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Any word on which three versed ones (intelligent ones) agree can be told anywhere; otherwise it must not be relied on. Do compare your word and the word of the others with the words of the versed ones (intelligent ones): if it will be in agreement you can say, otherwise there is no way to say.

Whoever lies with intention or through sorcery, or spies upon the behavior of others, or intervenes between the two arguing ones to help the one against the other is to be put to death.

Excerpts from Great Yassa of Genghis Khan

(An original list of the regulations legendarily declared by Genghis Khan on Kurultai in 1206 is not preserved. This text is based on reconstructions of Great Yassa by Rashid-al-Din Hamadani (1247 – 1318) and Al-Maqrizi (1364 – 1442) assembled by Erenzhen Khara-Davan in the work "Genghis Khan as a Warlord and His Heritage" (in Russian), Belgrade, 1929)

I

Introduction

To a young boy, who is trying to build for the first time his own cosmological picture of the Universe consisting of myriads of galaxies, the endless space between stars may seem to be just an empty barrier, a necessary "evil" that has to be passed before reaching the next island of matter – a star system similar to our own. To me, the concept of interstellar medium was for the first time introduced by Stanisław Lem's novel 'The Magellanic Cloud' (1955), where the first human expedition, which undertakes the venture of leaving our Solar system and travelling to a nearby star in search for a new World, had encountered an unexpected problem. Their spaceship was overheated for unknown reasons. It took a while before engineers on the ship had realized the cause: "The source of the heat rise could only be outside, but outside there was the emptiness. One cubic centimeter of this emptiness contains only few atoms, and that is why it could be considered as an absolute vacuum in comparison to the gas density under terrestrial conditions, where one cubic centimeter of gas has several trillions of molecules. However, "Gaia" moved with such velocity, that every square centimeter of its surface collided with 800 billions of atoms per second; this was enough for friction to take place and overheat the rocket". This was the first time when I looked at the interstellar medium as a system that has its own structure and life. However, it was difficult to me to imagine at that time that the chemistry of this "emptiness" would eventually become the subject of my thesis.

1.1 Star evolution

The interstellar medium (ISM) is an extremely dilute environment; nonetheless, it plays an important role in the evolution of our Galaxy. The ISM is the place where new stars and planets are formed from the remnants of stars that died in a former star cycles. A simplified scheme of this cycle of life and death is depicted in Fig. 1.1. The ISM is filled with gas (99% in mass) and dust (1% in mass). The gas is composed by hydrogen (H, 70%), helium (He, 28%), and a fraction of heavier elements; the dust comprises mainly silicate grains and carbonaceous material. Gas and dust are not distributed uniformly over the ISM. Therefore, there exist regions that are dominated by high densities and lower temperatures. With time, gravitational attraction or external shockwaves induce these cold regions to reach even higher densities (10^2-10^6 particles cm^{-3}). These values are still extremely low and can be considered as a perfect vacuum if compared to terrestrial standards. However, the size of these objects is so large (>10000 astronomical units) that the visual extinction by the dust grains does not allow visible light to pass through and therefore does not reach the observers, *i.e.*, us (Tielens 2005). This explains the name given to these objects, dark (molecular) clouds (see Barnard 68 in Fig. 1.1). When gravitational attraction induces further collapse of the cloud over a period that depends on the mass of the dark cloud (10^5-10^6 years for a cloud resulting in a Solar mass star), the innermost regions reach high enough density and temperature for a protostar (a future star) to be formed inside. For the conservation of the angular momentum, this process is accompanied by the formation of a protoplanetary disk and outflows (see DG Tau B in Fig. 1.1). This is not yet a star system, but also not a cloud anymore and therefore is called a young stellar object (YSO). It takes about 10 millions years before a star finally accretes most of the nearby material and reaches its final mass, while the protoplanatery disk is segregated and gives birth to future planets. A low-mass star with a planetary system similar to our own Solar system usually lasts for about 10^{10} years before most of the hydrogen fuel inside the star is consumed and it becomes a Red Giant, approaching the end of its life cycle. During all these stages, starting from YSO and ending with the Red Giant, the system releases gas and dust into the ISM that in turn provides material from which new stars are formed. Our own Sun belongs to the second-third generation of stars.

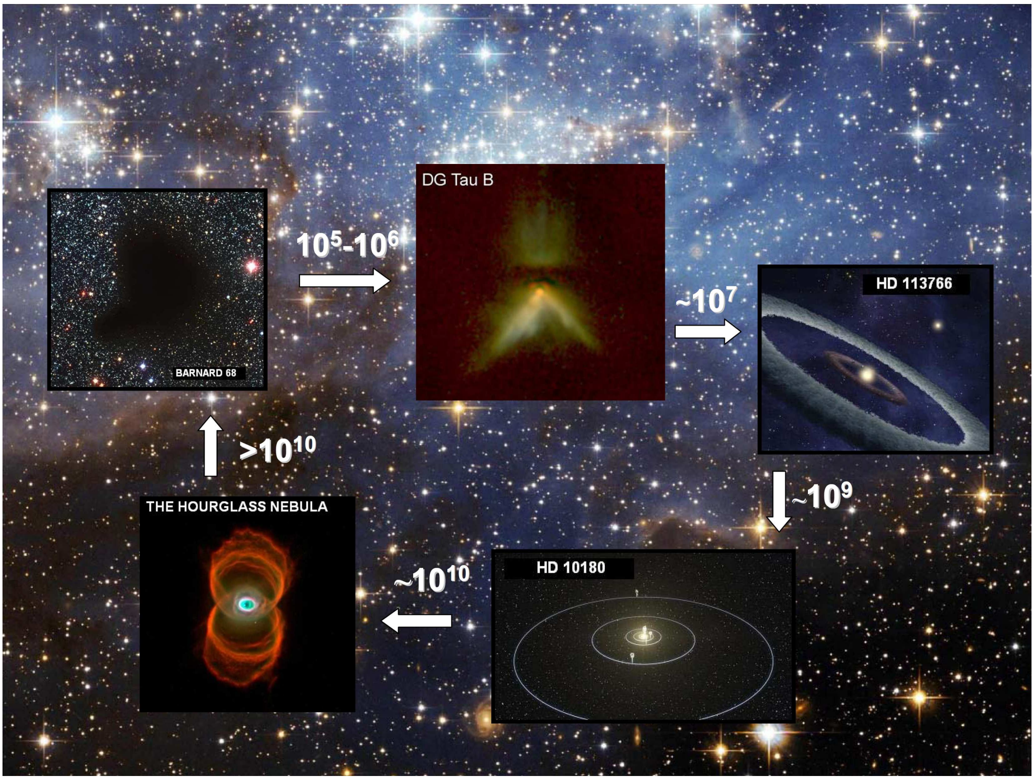

Figure 1.1. Artistic representation of a star formation cycle in the ISM. All objects are chosen to be close to the solar mass. Arrows indicate time in years. Pictures are taken from ESO and NASA web pages.

