One

Introduction
Abstract

Space is filled with billions of stars, which are clustered in larger structures, named galaxies. Beyond our own galaxy (called Milky Way), there are billions of other galaxies. The space between the stars (the interstellar medium, ISM) and between the galaxies (intergalactic medium, IGM) was long thought to be vacuum. While these media are indeed relatively empty compared to a more familiar medium like the Earth’s atmosphere, they do contain a certain level of matter in the form of gas and tiny solid particles. When atoms are present, chemistry can take place and molecules can be formed.

Organic molecules consist primarily of carbon and hydrogen atoms, but may also contain other atoms like oxygen and nitrogen. Organic molecules can grow up to very large sizes and may also form supramolecular structures. On Earth, all living organisms—from the simplest bacteria to complex mammals including human beings—are built from a collection of small organic molecules including amino acids, nucleotides, sugars, fatty acids, that can assemble into larger polymers such as proteins, RNA, and DNA, and large complexes (e.g. membranes). These building blocks need to be available on a planet before life can emerge. The central question in the origin of life is where organic chemistry started and how organic molecules assembled into self-organizing systems. It is likely that a combination of terrestrial (e.g. hydrothermal vents) and extraterrestrial sources (comets and meteorites) provided the first building blocks for life on the young Earth.

This introduction gives an overview of the organic chemistry that proceeds in interstellar, interplanetary, and planetary environments. During their life cycle, organic molecules formed in space may encounter degrading environmental conditions, such as ultraviolet (UV) radiation, cosmic rays, shocks, and elevated temperatures. The following chapters in this thesis investigate the stability of a variety of organic molecules and a salt-loving microorganism in interstellar and planetary environments.

1.1 Organics in space

Origin of the elements

The field of chemistry had its coming of age as a scientific discipline with the compilation of the periodic table by Mendeleev in 1869. Later, astronomers created their own version of the periodic table, aptly named the astronomer’s periodic table, see figure 1.1. Here, the elements are sorted based on their universal abundance, rather than their mass or atomic number. The elemental composition of the Universe is primarily based on the nucleosynthesis during the Big Bang. Between 100 and 300 seconds after the Big Bang, all the hydrogen and most of the helium in the universe, and small traces of deuterium, tritium, lithium, and beryllium were formed (see Schramm (1998) for an overview). All elements heavier than beryllium were formed later by nucleosynthesis during stellar evolution, probably starting as early as 300–500 My after the Big
Figure 1.1
The astronomers’ periodic table (left). The sizes of the boxes represent the relative cosmic abundances of the elements. The table (right) gives the cosmic abundances by number of atoms relative to hydrogen for those elements.

Bang (Stark et al. 2007).

Star formation
Stars are formed when a cloud of gas and dust contracts due to its own gravity. Heat generated by compression of the gas is initially dissipated in the infrared, mainly through emission of rotational lines by molecules such as CO. In this stage cloud contraction proceeds isothermally. When the density is high enough to trap the cooling radiation (at $\sim 10^7$ cm$^{-3}$), the cloud core starts to heat up. When the core temperature reaches $10^7$ K, nuclear fusion of hydrogen ($^1$H) to helium ($^4$He) is initiated. The formation of helium is a highly exothermic reaction and the heat produced by this reaction keeps the star from further gravitational collapse. The star then reaches a temporary equilibrium, the duration of which is determined by the star’s mass. During that period the star is called a main-sequence star. The Sun is an example of a star in its main sequence. For a recent overview of star formation, see Lada (2005).

When the hydrogen that fuels nuclear fusion reactions in the stellar core is consumed (approximately 10 Gyr for a star with the mass of the Sun), the pressure balance is no longer maintained and the star starts to gravitationally contract once more. While the core of the star contracts the outer layers expand, causing the star to increase in size. The compression of the core causes the temperature to rise further. When the
core temperature reaches $10^8$ K, helium starts to fuse, forming carbon ($^{12}$C) and oxygen ($^{16}$O). Stars in this phase of their existence are called asymptotic giant branch (AGB) stars.

Circumstellar envelopes

Elemental carbon and oxygen are ejected from AGB stars by solar winds (Willson 2000). At a distance $>10^{13}$ cm from the central star, the temperature of the outflows has dropped enough for the carbon and oxygen atoms to form molecular bonds. C and O react quickly to form CO, which continues to be formed until one of the two elements is depleted. Early in the AGB phase of the star, O is the more abundant element and all C will be locked in CO. During that phase, the AGB produces O-rich silicate dust particles. Later, more C is dredged up from the star’s core and when C/O $>1$, oxygen will be depleted due to CO formation. The remaining C then forms molecules such as C$_2$H$_2$ and HCN. These molecules can engage in a rich gas-phase chemistry, initiated by shock waves from stellar pulsations. An important reaction that takes place is the polymerization of acetylene to benzene and larger polycyclic aromatic hydrocarbons (PAHs) (Frenklach & Feigelson 1989, Cherchneff et al. 1992). Benzene was tentatively detected in CRL618 by Cernicharo et al. (2001). These reactions take place in the region from $4 \times 10^{13}$–$10^{14}$ cm. Figure 1.2 shows the temperature profile through the circumstellar envelope of a typical AGB star. The plot is divided in five regions, each displaying a distinct type of chemistry as described above (adapted from Millar 2003).

