Dark ice chemistry in interstellar clouds

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Summary

Between (inter) the stars (stellar) lies what is called the interstellar medium (ISM), which consists of highly dilute and very cold clouds of dust and gas. Although this medium is largely composed of gas, the role of the dust in the chemistry of the ISM is significant. The dust acts as a platform for simple atoms and molecules to "accrete, meet, and greet" (i.e., freeze out, directly collide or diffuse on the surface, and react). When these species react with each other on the dust grain, such a reaction typically releases a certain amount of energy, which gets absorbed by phonons in the solid lattice. This is an important stepping stone to the formation of large molecules, as the excess energy could otherwise break apart the product species, as sometimes observed in gas-phase reactions. The dust also contributes to blocking external UV-radiation from penetrating the cloud, which increases the role of 'dark' or 'non-energetic' processes (i.e., processes absent of 'energetic' particles) to the formation of ice species. When the cloud eventually collapses onto itself to form a young stellar object (YSO), the UV-light emitted induces a rich ice chemistry largely governed by 'energetic' processes, as investigated in numerous observational surveys, laboratory experiments, and computational simulations.

This thesis focuses on the 'dark' ice chemistry, which has received less attention in the literature compared to the ice chemistry involving 'energetic' processes, but is equally important to understanding the chemical inventory of interstellar clouds. The formation and formation parameters of simple and complex organic molecules (COMs) through 'non-energetic' processes are experimentally demonstrated and complemented by quantum chemical calculations. The findings from the experimental studies are strongly linked to astronomical observations of both, gas-phase and ice species.

Dark to light ice chemistry in interstellar clouds

At the edges of interstellar clouds, which has a visual extinction (A_V) of just below 1.6 mag, the molecular hydrogen density is relatively low ($\sim10^3$ cm^{-3}). External UV photons are present, which causes the photodesorption of certain species, like carbon monoxide (CO), from dust grains that have temperatures of ~10-20 K. However, the density is high enough to somewhat shield gas-phase species from 'energetic' particles, which mitigates further ionization of gas-phase species. The ionized species present will recombine (i.e., positive ion combines with electrons or negative ions) to form neutral atoms, such as C, H, N, and O. If not photodesorbed, these simple atoms will hit and stick to the dust surface, and subsequently react to form molecules such as water (H_2O), ammonia (NH_3), and methane (CH_4) ices, with water being the most abundant. Although not yet observationally constrained, recent laboratory experiments, some of which are presented in this thesis, demonstrate that COMs can also be formed in this H_2O-rich ice phase. Carbonaceous grains may contain hydrocarbons, such as propyne and acetylene. These molecules can react with nearby OH radicals almost barrierlessly to form aldehydes and alcohols, for example.

Traveling deeper into the cloud (A_V > 9 mag), the density is increased by orders of magnitude ($\sim 10^5$ cm^{-3}), which severely blocks external UV radiation from penetrating the cloud, and also causes a further drop in the temperature (to ~10 K). This is the time period when the ‘dark’ ice chemistry largely comes into play, as certain ‘energetic’ particles are not readily available to induce chemical reactions. Much of the remaining carbon in the gas-phase is destroyed by O to form CO. This CO freezes out on top of the H_2O-rich ice "heavily" and then "catastrophically", and is subjected to hydrogenation to form species such as H_2CO, CH_3OH, glycolaldehyde, ethylene glycol, and methyl formate. Recent laboratory experiments from our group have also demonstrated that biologically relevant species can be formed, such as glycerol. In modern life, cell membranes are composed of glycerophospholipids, which contain glycerol molecules. Thus, this ‘dark’ and ‘non-energetic’ chemistry can lead to the formation of simple, complex, and biologically relevant organic species.

At a certain point, the cloud will eventually collapse under its own gravity, which then triggers an increase in the density and temperature. A YSO is created and emits radiation, which can process the ices formed in the ‘dark’ period. Laboratory experiments have demonstrated that radiation-induced processes lead to the formation of residues consisting of polymers and amino acids, in addition to simpler species.

