic hydrocarbons (PAHs) are found widely throughout space by their infrared emission signatures (Allamandola et al., 1989; Draine and Li, 2007; Tielens, 2008). Emission from dust-rich regions such as photodissociation regions, planetary nebula and even nearby galaxies show the presence of aromatic bonds, indicating wide abundance of this class of molecules (Draine and Li, 2007; Tielens, 2008). PAHs consist primarily of six carbon atoms fused into aromatic rings, but may also contain oxygen or nitrogen insertions (Tielens, 2013). Aromaticity occurs when one electron on each atom in a six-membered carbon ring is delocalized, resulting in so-called conjugated molecular bonds,

which effectively allows the electrons to roam free around the atomic skeleton. The direct consequence of aromaticity is a significant stabilization of the molecule. Inherent to aromaticity are large electronic absorption cross-sections, and as a result, PAHs are generally strong absorbers of UV light. In space, in the gas phase, the absorbed energy is re-emitted as infrared radiation – which is how the presence of PAHs is revealed – and that is in turn easily absorbed by other molecules, effectively leading to local heating (Draine and Li, 2007). Another consequence of the electron delocalization in PAHs is the relative stability of charged PAHs. Most organic molecules are likely to fragment upon vacuum UV excitation instead of being ionized, but PAHs are relatively stable as ions. Hence, PAHs are thought to be present both positively and negatively charged in the ISM and to contribute significantly to the ionization balance in the ISM (Tielens, 2008). Identification of a specific PAH, however, has remained elusive, as the infrared emission features are rather similar for different. Based on the ubiquitous detection of PAH emission features in the ISM, the estimate is that PAHs carry up to 10 % of the cosmic carbon, contingent on assumptions about the infrared band strengths and molecular size (Tielens, 2013). PAHs features are not visible in the colder environments of the ISM, which suggests that these non-volatile species accrete onto dust grains and end up in the ice layers. This is interesting, both from an astronomical and a physical-chemical point of view. Once embedded in an ice matrix, the ionization potential of the PAHs is thought to be lowered, which further enhances the formation of PAH cations (Gudipati and Allamandola, 2004). PAHs embedded in ice offer different starting conditions for chemical processes than bottom-up reaction schemes in which smaller species merge into larger ones; in the case of PAHs a large precursor stage (e.g. a carbon skeleton) has already been realized and this may react with for instance OH radicals which form upon water photolysis (Nuevo et al., 2014; Cook et al., 2015).

As in the gas phase, in the solid state it is hard to discriminate between different PAHs using infrared (i.e. vibrational) spectroscopy; similar modes exhibit similar spectral features, resulting in non-unique and overlapping spectra. Moreover, in the infrared, many of the PAH and PAH-cation features will be hidden in the strong water absorptions of the ice they are embedded in. In a number of experiments conducted in the past, this has been overcome by using high PAH abundances in ice mixtures, conditions not necessarily representative for the ices in the ISM. Optical (i.e. electronic) spectroscopy may offer an alternative way for studying ice embedded PAHs, both in the laboratory and possibly also in space (Salama, 2008; Linnartz, 2014). As stated before, aromatic molecules tend to have strong transitions in the UV-vis range. These transitions do not coincide with water absorption, as water is transparent

in this wavelength range. Moreover, electronic spectra are very distinctive for individual PAHs (i.e. practically unique, as apposed to the very similar infrared spectra), and change completely upon ionization of the PAH. In this thesis the experimental procedure to study PAHs and PAH-cations embedded in water ice, both in the UV-vis and IR will be discussed.

1.5 Laboratory studies of astrophysical ice mixtures

It is only through dedicated laboratory astrochemical studies that the chemistry in dark clouds, protoplanetary disks, and star-forming regions can be understood, as the physical and chemical conditions in these locations is vastly different from what is typically considered in physical chemistry studies on Earth. As the composition of the ice is reflected in the gas phase upon evolution of the molecular cloud into a YSO, understanding of molecular formation mechanisms in the solid-state is crucial for our understanding of the molecular inventory of star and planet forming regions. Without constraining the reactions taking place in the solid phase, the ISM would not be understood as well as we do now.

