Shining light on interstellar matter : a laboratory study

Paardekooper, D.M.

Citation

Paardekooper, D. M. (2016, July 5). *Shining light on interstellar matter : a laboratory study*. Retrieved from https://hdl.handle.net/1887/41186

Author: Paardekooper, D.M.
Title: Shining light on interstellar matter : a laboratory study
Issue Date: 2016-07-05

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INTRODUCTION

The conditions in the space between the stars, the so-called interstellar medium (ISM), vary strongly from the conditions we are familiar with on the planet Earth. Temperatures range from 10^{6} down to 10 K, while densities can range from 10^{-4} up to 10^{8} particles cm^{-3} (van Dishoeck, 2014). Compare these conditions to an exceptional summer day in the Netherlands at sea level with a temperature of 20° (293 K) and density of $2.7\text{x}10^{19}$ particles cm^{-3}! The density in the ISM is *eleven* to *twenty-three* orders of magnitude lower. On Earth, the high density and temperature stimulate chemical reactions; reaction barriers can be overcome and excess reaction energy is removed by surrounding particles acting as a third body. In the ISM however, due to the low density the probability of two species colliding is small. The probability of species reacting is even more unlikely, since usually no third body is present to remove the excess reaction energy. Therefore, the chemical network in the gas phase is mainly driven by (exothermic) ion-molecule reactions. Next to these extreme physical conditions, cosmic rays are continuously penetrating the ISM that is also affected by the interstellar radiation field containing high energy photons (Tielens, 2005). Both of these are capable of effectively ionising or fragmentating species. Considering the harsh environment described above, the molecular complexity actually found in the ISM is astonishing. Up to date, over 185 different species (not including isotopes) have been detected in interstellar and circumstellar environments.[1]

The ISM consists of 99% of gas and 1% of dust, with an inhomogenous distribution of the mass. The gas consists of hydrogen (89%), helium (9%) and heavier elements (2%). Gas and dust gather in molecular clouds in the ISM, and within these clouds, dense and diffuse regions exist with number densities of $10^{4} - 10^{5}$ cm^{-3} and 10^{2} cm^{-3}, respectively (van Dishoeck et al., 2013). Typical temperatures in dense regions range from 10 to 20 K. Visible light is unable to penetrate these regions, which are therefore referred to as 'dark clouds'. The dense regions are fed from diffuse regions upon gravitational attractions or external shocks (Shu et al., 1987). Photons from the interstellar radiation field can penetrate the diffuse regions, leading to the photodestruction of species present. In the dense regions of the molecular clouds, photons are absorbed by the edges, effectively protecting the inner parts of the clouds. When the density in these molecular clouds reaches a critical point, the cloud can gravitationally collapse and a star can form. Conservation of momentum leads to a disk surrounding the star, in which planets are thought to be formed (Armitage, 2011).

It has become clear that the dust present in the molecular clouds plays an essential role in the cosmochemical evolution from diffuse clouds to planets and stars, since gas phase chemistry only cannot explain the observed abundance of species. The cold (10 to 20 K) dust grains, with a typical dimension of up to $0.1\ \mu m$ in size acts as a small cryostat. Atoms and molecules collide and stick, over time an ice can be formed. It provides a meeting place, where atoms and molecules can accrete, meet and react. The grain and ice act as a third body, effectively facilitating chemical reactions. The accretion of species depends on the gas composition, carbon is locked in CO and oxygen atoms are present. Hydrogen is abundant and on top of the grain still mobile at these temperatures. CO and oxygen atoms, undergo several hydrogenation reactions forming CH_3OH and H_2O, respectively.

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[1] https://www.astro.uni-koeln.de/cdms/molecules

For many ice components, only efficient surface formation routes are known (Linnartz et al., 2015). Inside dark clouds, the dust grains act as molecular reservoirs, which are continuously energetically processed by an internal radiation field driven by the interaction of penetrating cosmic rays with molecular hydrogen (H_2). This processing can leads to an increase of molecular complexity, resulting in the formation of so-called Complex Organic Molecules (COMs).

As mentioned before, shortly after a star is formed, the conservation of momentum results in a disk surrounding the star. This protoplanetary disk consists of the remnants of the molecular cloud, including the (icy) dust grains. Planets like Earth are thought to form in these disks. It has been hypothesised that water and prebiotic species in this stage can be delivered to planets by cometary bodies, hereby effectively kickstarting life. Therefore, it is key to understand the fundamental processes occurring in interstellar ices and into what degree of molecular complexity this can result. This is the topic of the present thesis.