Upon further migration outward from the star ($10^{14}$–$10^{15}$ cm) and subsequent further cooling, PAHs and other molecules coagulate to form small amorphous dust particles. These dust particles attenuate the UV light from the star on the inside and the interstellar UV radiation on the outside. In the region $10^{15}$–$10^{16}$ cm, these dust grains create a high visual extinction that lowers the photodissociation rates and this zone is considered chemically quiet. Beyond $10^{16}$ cm the dust is diluted and the visual extinction A$_V$ drops, allowing photodissociation and photoionization of molecules by the interstellar UV field to occur. This leads to a photon-driven type of chemistry and a wealth of reactions.

The carbon-rich envelope of IRC+ 10216, the prototypical example of an high mass-loss carbon star, contains a large variety of organic molecules (Glassgold 1996) and is dominated by the presence of carbon molecules, such as polyacetylenes (e.g. C$_8$H, Cernicharo & Guélin 1996), cyanopolyynes (e.g. the largest uniquely identified interstellar molecule: HC$_{11}$N, Bell et al. 1982), sulfuretted chains (e.g. C$_2$S, C$_3$S, C$_5$S, Cernicharo et al. 1987, Bell et al. 1993), structural isomers (HCCNC vs. HCCCCN, Gensheimer 1997), and the recently detected carbon-chain anions (C$_6$H$^-$ and C$_4$H$^-$, McCarthy et al. 2006, Cernicharo et al. 2007). These molecules are formed in the inner parts of the circumstellar envelope, where the interstellar UV field is attenuated by the dust. Once these molecules reach the outer regions of the envelope, the outflowing gas is photodissociated and photoionized by the interstellar UV field to produce ions and radicals. Except for the most photochemically stable
Figure 1.2
Temperature profile of a circumstellar envelope surrounding an AGB star with an effective temperature ($T_{\text{eff}}$) of 2215 K and a radius ($R_\star$) of $2 \times 10^{13}$ cm. The plot is divided into five regions, each having a distinct type of chemistry. Adapted from Millar (2003).

Species (PAHs, dust grains), molecules formed in the circumstellar envelopes are destroyed in the outermost layers as they leave the circumstellar envelope and enter the diffuse ISM.

Near the end of the AGB phase, the star begins to pulsate. The pulses blow away its outer shells and the circumstellar envelope, thereby enriching the surrounding medium with the elements, molecules and dust grains it produced. The expanding cloud of gas and dust is called a protoplanetary nebula, and later (when the temperature of the central star rises above 30,000 K) a planetary nebula. When the AGB star has converted all its helium into carbon and oxygen, the central star collapses into a white dwarf. For stars that started out with a mass $>8$ solar masses, nucleosynthesis continues to produce heavier elements up to $^{56}\text{Fe}$. High mass stars end their lifetime in a violent supernova explosion.
Interstellar medium

The interstellar medium (ISM) comprises many different environments, with distinct physical properties. These environments can be divided into five main categories: the hot ionized medium, the warm ionized medium, the warm neutral medium, the atomic cold neutral medium, and the molecular cold neutral medium (Spitzer 1985). These categories are based on differences in temperature, hydrogen density, and the ionization state of hydrogen. A summary of these properties for each of the ISM components is given in table 1.1. A comprehensive overview of the composition and evolution of interstellar clouds is given by Wooden et al. (2004). Of the five categories listed in table 1.1, the warm neutral medium (T ∼ 10^4 K, n_H ∼ 0.1 cm^-3, neutral H) is generally regarded as the intercloud medium. Outside areas where gravity dominates, the Milky Way is roughly in pressure equilibrium, with an average pressure (P/k) of ∼10^4 K cm^-3 (Field et al. 1969, McKee & Ostriker 1977).

Diffuse clouds

Diffuse clouds (atomic cold neutral medium) often surround denser and colder regions (Heiles 1967) and have filamentary or sheet-like structures. The main component of diffuse clouds is neutral atomic hydrogen (H) at densities ranging from 10–300 cm^-3. The temperature varies in the range 50–200 K. Due to a low visual extinction (A_V ∼ 1 magnitude), UV photons can easily penetrate the cloud to photodissociate and photoionize molecules. The molecules found in diffuse clouds are therefore usually simple species such as CH^+, CH, HCO^+, HCN, HNC, CS, H_2CO, CO, OH, and C_2 (Lucas & Liszt 1997), or large UV-resilient molecules such as polycyclic aromatic hydrocarbons (PAHs) or other carbon clusters (Ehrenfreund & Charnley 2000). UV radiation in those clouds is dictated by the interstellar UV field as described by Draine (1978) that integrates to ∼10^8 photons cm^-2 s^-1 for the wavelength range 100–200 nm.

