# From clouds to comets: tracing the molecular journey of interstellar ices in the JWST era

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# English summary

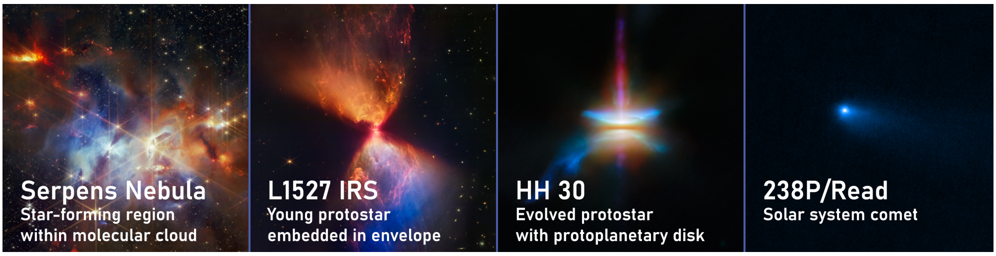


**Figure 1:** Four cosmic objects representing different stages of the star and planet formation sequence captured with the *James Webb* Space Telescope (JWST). All of their spectra indicate chemical inventories rich in icy volatiles. Image credits: NASA/ESA/CSA/STScI and, from left to right, 1. Klaus Pontoppidan (NASA-JPL)/Joel Green (STScI). 2. Joseph DePasquale (STScI)/Alyssa Pagan (STScI)/Anton Koekemoer (STScI). 3. Ryo Tazaki et al. 4. Mike Kelley/Henry Hsieh (PSI)/Alyssa Pagan (STScI).

Deep in the remote interstellar medium, clouds of gas and microscopic dust grains are shaped by physical processes into swirling webs of pillars, globules, and filaments. The densest depths of these clouds are largely shielded from the surrounding interstellar radiation, creating exceptionally cold and dark conditions that are, perhaps counterintuitively, ideal for chemical reactions. The cooling of the dust grains within these clouds turns them into catalytic surfaces – gaseous species stick to them and subsequently react with each other to form a plethora of volatile biogenic molecules in the form of ice layers that grow on top of the dust grains.

The most abundant of these molecules is water, which is produced particularly efficiently under such dark and dusty conditions. However, a variety of other species like methanol, formaldehyde, and ammonium salts can also be found in these ices. Eventually, the dust cloud may collapse due to its own gravity, allowing a *protostar* to begin forming at its center. The icy dust particles from the cloud – now enriched with volatile molecules – then feed the growing star and the surrounding protoplanetary disk, where its planets form. In this way, the ices grown in interstellar dust clouds become one of the primary ingredients of planetary systems and serve as a key source of biogenic volatiles during planet formation.

The work presented in this thesis investigates 1) the chemistry that occurs in interstellar ices during these earliest stages of star and planet formation, and 2) how that chemistry sets the stage for the formation of solar systems like our own and the distributions of volatiles within them. To do so, it employs infrared (IR) spectroscopy in a combined experimental and observational approach, where data collected in Earth-based laboratories that simulate interstellar conditions are used to analyze interstellar spectra observed by powerful IR facilities like the *James Webb* Space Telescope (JWST) and its predecessors. The presented studies largely target molecules that have been detected in volatile-rich and primitive small solar system bodies – particularly comets – to assess the chemical link between the interstellar medium and planetary systems.

# Ice chemistry during star and planet formation

The chemical inventory of the interstellar medium (ISM) mainly consists of hydrogen and some helium atoms formed via fusion shortly after the Big Bang. Additionally, outflows from exploding dying stars supply trace amounts of heavier elements like carbon, nitrogen, oxygen, sulfur, and silicon in the form of atoms, ions, and microscopic grains of highly radiation-resistant molecules like polycyclic aromatic hydrocarbons (PAHs) and silicate minerals.