1.1 ICE COMPOSITION

Infrared (IR) observations from the ground are limited to spectral windows, due to obscuring effects of the Earth's atmosphere. This has posed the requirement of space based observations to derive the composition of interstellar ice. These observations have been mainly performed using the Interstellar Space Observatory (ISO) and the Spitzer Space Telescope (SST) (Gibb et al., 2000; Boogert et al., 2004, 2008). Figure 1.1 presents spectra of line of sight infrared observations from different protostars towards background stars. Via these observations the main composition of interstellar ices has been obtained. These mainly consist of H_2O, CO, CO_2, CH_4, CH_3OH, H_2CO, HCOOH and NH_3. Also other constituents like OCN^- and $NH_4{}^+$ have been detected. Both telescopes (ISO and SST) have become inactive after running out of helium, and currently there is no space based telescope active in the IR range. Late 2018, the James Webb Space Telescope (JWST) will be launched and will have IR-spectroscopic instruments to perform observations of interstellar ices with unprecedented sensitivity and spatial resolution.

Most components of these ices can be explained by non-energetic atom addition processes (Tielens & Hagen, 1982; Linnartz et al., 2015), while the presence of OCN^- is an indication that interstellar ice undergoes energetic processing (Bernstein et al., 1995; Palumbo et al., 2000). The interaction of penetrating cosmic rays with matter can in turn produce secondary particles, such as VUV photons (Prasad & Tarafdar, 1983; Shen et al., 2004), electrons and low-energy cosmic rays. The secondary particles are capable of energetically processing the ice, which can lead to an increase of molecular complexity. Next to these effects, the temperature increase in different stages of the star formation sequence can facilitate thermal reactions in interstellar ice (Theulé et al., 2013).

Direct IR observational evidence for molecular complexity is however lacking. Ice spectra are dominated by the abundant ice components; weak features of minor ice components are bound to overlap since the cold environment results in line broadening. Additionally, the abundance of these species is low, since it decreases with increasing molecular complexity. However, in later stages during the star formation sequence, the temperature of the grains increases. This leads to the thermal desorption of (volatile) species present in the ice, after which they can then be observed in gas phase. Moreover, icy bodies may impact on planets delivering H_2O and COMs.

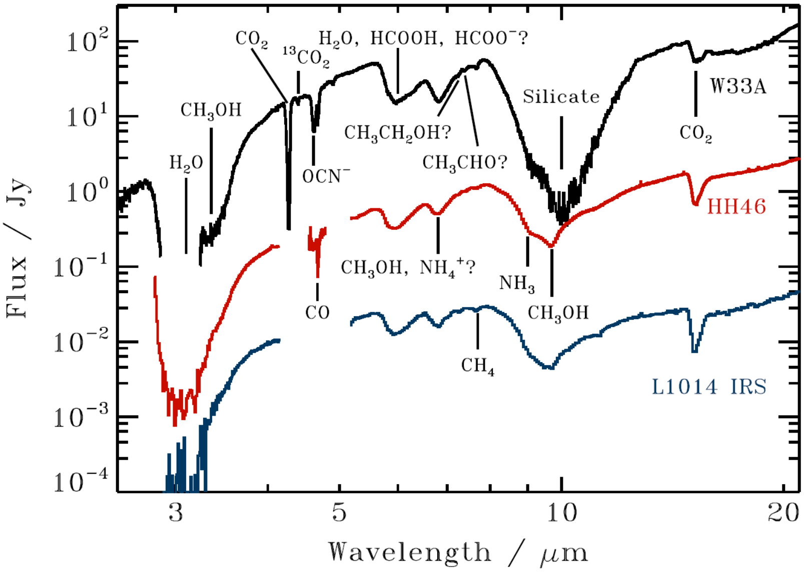

Figure 1.1: Ice spectra toward the protostars W334A ($10^5 L_\odot$), HH46 ($12 L_\odot$), and L1014 IRS ($0.09 L_\odot$) (Gibb et al., 2000; Boogert et al., 2004, 2008). The 3 µm portions of the spectra have been binned to increase the signal-to-noise ratio. Figure from Öberg et al. (2011).