In the laboratory, the conditions in the ISM can be mimicked, allowing us to simulate the reactions taking place. Pressures reached in state-of-the-art ultra-high vacuum setups regularly are below the 10^{-10} mbar range, which correspond to molecular mean free path lengths of hundreds to thousands of kilometers m. These particle densities are still higher than what is expected to be present in molecular clouds, but enables nearly complete control over the species involved in an experiment. In the high-vacuum regime, such as reached in the experiment in this thesis (pressures above 10^{-8} mbar), water remains a background gas, which may affect surface reactions. Temperatures reached in the laboratory are often between 10 and 15 K, but reaching 4 K is possible using commercial equipment. Considering that the temperatures even deep inside molecular clouds are in the 10 K range, the physical conditions in can be adequately constrained in laboratory astrophysical studies. See van Dishoeck (2014) and Öberg (2016) for recent overviews of developments in the field.

A number of wavelength regimes are considered in this thesis, which we will define as following. The vacuum ultraviolet (VUV) is defined by the MgF₂ cut-off value assumed to be at 120 nm, i.e. including the hydrogen Lyman α transition, but not the more energetic Lyman transitions. The long-wavelength

edge of the VUV is 200 nm, where the ultraviolet region starts (200–400 nm). The visible describes the wavelength range between 400 and 750 nm. Here, we consider the near-infrared to be between 750 and 2500 nm, where the mid-infrared range starts until 25,000 nm. In the mid-infrared the wavelengths are reported in wavenumbers (i.e. between 4000 and 400 cm^{-1}).

Infrared spectroscopy is most often applied to study astronomical ice mixtures, as the ice is directly probed, it is non-destructive, and the obtained spectra can directly be applied to observations of ices in space. UV-vis and VUV spectroscopy, and more recently far-IR or terahertz spectroscopy are also used to investigate the molecular properties of interstellar ice analogs. Particularly in the case of VUV spectroscopy, the photons are destructive for the ice and thus the diagnostic capacity of VUV spectroscopy is limited. The photons used in UV-vis spectroscopy are typically not energetic enough, and the fluxes too low to induce significant chemical changes in the ice sample. Other approaches, such as temperature programmed desorption-quadrupole mass spectrometry (Collings et al., 2004; Öberg et al., 2009a; Ligterink et al., 2018) or laser ablation-mass spectrometry (Paardekooper et al., 2014; Henderson and Gudipati, 2015) enable very sensitive detection of ice constituents at the expense of destruction of the ice. The use of isotopic labeling provides additional diagnostic information, by enabling the following labelled atoms in a reaction. Isotopic labelling is used in the infrared but particularly powerful in mass spectrometric techniques.

In this thesis, the focus is on vacuum UV induced processes in interstellar ices. Spectroscopic analyses are performed in the UV-vis and infrared. In order to simulate the radiation in space, a microwave discharge hydrogen plasma lamp is used (Warneck, 1962). The light emission from the plasma mimics the VUV radiation in space, providing a relatively accessible way to simulate the part of the radiative conditions in space (Cruz-Diaz et al., 2014; Ligterink et al., 2015; Heays et al., 2017). The flux of the lamp is many orders of magnitude larger than is expected to be present in dark clouds (see Chapter 5), but it should be noted that the photon flux applies is still far below what would be required for multi-photon processes. This ensures the results from the laboratory can safely be extrapolated to what ice would experience in dark clouds.

1.6 This thesis

The studies in this thesis are performed with an experimental setup capable of measuring the IR and UV-vis spectra of interstellar ice analogs, with the option of embedding non-volatile species within these ices. Ices and the embedded species are continuously studied while being exposed to vacuum UV radiation. The setup was redesigned and extended as part of this thesis project. A new method to determine ice thickness has been developed, which also allows determining optical constants of the ice under investigation. A special focus is on water ice, given its important role in the ISM. The optical and photochemical properties of amorphous solid water, and its influence on embedded species are investigated. If PAHs are abundantly present in water ice, and easily ionized, can we identify a unique spectral signature to search for PAHs in the ice in space? If complex molecules, like amino acids, are formed in the ice, how likely are they to survive the radiation in space? What is the protective role of ASW? What are the optical properties of ASW at different wavelengths? These questions are addressed in the next chapters.