The study of every single stage of the star formation cycle involves different physical and chemical branches of science and faces many unresolved issues. This thesis mostly focusses on the very first steps of star formation, *i.e.*, the dark cloud stage and the formation of YSOs. This focus has two reasons: on one hand, infrared (IR) observations toward dark clouds show that these regions already possess a rich chemistry even before stars and planets are formed. On the other hand, an exact understanding of the chemical processes involved in the formation of interstellar species observed in these regions will help scientists to unlock the origin and fate of the organic molecules that are present on Earth and that at some point contributed to the formation of life.

1.2 Molecules in star forming regions

1.2.1 The role of dust and ice

More than 180 different molecules have been identified in the circumstellar and interstellar media (Woon 2014). These species comprise simple molecules, like H_2 or CO – two of the most abundant molecules of the ISM – as well as about 50 molecules with 6 and more atoms, organic molecules, and structural isomers (Herbst & van Dishoeck 2009). This observed chemical complexity in space is the cumulative outcome of gas, dust, and gas-dust interactions. Many species can be formed in the gas-phase. However, gas-phase reactions alone cannot explain the observed abundances of many detected molecules, particularly the more complex organic species. Therefore, solid state processes become important. At low temperatures (~10 K), (sub)micrometer-sized dust grains act as small cryopumps onto which gas-phase molecules accrete. In dense cores (the innermost part of Molecular Clouds), the approximate timescale at which gas-phase species deplete onto grains is about 10^5 years, that is comparable to the lifetime of a dark cloud. Therefore, during the first stage of star formation, most of the species, with the exception of the lightest ones (H_2, He), are expected to be largely frozen-out onto interstellar grains. The resulting ice mantle provides a local molecule reservoir, which may be as thick as several tens of monolayers (ML, where 1 ML = 10^{15} molecules cm^{-2}). It also provides a 'third body' to which two reactive species can donate excess energy allowing formation of a stable molecule, a process that otherwise is impossible in two body gas-phase collisions. Although accretion rates on the surface of interstellar grains are extremely low, over thousands of years grains accumulate enough material for complex chemistry to take place. It is generally accepted nowadays that solid state astrochemistry plays an important role in the chemical enrichment of the ISM. Grains play here the same role of a solid-phase catalyst in gas-phase chemical synthesis.

1.2.2 Interstellar ice composition

The interstellar ice composition can be derived from mid-infrared observations of molecular clouds along the line of sight to a background star. Alternatively, a newly formed protostar embedded into a young stellar object can be used as a source of light. The ice absorption spectra are then obtained by subtracting the emission profile of a background star or embedded protostar from the observed spectra. The features leftover correspond to the absorbance of molecules in the line of sight between the emitting object and the observer. Observations in the mid-IR range from ground-based telescopes are limited to a few spectral windows, because of the presence of telluric lines in the Earth atmosphere. This limitation is overcome by airborne and space observations. Observations with the Infrared Space Observatory (ISO) (Whittet *et al.* 1996, Gibb *et al.* 2000, Gibb *et al.* 2004) and the Spitzer Space Telescope (, Boogert *et al.* 2008, Pontoppidan *et al.* 2008, Bottinelli *et al.* 2010 and Öberg *et al.* 2011) greatly improved our knowledge on interstellar ice composition by exploring wavelength ranges inaccessible from Earth. Some examples of ice spectra toward three chosen protostars are shown in Fig. 1.2.

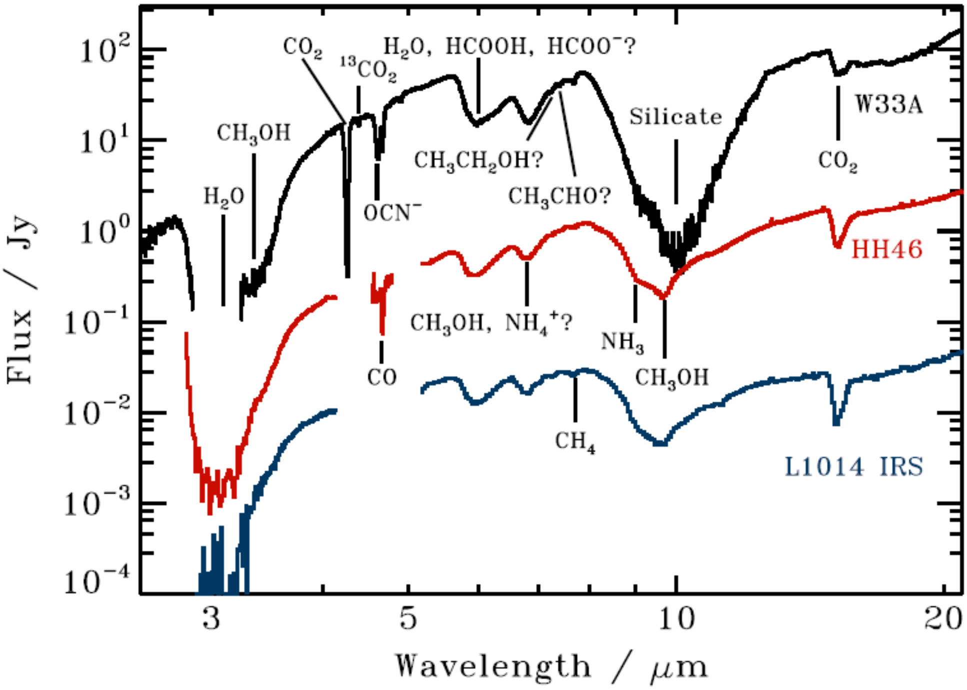

Figure 1.2. Ice spectra towards star forming regions W33A , HH46 and L1014 IRS with solar luminosities of 10^5, 12 and 0.09, respectively, obtained from ISO, Spitzer, and ground-based observations (Gibb *et al*. 2000, Boogert *et al*. 2004). The Figure is taken from Öberg *et al*. (2011).

Despite the different nature of the three objects reported in Fig. 1.2 (low-, high-mass YSO, and background star), similar spectral features are present in all these sources. A detailed and quantitative study of these bands, however, would not be possible without the use of laboratory ice spectroscopy (Hudgins *et al*. 1993, Gerakines *et al*. 1995, Baratta & Palumbo 1998, Cuppen *et al*. 2011). The systematic laboratory investigation of IR band profiles of pure and mixed ices (*i.e.*, containing two or more species) over a wide range of temperatures combined with the knowledge of all the absorption band strengths of each molecule allows for the identification of the components of the interstellar ice mantles. The main components of interstellar ices are reported in Table 1.1 and are – in order of decreasing abundance – H_2O, CO, CO_2, CH_3OH, NH_3, CH_4, and XCN. The latter is likely due to OCN^-. Moreover, from a comparison between laboratory work and observations, interstellar ices appear to be layered. The first layer is a H_2O-rich polar-ice with embedded CO_2, CH_4, and NH_3. The observed abundances of these species correlate with the abundance of solid H_2O. The second, top, layer is a non-polar CO-rich ice, which likely contains also most of the solid CH_3OH and OCN^- (Fuchs *et al*. 2009, Cuppen *et al*. 2011, Fedoseev *et al*. 2014). There is also evidence for the presence of more complex molecules, like HCOOH, CH_3CHO, and C_2H_5OH (Schutte *et al*. 1998, Boudin *et al*. 1998). However, better constraints, *i.e.*, higher quality spectra, especially at 5-10 μm, are needed to unambiguously identify these species in the solid phase. Moreover, mid-IR observations are insensitive to homonuclear diatomic molecules, like O_2 and N_2. Although O_2 is not expected to be observed in the ice due to its chemical reactivity, N_2 may be in fact one of the most abundant ice components, because of its chemical inertness and stability.

