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Title: The formation of complex organic molecules in dense clouds: sweet results from the laboratory
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Large areas of space are filled by molecular clouds that consist of gas (mainly hydrogen) and (sub)-micron sized silicate and carbonaceous dust grains that are the remnants of dead stars. These interstellar clouds are optically opaque and cold as light penetration is hindered. With decreasing temperature and increasing density, gas starts accreting onto dust grain surfaces that act as highly effective cryopumps. This results in layered geometries of partially mixed ices on top of the grains. It has become clear that these icy dust grains act as molecule reservoirs and cryogenic catalysts on which both simple and complex molecules form in surface reactions, triggered by impacting atoms, electrons and cosmic rays or irradiation by vacuum UV light. Moreover, these grains form the material from which planetesimals and later larger celestial bodies—comets and planets and their moons—are formed. A good understanding of the elementary processes taking place in dark interstellar clouds is necessary to understand the chemical inventory of stellar systems, like our own Solar system.

This thesis focuses on laboratory studies investigating the surface chemistry of CO-rich ices on dust grains under dense interstellar cloud conditions. The formation mechanisms of complex organic molecules (COMs) are investigated by non-energetic processes (e.g., hydrogenation) and energetic processes (e.g., photolysis) of simple molecules, like CO and other interstellar relevant precursor species. Moreover, the net transfer of the newly formed hydrogenated species from grain surfaces into the gas phase through non-thermal desorption is investigated. All work described in the previous chapters has been performed in the Sackler Laboratory for Astrophysics at Leiden University.

Interstellar ice in dense clouds

Astronomical observations show the presence of frozen molecules on dust grains, such as H$_2$O, CO, CO$_2$, and CH$_3$OH, through their vibrational transitions in the infrared. In dense clouds, the density ($n_H$) increases to $10^{4-5}$ cm$^{-3}$ and temperature drops to $\sim$10 K; carbon monoxide (CO), which is the second most abundant gaseous species (i.e., $\sim$10$^{-4}$$n_H$) after H$_2$, abundantly condenses on the pre-formed H$_2$O-rich ice mantle. This stage is known as the 'catastrophic CO freeze-out stage'. The simultaneous accretion of CO and H-atoms primarily leads to hydrogenated species formation, e.g., H$_2$CO and CH$_3$OH, through successive H-atoms addition reactions forming a CO-rich apolar ice coating. This non-energetic mechanism (e.g., hydrogenation) dominating the ice chemistry on grain surfaces is widely considered as the pathway to explain the observed CH$_3$OH abundance in space. In this thesis it is shown that along this reaction chain also larger complex organic molecules (COMs), such as glycolaldehyde, ethylene glycol and glycerol can be formed.

In dense clouds, the moderate UV-photons induced by cosmic rays interacting with H$_2$ molecules also affect the surface chemistry of interstellar ices. The flux of the secondary UV-photons ($\leq 10.2$ eV) is lower than the typical flux of H-atoms ($\sim 1 \times 10^4$ atoms cm$^{-2}$ s$^{-1}$). However, such UV-photons can easily penetrate the entire ice mantle resulting in photolysis reactions. The energy of impinging UV-photons cannot dissociate simple molecules, e.g., CO and H$_2$, but is enough to photo-pump CO into its first electronically excited state or to photo-dissociate the CO hydrogenated species, e.g., H$_2$CO and CH$_3$OH. The photolysis of CH$_3$OH also leads to the formation of interstellar complex organic molecules through the photo-fragment recombination reactions.
The work presented in this thesis shows that molecules of prebiotic interest are already formed during the very first stages of star and planet formation. Complex organic molecules are generally believed to be precursors of the building blocks that are inherent to life and that may have been delivered to early Earth by impacting celestial bodies. Glycolaldehyde, for example, is an important ingredient for ribonucleic acid (RNA) and has been astronomically observed with methyl formate (one of its isomers) and ethylene glycol (a sugar alcohol) toward a number of high- and low-mass protostars. The formation mechanism of COMs is generally accepted to take place on icy dust grains through the recombination of radicals that are generated upon both energetic triggers (e.g., UV-photons, electrons, and ions) and non-energetic triggers (e.g., H-atoms). Recently, the ‘cold’ discovery of gaseous COMs in dense clouds and prestellar cores (at temperatures as low as 10 K) has challenged the conventional synthesis scenario where CH$_3$OH undergoes intense energetic particle bombardment and ‘warm ice chemistry’ forming COMs in high-mass protostars. In cold regions, therefore, hydrogenation starting from CO ice offers an alternative mechanism to explain the presence of COMs in the early phase of star formation. This mechanism is proven in this thesis.