These grains shield, absorb, and scatter interstellar radiation and catalyze reactions on their surfaces, cooling their surroundings and enabling chemical reactions. In the densest regions of interstellar dust clouds, temperatures can be as low as 10 K (-263.15°C). At these temperatures, gaseous atoms and molecules that stick to the grains form layers of ices. The high abundance and mobility of hydrogen atoms on the surfaces of these grains lead to the production of reduced species such as $H_2O$, $CH_4$, and $NH_3$, with water being by far the most abundant. Species that are acidic can react with the base $NH_3$ to form ammonium salts, like $NH_4SH$ and $NH_4OCN$. Organic molecules like $H_2CO$ and $CH_3OH$ can also form via the hydrogenation of CO that freezes out onto the grains from the gas phase. During the evolution of the cloud, different species dominate the ice chemistry at different cloud stages and cloud locations, resulting in a chemical stratification within the ice layers formed throughout a cloud's lifetime (Fig. 2). Namely, ice layers rich in water are produced largely at early, less dense cloud stages, while ice layers rich in CO and its products like $CH_3OH$ are produced in the later, denser cloud stages.

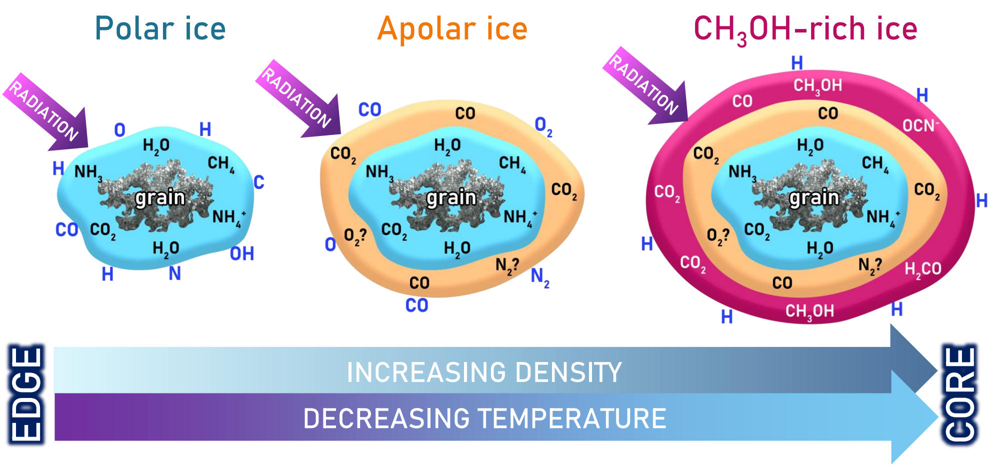


**Figure 2:** Different stages of ice growth in molecular clouds. In the first ice layers grown in the less dense translucent regions closer to the cloud edges, $H_2O$, $CO_2$, and hydrogenated species like $NH_3$ and $CH_4$ form. As densities increase, temperatures drop, enabling the growth of an apolar layer dominated by CO and $CO_2$. In the densest regions, CO is efficiently hydrogenated to form $CH_3OH$, resulting in a $CH_3OH$-rich layer that includes other species formed from CO like $CO_2$, OCS, and $OCN^-$.

If a molecular cloud is sufficiently massive and dense, gravitational instabilities and turbulence can trigger the cloud's gravitational collapse, initiating the formation of a protostellar core. The nascent protostar follows an evolutionary sequence that ends in the formation of a star and sometimes planets. First, molecular cloud material feeds the core source, and gravitational potential energy is converted into thermal energy as the material collapses, heating the surrounding envelope of material. As the protostar continues to accrete surrounding envelope material, conservation of angular momentum results in outflows of accreted material from the source poles as well as the flattening of the inner portion of the envelope into a *protoplanetary disk*. Matter within the disk starts to coagulate into larger bodies, marking the beginnings of planetary formation. Eventually the envelope material is completely depleted via outflows and accretion, leaving only the disk and a central pre-main sequence star. Finally, the disk material is also depleted via disk winds and accretion by the source or disk planetesimals.