Cometary bodies contain a wealth of information, they preserve the earliest record of material about dust grains and ice, from the molecular cloud out of which our Sun and Earth have been formed. Recently, after a 10 year journey Rosetta has visited the comet 67P/Churyumov-Gerasimenko. Rossetta's lander Philea has achieved the first-ever landing on a comet. Philea detected organic compounds (Goesmann et al., 2015), of which some can play an important role in the prebiotic synthesis of amino acids, sugars and ribonucleic acid (RNA). Interstellar ice cannot directly be compared to cometary ice, but this detection does support the presented hypothesis about the origin of life on Earth, i.e., that COMs were delivered from space.

1.2 ICE EVOLUTION THROUGH DIFFERENT STAGES OF STAR FORMATION

In the cartoon presented in figure 1.2 (Herbst & van Dishoeck, 2009), the evolution of ice through different stages of star formation is depicted. During the precollapse stage (dense regions, dark cloud), the continuous hydrogenation of oxygen atoms on the surface leads to a water rich layer. With increasing density ($10^4 - 10^5$ cm^{-3}), CO starts freezing out. The hydrogenation of CO leads to the formation of CH3OH (Hiraoka et al., 2002; Watanabe & Kouchi, 2002; Fuchs et al., 2009). Cosmic rays interacting with matter, produce secondary particles such as electrons, low energy cosmic rays and VUV photons. These secondary particles can induce (photo)desorption or bond cleavages of ice species. Desorption effectively influences the molecular reservoirs in the gas and solid phase while highly reactive radicals can recombine reforming the original species, or move around the ice to eventually meet a different reaction partner (Öberg et al., 2009). This can result in an increase of molecular complexity, forming COMs. During the core collapse, the temperature increases and volatile species will move from the grains into the gas phase.

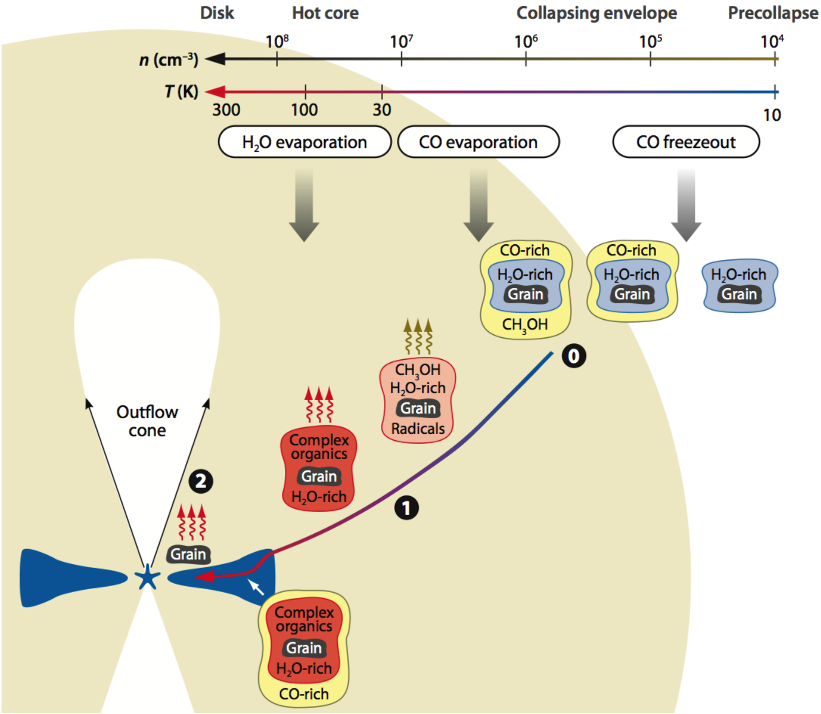

Figure 1.2: Cartoon representation of the evolution of material from the prestellar core stage through the collapsing envelope into a protoplanetary disk. The dust grains are typically 0.1 μm and are not drawn to scale. Figure by E.F. van Dishoeck and R. Visser. Figure from Herbst & van Dishoeck (2009).

Apart from directly detecting species through IR observations in the ice, it is also possible to indirectly detect gas phase species which have been evaporated from the dust grains. A large variety of complex organic molecules have been detected in the gas phase in a number of astronomical environments (see Fig. 1.3, Jørgensen et al., 2012). Gas phase chemistry fails to explain the observed abundances while astrochemical models indicate that the majority of complex organic species must have its origin in the solid state, i.e., on icy surfaces (Garrod & Herbst, 2006; Garrod et al., 2008; Balucani et al., 2015).