Table 1.1. Abundance medians and lower and upper quartile values of ices and individual ice components with respect to H_2O ice. Taken from Öberg *et al*. (2011).

Ice Feature	Low Mass Protostar	High Mass Protostar	Background Star
H_2O	100	100	100
CO	38^{61}_{20} (29)	13^{19}_{7}	31
CO_2	29^{35}_{22}	13^{22}_{12}	38^{41}_{32}
CH_3OH	7^{12}_{5} (3)	8^{16}_{8} (4)	8^{10}_{7} (4)
NH_3	5^{6}_{4}	16^{17}_{10} (5)	-
CH_4	5^{7}_{4}	4^{4}_{2} (2)	-
XCN	$0.6^{0.8}_{0.2}$ (0.3)	$0.8^{1.4}_{0.4}$ (0.6)	-
CO (pure)	21^{36}_{7}	3^{6}_{2}	-
CO in H_2O	13^{19}_{7}	10^{12}_{5}	-
CO in CO_2	2^{3}_{1}	$1.3^{1.6}_{0.4}$ (0.3)	-
CO_2 (pure)	$2^{4}_{0.3}$	2^{2}_{1}	-
CO_2 in H_2O	20^{23}_{15}	9^{15}_{6}	24
CO_2 in CO	5^{7}_{4}	5^{6}_{2}	6
OCN^-	$0.4^{0.4}_{0.3}$ (0.2)	$0.6^{1.4}_{0.4}$	-

1.3 Interstellar ice evolution and chemistry

To date, it is generally accepted that a substantial part of the stable and complex species identified so far, is formed on icy dust grains *via* non-energetic atom addition induced reaction schemes. Since solid-state radical-radical and radical-molecule reactions often do not require any activation energy, they can occur even at extremely low temperature (10 K): *i.e.*, in the innermost part of molecular clouds, where newly formed molecules are largely shielded from radiation by dust particles. These regions are part of collapsing envelopes that feed new stars - young stellar objects - and provide the original material from which comets and ultimately planets are made.

Grain surface chemistry is governed by the accretion rate of gas-phase species onto the grains, the surface migration rate which sets the reaction network, and the desorption rate. Therefore, it also depends on a number of physical parameters, such as cloud density, ice temperature, and chemical composition of the grain surface. Figure 1.3 shows a schematic representation of ice evolution starting from the prestellar stage (dark cloud) through the collapsing envelope resulting in the formation of a protoplanetary disk around the protostar. In short, a less-volatile water-rich ice is formed on top of bare grains. Then, with increasing densities to 10^4-10^5 cm^{-3}, CO freeze-out occurs and CO-rich ice mantles are formed on top of the water-rich ice. This newly formed CO-rich ice is hydrogenated to form most of the interstellar CH_3OH observed in space. Molecules formed on the surface of dust grains can in turn desorb to the gas phase. At low temperature, this can be achieved by the interaction of the ice with cosmic rays, cosmic ray induced UV-photons, or as the result of grain collisions. When the core collapses and a protostar is formed, ice will further experience heat, UV- and cosmic rays induced reactions in the region close to the newly formed protostar. At this stage, volatile species desorb, while less-volatile species undergo a “warm” ice chemistry**,** and, as a result, more complex (organic) species are formed in the ice mantles. When the temperature reaches values of 100 K and higher, water ice and other less-volatile species trapped in the ice start to sublimate. Alternatively, some of the icy grains will flow into the mid-plane of protoplanetary disk, where they are shielded from heat and UV irradiation caused by the newly formed protostar and from the external UV-field. In this region, planets and comets are formed. Therefore, understanding formation mechanisms and delivery processes of complex and even prebiotic molecules to planets is fundamental for a better understanding of the early composition of Earth, and its primordial oceans.

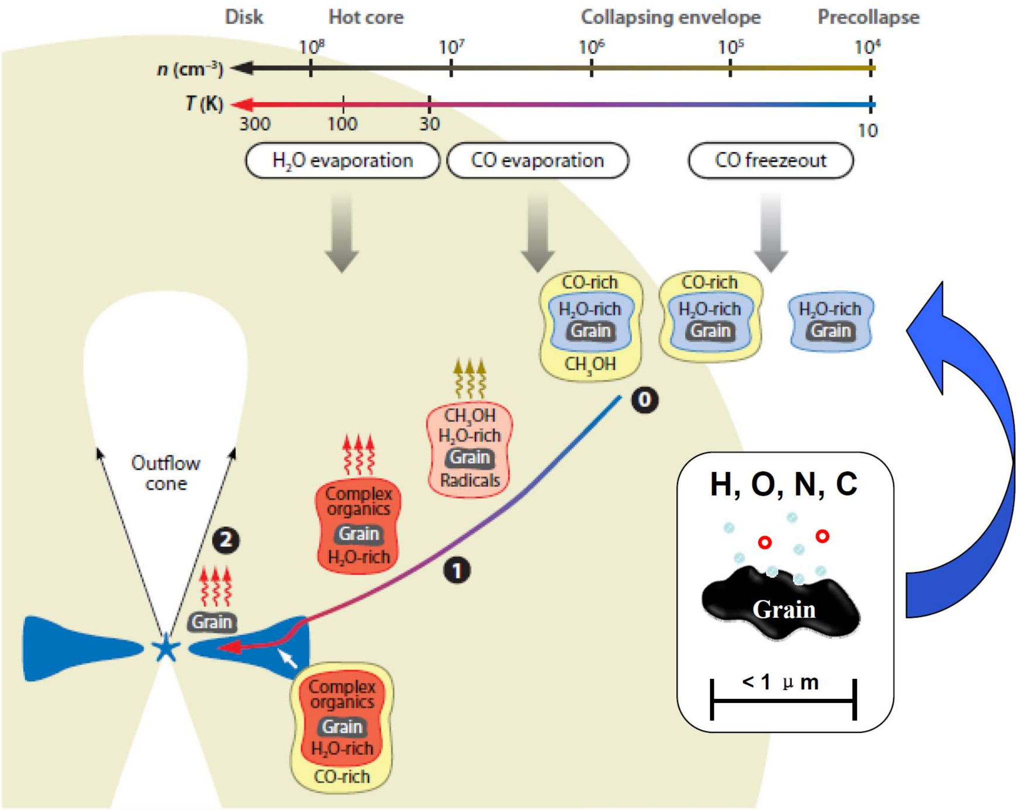

Figure 1.3. Evolution of the ice composition starting from the prestellar stage through the collapsing envelope, and into a protoplanetary disk. Adapted from a figure by van Dishoeck & Visser (Herbst & van Dishoeck 2009).

