Transformation and sublimation of interstellar ices: insights from laboratory experiments and astronomical observations

Carvalho Santos, J. de

Citation

Carvalho Santos, J. de. (2025, July 2). *Transformation and sublimation of interstellar ices: insights from laboratory experiments and astronomical observations*. Retrieved from https://hdl.handle.net/1887/4252309

English summary

Stars are born within immense, inhomogeneous clouds of gas and dust that drift through space. Over time, denser pockets within these clouds accumulate enough material to collapse under their own gravity, giving rise to a young star. Surrounding each newborn star is a swirling disk of leftover cloud material, where planets, moons, asteroids, and comets gradually take shape (Figure 1).

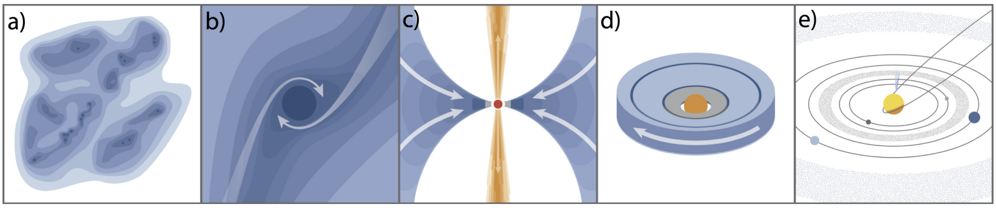

Figure 1: Stages of star and planet formation in Sun-like systems. (a) Dense pockets exists in inhomogeneous clouds of gas and dust. (b and c) These pockets collapse under gravity to form a young star. (d) The surrounding cloud material is dispersed, leaving a young star with a disk where planets can form. (e) Eventually, the disk disappears and gives rise to a planetary system. Adapted from Öberg & Bergin (2021).

These stellar nursery clouds—whose material eventually forms solar system bodies—are made up of about 99% gas and just 1% dust. Yet, despite being scarce compared to gas, dust grains play an outsized role: they provide surfaces where various chemical reactions take place. On these tiny particles, smaller than the width of a human hair, atoms and molecules combine to form essential ingredients for life, including water and organic compounds. As these species accumulate, they create a coating of frozen material—known as interstellar ices—that envelops the dust grains. When a young star forms and heats its surroundings, the icy grains that drift close enough to it experience rising temperatures. This causes the ices to sublimate, releasing into the gas the material that was previously locked in solid form.

Interstellar ice processes

Dust grains—and the ices that form on them—create a fertile environment where chemistry can thrive. First, because temperatures in interstellar clouds are extremely low (around 10 K, or –263°C), gas-phase molecules readily stick to the cold dust surfaces. This allows chemical species to accumulate, come into contact more easily, and react. Second, the solid surface provides a way for the excess energy released during molecule formation to dissipate. This helps stabilize the newly formed molecules, preventing them from immediately breaking apart—a common hindrance to gas-phase chemical reactions in interstellar environments.

Altogether, the physicochemical processes taking place in interstellar ices play a central role in shaping the molecular makeup of the environments where stars and planets begin to form. These ice processes can generally be grouped into four main categories (Figure 2): adsorption, desorption, diffusion, and reaction. When a gas-phase molecule encounters a cold dust grain and sticks to its surface, this is called adsorption. On the other hand, if an adsorbed molecule gains enough energy to overcome the forces holding it to the surface, it is released into the gas phase in a process known as desorption. Molecules on the surface can also move around without detaching from it, in a set of motions called diffusion. Finally, when two species come into contact under the right conditions, a reaction can take place, resulting in the formation of a new molecule.

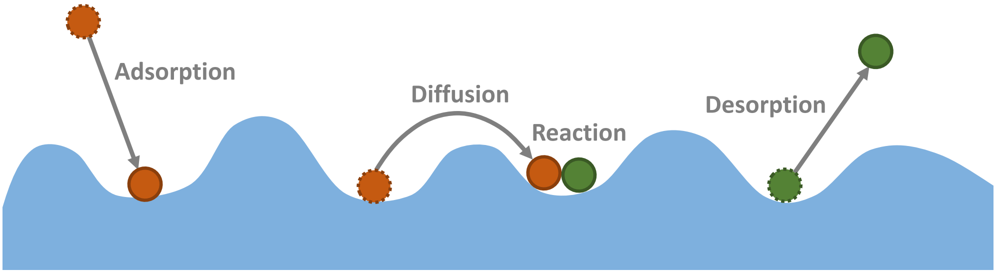

Figure 2: Cartoon of the four categories of ice processes: adsorption, desorption, diffusion, and reaction.

The interplay among these ice processes determines which molecules are formed or destroyed on dust grains, as well as how, and when, they are released into the gas phase. Unraveling the outcomes of these ice processes is therefore essential for understanding which molecules are produced in prestellar and protostellar environments and to what extent they can be incorporated into forming planetesimals. This is the central goal of the present thesis.