Molecular clouds

Molecular clouds are dense, cold regions of the ISM with hydrogen densities (H_2) in the range 10^3–10^4 cm^-3. The temperature in a molecular cloud is low, generally between 10–50 K. Molecular clouds can contain many substructures, some of which are referred to as dense cores or clumps. These cores have a higher density than the surrounding cloud, ranging 10^4–10^6 cm^-3. The temperature of dense cores generally does not rise above 10 K. The visual extinction is usually very high and can reach up to hundreds of magnitudes. Because of this high extinction, photons from the interstellar UV field can not penetrate the cloud — hence its moniker dark cloud. Despite the high extinction, the UV field inside a dense core is not zero. Cosmic rays can penetrate the cloud and ionize hydrogen. Secondary electrons excite the surrounding hydrogen, which produces a low level of UV photons upon de-excitation (Prasad & Tarafdar 1983). This yields a UV flux of ∼10^3 photons cm^-2 s^-1 in the wavelength range 100–200 nm, with two main bands at 120 and 160 nm (Gredel et al. 1989). The low UV flux allows a large number of molecules to exist in dense clouds. A comprehen-
Table 1.1
Phases of the interstellar medium (adapted from Wooden et al. 2004).

<table>
<thead>
<tr>
<th>ISM component</th>
<th>common designation</th>
<th>T (K)</th>
<th>density (cm$^{-3}$)</th>
<th>state of hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>hot ionized medium</td>
<td>coronal gas</td>
<td>10$^6$</td>
<td>0.003</td>
<td>H$^+$</td>
</tr>
<tr>
<td>warm ionized medium</td>
<td>diffuse ionized gas</td>
<td>10$^4$</td>
<td>&gt;10</td>
<td>H$^+$</td>
</tr>
<tr>
<td>warm neutral medium</td>
<td>intercloud H i</td>
<td>10$^4$</td>
<td>0.1</td>
<td>H</td>
</tr>
<tr>
<td>atomic cold neutral medium</td>
<td>diffuse clouds</td>
<td>100</td>
<td>10–100</td>
<td>H + H$_2$</td>
</tr>
<tr>
<td>molecular cold neutral medium</td>
<td>molecular clouds</td>
<td>&lt;50</td>
<td>10$^3$–10$^4$</td>
<td>H$_2$</td>
</tr>
<tr>
<td></td>
<td>dense cores</td>
<td>10</td>
<td>10$^4$–10$^6$</td>
<td>H$_2$</td>
</tr>
<tr>
<td>hot molecular cores</td>
<td>protostellar cores</td>
<td>100–300</td>
<td>&gt;10$^6$</td>
<td>H$_2$</td>
</tr>
</tbody>
</table>

A comprehensive and up-to-date list of all molecules detected in interstellar space (not only in dense clouds) can be found at http://www.astrochemistry.net. At the time of this writing, the counter for detected molecules rests at 151 unique molecules, or 231 including isotopomers. Of the 151 molecules currently identified, the majority is detected in dense clouds.

Chemistry in dense cores is dominated by solid-phase reactions on grain surfaces. Due to the low temperature in the cloud, sticking coefficients are close to unity and most molecules are condensed on dust grains. Consequently, these dust grains are covered by icy mantles. Methanol, for example, is formed efficiently in the solid phase in dense cores. In regions where the temperature is below 25 K, CO is depleted onto dust grains and successive additions of hydrogen atoms leads to the formation of CH$_3$OH (Charnley 1997).

\[
\begin{align*}
\text{CO} & \xrightarrow{H} \text{HCO} \xrightarrow{H} \text{H}_2\text{CO} \\
& \xrightarrow{H} \text{CH}_3\text{O} \xrightarrow{H} \text{CH}_3\text{OH}
\end{align*}
\]

When the temperature rises above 140 K (e.g. in hot molecular cores), methanol is evaporated into the gas phase. Once in the gas phase, protonated methanol can react to form dimethyl ether (DME, CH$_3$OCO$_3$) via methyl cation transfer (Karpas & Mautner 1989),

\[
\text{CH}_3\text{OH}^{+} + \text{CH}_3\text{OH} \rightarrow (\text{CH}_3)_2\text{OH}^{+} + \text{H}_2\text{O}
\]

followed by electron dissociative recombination to yield CH$_3$OCH$_3$. Both cosmic rays and the cosmic ray induced UV field can deposit energy into the ice mantles, but the UV field is about 10 times more efficient than cosmic rays (Shen et al. 2004). UV photons can create radicals in the ice mantles. This has two consequences. First, UV-induced radical chemistry in the mantle can create molecules that may not have formed in the
gas-phase. Secondly, the energy released by the radicals causes the grain to heat and molecules to desorb into the gas-phase (Shen et al. 2004).