Some of the most important mechanisms that rule the interstellar ice chemistry are discussed below**:**

1) *Atom and radical addition reactions*. Among all the possible atom addition reactions (*e.g.*, H, O, N, and C) occurring in space, the most important one is the hydrogenation of the ice. This is not surprising since hydrogen is the most abundant element in the Universe. Some of the species formed through hydrogenation reactions on the surface of dust grains are H_2 (through H + H), H_2O (through hydrogenation of $O/O_2/O_3$), NH_3 (through hydrogenation of N atoms), CH_3OH (through hydrogenation of CO), and possibly CH_4 (through the hydrogenation of C atoms). CO_2 can be formed through atom and radical addition reactions: CO+O and CO+OH. Radical-radical and radical-molecule reactions often do not require any activation energy and therefore can easily proceed even at low temperature (10 K). Three of the most relevant reaction mechanisms on the grain surface are the Langmuir-Hinshelwood (L-H), Eley-Rideal (E-R), and hot-atom mechanisms (see Figure 1.4). In the case of the

Langmuir-Hinshelwood mechanism, two reactants are adsorbed on different surface spots of an interstellar grain and reach thermal equilibrium with the surface before one or both of them diffuse to find each other and react. In the Eley-Rideal mechanism, one of the reactive species directly lands on top of the other and the reaction immediately occurs before thermal equilibrium is reached. The hot-atom mechanism is a combination of both: one species is located on the surface in thermal equilibrium, while the second one lands on the nearby surface spot; migration and reaction occur before the thermal equilibrium is reached.

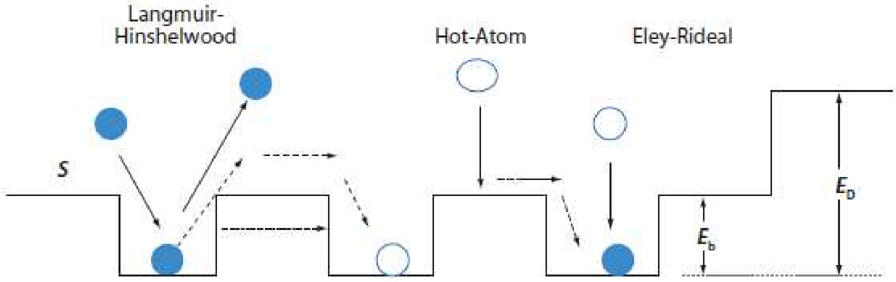

Figure 1.4. Three mechanisms for surface reaction on the grain surface. E_d is the desorption activation barrier; E_b is an activation barrier of the diffusion from a surface spot to another. The figure is taken from van Dishoeck & Herbst (2009).

Distinguishing between Langmuir-Hinshelwood, Eley-Rideal, and Harris-Kasemo ("hot-atom") mechanisms is of great importance when the temperature of the adsorbing species is significantly higher than the temperature of the surface. For the Eley-Rideal and the hot-atom mechanisms, the high energy of the incoming species helps to overcome the activation barrier of the reaction. This is not the case if the Langmuir-Hinshelwood mechanism takes place, where both the reactants are in thermal equilibrium with the ice surface. In cold dark molecular clouds, the difference in temperature between the accreting species and the ice surface is not large. Furthermore, the Langmuir-Hinshelwood mechanism is the most important mechanism in non-energetic surface reactions, because of the extremely low accretion rates even in the densest regions of molecular clouds. However, under laboratory conditions, the temperature of the exposing atom beams is often equal or higher than the room temperature. This deviation from the conditions found in space has to be taken into account during the interpretation of laboratory data. Monte Carlo (MC) simulations (Cuppen *et al*. 2013) can be used to simulate and reproduce laboratory results to investigate qualitatively and quantitatively all the mechanisms at play in the solid phase (*e.g.*, deposition, diffusion, segregation, reaction, and desorption). Results from these models can then be included into astrochemical MC models to extend laboratory results to interstellar timescales and fluxes (Fuchs *et al*. 2009, Cuppen *et al*. 2009, Vasyunin & Herbst 2013). The experimental investigation of non-energetic reaction routes is the main subject of this thesis.

2) *UV-induced reaction routes*. As opposed to the neutral-neutral, atom, and radical addition surface reactions discussed above, UV processing of ices provides an energetic input that leads to the excitation of molecules and dissociation of molecular bonds followed by the formation of “hot” fragments, *i.e.*, radicals, atoms, and ions with high internal energy. These “hot” fragments can in turn react with the surrounding molecules and easily overcome activation barriers, desorb from the ice surface, or diffuse into the bulk of the ice and even eject other molecules from the surface (Arasa *et al*. 2010). A complete analysis of the UV-induced reaction network is often challenging without the knowledge of photodissociation and photoionisation cross sections for all the molecules involved in the UV photolysis process. Furthermore, these cross-sections and photodissociation branching ratios are wavelength dependent and, therefore, significant variations in the final outcome may occur, depending on the energy of the UV-photon applied. Secondary processes, like photodesorption, and structural changes in the ice morphology should also be taken into account. UV-photon induced chemistry can efficiently lead to the formation of complex organic species in the ice mantles. Therefore, UV-photolysis significantly increases complexity in the ice (see Öberg *et al*. 2009). At high doses and high enough thickness of the ice, a complex polymeric refractory residue can be formed as well (D'Hendecourt *et al*. 1996, Allamandola *et al*. 1988, Greenberg *et al*. 1995, Herbst & van Dishoeck 2009).

3) *Cosmic rays*. The chemical composition of the ices can be further modified by ion and electron bombardment. For example, the energy released by a highly energetic ion passing through a material causes the dissociation of hundreds of molecules along their path. These fragments can then recombine. As a result of the interaction between a cosmic ray and the ice, hundreds of new molecules including both simple and more complex molecules are formed. Moreover, the impact of a cosmic ray with the ice surface causes the release of some of the ice material into the gas phase through sputtering and local heating. In this respect, cosmic ion irradiation is a more complex mechanism than UV-photolysis that involves only a single-photon event (Baratta *et al*. 2002).

4) *Thermal processing*. During their evolution, star-forming regions are exposed to thermal processing. Most of the chemistry in interstellar ices takes place within the range of temperatures 10-100 K. Thermal processes can induce sublimation of ice material, changes in the ice morphology, segregation of species in the ice, neutral-neutral reactions – such as deuterium-exchange reactions – and charge transfer within the ice (Ratajczak *et al* 2009, Novozamsky *et al*. 2001 and Theule *et al*. 2011).