Laboratory astrochemistry

Due to the large distance between the Earth and the interstellar clouds where ices grow (typically over 100 pc, or 325 light years), direct experimentation on the icy dust grains within these regions is not possible. Space missions such as Rosetta, which targeted comet 67P/Churyumov–Gerasimenko, and sample-return missions like Hayabusa and OSIRIS-REx can offer some insight into the fate of interstellar ices after they have become part of comets or asteroids; but the earlier stages remain out of reach. To study the physicochemistry taking place in these earlier stages, we recreate the physical conditions of their environments in laboratory settings here on Earth. This is made possible by advanced experimental setups that can reach extremely low temperatures (around 10 K, or −263°C) and pressures (around 10^{-10} mbar, or nearly a quadrillion times below atmospheric pressure). These apparatuses allow us not only to simulate the formation and evolution of interstellar ices, but also to accelerate processes that would naturally take at least millions of years, condensing them into timescales of just a few hours. These controlled experiments also allow us to isolate and study specific mechanisms in simplified systems, offering a more focused view of the chemistry under investigation.

In this thesis, several such vacuum cryogenic apparatuses were utilized. The main one was SURFRESIDE^3, located at Leiden University in the Netherlands, which is specifically built to study surface reactions on interstellar ice analogues triggered by atoms and radicals. Other setups featured in this thesis are LISA (Radboud University, the Netherlands), which focuses on the interaction of interstellar ice analogues with infrared light; and SPACE-KITTEN (Harvard University, United States), designed to investigate how ices respond to thermal processing that mimics heating by a young star.

Observational astrochemistry

To design meaningful experiments, we first need to know which molecules are present in different space environments, and in what physical state. Observations are crucial for this, as they provide the only direct, empirical evidence of the chemical inventory of regions where stars and planets are forming. They also allow us to test and validate hypotheses drawn from laboratory experiments and models of interstellar chemical evolution. In this way, observations form a fundamental pillar of astrochemical research, anchoring experimental and theoretical studies in real astronomical data.

In this thesis, two types of astronomical observations are particularly relevant: those made at radio frequencies and those using infrared light. Radio observations allow us to detect molecules present in the gas phase of interstellar environments, including species that were once frozen in ices and have since sublimated. These observations are carried out using radio antennas, either individually or in coordinated arrays known as interferometers. Infrared observations, on the other hand, are crucial for detecting molecules in ices, which mostly remain invisible at radio frequencies. Together, these two techniques offer complementary views of the chemical composition of star- and planet-forming regions.

This thesis

This thesis investigates the physicochemical evolution of interstellar ices across the various stages of star and planet formation. This includes understanding their formation mechanisms in cold molecular clouds, their transformation during star and planet formation, and their eventual sublimation and potential incorporation into forming planets and planetesimals. To achieve this, we combine experiments using apparatuses that mimic interstellar conditions with astronomical observations of the molecular content in these environments. The chemical pathways discovered in this thesis are highlighted in Figure 3, and below is a summary of the key findings from each chapter:

Chapter 2. In this chapter, we study the formation of methanol (CH_3OH) ice, a major component of interstellar ices that serves as a key precursor to complex organic molecules in space. Our experimental results demonstrate that the dominant final step in the pathway for methanol formation occurs through a reaction between CH_3O and H_2CO, rather than the previously proposed mechanism involving CH_3O and H. These findings align with theoretical model predictions under laboratory settings, which in turn extend to conditions representative of interstellar clouds and suggest that this alternative mechanism is also the dominant process in space. This has significant implications for modeling the chemistry of these environments and interpreting the distribution of deuterated methanol in these regions.

Chapter 3. This chapter investigates experimentally the influence of infrared radiation on interstellar ices, finding that infrared light in resonance with the vibrations of

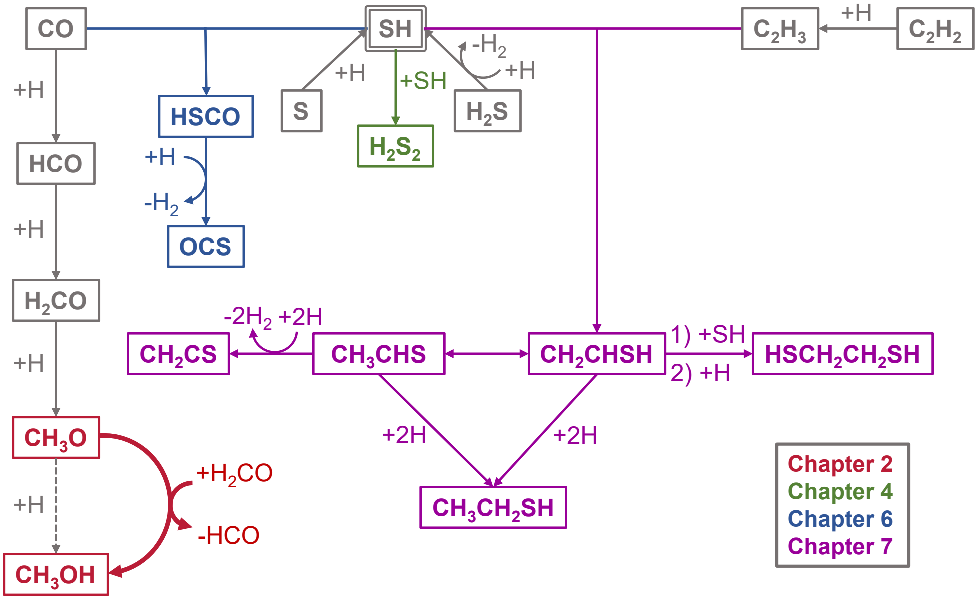

Figure 3: Summary of the interstellar ice reaction routes discovered in this thesis.