Experimental simulations of dark ice chemistry with SURFRESIDE^3

All experiments presented in this thesis were performed with the cryogenic ultrahigh vacuum setup, SURFace REaction SImulation DEvice (SURFRESIDE^3), which is uniquely equipped with three atomic beamlines, along with gas deposition lines, to study solid-state chemical reactions that simply involve radicals. A photograph of the setup is shown in Figure 1 and on the cover of this thesis. For over a decade, SURFRESIDE has been used to study the ‘non-energetic’ processes that take place in the ices of translucent and dense interstellar clouds. Details on the formation of simple hydrides (e.g., H_2O, NH_3, and CH_4) as well as COMs (e.g., glycolaldehyde, glycerol, and propanal) have been explored, primarily on 10-20 K surfaces cooled by a closed-cycle helium cryostat. The components of the setup are described in the text below.

The three atomic beamlines are collectively able to produce C, H/D, O, and N atoms, along with molecular fragments. The newest addition – the atomic carbon source – produces atomic carbon by the heating of carbon powder within a tantalum tube. This tube is heated to at least ~2000 K in order to sublimate the carbon. The sublimated carbon reacts with the tantalum to form tantalum carbide, which ultimately breaks apart molecular carbon, leading to the formation of atomic carbon that eventually is released into the gas-phase. The hydrogen

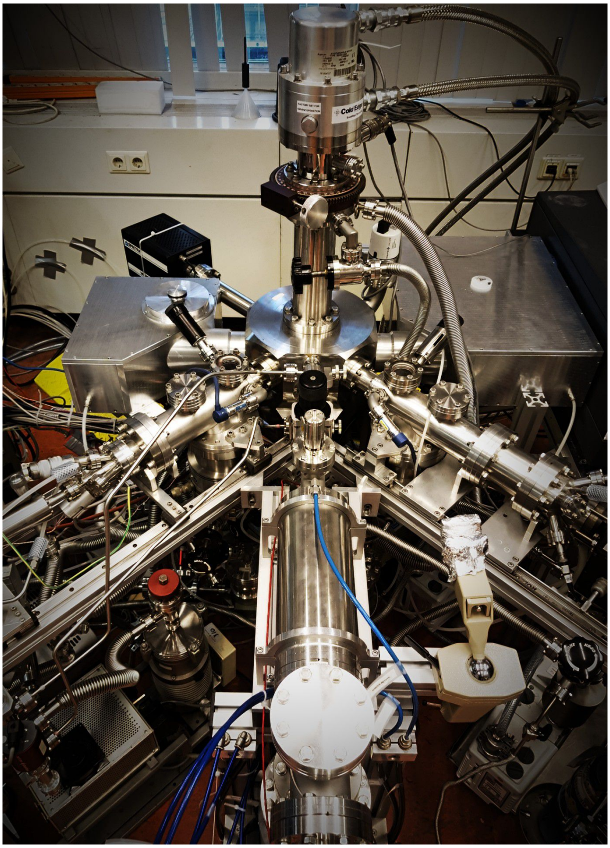

Figure 1: A photo of SURFRESIDE^3.

atom beam source is used primarily to form H(D) atoms by thermally cracking hydrogen (deuterium) molecules with a filament. The microwave atom beam source exploits the electron cyclotron resonance effect to create electrons with kinetic energies sufficient to break apart molecules into atoms and molecular fragments, such as N, O, OH, NH_x, and so on. The absence of a hot filament in the microwave atom beam source allows reactive species, such as oxygen, to be dissociated in the chamber in an experimentally friendly way. For the deposition of stable molecules, two independent dosing lines, which are also pumped by a turbomolecular pump, are used to transfer gases and vapors into the main chamber of SURFRESIDE^3.