The aforementioned mechanisms may dominate in different regions of the ISM or at different evolutionary stages in star-forming regions, but all mechanisms have in common that they contribute to a higher molecular complexity in space.

1.4 Chemistry of interstellar ices in the laboratory

1.4.1 Experimental setups

SURFRESIDE

Atom and radical addition reactions in interstellar ice analogues are here studied using SURFRESIDE, an ultrahigh vacuum (UHV) setup, and its more recent upgrade SURFRESIDE^2, operational since 2012. SURFRESIDE^2 is an extended version of the former system and comprises a second atom line to allow the simultaneous use of two atom-beams together with regular molecular dosing lines. Details of both setups are available from Fuchs *et al*. (2009) and Ioppolo *et al*. (2013) (Chapter 2 of this thesis). The use of an UHV setup (base pressure ~10^{-10} mbar of mainly H_2) allows us to grow ices with submonolayer precision. Extremely low background gas deposition rates provide enough time to perform selected atom-bombardment experiments under fully controlled laboratory conditions (*i.e.*, the exposure of background gas H_2O, N_2, and CO_2 to a cold sample at 10^{-10} mbar requires almost 4 hours to obtain 1 ML surface coverage).

Ices are deposited with controllable deposition rates on a gold substrate at a selected temperature. Deposition with a variable incident angle is possible. The substrate is mounted on the tip of a cold head of a He close-cycle cryostat and a temperature regulation is realized by means of a heating wire. The absolute temperature precision is ~2 K while the relative precision is as high as 0.5 K

The setup comprises two molecular deposition lines and two atom-beam lines. In order to provide diversity in the way atoms beam are generated two different atom sources are used: (*i*) a Hydrogen Atom Beam Source (HABS, Dr. Eberl MBE-Komponenten GmbH, see Tschersich 2000) that produces H or D atoms through thermal cracking of H_2 or D_2; (*ii*) a Microwave Atom Source (MWAS, Oxford Scientific Ltd, see Anton *et al*. 2000) that generates H, D, O, and N atoms as well as OH, NH, and NH_2 radicals by using a microwave discharge (125-300 W at 2.45 GHz). In the following chapters of this thesis, various parent molecules are used to generate atom beams: H_2(D_2) for H(D) atoms, O_2 and

N_2O for O atoms, N_2 and NH_3 for N atoms, H_2O for OH radicals, and NH_3 and even mixtures of two gases N_2 and H_2 for NH and NH_2 radicals. A nose-shaped quartz pipe is placed along the path of each of the atom beams to efficiently quench the excited electronic and ro-vibrational states of the formed atoms and non-dissociated molecules through collisions with the walls of the pipe before they reach the ice sample. Furthermore, the experimental results on hydrogenation (deuteration) of interstellar ice analogues can be repeated sequentially by using the thermal cracking source and then the microwave discharge to increase the "confidence" level of the obtained results.

Two molecular deposition lines that allow for separate depositions of stable molecules are used to simulate different molecular environments as typical for different evolutionary stages of interstellar ices (*i.e.*, polar, H_2O-rich, or non-polar, CO-rich, interstellar ice analogues) In this way, it becomes possible to co-deposit a number of various atoms and molecules together, simulating selected astrophysical conditions. Furthermore, experiments performed in a H_2O or CO environment have the advantage that reactive species can donate their excess energy to the surface (H_2O or CO) before they participate into reactions through the Langmuir-Hinshelwood mechanism. Thus, reactants are most likely thermalized to the surface temperature and their kinetic energy should not affect the final results. Another advantage of using H_2O and CO matrices is to make sure that the reactive atoms participating in the selected reaction routes are deposited isolated and not as dimers, trimers, or even larger oligomers.

Two different experimental procedures are here regularly applied. In "pre-deposition" experiments, ices are first deposited on the sample and are subsequently exposed to a thermal atom-beam. In this case, the formation and consequent destruction of the intermediate products followed by the formation of final products can be monitored. This allows us to obtain kinetic curves that then can be fitted by a system of differential equations in order to obtain formation rates. However, this technique has considerable drawbacks. Limited penetration depth of atoms into the pre-deposited ice causes low final yields of the products. Furthermore, unstable intermediate radicals are rapidly converted to the stable species and consequently hard to identify. These drawbacks can be overcome by using a "co-deposition" technique. In the latter case, molecules and atoms are deposited simultaneously with specified rates. Varying the ratio with which reactive species are deposited, formation of only first intermediate products without further conversion into the stable final products or, on the contrary, a thick ice of only final products can be obtained. These two techniques fully complement each other.

CRYOPAD

Several UV photolysis experiments shown in this thesis are performed by using the

CRYOgenic Photoproducts Analysis Device (CRYOPAD), which is described in details by Öberg *et al*. (2009) and references therein. As for SURFRESIDE, the rotatable gold-coated substrate in CRYOPAD is mounted on the tip of a cold head of a He close-cycle cryostat in the centre of a stainless steel UHV chamber. The temperature of the substrate is controlled between 15 and 300 K by means of a heater and a temperature controller. Ice deposition proceeds through a molecular dosing line by injecting either pure gases or preliminarily prepared gas mixtures. After deposition of an ice, the film is irradiated by UV light from a broadband hydrogen microwave discharge, which peaks at Ly-α (121 nm) and around 160 nm. The experiments discussed in chapter 4 are performed sequentially, but the system also allows the simultaneous molecular deposition and UV irradiation of the growing ice.

1.4.2 Measuring techniques

In both SURFRESIDE^2 and CRYOPAD, ice composition is monitored *in situ* by means of Reflection Absorption Infrared Spectroscopy (RAIRS) using a FTIR spectrometer, which covers the range between 4000 and 700 cm^{-1}. While 1 cm^{-1} is the typical spectral resolution used in the chapters of this thesis, spectral resolution can be varied between 0.5 and 4 cm^{-1}. The main advantage of the RAIRS technique is the ability to detect products of the reactions investigated in the solid phase at the sample temperature and to monitor the amount of products over time, *i.e.*, to obtain kinetic curves. The choice of RAIRS over transmission infrared spectroscopy is due to the higher sensitivity of the RAIR technique: the glancing angle of an infrared beam (*e.g.*, 8° to the substrate plane) results in enhancement of the *p*-polarized electric field at the surface and, therefore, to a gain in sensitivity. Furthermore, this effect is further enhanced by the increase in the path length of the beam through the deposited ice film and by the fact that the beam has to pass through the ice film twice, once before reaching the sample (gold-coated mirror) and a second time after reflecting from the sample. Such geometry improves the minimal detection limits of the infrared technique. Another great advantage of the RAIR technique is that only the ice deposited on one side of the substrate is probed. This is because the substrate is a gold-coated piece of copper, which reflects IR light. In the case of transmission spectroscopy, an infrared transparent material is used as a substrate window. Therefore, molecules are deposited on both sides of the window through direct or background deposition, as the result the final IR spectrum is a combination of the two ices. This can potentially be an issue during data analysis when only one of the two sides of the substrate window is processed to induce chemistry.