The astronomical gas-phase observation of simple species and organic molecules in dense clouds, with abundance as high as $10^{-9}$ to $10^{-8} \text{H}_2$, contradicts the concept that at such low temperature all species (except H$_2$ and He) should condense onto dust grains. A physical or chemical mechanism that transfers the ice species from the solid state into the gas phase offers a possible explanation. A direct thermal desorption is forbidden due to the very low temperature ($\sim 10$ K) at this stage. Therefore, different non-thermal desorption mechanisms have been proposed to bridge the grain-gas gap. Photo-desorption is an efficient mechanism to non-thermally desorb simple species, e.g., CO, CO$_2$, H$_2$O, and CO:N$_2$ ices. However, for the hydrogenated species CH$_3$OH, photo-dissociation becomes a dominating channel resulting in fragment formation, e.g., CH$_3$, CH$_2$O, and CH$_2$OH. For this reason, a different mechanism has been studied here; reactive desorption (RD) may offer a gas-phase enrichment of both simple species and organic molecules through desorption following exothermic reactions along the CO-H$_2$CO-CH$_3$OH hydrogenation scheme.

INTERSTELLAR ICE IN LABORATORY

The solid-state chemistry in interstellar ice analogues described in this thesis has been studied in the Sackler Laboratory for Astrophysics by using Surface Reaction Simulation Device$^2$ (SURFRESIDE$^2$; Figure 1), an ultra-high vacuum system fully optimized to study atom reactions and UV-photolysis under dense cloud conditions, i.e. at very low temperatures. Two atom beam lines, i.e., a Hydrogen Atom Beam Source (HABS) and Microwave Atom Source (MWAS), are available to generate interstellar atomic (or molecular) radicals that are co- or pre-deposited with simple species from molecular dosing line onto a cryogenically cooled surface that mimics the grain surfaces in space. A Microwave Discharge Hydrogen-flow Lamp (MDHL) is used to simulate the secondary UV-photons induced by cosmic rays excited molecular hydrogen in dense clouds. The wide range of available substrate temperatures, which are set by the cryostat and resistive heating wire, makes it possible to study the cold surface chemistry that happens in interstellar cores at low temperatures and to simulate thermal desorption, when icy species sublime into the gas phase, during the later stages of star evolution.

The interstellar ices in SURFRESIDE$^2$ are in situ monitored by means of Reflection-Absorption InfraRed Spectroscopy (RAIRS). The icy constituents are identified by their characteristic vibrational modes that are linked to the various chemical functional groups, and their abundances are derived by the IR absorption band strength (A value) that is carefully calibrated.
by a HeNe laser interference technique. A Temperature Programmed Desorption (TPD) experiment in combination with Quadrupole Mass Spectrometry (QMS) providing a very high detection sensitivity is used as a complementary tool to identify the newly formed products. Species desorb at very specific temperatures and are relatively easily distinguished through their characteristic fragmentation patterns upon electron impact ionization. In the case of ambiguity, isotopically enriched species can be used. This all makes SURFRESIDE\textsuperscript{2} a very versatile tool to investigate molecular complexity in interstellar ices, for settings that are fully controlled and with a precision that allows to quantitatively investigate the underlying physical/chemical processes on icy grain surfaces.

**NON-ENERGETIC FORMATION MECHANISM OF COMS IN DENSE CLOUDS**

The laboratory studies of the solid-state interaction between H\textsubscript{2}CO and H-atoms not only leads to the hydrogenated species, i.e., CH\textsubscript{3}OH, but also results in dehydrogenated species, i.e., CO, through HCO radical. The H-atom abstraction reactions are also found in CH\textsubscript{3}OH ice interacting with H-atoms to form H\textsubscript{2}CO through CH\textsubscript{2}OH radical. The simultaneous forward (hydrogenation) and backward (dehydrogenation) reactions of CO-rich species increase the lifetime of the intermediate radicals on grain surfaces. As a consequence, a barrierless radical-radical recombination can explain the formation of oxygen-bearing complex organic molecules, e.g., methyl formate (HC(O)CH\textsubscript{3}), glycolaldehyde (HC(O)CH\textsubscript{2}OH) and ethylene glycol (H\textsubscript{2}C(OH)CH\textsubscript{2}OH), on dust grains under dense cloud conditions without the presence of energetic particles (e.g., UV-photons, electrons, and ions) or the central star. The experimental findings presented here are in strong support of COM formation during the ‘catastrophic CO freeze-out stage’. This formation scheme goes beyond the formation of two-carbon bearing species.