A number of molecules in interstellar ices have been detected in the infrared spectrum of dense clouds towards massive protostars (Gibb et al. 2004). The most abundant molecules in these ices are H$_2$O, CO, CO$_2$, CH$_3$OH, and NH$_3$ (Whittet et al. 1996). Other species including OCS, H$_2$CO, HCOOH, CH$_4$, and OCN$^-$ have been observed towards massive protostars (d’Hendecourt et al. 1996) and low-mass protostars (Boogert et al. 2004). In laboratory simulations many other species have been produced by radiative processing of similar ices. The products that have been formed include radicals, new molecules, and complex organic materials (Gerakines et al. 2000).

Hot molecular cores
Stars are formed in the interiors of dense clouds. As described in section 1.1, stars form through the collapse of a dense cloud. This might be triggered by an energetic event such as a nearby supernova that generates shockwaves. These shockwaves create regions with higher local density, which act as the nucleation points for gravitational collapse. Such higher-density regions are also known as hot (molecular) cores, or hot corinos in the case of low-mass protostellar objects (Ceccarelli 2004). Hot molecular cores have temperatures in the range of 100–300 K and densities well over $10^6$ cm$^{-3}$ (table 1.1). Their lifetime is rather short, in the order of $10^5$ years. Due to the higher temperature, the molecules that were originally condensed on the dust grains, evaporate into the gas-phase. In the warm gas-phase, reactions can take place that form a wealth of new complex molecules (see e.g. Charnley et al. 1992).

Table 1.2 shows a list of molecules with their abundances that have been detected in a dense cloud (L134N), in protostellar ices (NGC 7538:IRS9), a protostellar hot core (Orion KL), in a low-mass protostellar hot corino (IRAS 16293-2422), the cooler and less dense outer part of IRAS 16293-2422, and in a cometary coma (Hale-Bopp) (adapted from Schöier et al. 2002). A remarkable recent detection is the first interstellar amino acid glycine towards the hot molecular cores Sgr B2(N-LMH), Orion KL, and W51 e1/e2 (Kuan & Charnley 2003), although the results are debated (Snyder et al. 2005, Cunningham et al. 2007).

1.2 Organics in the solar system
Solar system formation
During the collapse of a dense cloud into a protostellar object, not all gas and dust is incorporated into the central object. The slowly rotating presolar nebula shrinks in size and because of the conservation of angular momentum the rotation speed increases. As a result, the presolar nebula flattens into a disk. In the rotating protoplanetary disk, dust grains collide and stick together electrostatically (Blum 2000). This causes the grains to gradually grow in size which, in turn, increases the chance for collisions. The gas molecu-
Table 1.2
Selected molecules detected in the gas of a molecular cloud (L134N), protostellar ices (NGC 7538:IRS9), protostellar hot core (Orion KL), protostellar hot corino of IRAS 16293-2422 (I16293 HC), surrounding colder, less dense outer part of IRAS 16293-2422 (I16293 OP), and in a cometary coma (Hale-Bopp). Adapted from Schöier et al. (2002).

<table>
<thead>
<tr>
<th>molecule</th>
<th>L134N</th>
<th>NGC7538:IRS9</th>
<th>Orion KL</th>
<th>I16293 HC</th>
<th>I16293 OP</th>
<th>Hale-Bopp</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>$1 \times 10^{-4}$</td>
<td>$(1-5) \times 10^{-6}$</td>
<td>$1 \times 10^{-4}$</td>
<td>—</td>
<td>$4.0 \times 10^{-5}$</td>
<td>$1 \times 10^{-5}$</td>
</tr>
<tr>
<td>HCN</td>
<td>$7 \times 10^{-9}$</td>
<td>$&lt;2 \times 10^{-6}$</td>
<td>$4 \times 10^{-7}$</td>
<td>—</td>
<td>$1.1 \times 10^{-9}$</td>
<td>$1 \times 10^{-7}$</td>
</tr>
<tr>
<td>HC$_3$N</td>
<td>$4 \times 10^{-10}$</td>
<td>—</td>
<td>$2 \times 10^{-9}$</td>
<td>$1.0 \times 10^{-9}$</td>
<td>$&lt;1.0 \times 10^{-10}$</td>
<td>$1 \times 10^{-8}$</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>$&lt;4 \times 10^{-10}$</td>
<td>—</td>
<td>$2 \times 10^{-8}$</td>
<td>$7.5 \times 10^{-9}$</td>
<td>$&lt;8.0 \times 10^{-11}$</td>
<td>$1 \times 10^{-8}$</td>
</tr>
<tr>
<td>H$_2$CO</td>
<td>$2 \times 10^{-8}$</td>
<td>$(1-4) \times 10^{-6}$</td>
<td>$1 \times 10^{-8}$</td>
<td>$6.0 \times 10^{-8}$</td>
<td>$7.0 \times 10^{-10}$</td>
<td>$5 \times 10^{-7}$</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>$5 \times 10^{-9}$</td>
<td>$(2-10) \times 10^{-6}$</td>
<td>$2 \times 10^{-7}$</td>
<td>$3.0 \times 10^{-7}$</td>
<td>$3.5 \times 10^{-10}$</td>
<td>$1 \times 10^{-6}$</td>
</tr>
<tr>
<td>CH$_3$OCH</td>
<td>—</td>
<td>—</td>
<td>$1 \times 10^{-8}$</td>
<td>$2.4 \times 10^{-7}$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>HCOOH</td>
<td>$3 \times 10^{-10}$</td>
<td>$(2-10) \times 10^{-7}$</td>
<td>$8 \times 10^{-10}$</td>
<td>$6.2 \times 10^{-8}$</td>
<td>—</td>
<td>$5 \times 10^{-8}$</td>
</tr>
<tr>
<td>HCOOCH$_3$</td>
<td>—</td>
<td>—</td>
<td>$1 \times 10^{-8}$</td>
<td>$&lt;6.0 \times 10^{-8}$</td>
<td>—</td>
<td>$4 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