ice molecules can induce structural rearrangements and even trigger the desorption of ice material. These effects have potential implications for the observed abundances of complex molecules, particularly those thought to be formed in ices, in the gas phase of regions where thermal sublimation is not feasible.

Chapter 4. This chapter explores the interaction between solid H_2S, a key volatile sulfur carrier in interstellar ices, and hydrogen atoms in the laboratory. We show that H_2S reacts with hydrogen to form HS radicals and H_2, with most of the HS either recombining to form H_2S_2 or reacting again with hydrogen to reform H_2S. A significant fraction of the reformed H_2S promptly desorbs due to its excess formation energy, resulting in a loss of H_2S ice. In this study, we develop a novel approach to directly quantify this chemistry-induced desorption and disentangle its contribution from that of H_2S_2 formation in the net destruction of the original H_2S ice.

Chapter 5. This chapter experimentally characterizes the desorption behavior of H_2S ice. We determine how strongly H_2S adheres to itself and to water ice—the main constituent of interstellar ices—by measuring its desorption behavior when deposited as pure H_2S ice and on top of water ice. We also investigate the desorption behavior of H_2S in mixed ices dominated by water and find that a surprisingly large fraction of H_2S remains trapped well above its normal sublimation temperature. Using these results, we estimate the location in a planet-forming disk where H_2S transitions from ice to gas and find that it likely remains solid within the region where comets and icy planetesimals form.

Chapter 6. In this chapter we build on the findings from Chapter 4 and investigate experimentally the chemical network initiated by interactions between HS, CO, and H. We find that this network leads to the formation of OCS ice—a major volatile sulfur carrier in interstellar ices—even at unfavorable conditions such as in scarcity of H atoms. We also argue that this new potential route to form OCS in ices can occur throughout a wide range of a cloud lifespan, and is more consistent with the proposed ice phase (and therefore cloud collapse timescale) in which OCS is thought to be observed than other commonly invoked OCS formation mechanisms.

Chapter 7. This chapter extends the sulfur ice chemistry explored in Chapters 4 and 6 by experimentally investigating the formation of sulfur-bearing complex organic molecules with two carbon atoms. We study the reactions of HS with C_2H_2 and H and find that this network leads to a rich chemistry, producing at least six sulfur-containing products, five of which are organic. The dominant product is ethanethiol (CH_3CH_2SH)—a molecule already detected in the interstellar gas phase—which appears to act as a chemical sink, forming efficiently as long as hydrogen atoms are present, at the expense of the other products.

Chapter 8. In this chapter, we present gas-phase observations of two major volatile sulfur carriers, OCS and SO_2, around a large sample of massive young, forming stars. We find that their abundances with respect to methanol (CH_3OH; a common reference molecule found in ices), do not display any trends across stars of different brightnesses. This suggests that both molecules are predominantly formed in ices before the star itself is formed—that is, in clouds. However, despite this shared origin, their abundance distributions and how they compare to ice observations point to different histories: OCS appears to form later in the cloud's evolution, in tandem with CH_3OH ice, while SO_2 likely forms earlier, simultaneously to H_2O ice, and/or may be significantly altered after it sublimates due to gas-phase reactions happening close to the newly forming star.

Chapter 9. This chapter presents gas-phase observations of the organic molecule CH_3CCH around a massive young star in formation. This molecule is thought to form through a combination of gas and ice chemistry and is commonly used to trace gas temperatures. By analyzing the kinematics of the gas, we find that the emission is dominated by the quiescent, outer layers surrounding the protostar and likely contains two distinct components—one warmer than the other. Additionally, thanks to the spectroscopic properties of CH_3CCH, we are able to indirectly trace the overall temperature range of this gas in more detail than is typically achievable with observations from a single-antenna radio telescope.

Future look

Overall, this thesis shows how laboratory experiments and telescope observations work together to reveal the chemical story of the ices and gases that form stars and planets. This is an exciting era for this field: thanks to cutting-edge laboratory technology and powerful telescopes like ALMA and JWST, we are offered an unprecedented look at the building blocks of planets and planetesimals in both gas and ice. With JWST also providing new insights into the materials present where planets are forming, the combined efforts of observations, lab work, and computer models will soon give us our best picture yet of the chemistry at play in the birthplaces of planets.