Recent results from the Atacama Large Millimeter/submillimeter Array (ALMA) have shown the presence of the simplest sugar glycolaldehyde in the protostars IRAS 16293A and B (Jørgensen et al., 2012). The detected glycolaldehyde is thought to form on top of dust grains either by photochemistry of solid methanol (see Öberg et al. (2009) and Chapter 5) or by surface hydrogenation of CO (Fedoseev et al., 2015; Chuang et al., 2016). Glycolaldehyde is an ingredient for the chemical reactions that can create ribonucleic acid (RNA), a molecule which is essential for all known forms of life. The position where these molecules have been found is located near the position where planets are thought to form (Jørgensen et al., 2012).

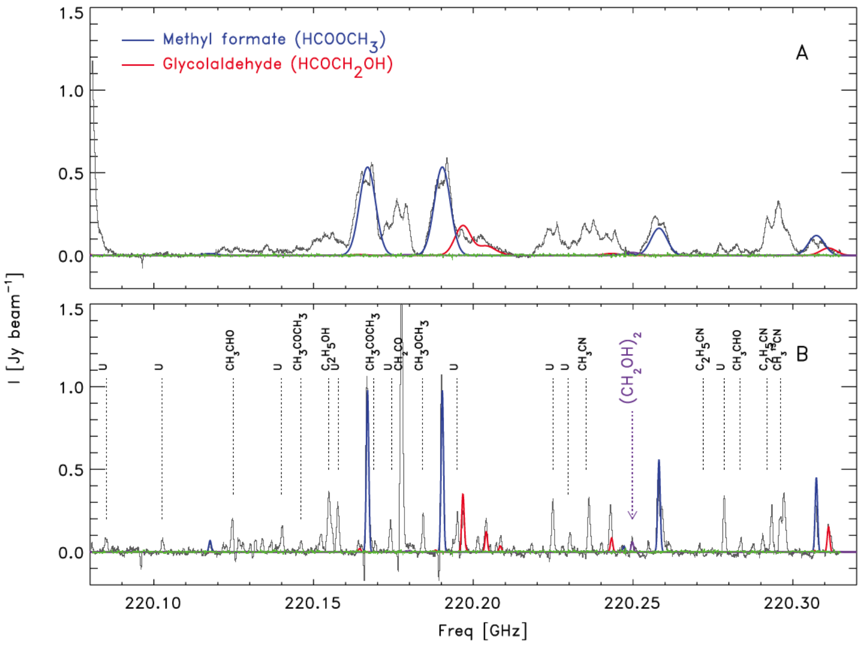

Figure 1.3: Spectra in the central beams toward the continuum peaks of IRAS16293A (upper) and IRAS16293B (lower). The X-axis represents the frequencies in the rest frame of the system. Note the much narrower lines toward IRAS16293B which facilitate identification of individual feature. Figure from Jørgensen et al. (2012).

1.3 LABORATORY ASTROCHEMISTRY

Solid state laboratory experiments aim at increasing our understanding of the fundamental processes occurring in ices, containing molecules of astrochemical interest. Over the years a large variety of experimental techniques and detection schemes have been developed and applied. It started with fundamental studies using IR spectroscopy[2] in a high vacuum (10^{-7} mbar) environment (Hudgins et al., 1993). This has led to the detection of molecules condensed on top of small dust grains in molecular clouds (see Fig. 1.1). Since the main constituent of interstellar ices is now known, pure ices containing these molecules have been processed using vacuum ultraviolet (VUV) photons produced by a hydrogen microwave discharge lamp (Gerakines et al., 1996), resembling the radiation field in such environments.