$^a$ from Cazaux et al. (2003)

Les and dust grains in the disk start to coagulate and form larger particles. When the bodies reach kilometre size, gravitational interactions become dominant in the process (Safronov & Zvjagina 1969). The solid bodies (now called planetesimals) continue to grow by accretion, but gravitational pull can attract gas, dust, and other bodies over a longer range. When the planetesimals reach a size where gravitational pressure and heat from radioactive decay in the center causes the core to melt, the body is referred to as protoplanet. These protoplanets collide violently to form the terrestrial planets and the cores of the gas giants. Lissauer (1993, 2005) and Goldreich et al. (2004) give excellent overviews of the process of planet formation in the solar system.

The chemistry that started in the hot molecular cores, evolves during the presolar nebula and protoplanetary disk phases. With the formation of a disk a range of new interactions influence the molecular composition and distribution in the protostellar region. The central young stellar object heats the disk from the inside, evaporating the grain-mantle ices and driving gas-phase chemistry. Further outward from the central young stellar object, a high dust abundance attenuates the light from the central object and keeps the temperature low. This allows molecules such as H$_2$O, CO, CO$_2$, NH$_3$, and CH$_4$ to condense onto cold dust grains. Cosmic rays can penetrate deep into the disk and may produce ions and radicals, which drive ion-molecule and neutral-neutral reactions in the outer regions of the disk. For a recent overview of the chemistry in protoplanetary disks, see Bergin et al. (2006). Turbulent mixing of the disk can dis-
tribute material throughout the disk. An important result from the recently returned Stardust mission, which collected dust particles from the tail of comet 81P/Wild2, is that mixing in the solar nebula occurred on a large scale and much more efficient than models previously predicted (Brownlee et al. 2006).

**Planets**

The International Astronomical Union recently adopted a new definition for planets and other solar system bodies (IAU 2006). The following three criteria were formulated:

1. a body has an orbit around the Sun,
2. a body has sufficient mass to assume hydrostatic equilibrium shape (nearly round), and
3. a body has cleared the neighbourhood around its orbit.

A *planet* is a body that fulfils all three of the above criteria, while a *dwarf planet* complies only with criterion 1 and 2 and, additionally, is not a satellite. All other objects that are in orbit around the Sun and are not satellites, will be referred to as *small solar system bodies*.

The planets can be divided into two groups: the terrestrial (or rocky) planets (Mercury, Venus, Earth, and Mars) and the Jovian planets (or gas giants, with Jupiter, Saturn, Uranus, and Neptune). Pluto, formerly the ninth planet, is now the prototype of the new class of dwarf planets. The division between the terrestrial planets and the gas giants relies upon the location of the snowline, the distance from the Sun beyond which the temperature is low enough for a volatile molecule to condense. For water in the solar system this transition occurs around 3 AU. During the formation of the outer planets, dust grains in the protoplanetary disk beyond the snowline retained an ice mantle, causing the planetesimals in this region to grow faster and taking up a larger part of the material in the disk. In their present form, the gas giants are characterized by a mass that is high enough to gravitationally trap even the lightest gas, H₂ (between 15 M⊕ for Uranus and 318 M⊕ for Jupiter, where M⊕ is the mass of the Earth, 6.0×10²⁴ kg). These planets do not have a distinct surface, but a gradually increasing density of gas, which becomes a supercritical fluid above the critical temperature and pressure.

The terrestrial planets have much lower masses than the gas giants (between 0.055 M⊕ for Mercury and 1 M⊕ for Earth). The composition of the terrestrial planets’ atmospheres depends on the mass of the planet and the surface temperature. On Earth, N₂, O₂, and H₂O are stable in the atmosphere, while on Mars these compounds have escaped and CO₂ is the major atmospheric component.