The formation of a three-carbon simple sugar, e.g., glyceraldehyde (HOCH\textsubscript{2}CH(OH)CHO), and a three-carbon sugar alcohol, e.g., glycerol (HOCH\textsubscript{2}CH(OH)CH\textsubscript{2}OH), is demonstrated by recombining single- and double-carbon radicles under dense cloud conditions. From this it
is concluded that the non-energetic mechanism also holds much potential to form even larger complex organics in the space. The COM formation scheme is presented in Figure 2.

**ICE CHEMISTRY INVOLVING UV-PHOTONS**

In dense clouds, the interstellar ice chemistry is simultaneously triggered by both H-atom addition reactions and UV-photon irradiation on dust grains. A systematic experimental study presented in this Thesis shows a quantitative comparison between hydrogenation and UV-photolysis in interstellar relevant ice analogues resulting in different COM formation compositions. COM formation ratios derived from the laboratory results can be used as a diagnostic tool to determine how such species may have formed in interstellar ice. A comparison between laboratory data as discussed here and observational results toward comets and solar-mass protostars suggests that COMs, e.g., glycolaldehyde and ethylene glycol, have a solid-state formation pathway.

UV-photolysis can play an important role to associate a carbon- and nitrogen-bearing species forming prebiotic molecules (peptide-bearing compound). Nitric oxide (NO) has a very high chemical reactivity compared to other N-bearing simple species (e.g., N2) and accretes with H-atoms on grain surfaces in the CO freeze-out stage. Therefore, the fully saturated NH2OH from NO hydrogenation is expected to be mixed with other CO-rich ices, e.g., H2CO and CH3OH. The UV-photons can efficiently dissociate the hydrogenated products resulting in photo-fragments, such as NH2 and HCO. The experimental findings show that these energetic radicals can further undergo radical-radical recombinations forming NC-bearing biological species, such as HNCO and NH2CHO that have been observed toward various star evolutionary and cometary objects.

Clearly, hydrogenation reactions involving CO ice on dust grains are important to form both smaller and larger complex organics, in dense clouds. However, molecular hydrogen (H2), with an abundance four orders of magnitude higher than that of H-atoms, does not actively participate in non-energetic ice chemistry, despite its overabundance and this is due
to the high activation energy of the involved reactions. The experimental study of CO:H$_2$ ice photolysis results in the unambiguous identification of HCO and H$_2$CO under dense cloud conditions. It is concluded that the electronically excited carbon monoxide (CO$^*$) induced by UV-photons can react with a ground-state H$_2$ molecule to form HCO and a free H-atom that then becomes available for H-atom addition reactions. The interaction between CO$^*$ and H$_2$ enhances the production of H$_3$CO species in the ice mantle and introduces a new solid-state channel involving electronically excited molecules and abundant H$_2$ in dense clouds.

**NON-THERMAL DESORPTION IN DENSE CLOUDS**

Reaction desorption (RD) is one of the crucial non-thermal desorption mechanisms to explain the net transfer of icy species from grain surfaces into gas phase at temperatures of which all molecules should be frozen out in the solid state. An accurate laboratory study of the solid-state elemental carbon budget monitored kinetically by RAIRS shows an upper limit of overall RD efficiency, i.e., 0.24, along the CO-H$_2$CO-CH$_3$OH hydrogenation scheme. Furthermore, the derived effective desorption fraction for single hydrogenation reaction and for each surface reaction induced by H-atoms (i.e., addition and abstraction) are \( \leq 0.07 \) and \( \leq 0.02 \), respectively, favoring the lower range of RD efficiencies of \( 0.01 - 0.10 \) which is currently applied as a free parameter in astrochemical simulations.

This thesis experimentally demonstrates that the building blocks of life are already formed on icy dust grains at low temperatures before the presence of a protostar, and shows an unexpected molecular complexity following non-energetic processes in dense clouds. Upon UV irradiation this level of complexity is even enhanced. We clearly live in an icy universe and with the launch of the JWST, for the moment scheduled for 2020, a new tool will become available to study interstellar ices. Exciting times are ahead.