In a later stage, an interstellar ice mixture of H_2O:CH_3OH:NH_3:CO:CO_2 (2:1:1:1:1) has been irradiated for 24 hour using a hydrogen microwave discharge lamp (Muñoz Caro et al., 2002). This has been performed at 12 K in a high vacuum environment. The sample was warmed to room temperature and the residuals have been analysed using a gas chromatograph mass spectrometer (GC-MS). This was the first *ex situ* detection of the formation of amino acids from photoprocessing such an interstellar ice mixture, demonstrating that under these conditions prebiotic species can be formed from energetically processing the basic interstellar ice ingredients (Fig. 1.4). It remains however unclear if these molecules have been formed at low temperature or during a later stage in the analysis. Technological

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[2] http://home.strw.leidenuniv.nl/ linnartz/leiden-ice-database.html

improvements have provided more details about the residual (de Marcellus et al., 2015). Recent efforts have been made in order to improve on such techniques by performing the analysis *in situ* (Mrad et al., 2016), minimizing possible chemical alternations during the analysis. All these methods, however, need the heating of the ice sample and thermal effects cannot be fully excluded.

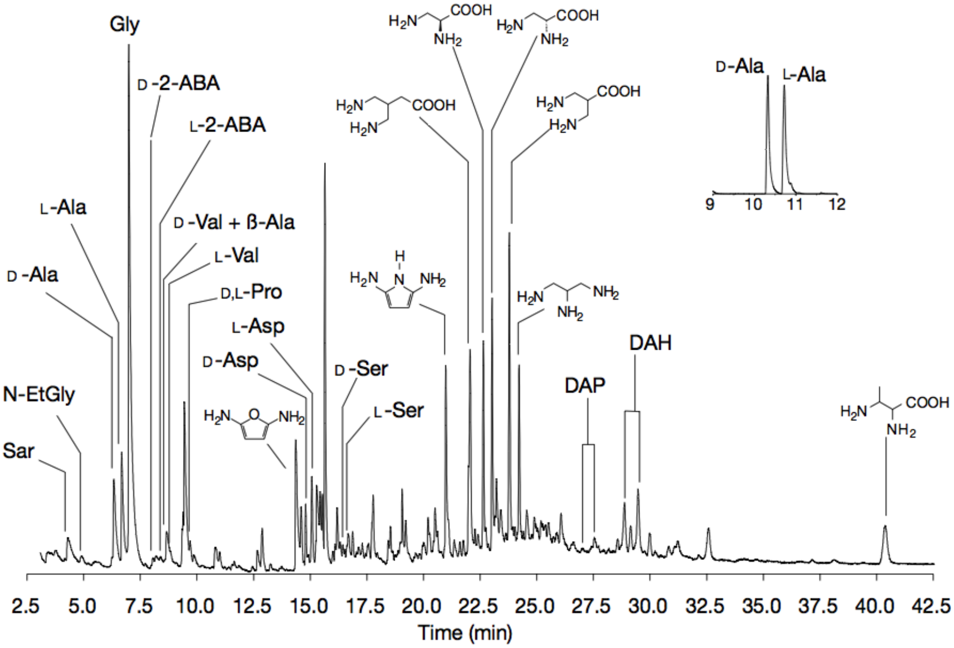

Figure 1.4: Mass spectrum recorded by GC of a VUV photoprocessed interstellar ice analogue. Figure from Muñoz Caro et al. (2002).

In the ISM in dense cores, at low temperatures the dust grains are covered with an ice mantle consisting primarily of H_2O. A typical 0.1 μm sized dust grain is surrounded by about 100 monolayers of water ice (1 ML = 10^{15} molecules/cm^2) (van Dishoeck, 2014). Combined with the importance of surface reactions, this has posed requirements on the vacuum conditions of solid state laboratory experiments simulating these environments. In a high vacuum (10^{-7} mbar) environment, every 25 seconds a cold substrate will be coated with a ML, while in an UltraHigh Vacuum (UHV) environment (10^{-10} mbar) this will require almost 7 hours. This has substantially improved the experimental conditions for which interstellar ices can be studied. *In situ* diagnostics such as InfraRed (IR) spectroscopy (reflection or transmission) are used in conjunction with Quadruple Mass Spectrometry (QMS) and Temperature Programmed Desorption (TPD). Although powerful and versatile, both methods come with disadvantages. Only molecules with a dipole moment can be monitored using IR spectroscopy. It traces functional groups, and can suffer from overlapping bands. TPD can accommodate thermal reactions during the warm up phase, which can result in chemical changes in the ice (Öberg, 2009; Ioppolo, 2010).