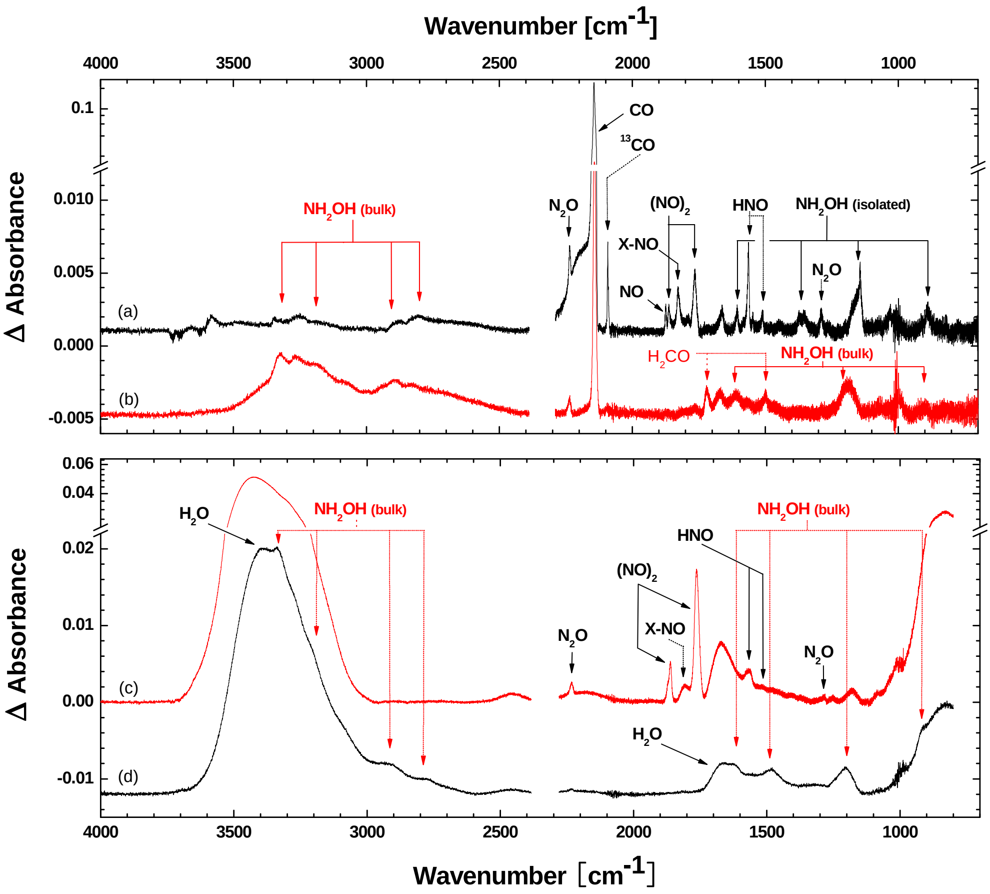

Figure 1.5. RAIR spectra of NO hydrogenation experiments taken from chapter 4. The upper panel shows co-deposition spectra of NO, CO and H atoms with NO:CO:H = 1:6:15 (a) and 1:1:20 (b). On the lower panel co-deposition spectra of NO and H_2O with H atoms for NO:H_2O:H = 1:6:3.5 (c) and 1:6:15 (d) are shown. All spectra are acquired at 15 K.

Species in the ice are identified according to their specific frequency fingerprint at which infrared light is absorbed. These specific frequencies, in turn, can be the same for few different species that share same functional groups or can shift for the very same species according to the specific molecular environment that surrounds them (polar vs. non-polar ice). For example, in Figure 1.5, one can see that the absorbance features of H_2O overlap with the NH_2OH bands. Moreover, the NH_2OH absorption features in Fig. 1.5(b) are shifted compared to those of NH_2OH in Fig. 1.5(a), where 6 times more CO is co-deposited and the formed NH_2OH molecules are in a way more isolated from each other. In addition, hydrogen bonds formed between polar species significantly broaden their absorption features making their exact assignments and quantification harder. The band broadening effect is illustrated in Fig. 1.5, where hydroxylamine (NH_2OH) absorbance features are significantly wider in presence of water (lower panel of Fig. 1.5), and narrower when NH_2OH is mixed with CO (upper panel of Fig. 1.5). Low amounts of products formed in the experiments may significantly affect a correct assignment of the formed species and a quantitative analysis of the results. Furthermore, diatomic homonuclear molecules (*e.g.*, N_2, O_2, and H_2) are infrared inactive and their detection is not trivial if only infrared techniques are used. Therefore, a second analytical technique is routinely used to constrain the obtained IR results. This is Quadrupole Mass Spectrometry (QMS) in combination with Temperature Programmed Desorption (TPD) experiments.

In a TPD experiment a deposited ice sample is heated linearly with a selected rate (normally 1-10 K/min), molecules eventually desorb and their gas-phase signal is monitored by means of the QMS. Every chemical species has a specific desorption temperature, depending on its binding energy to the surface spot it occupies. When the temperature of the ice sample reaches the desorption temperature of a constituent, the latter evaporates into the gas phase, where it can be ionized in the ion source of the QMS. Ionization is realized through the impact with electrons that are produced by a hot filament. When ions are produced, they undergo a selection process that takes place in the quadrupole mass filter in a way that only the ions with a selected mass-to-charge (m/z) ratio can reach the detector at any given time. The detected signal is proportional to the density of the produced ions of a given m/z ratio. Up to twelve m/z signals can be recorded in series over time. As a result, a three dimensional plot of temperature *vs*. m/z *vs*. intensity of the signal can be obtained. However, the analysis of such plots is not trivial. The temperatures at which different species desorb can be close or even overlap. Furthermore, for the very same species the desorption temperature depends on the binding energy to the surface and therefore on the chemical composition of the surface (*e.g.*, H_2O ice, CO ice, amorphous carbon, and amorphous silicates) and even for the same type of surface, the binding energy can vary a lot because the surface is usually not uniform and different adsorption spots can have different binding energies. Moreover, TPD experiments of mixed ices are even harder to analyze because, for instance, volatile species can react or be trapped in a matrix of non-volatile species during a TPD. This way, they can only desorb at higher temperatures, together with the non-volatile species. The full picture is further complicated by the fact that species are fragmented upon electron impact in the ion source of the QMS, and a number of charged fragments are produced with a certain ratio (depending on the electron energy), forming a unique pattern for each species. This is illustrated in Fig. 1.6.