### 1.3 Mars

Known as *Nergal* in Babylonian astronomy, as *Mangala* in Hindu mythology, as *Ηρ δῆς* (Horus the Red) to the ancient Egyptians (see textbox 1), as *מאמדָמ* (Ma’adim, the one who blushes) in Hebrew, as *Ἄρηος ἀστήρ* (Ares’ star) by the Greeks, the planet is in modern times better
known as the Red Planet, or simply Mars. Mars is a close neighbour to Earth, both in distance and in other properties\(^1\). Because of the resemblance and proximity to Earth, Mars has been the subject of many past and ongoing space missions that search for clues of extinct or extant life.

**Water on Mars**

Images returned from Mars by the Mars Global Surveyor show the presence of gullies, features which may be explained by ground water seepage and surface run off (Malin & Edgett 2000). Malin et al. (2006) have also found gullies that formed in the past decade, by comparing images of the same area from 1999 and 2006, which suggests that, at least occasionally, liquid water may flow on Mars in the present day. The water that formed these gullies might come from large subsurface ice deposits, detected by the gamma-ray spectrometer on board the Mars Odyssey mission (Feldman et al. 2002). Cementation and bleaching along joints in layered deposits have been discovered in observations from the Mars Reconnaissance Orbiter (Okubo & McEwen 2007), indicating fluid alterations in the geological past by subsurface flows.

**Martian mineralogy**

Data returned from the Observatoire pour la Mineralogie, l’Eau, les Glaces et l’Activité (OMEGA) spectrometer on Mars Express, the Thermal Emission Spectrometer (TES) on Mars Global Surveyor, the Thermal Emission Imaging System (THEMIS), and the Mössbauer spectrometers on the Mars Exploration Rovers have provided many new insights into the planet’s mineralogy. The main mineral on the surface of Mars are the silicates olivine, pyroxene, and plagioclase (Bibring et al. 2005). Clay minerals including Fe-rich smectites (such as nontronite), Fe/Mg-phyllosilicates (e.g. chamosite), and Al-rich phyllosilicates (such as montmorillonite) have also been identified (Poulet et al. 2005). These clays are mainly localised on the south Noachian crust. Iron oxide minerals have long been considered to be present on Mars due to the typical red colour of the surface. Iron oxides have been found in various forms of hematite (Morris et al. 1997) and goethite (Kirkland & Herr 2000). Sulfate minerals have been discovered as jarosite (Klingelhöfer et al. 2004), gypsum (Langevin et al. 2005) and kieserite (Wang et al. 2006). Jarosite, hematite, and several other minerals found on Mars, are usually formed in the presence of water. This notion, along with the above mentioned gullies, indicate that there was probably liquid water on Mars for a geologically relevant period. Chevrier & Mathé (2007) give an comprehensive overview of the mineralogical and geological results from the recent Mars missions.

Based on the impact cratering records of the martian surface Hartmann & Neukum (2001) have derived absolute dates for the relative peri-

\(^1\) Actually, Venus is closer in distance, 0.72 AU compared to 1.52 AU for Mars. Also Venus’ mass (0.81 M\(_\oplus\)) is a closer match to Earth than Mars (0.11 M\(_\oplus\)), but with an average surface temperature of 750 K and an atmosphere of 86 bar CO\(_2\) Venus is inhospitable to Earth life.
Textbox 1: Mars in ancient Egypt

In Egyptian mythology stars and planets were thought to represent gods. In the case of Mars, this was the god Horus (Hr, pronounced as Her). The symbol of Horus was the falcon, which is the first character in each of the hieroglyphs depicted here. The names used to point out Mars changed over time. The oldest of the three hieroglyphs shown here (a) was in use during the New Kingdom and the third Intermediate Period (around 1539–715 BC). It can be translated as ‘Horachte is his name’, where Horachte means ‘Horus of the horizon’. The second hieroglyph (b) is usually transliterated as Hr dšr and pronounced as Her desjer. This name was in common use during the Greco-Roman period (332 BC – 395 AD) and is translated ‘Horus the Red’. Hieroglyph (c) is an alternative spelling of (b) and is transliterated as Ḥr dš. For an extensive overview of the names given by the ancient Egyptians to astronomical objects, see Neugebauer & Parker (1969).

ods in the martian geological history defined by Tanaka (1986). Bibring et al. (2006) overlaid the impact cratering timeline with a timeline based on mineralogical data. They define three periods: the phyllosian (early, characterized by the presence of phyllosilicates, found on Noachian terrains), the theiikian (mid period, characterized by the presence of sulfates, linked with Hesperian terrain), and the siderikian (mid to late, characterized by the presence of iron oxides, overlaps with Amazonian period). The different periods are represented in figure 1.3. During the phyllosian, phyllosilicates were formed, which indicates the presence of liquid water during that period. This suggests a warmer and wetter climate in the past. In the interval between the phyllosian and the theiikian, there was probably a period of global change which included high volcanic activity. Large amounts of sulphides were released by the volcanic activity, which acidified the water. As the water gradually evaporated during the theiikian, sulfate minerals were formed. When water evaporation completed, the dry and oxidizing siderikian period started (Bibring et al. 2006).