Recently, Jones & Kaiser (2013) have implemented a different detection scheme. After processing an ice at low temperature, the sample is slowly warmed to high temperature by performing a TPD. Species will sublimate, and the gas phase species desorbing from the ice are ionised using Single Photon Ionisation (SPI, 10.49 eV). Subsequent detection is performed using a time-of-flight mass spectrometer. Since the energy of the photon is chosen slightly above the ionisation potential of the species, this mainly leads to ionisation without fragmentation. An update of the system allows to distinguish between isomers by using tunable SPI (Abplanalp et al., 2016).

So far, the composition of ice is measured either by *in situ* IR spectroscopy, or by detecting the species moving into the gas phase using either QMS or SPI ReTOF. The next step forward is inducing desorption using alternative methods. Using an IR laser pulse (~ 3 μm), Gudipati & Yang (2012) and Henderson & Gudipati (2015) induce desorption, transferring species from an ice into the gas phase. Species are ionised using a focused UV laser, and detected by time-of-flight mass spectrometry.

In the Sackler Laboratory for Astrophysics in Leiden an experimental setup has been developed, aiming at measuring the composition of ices; MATRI^{2}CES (Mass-Analytical Tool for Reactions in Interstellar ICES, Fig. 1.5). Desorption of the ice is induced using an unfocused UV laser. Gas phase species are subsequently ionised using electrons with a mean energy of 70 eV, after which the ions are extracted and measured by time-of-flight mass spectrometry (Paardekooper et al., 2014; Bossa et al., 2015). The ice can be photo-processed using a hydrogen discharge lamp; at different fluences the ice constituents can be tracked. It has an improved sensitivity compared to IR spectroscopy, and compared to TPD/QMS the advantage that all ice constituents can be desorbed and traced *at low temperature*.

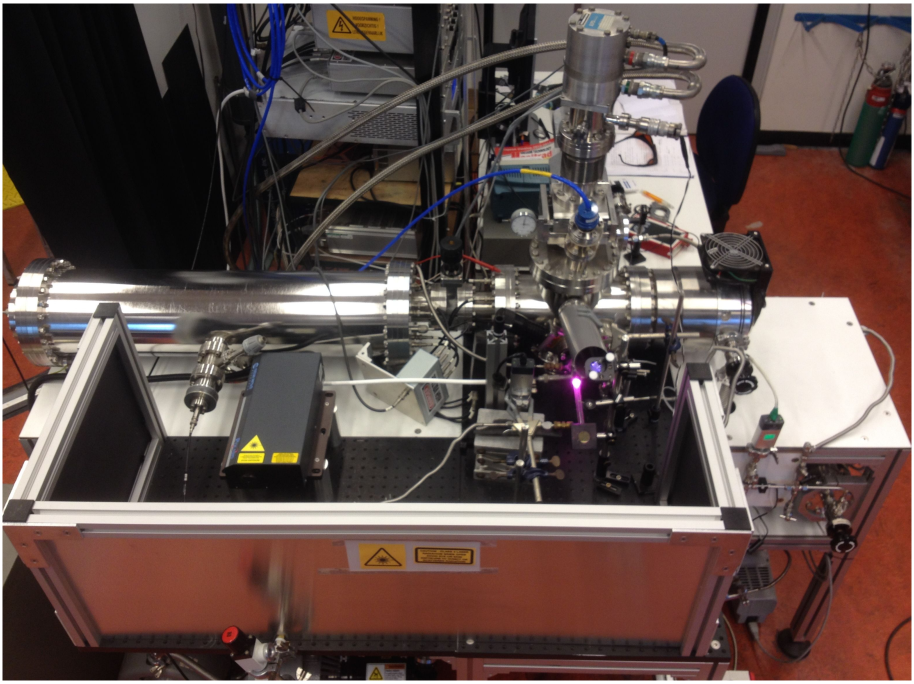

Figure 1.5: Picture of MATRI^{2}CES, the system is described in detail in Paardekooper et al. (2014) and Chapter 2.