Ices from the molecular cloud stage are inherited by the protostellar envelope and disk, where they can transform through various physical processes (Fig. 3). One of the processes most central to this transformation is the desorption of ice species into the gas phase, which is governed by molecular *snowlines*: the thermal boundaries that define the regions where envelope or disk temperatures become warm enough to sublimate specific ice species.

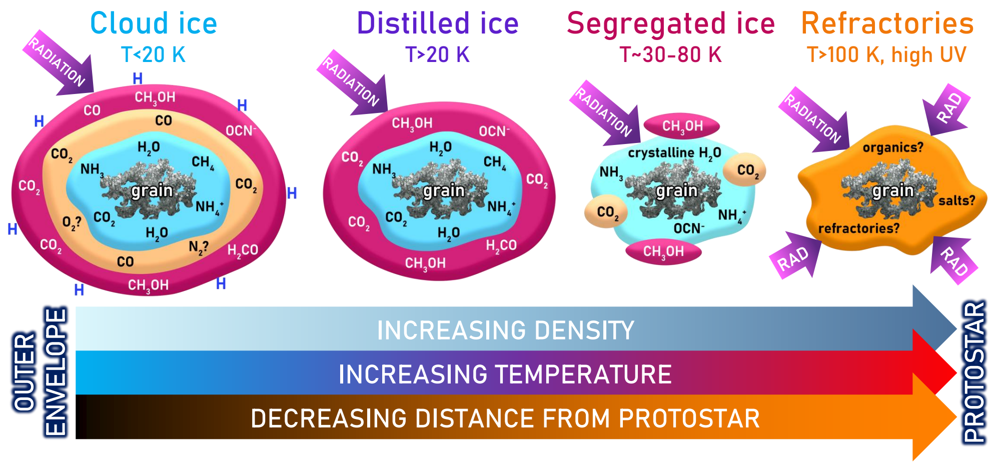


**Figure 3:** Changes in ice chemistry during processing in protostellar envelopes and protoplanetary disks. In the coldest envelope and disk regions, ice structures mimic those seen toward molecular clouds. As the ices move into warmer regions, hypervolatile species desorb into the gas phase, distilling the ice. Even warmer temperatures drive the segregation of certain species within the ice matrix and crystallization of the amorphous ices. Past 100 K, most of the volatile ices are expected to have desorbed into the gas, leaving behind on the grain more refractory species like salts and larger complex organics.

In younger and colder protostellar envelopes as well as the coldest, outermost regions of more evolved protostellar envelopes and the cold midplanes of protoplanetary disks, molecular cloud ices remain largely intact. As the ices move into warmer regions, they cross molecular snowlines in order of decreasing volatility, effectively *distilling* the ice layers as various ice species desorb into the gas phase, where they can further react with other gaseous species. Before inducing desorption, warmer temperatures also increase the mobility of species within the ices, leading to restructuring of the ice matrix. Additionally, increased mobility can increase rates of reactions that involve heavier species.

Snowlines in protoplanetary disks are a key factor that partially dictates the compositions of planetary objects based on their formation locations within the disk. A given species can be accreted by planetesimals that form outside of the snowline of that species, so the starting material that forms a planetary body will depend on where that body lies in the protoplanetary disk in relation to molecular snowlines. This initial chemical record is subsequently altered by snowline changes during disk evolution, the dynamic scattering of planetary objects into different disk regions, and the geologic, atmsopheric, and space-weathering processes that planetary bodies undergo.

Small airless bodies formed in the outermost reaches of the solar system are thought to contain some of the most pristine records of volatiles inherited from interstellar ices because their small sizes preclude significant geologic or atmospheric processing, and their formation locations in the cold outer solar system allowed them to retain volatiles after their formation. Comets are a prime example, and comparisons between their volatile inventories and those of interstellar ices and protostellar gases have revealed some striking similarities. However, systematic differences between cometary and interstellar chemical inventories also point toward cometary material undergoing at least some degree of chemical processing within the protoplanetary disk.