Two analytical techniques are collectively used to probe the reactive intermediates and products formed: reflection-absorption infrared spectroscopy (RAIRS) and temperature programmed desorption-quadrupole mass spectrometry (TPD-QMS). With RAIRS, the vibrational signatures of the ice species are probed. This method allows *in situ* observations, however with the disadvantage that vibrational modes are typically broad and semi unique. TPD-QMS is the higher sensitivity technique within the experimental setup that can typically distinguish the different species formed more effectively. However, TPD-QMS is an *ex situ* technique as it involves the sublimation of the ice sample, and is also not ideal to probing transient intermediate species. The coupling of RAIRS and TPD-QMS to understand the ice chemistry is powerful, however, in that the disappearance of vibrational signatures and the subsequent rise of desorption signals can be used to piece together the ice species formed. Additional spectroscopic and mass spectrometric information are obtained by using isotopically enriched precursor species.

Non-energetic solid-state formation of simple molecules: CH_4, HCOOH, and CO_2

CH_4 is in the top six most abundant ices to be detected towards young stellar objects. Observational surveys of CH_4 ice show that the probed CH_4 is expected to be formed by the hydrogenation of solid C in H_2O-rich ices. This pathway has also been adapted in some astrochemical models, with however no experimental confirmation of this. In this thesis, it is experimentally demonstrated that CH_4 can be formed by the solid-state hydrogenation of C in a H_2O-rich ice. Additional details to the CH_4 formation pathway are also discussed, such as 1) The formation rate of CH_4 is twice as high in a H_2O-rich ice compared to an ice without H_2O. This is partially due to the increase in the residence time of hydrogen in H_2O ices. 2) Under our laboratory conditions, the competing abstraction reactions appear to not dominate. CH_n radicals readily react with H, as CH_n radicals nor their recombination products are observed. This implies that the H-addition pathway to form CH_4 dominates the H-abstraction pathway to form CH_n radicals, at least with the chosen laboratory settings. As CH_4 is best observed with space-based observatories due to the interference of telluric contamination, the anticipated James Webb Space Telescope (JWST) will be a promising facility to probe CH_4 ice. It's high sensitivity in the mid-IR may also allow direct observations of CH_4 in the H_2O-rich ice phase of quiescent molecular clouds.

HCOOH and CO_2 ices have been recognized through multiple studies to be largely formed also in the H_2O-rich ice phase. Yet, ice observations of CO_2 additionally show that a smaller fraction (~1/3) of the sampled ice is detected in a CO environment. It is explored here the experimental formation of both, HCOOH and CO_2 ices, starting from H_2CO. As H_2CO is a product of CO hydrogenation, this investigation supports the idea that HCOOH and CO_2 should also be formed in the CO-rich ice phase. By combining the experimental results with quantum chemical calculations from the literature, it is found that HOCO and HCO intermediates are responsible for the formation of HCOOH, and that CO_2 is predominantly formed from HOCO. As HCOOH has yet to be securely detected in interstellar ices, this study provides more hope for the presence of HCOOH in the ices of quiescent clouds, as HCOOH ice should be more abundant than previously thought. It is suggested that future observational surveys targeting 'non-energetically' formed HCOOH should not probe beyond the sufficient conversion of H_2CO to CH_3OH in order to reduce complexity in the ice spectra.

The CH_3OH ice dilemma in interstellar clouds

The solid-state CO hydrogenation pathway is regarded as the dominant pathway to forming CH_3OH (ice and gas-phase) in interstellar clouds. But is this scenario truly uniform across all interstellar clouds? Observations of CH_3OH ice in quiescent cloud environments show that CH_3OH upper limits are at least a factor of 3 below CH_3OH ice detections at high visual extinctions (i.e., at cloud depths where CH_3OH should be sufficiently formed). Note, however, that a high visual extinction does not necessarily imply a high density, which would affect CH_3OH formation. This indicates that CH_3OH ice is not effectively formed by the CO hydrogenation pathway in some clouds. Instead, a potential situation may be that CH_3OH is formed by less efficient reactions, such as the CH_4 + OH route, as supported from laboratory experiments presented here. It is found that the CH_4 + OH reaction pathway is around 20 times less efficient than the CO + H pathway to forming CH_3OH. If interstellar CH_3OH ice can also be formed from CH_4, then CH_3OH may be formed earlier than expected. Currently, CH_3OH is constrained to be formed at $A_V \sim 9 \pm 3$ mag, which is after H_2O has formed ($A_V \sim 2$ mag) and after the heavy CO freeze-out ($A_V \sim 3$ mag). Note that the CH_3OH ice formation threshold is only based on 7 detections. Simply based on these formation threshold values, it is thought that the CH_3OH formation threshold should at least be dropped to when CO heavily freezes out.