1.4 THIS THESIS

This thesis is dedicated to studying the interaction of photons with matter of astrochemical interest. For the field of astrochemistry, a new *in situ* experimental technique, Laser Desorption Post-Ionization Time-Of-Flight Mass spectrometry (LDPI TOF-MS) is applied to study the photochemistry in ice (Chapter 2, 4 and 5) containing molecules of astrochemical interest. Apart from the chemistry occurring upon absorption of photons and photodissociation, photons can induce desorption of molecules in ice, so called photodesorption. We have applied a novel approach to accurately derive the photodesorption rate (Chapter 6) for CO ice. Since light plays an essential role throughout the different chapters of this thesis, a chapter has been dedicated to characterize a commonly used light source in laboratory astrochemistry, the hydrogen microwave discharge lamp (Chapter 3). As molecular complexity is the leading topic in this thesis, the last chapter focusses on the influence of light on a large Poly Aromatic Hydrocarbon (PAH). The data are recorded with a different setup, also using TOF methodology. The photo-fragmentation of the hexa-benzo-coronene (HBC) cation, a large PAH cation of potential astrophysical interest is presented in Chapter 7.

Chapter 2 introduces a new experimental technique to study the formation of complex organic molecules (COMs) in (interstellar) ice analogous. Species of astrophysical interest are deposited on top of a cold substrate (20 K) and subsequently photo-processed using a hydrogen microwave discharge lamp. The composition of the ice is traced using LDPI TOF-MS. Briefly, desorption is induced using a laser pulse, species in the desorption plume are then ionised using electrons, after which they are extracted into a field-free time-of-flight tube. Subsequent detection of the ions is realised using a Multi Channel Plate (MCP) detector. Based on their time of arrival, the m/z is determined. Detailed description and calibration of the system are provided, and the system capabilities are demonstrated on the example of photo-processed methane (CH_4) ice at 20 K.

Chapter 3 describes the spectral characterisation of the hydrogen microwave discharge lamp, commonly used to simulate interstellar radiation fields in laboratory experiments. Recent discrepancies between identical measurements in different laboratories, as well as clear wavelength dependent results obtained in monochromatic (synchrotron) experiments, hint at a more elaborate dependence on the exact discharge settings than assumed so far. A sophisticated plasma lamp calibration set-up has been used to record the vacuum ultraviolet (VUV) emission spectra. Spectra are compared with the output of a calibrated D_2 -lamp which allows a derivation of absolute radiance. The direct influence of using two lamp spectra on the CO photodepletion rate is presented.

Chapter 4 presents the ice photochemistry of pure methane (CH_4), studied at 20 K. VUV processing is performed using photons produced by a hydrogen microwave discharge lamp. LDPI TOF-MS is used for the first time to determine branching ratios of primary reactions leading to CH_3, CH_2, and CH radicals, typically for fluences as expected in space. The study is based on a stable end-products analysis and the mass spectra are interpreted using an appropriate set of coupled reactions and rate constants, yielding clear differences compared to previous gas phase studies. The matrix environment as well as the higher efficiency of reverse reactions in the ice favor CH_3 radical formation as the main first generation photoproduct.

Chapter 5 describes a study of the photoprocessing of pure methanol (CH_3OH) ice at 20 K. Condensed methanol is observed in molecular clouds. Its solid formation route is well studied in the laboratory through subsequent hydrogenation events of CO. In the past, the ice photochemistry of methanol has been studied with various techniques, it is a known precursor for the formation of various COMs. Using LDPI TOF-MS, we study the formation of COMs as function of VUV fluence, and for the first time the formation of $(CO)_3H_x$ species is detected *in situ* after the VUV photoprocessing of methanol ice.

Chapter 6 presents a novel approach to study the photodesorption rate of molecules of astrochemical interest, on the example of CO ice. Complete desorption of the ice is induced using a laser pulse. The desorption profile is sampled at different extraction times relative to the laser pulse. Using this approach we track the composition and surface coverages of species of the ice as function of VUV fluence. Accurate surface coverages and flux calibration have been performed using HeNe interferometry and *in situ* NIST photodiode measurements.

Chapter 7 describes a study of the photo-fragmentation of the hexa-peri-hexabenzocoronene HBC cation -$C_{42}H_{18}^+$ - a large PAH cation of potential astrophysical interest. HBC cation photo-fragment patterns are measured upon irradiation by an unfocused Nd:YAG laser (532 nm) for different experimental conditions, using quadrupole ion trap, time- of-flight mass spectrometry. Both stepwise dehydrogenation of $C_{42}H_{18}^+$ and C_2/C_2H_2 loss pathways are identified as relevant photodissociation routes. Whereas the majority of the experiments presented focuses onto COM formation in bottom-up approaches, the research presented here follow an opposite route, namely top-down, starting from large complex precursor species.

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