# Infrared spectroscopy of ices

Molecules absorb or emit light by transitioning between their quantized energy states. Molecules in space can be identified and quantified by their unique emission or absorption features in telescopic spectra. The ice chemistry described in this thesis is uncovered using absorption features at infrared (IR) wavelengths, which probe vibrational energy transitions.

The positions, shapes, and intensities of IR absorption peaks observed toward interstellar regions contain information about the chemical identities, quantities, and the physical and chemical environments of interstellar ices. Extracting this information requires an integrated approach in which observations are compared to models that use laboratory data.

## Observational methods

Fig. 4 provides a schematic of the observing geometry used to acquire interstellar ice spectra. The telescope is aimed toward an IR light source, which can be either a background star located behind an interstellar cloud, or a protostar that is embedded within the cloud. Species located along the line of sight from the light source to the telescope are then observed against the (proto)stellar continuum. A large portion of the observational work utilized in this thesis was collected with the JWST, which has superior sensitivity, wavelength coverage, and spectral and spatial resolution compared to most previous IR telescopes. An example JWST spectrum of interstellar ices observed toward a protostar is presented in Fig. 5.

A specific molecule can be identified or ”assigned” in an interstellar IR spectrum if its characteristic IR features, defined via controlled laboratory experiments or theoretical quantum calculations, are observed. Assignments can be ascertained by comparing how closely observed peak shapes and wavelengths match those in laboratory data. Once assigned, an IR peak can be used to quantify molecules along a line of sight. In addition, peak shapes can be used to infer the physical and chemical properties of their ice carriers.

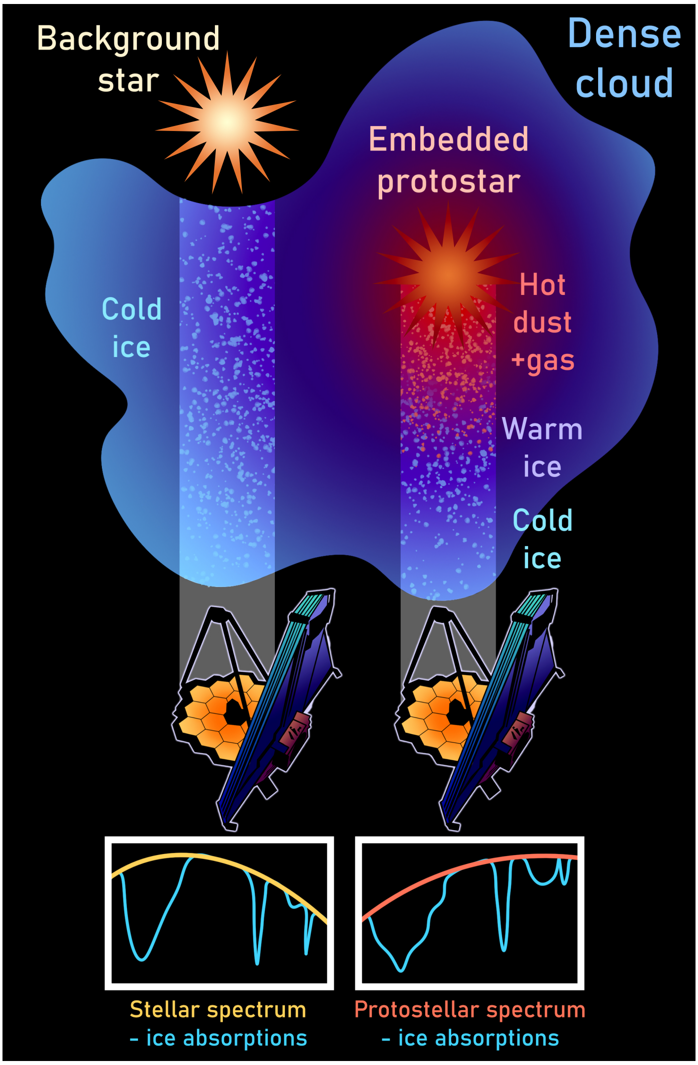


**Figure 4:** A schematic of how telescopes observe absorption features of interstellar ices in dense clouds and protostellar envelopes. The ices are observed along a pencil beam that traces the path from an IR light source (either an extincted background star or a protostar) to the telescope.