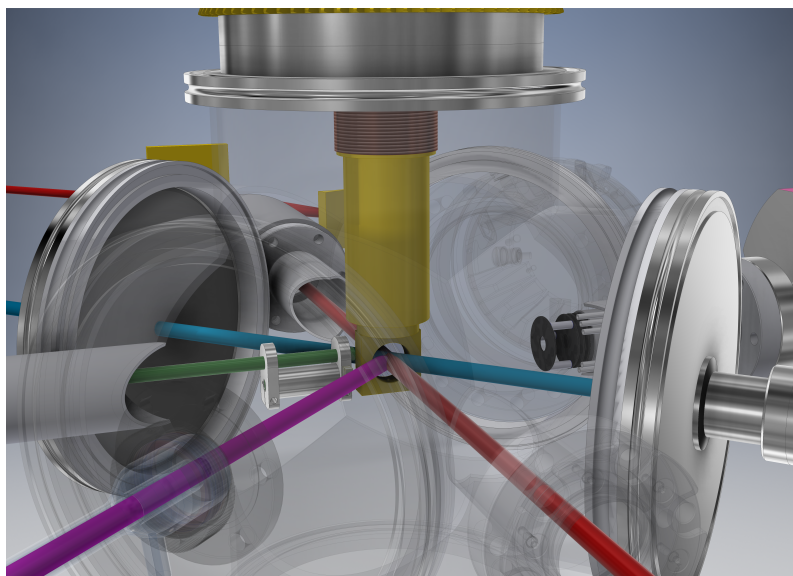


FIGURE 1.3: Schematic drawing of the setup used in this thesis. It shows the transparent window in the center, suspended in the gold-colored cold head. The different light paths are colored: VUV light in magenta, IR in red, UV-vis in blue. The gas deposition tube, with the oven suspended underneath it, is shown in green.

- **Chapter 2** describes the experimental setup and measurement procedures in detail. The setup was constructed for the research described here, and is capable of simultaneous UV-vis and IR spectroscopy of interstellar ice analogs. A custom made sublimation oven enables the controlled co-deposition of non-volatile molecules like PAHs and amino acids. Ices can be processed by exposing them to the VUV radiation from a hydrogen plasma lamp, which mimics the radiation in dark clouds. The capability of simultaneous UV-vis and IR spectroscopy allows probing both the bulk species in the ice by the vibrational transitions, and the highly molecule-specific electronic transitions. By detecting species in the UV-vis which are invisible in the IR and vice versa, it is demonstrated that these methods are not only complementary, but that both techniques also enhance one another by using accurate quantification of molecules in the UV-vis to constrain infrared band strengths. By combining both techniques the ice can be very well characterized and monitored while active processing takes place.
- **Chapter 3** presents a new method to determine the refractive index of ice. In order to characterize interstellar ice, it is crucial to know the refractive index n as a function of the wavelength (λ) accurately, as this describes the propagation of light through the ice. Water is by far the most abundant ice component, and its optical properties are needed for a correct interpretation of astronomical observations and astrochemical modeling. Prior to these studies, the refractive index of amorphous ice, the state in which most ice in space is in, was not well constrained, and $n(\lambda)$ of crystalline ice in the UV-vis was only known at moderate resolution. The new method relies on dynamic broadband UV-vis interferometry to derive a continuous function of $n(\lambda)$ of amorphous solid water between 10 and 130 K, as well as crystalline ice at 150 K. A general formula for calculating the refractive index of water ice as a function of the porosity and wavelength, applicable between 210 and 757 nm, is provided.
- **Chapter 4** investigates the polycyclic aromatic hydrocarbon triphenylene ($C_{18}H_{12}$) embedded in water ice. Triphenylene is symmetrical and fully benzenoid and has strong absorptions in the UV. It has been detected in meteorites, and because of its relative photo-stability, it may be abundant in the ISM. Although the ions of PAHs are relatively stable compared to other organic molecules, preparing these in sufficient quantities to measure the absorption spectra is challenging. The UV-vis spectrum of the cation of triphenylene is recorded in high resolution, and, in line with expectations, show strong absorption in the near-UV. The absorption

spectrum in water is provided, which can be used to search for the triphenylene cation in interstellar ice.

- **Chapter 5** constrains the role of water ice in the VUV induced photochemistry of glycine embedded in ASW. Glycine is exposed to VUV radiation, and the reactions and products are studied using both UV-vis and infrared spectroscopy. By comparing the reaction in water and a chemically inert host, the role of ASW can be deduced. The laboratory results are used to conclude on how frozen amino acids behave in space. The penetration depth of VUV photons into the water ice is determined, revealing 152 nm of water ice decreases the VUV radiation by half. The amount of ice required for glycine to survive in dark clouds is determined.