Organics on Mars

Based on the recent discoveries concerning the mineralogy and geology of Mars (see previous
Figure 1.3
The major epochs in Mars’ geological history, based on mineralogical data (top) and cratering data (bottom). Phyll. stands for Phyllosian and Theii. is short for Theiikian. Adapted from Bibring et al. (2006), cratering chronology from Hartmann et al. (2001).

section), the current view holds that Mars was warmer and wetter in the past. If there was indeed a prolonged period of liquid water on the surface of Mars, the possibility exists that life emerged. One of the goals of the 1976 Viking Landers was to find life on Mars. The Labeled Release (LR) experiment mixed an aqueous growth medium containing $^{14}$C-labelled organic compounds with collected martian soil samples and monitored the head space for release of $^{14}$CO$_2$. The Gas Exchange (GEx) experiment also introduced an aqueous growth medium to soil samples, but monitored the head space for any change in gas composition. A gas-chromatograph–mass-spectrometer (GCMS) measured the volatile organic content of the soil samples, as they were heated to 200, 350, or 500 °C. The LR and GEx experiments both showed a rapid release of $^{14}$CO$_2$ (LR) and O$_2$ and CO$_2$ (GEx), but the gas evolution quickly ceased and did not recover when new medium was added. Also, the GCMS did not detect any organic molecules above the detection limit of several parts per billion (Biemann et al. 1976, 1977). These results lead to the conclusion that the Mars soil is probably not biologically active and that chemical reactivity of the martian soil caused the positive responses in the LR and GEx experiments (Klein 1979).

Although the Viking GCMS may have missed certain types of molecules (Benner et al. 2000, Glavin et al. 2001), the non-detection of organics is still surprising because some organic molecules were expected to be present as a result of meteoritic influx (Flynn 1996). The discrepancy between expected and detected levels of organics is usually attributed to degradation. Solar UV photolysis of atmospheric gas molecules, and subsequent recombination, can produce oxidizing species in the atmosphere, such
as H, OH, HO$_2$, H$_2$O$_2$, O, and O$_3$ (see e.g. Nair et al. 1994). These species are relatively stable in the martian atmosphere and can diffuse into the soil, where they may oxidize organic compounds (Hunten 1979). H$_2$O$_2$ was detected in the martian atmosphere by Encrenaz et al. (2004). Besides an atmospheric origin, oxidants may also be produced by interaction of UV radiation with minerals (Quinn & Zent 1999, Yen et al. 2000). Another relatively unexplored source of degradation is cosmic rays. While UV radiation is attenuated by the soil within a few millimetres, energetic solar protons and cosmic rays have a much greater penetration depth. Dartnell et al. (2007) have shown that cultures of E. coli, B. subtilis, and D. radiodurans at a depth of 2 m in the martian soil would be inactivated by cosmic rays within 30,000, 250,000, and 450,000 years, respectively. MeV protons can destroy organic molecules like benzene (Ruiterkamp et al. 2005), although larger PAH molecules are altered rather than destroyed by fast protons (Bernstein et al. 2003).

1.4 Thesis outline

The previous sections explained the formation and evolution of organic molecules in different interstellar and planetary environments. A prerequisite for the formation of molecules is the presence of elements. The elements are formed in the early universe and during nucleosynthesis in stars. From those elements, large organic molecules are most efficiently formed in cold dense regions in the interstellar medium. Collapsing dense interstellar clouds provide the raw material for star and planetary formation.

Tiny interstellar dust particles grow to large kilometre-sized planetesimals in the protoplanetary disk. These planetesimals collide to form planets. Not all the material of the protoplanetary disk is incorporated into the planets during planetary formation. Some material remains in the planetary system as small solar system bodies, grouped into comets and asteroids. In the early history of our solar system, these small bodies frequently impacted the young planets. By this process, comets and asteroids delivered their molecular inventory to the young planetary surfaces.

Liquid water seems to be essential for all biological systems on Earth. On a planet where liquid water is present, organic molecules may engage in a wide range of reactions. Prebiotic chemistry on Earth involving terrestrial and extraterrestrial matter, probably led to complex structures with emerging functions that subsequently formed the first living cells. Organic compounds in interstellar and planetary environments follow an evolutionary cycle and may be exposed to harsh environments during their lifetime. Investigating the stability of these compounds may provide insight in the link that connects the chemistry in interstellar space and the origin of life of Earth.