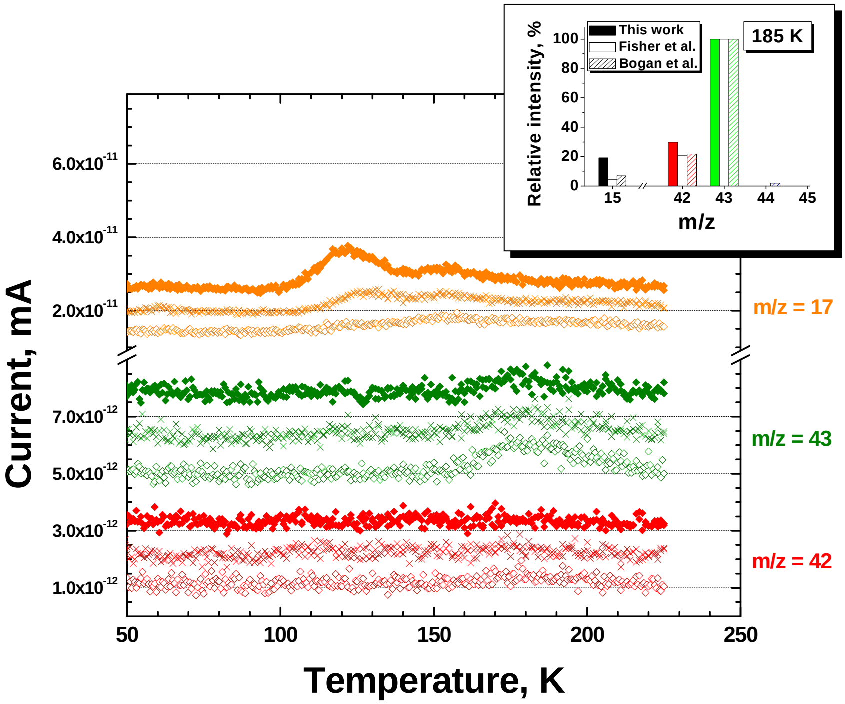

Figure 1.6. TPD spectra of three distinct experiments (this figure is taken from chapter 6 of this thesis). Three curves for each of the m/z values are shown. These curves from top to bottom correspond to smaller amounts of NH_3 formed in the ice (peak starting at 100 K for m/z = 17) and higher amounts of HNCO formed (peak starting at 160 K for m/z = 43). In the inset in the right top corner of the figure, a comparison between fragmentation pattern taken from the literature and fragmentation pattern obtained in our experiment is given.

Figure 1.6 shows that the desorption peak of NH_3 is slightly shifted toward higher temperatures when smaller amounts of NH_3 are formed. This can be explained as follow: when a smaller amount of NH_3 is adsorbed on the surface of the sample, it mainly occupies the "best" surface spots, *i.e.*, with high binding energy, while for a higher amount of NH_3, also spots with low energy are occupied and as a consequence the desorption peak shifts toward lower temperatures. The fragmentation pattern of HNCO (inset in the Fig. 1.6) is quite similar to the one reported in literature. In return, this greatly enhances the level of confidence of this assignment. In this thesis, care has been taken always to analyze more than one m/z value for the same chemical species in order to achieve reliable results.

TPD experiments can also be performed by using RAIRS as an analytical tool. In this case, RAIR difference spectra monitor the chemical composition of the ice that is not desorbed yet. In this thesis, the same experiment is often repeated twice to use both techniques, or both RAIR and QMS spectra are recordered simultaneously during a single experiment. This procedure allows making unambiguous identifications of several surface reaction products (see next chapters). Finally, it is important to note that, although QMS is a more sensitive technique than RAIRS, QMS data of a TPD experiment do not provide *in situ* information. Therefore, RAIR spectroscopy at low temperatures is considered the primary analytical tool in all the following chapters.

1.5 This thesis

This thesis presents detailed laboratory based research on solid-state atom and radical addition reactions aimed to increase our understanding of the chemistry that occurs in interstellar ices. The focus here is on the chemistry of nitrogen-bearing species as well as on the formation of molecules of astrobiological importance. An attempt to provide a link between the formation of the simplest nitrogen-bearing molecules and simplest amino acids is made. In addition to amino-acid formation routes, the simplest representatives of two other classes of prebiotic compounds - aldoses (polyhydroxy aldehydes) and polyols - with their corresponding formation routes are presented. The main conclusions for each chapter are linked to Fig. 1.3 and in particular to the corresponding stages of interstellar ice evolution. Here, a brief description of every chapter is made.

Chapter 2 presents the new setup SURFace Reaction SImulation DEvice (SURFRESIDE^2) that allows a systematic investigation of solid-state reaction pathways resulting in the formation of molecules of astrophysical interest. This ultrahigh vacuum setup focuses on studying atom and radical addition reactions in interstellar ice analogues at astronomically relevant cryogenic temperatures. The implementation of two atom-beam lines along with two molecular beam deposition lines makes it possible to expose deposited ice molecules to different atoms and/or radicals sequentially or at the same time. Special efforts are made for precise atom flux determinations, in order to quantitatively characterize different reaction channels. In addition, we demonstrate the performance of the new setup on the example of carbon dioxide formation by comparing the efficiency of two different solid-state formation routes of CO_2 ($CO + OH = CO_2 + H$ and $CO + O = CO_2$). We find that under the same experimental conditions formation of CO_2 through the reaction CO+OH takes place more efficiently than through the reaction CO+O. We further discuss the potential of SURFRESIDE^2 to study complex molecule formation, including nitrogen-containing (and even prebiotic) compounds. This is indeed the focus of the next chapters.

Chapters 3 and **4** investigate in detail the surface hydrogenation of NO molecules in polar (water-rich) and non-polar (carbon monoxide rich) interstellar ice analogues. A complex reaction network involving both final (N_2O, NH_2OH) and intermediate (HNO, $NHOH/NH_2O\cdot$) products is discussed. We demonstrate that hydroxylamine formation takes place efficiently *via* a fast mechanism and it is found to be even more abundantly formed in a water-rich environment at lower temperatures. In parallel, we experimentally verified the non-formation of hydroxylamine upon UV photolysis of NO containing ices at cryogenic temperatures as well as the non-detection of NC- and NCO-bond bearing species after UV processing of NO in carbon monoxide-rich ices. Our results are implemented into an astrochemical reaction model, which shows that NH_2OH is supposed to be abundant in the solid phase under dark molecular cloud conditions. The assumed abundant presence of NH_2OH in interstellar ices adds a new perspective to the way molecules of biological importance may form in space. For instance, once NH_2OH desorbs from the ice grains, it becomes available to form more complex species (*e.g.*, glycine and β-alanine) in gas-phase reaction schemes. The possible formation scheme of these two molecules of astrobiological importance is discussed.

In **Chapter 5** a full reaction network involving nitrogen oxides (NO, NO_2, N_2O) and H, O, and N atoms is described. Here we show that NO_2 is efficiently formed in the reaction of NO with O atoms, and then rapidly destroyed in NO_2 + H/O/N reactions, which proceed in a barrierless way or with a very low barrier. The surface destruction of solid NO_2 leads to the formation of a series of nitrogen oxides of which the most important ones are NO, N_2O, as well as to the formation of HNO, NH_2OH, and H_2O. It is shown that the final stable products of the joint NO+H/O/N and NO_2+H/O/N reaction network are NH_2OH, H_2O, N_2, and N_2O. When NO_2 is mixed with an interstellar more relevant CO-rich ice, solid CO_2 and HCOOH are also formed due to interactions between the investigated reaction routes and CO-molecules. The astrophysical implications of the full reaction network are discussed.