## Laboratory methods

Laboratory measurements provide experimental data that is essential to interpreting ice observations. In such experiments, interstellar ice analogs are deposited upon a cryo-cooled flat substrate within an ultrahigh vacuum chamber with typical pressures on the order of $\leq 10^{-8}$-$10^{-10}$ mbar (up to trillions of times lower than standard atmospheric pressure on Earth). The resulting lab-grown ice is a physical approximation of the ice layers on top of interstellar dust grains. Laboratory IR spectra of these ices are then collected, which can in some cases

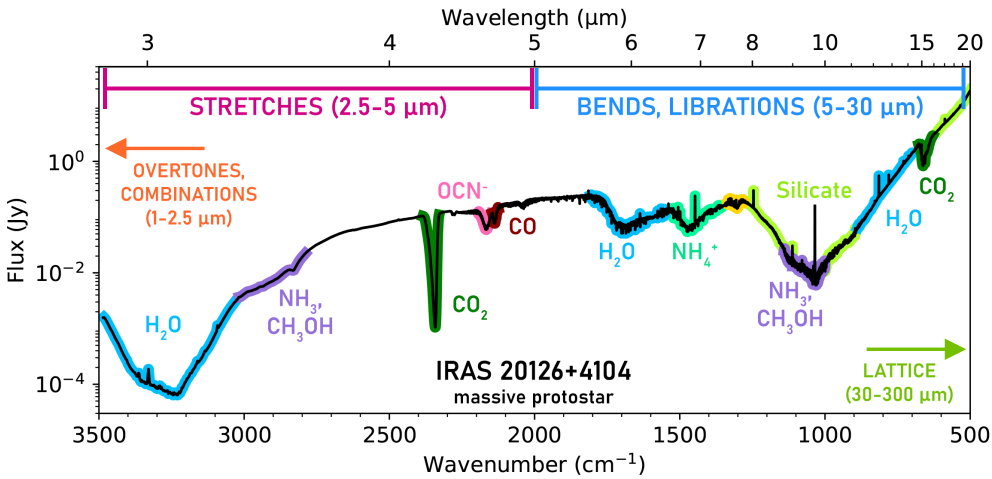


**Figure 5:** Example IR spectrum of a massive protostar (IRAS 20126+4104) showing interstellar ice and dust absorption features upon the protostellar continuum.

be directly compared to ice observations to identify species present in ices. Apparent band strengths of ice features can also be calculated, which can be used to quantify ice species in observations. The laboratory work presented in this thesis was conducted on the Infrared Absorption Set-up for Ice Spectroscopy (IRASIS) in the Leiden Laboratory for Astrophysics.

# Thesis overview

Infrared spectroscopy has continually revealed that interstellar ices are hosts to a rich chemistry foundational to the formation and transport of volatiles in planetary systems. However, a number of questions about this chemistry remained unanswered when this thesis work began: *To what extent is interstellar ice inherited versus chemically reprocessed in protostellar envelopes and protoplanetary disks before its accretion into planetary objects? What species are the major sulfur sinks in the densest stages of star formation? Which of the many complex organic molecules detected in the gas phase in protostars can be found also in ices, and what does that tell us about their formation histories?* The chapters in this thesis address these questions.