An updated observational study of CH_3OH ice is presented in this thesis, which includes one additional ice detection and a larger sample of CH_3OH upper limits measured over a range of A_V values (total A_V = 5.1-46 mags). A new CH_3OH ice formation threshold value of $A_V = 7 \pm 4$ mag is found, which shows that more CH_3OH ice observations are warranted due to the large error bar. The upper limits sampled are still much below the detections at high A_V, which confirms previous work that CH_3OH ice is indeed lacking in some clouds. To better understand this puzzling CH_3OH ice dilemma in interstellar clouds, a facility such as the JWST is desired for the following reasons but not limited to: 1) The sensitivity of the JWST in the mid-IR for the 3.53 μm band (S/N $\sim$100) and without the presence of tellurics will be ideal to probe CH_3OH ice. 2) Ice mapping, which allows a large number of sight-lines to be simultaneously probed at a wide range of A_V, is expected to provide a larger sample of CH_3OH ice detections. CH_3OH precursor species, such as CH_4 and CO, can be mapped alongside CH_3OH to observe potential trends between the precursor and product species in different clouds. If the density is indeed low at high A_V for certain clouds, then the CO:CH_3OH ratio will be affected by this, as less CO will be frozen out, and also the higher temperature in less dense regions will reduce the hydrogenation rate of CO to form CH_3OH.

Non-energetic solid-state formation of complex molecules: alcohols and aldehydes

At the low temperature of 10 K and under ultrahigh vacuum conditions, it is shown through experimental simulations complemented with theoretical calculations that various COMs can be formed ‘non-energetically’ (i.e., COMs can be formed by ‘dark’ ice chemistry on interstellar grains, assuming that the starting materials are available). If hydrocarbon radicals are present on/in CO-rich ices, then they should readily react with CO hydrogenation product species to form propanal (aldehyde) and 1-propanol (alcohol). In the experimental investigations, propanal is formed by the barrierless recombination of HCO and H_2CCH/H_3CCH_2 radicals. 1-propanol is formed by the hydrogenation of propanal, which comes with a barrier. The exact barrier value still remains to be explored through computational calculations, however the value is not expected to be below 2560 K, which promotes the idea that other pathways may be more effective to propanol formation. Indeed, it is also shown in this thesis that a variety of 3-carbon COMs, including 1-propanol, can be formed starting from the almost barrierless reaction of propyne/propene and OH radicals. The formation of 3-carbon alcohols can potentially be expanded to the formation of larger, more astrobiologically relevant species, such as fatty alcohols, which may have been part of the primitive material important to life on the early Earth.

In essence, this thesis exploits solid-state experimental techniques to unravel the formation details of simple and complex (organic) molecules on icy interstellar dust grains. Specifically, the study of such molecules through ‘dark’ or ‘non-energetic’ ice chemistry is explored to better understand the chemical inventory at the starting point of ice growth in interstellar clouds. Quantum chemical calculations are incorporated to better understand the experimental results, and to also understand the potential astrochemical relevance of certain studied formation pathways. Additionally, a dedicated observational study is presented, which links with experimental and computational findings to understand certain solid-state processes in interstellar ices. Once the JWST is launched and operational, this thesis work will be directly applicable to observational surveys of simple molecules and COMs in numerous quiescent cloud environments.