Dimethyl ether (DME) is one of the largest organic molecules detected in interstellar space. It is found in regions of high-mass star formation, but only in the hot cores where it exists in the gas-phase. In chapter 2 we present laboratory data on the UV photolysis rate of DME. These data were extrapolated to survival times
for relevant interstellar regions. The photolysis rates were also included in chemical models that calculate the evolution of a hot core. We found that DME is rapidly destroyed by UV radiation in the diffuse interstellar medium and the solar system at 1 AU. Furthermore, we found that UV photolysis of DME in hot molecular cores has a negligible effect on its chemical evolution.

Nitrogen-containing cyclic organic molecules (N-heterocycles) play an important role in terrestrial biology. For example, the nucleobases of the genetic material are N-heterocycles. In chapter 3, we report the destruction rates for the N-heterocycles pyridine, pyrimidine, and s-triazine, measured in the laboratory in a simulated interstellar environment. The results show that the photostability of the N-heterocycles decreases with an increasing number of nitrogen atoms in the ring (figure 1.4). All three N-heterocycles are rapidly destroyed in the diffuse interstellar medium and solar system environments. In dense clouds, pyridine and pyrimidine but not s-triazine, are stable for a period that is comparable to the average lifetime of a cloud (∼10^6 year). We discuss that the formation of N-heterocycles in the gas-phase follows a similar pathway as the formation of benzene, but that it is unlikely to produce molecules with more than 1 nitrogen in the ring. Several classes of N-heterocycles have been found in meteorites (carbonaceous chondrites), but stable isotope data are needed to determine the extraterrestrial origin of these molecules.

Nucleobases are the carriers of genetic information in all living cells. Extraterrestrial nucleobases have been detected only in carbonaceous meteorites. Chapter 4 reports on the UV photostability of the nucleobases adenine and uracil. We found that adenine and uracil are rapidly destroyed in the diffuse interstellar medium and the solar system at 1 AU, but both are stable in a dense cloud for at least the lifetime of the cloud. We discuss possible formation routes and conclude that nucleobases will be difficult to form outside the solar system. In the solar system they are likely synthesized on the parent bodies of meteorites or on comets, where they are protected from solar UV photons.

Mars is thought to receive 2.4×10^5 kg of carbon year^{-1} by meteoritic influx. However, the Viking missions did not detect any organic molecules above a detection limit of a few ppb in the martian surface. This discrepancy is usually attributed to oxidizing reactions in the martian soil. In chapter 5 we report on experiments that tested the stability of amino acids in Mars soil analogues exposed to a simulated martian environment. Mars soil analogues obtained from the Atacama desert were found to vary strongly in pH, ion concentrations, and redox potential, even when the samples were obtained only a few metres apart. The stability of embedded amino acids in the Atacama soil were compared with an iron-rich deposit form Denmark and a sample of the Orgueil meteorite. The differences in amino acid stability are attributed to a different mineral composition of the Mars soil analogues. We conclude that clay minerals can stabilize amino acids and protect them against destruction.

Halophilic archaea have the capability to survive in desiccated and high salt environments. In chapter 6 we tested the survival of halophilic
Figure 1.4
The UV photolysis half-life measured in the laboratory for four six-ring molecules containing 0 (benzene), 1 (pyridine), 2 (pyrimidine), or 3 (s-triazine) nitrogen atoms in the ring.

archaeon *Natronorubrum* sp. strain HG-1, when subjected to high temperature (70 °C), low temperature (4 and −20 °C), desiccation, and irradiation with wavelengths >200 nm. We also desiccated cells mixed with Atacama desert soil. The results show that *Natronorubrum* sp. strain HG-1 is not affected by storage at 4 or −20 °C, while storage at 70 °C completely inhibited growth. Desiccated samples were fully recovered upon rehydration, but desiccated samples mixed with Atacama soil did not show any growth. We conclude that *Natronorubrum* sp. strain HG-1 is not likely to survive on Mars. Additionally, *Natronorubrum* sp. HG-1 could not have survived the early Earth’s ocean, due to its vulnerability to high temperatures.

The origin of prebiotic molecules on Earth is currently unknown, but it is likely that both terrestrial and extraterrestrial sources contributed to the organic inventory on the early Earth. The research described in this thesis focuses on the stability of small organic molecules. The results show that amino acids, nucleobases, and their precursors are very fragile under most interstel-
lar conditions. Amino acids are also degraded by environmental conditions on Mars. Certain types of minerals may shield these compounds from degradation.

The formation of some prebiotic molecules, e.g. nucleobases, is unlikely to proceed efficiently in interstellar environments. The combination of a high formation reaction barrier and fast degradation by UV radiation, make it unlikely that those organic molecules are present when the planetary system is formed. Many organic molecules, including amino acids and nucleobases, have been found in meteorites, indicating that these molecules can be synthesized in the solar system on the meteoritic parent bodies.

In order to contribute to the organic inventory of a newly formed planet, prebiotic molecules must have formed in protected environments in the solar system, such as comets, meteorites, planetary oceans, or subsurface regions. Given the right conditions on the planet, this starting material may react to form larger structures and, ultimately, life.

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