Chapter 6 further expands the full nitrogen and oxygen reaction network as derived in chapters 3-5 by experimentally investigating the formation of NH_3 and HNCO through non-energetic surface reactions in interstellar ice analogues. It is shown that NH_3 is efficiently formed by three consecutive H-atom additions to N atoms. Furthermore, we show that in CO-rich interstellar ice analogues the formation of NH_3 is inhibited due to the surface formation of solid HNCO through the interaction of CO molecules with NH radicals – one of the intermediates in the formation of solid NH_3. This is an important experimental conclusion, since it shows that, in general, surface reaction routes cannot be treated independently. Moreover, possible reactions of intermediate products with different lattice molecules should always be taken into account. The surface formation route of HNCO is an important step to explain the observation of XCN spectral bands: HNCO can easily yield OCN^- in various thermally induced acid-base reactions. Finally, we discuss the implications of HNCO in astrobiology, and suggest a new possible solid-state formation route of peptides and their fragments.

In **Chapter 7**, the deuterium enrichment of species produced on the surface of interstellar grains is investigated. In Chapter 6, NH_3 was for the first time detected *in situ* through the N+H reaction route. This allows us to further expand this study and to perform the simultaneous addition of hydrogen and deuterium atoms to nitrogen atoms in CO-rich interstellar ice analogues in order to study the exact fractionation of the formed NH_3, NH_2D, NHD_2, and ND_3 isotopologues at low temperatures (<15 K). The experiments yield a deviation from a statistical distribution in favour of deuterium-enriched species. Deuteration events are estimated to have a 1.7 times higher probability to take place compared to a regular hydrogenation event. It is suggested that the most likely explanation for this laboratory result is a higher sticking coefficient of D atoms over H atoms to the surface of the ice. This results in a higher surface D-atom density and a preferred formation of deuterium enriched ammonia isotopologues.

Chapter 8 focuses on the formation of two molecules of astrobiological importance - glycolaldehyde ($HC(O)CH_2OH$) and ethylene glycol ($H_2C(OH)CH_2OH$) - by surface hydrogenation of CO molecules. This laboratory-based research is aimed to simulate the CO freeze-out stage in interstellar dark cloud regions, well before thermal and energetic processing become predominant. It is shown that along with the formation of H_2CO and CH_3OH – two well-established products of CO hydrogenation – side products containing more than one carbon atom are formed. The laboratory investigated reaction pathways are then implemented into a continuous-time random-walk Monte Carlo model to study their impact on the solid-state abundances of glycolaldehyde and ethylene glycol in space. This work is particularly important because glycolaldehyde and ethylene glycol are the two simplest components of two classes of prebiotic compounds - aldoses (among which the most important are sacharides) and polyols (with best-known representative glycerine – a basic compound of fats).

References

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

Anton R., Wiegner T., Naumann W., Liebmann M., Klein Chr., Bradley C., 2000, RSI, 71, 1177

Arasa C., Andersson S., Cuppen H. M., van Dishoeck E. F., Kroes G.-J., 2010, JCP, 132, 184510

Baratta G. A., Leto G., Palumbo M. E., 2002, A&A, 384, 343

Baratta G. A., Palumbo M. E., 1998, J. Opt. Soc. Am. A, 15, 3076

Boogert A. C. A. *et al*., 2008, ApJ, 678, 985

Bottinelli S., Boogert A. C. A., Bouwman J., Beckwith M., van Dishoeck E. F.; Öberg K. I., Pontoppidan K. M., Linnartz H., Blake G. A.; Evans N. J., II; Lahuis F., 2010, ApJ, 718, 1100

Bottinelli S., Boogert A. C. A., van Dishoeck E. F., Beckwith M., Bouwman J., Linnartz H., Öberg K. I., 2008, Proceedings of the International Astronomical Union, IAU Symposium, 251, 105

Boudin N., Schutte W., Greenberg J. M., 1998, A&A, 331, 749

Cuppen H. M., Karssemeijer L. J., Lamberts T., 2013, Chem. Rev., 113, 8840

Cuppen H. M., Penteado E. M., Isokoski K., van der Marel N., Linnartz H., MNRAS, 2011, 417, 2809

Cuppen H. M., van Dishoeck E. F., Herbst E., Tielens A. G. G. M., 2009, A&A, 508, 275

D'Hendecourt L. B., Allamandola L. J., Grim R. J. A., Greenberg J. M., 1986, A&A, 158, 119

Fedoseev G., Ioppolo S., Zhao D., Lamberts T., Linnartz H., 2014, submitted to MNRAS

Fuchs G. W., Cuppen H. M., Ioppolo S., Bisschop S. E., Andersson S., van Dishoeck E. F., Linnartz H., 2009, A&A, 505, 629

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

Gibb E. L. *et al*., ApJ, 536, 347

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

Greenberg M. J., Li A., Mendoza-Gomez C. X., Schutte W. A., Gerakines P. A., de Groot M., 1995, ApJL, 455, L177

Herbst E. & van Dishoeck E. F., 2009, Annu. Rev. Astron. Astrophys., 47, 427

Hudgins D. M., Sandford S. A., Allamandola L. J., Tielens A. G. G. M., 1993, ApJS, 86, 713

Ioppolo S., Fedoseev G., Lamberts T., Romanzin C., Linnartz H., 2013, Rev. Sci. Instrum., 84, 073112

Öberg K. I. *et al*., 2011, ApJ, 740, 109

Öberg K. I., Garrod R. T., van Dishoeck E. F., Linnartz H., 2009, A&A, 504, 891

Pontoppidan K. M., Boogert A. C. A., Fraser H. J., van Dishoeck E. F., Blake G. A., Lahuis F., Öberg K. I., Evans II N. J., Salyk C., 2008, ApJ, 678, 1005

Schutte W. A., Greenberg J. M., van Dishoeck E. F., Tielens A. G. G. M., Boogert A. C. A., Whittet D. C. B., 1997, Astrophys. Space Sci., 255, 61

Tielens A. G. G. M., 2005, The Physics and Chemistry of the Interstellar Medium, Cambridge University Press, Cambridge, UK

Tschersich K. G., 2000, J. Applied Phys., 87, 2565

Vasyunin A. I., Herbst E., 2013, ApJ, 762, 86

Whittet D. C. B., Schutte W. A., Tielens A. G. G. M., Boogert A. C. A., de Graauw T., Ehrenfreund P., Gerakines P. A., Helmich F. P., Prusti T., van Dishoeck E. F., 1996, A&A, 315, L357

Woon D. E., Interstellar & Curcumstellar Molecules, The Astrochemist, retrieved from http://www.astrochymist.org/astrochymist_ism.html