**Chapter 2:** This work makes the first robust detections of the O-D stretching mode of HDO ice at 4.1 $\mu$m with JWST. It then presents a method for quantifying ice HDO/$H_2O$ ratios toward protostars and uses this method to find this ratio toward two massive protostars observed with JWST. Ice HDO/$H_2O$ ratios of $4.6\pm1.8\times10^{-3}$ and $2.6\pm1.2\times10^{-3}$ are obtained for the two sources. These ratios are similar to the highest reported gas HDO/$H_2O$ ratios measured toward massive protostars and the hot inner regions of isolated low-mass protostars, suggesting that at least some of the gas HDO/$H_2O$ ratios measured toward massive hot cores are representative of those in ices.

**Chapter 3:** This work presents the first detection of the 4.1 $\mu$m HDO ice feature with JWST toward a low-mass Sun-like protostar, L1527 IRS. The method developed in Chapter 2 is used to measure an ice HDO/$H_2O$ ratio of $4.4^{+3.7}_{-1.7} \times 10^{-3}$, similar to the gas HDO/$H_2O$ ratios measured in the warm inner cores of other low-mass protostellar envelopes and protoplanetary disks found in comparably isolated star-forming regions. Such a similarity tentatively supports the assumption that water vapor detected in these regions is not significantly altered by gas-phase reactions following ice sublimation. It also supports the hypothesis that pre- and protostellar water ice is largely inherited in a chemically unaltered state by outer protoplanetary disks. However, the fraction is a factor of ~4-10 times higher than the gas HDO/$H_2O$ ratios measured toward comets and low-mass protostars in clustered star-forming regions, perhaps due to gas-phase water reprocessing in protostellar envelopes and protoplanetary disks or differences between prestellar conditions of isolated dense cores and the clustered star-forming regions that are more analogous to the environment in which our Sun formed.

**Chapter 4:** Laboratory IR spectra and apparent band strengths of ices containing $NH_4SH$ salt were collected to investigate whether $NH_4SH$ could be a major sulfur reservoir and a carrier of the 6.85 $\mu$m band in interstellar ices. The laboratory IR spectra were compared to those of four protostars and two dense clouds. The observed 6.85 $\mu$m feature toward these sources is fit well with laboratory $NH_4SH$:$H_2O$ ice spectra. Calculated $NH_4^+$ column densities range from 8–23% with respect to $H_2O$. The apparent band strength of the $SH^-$ feature is likely too low for the feature to be detectable, but the 5.3 $\mu$m $NH_4SH$ combination mode may be an alternative means of detection. Its tentative assignment supports the presence of $NH_4^+$ salts in ices and is the first tentative observation of the $SH^-$ anion toward interstellar ices. If the majority ($\gtrsim$80–85%) of the $NH_4^+$ cations quantified toward the investigated sources are bound to $SH^-$ anions, then $NH_4SH$ salts could account for up to 17–18% of their sulfur budgets.

**Chapter 5:** This chapter provides a library of new laboratory IR spectra and apparent band strengths of OCS in $CH_3OH$- and CO-rich ice mixtures, some of which also include $H_2S$ and $H_2O$, to aid future studies of the abundance, physicochemical environment, and evolutionary history of interstellar OCS ice. Of these new laboratory spectra, tertiary OCS:CO:$CH_3OH$ ice mixtures provide the best fits to observations of high-mass protostars, providing further evidence that OCS forms with $CH_3OH$, possibly via chemical pathways involving CO. A mass spectrometric calibration method for producing ice mixtures using gases and high vapor pressure liquids is described.

**Chapter 6:** Gaseous formamide has been detected in many interstellar regions, but whether it forms in the ice or gas is a topic of great debate. This chapter characterizes the IR spectra and apparent band strengths of pure and mixed formamide in interstellar ice analogs. Three formamide bands are identified as potential tracers in observational ice spectra. The laboratory spectra are compared to the 7.24 $\mu$m band in spectra of protostars and prestellar cores. If formamide ice contributes significantly to the observed band, it is more likely in a polar ice matrix, but other species provide better fits and are more likely to be the main carriers. Upper limits ranging from 0.35-5.1% with respect to $H_2O$ were calculated, in agreement with gas-phase protostellar as well as cometary formamide abundances.

## Scientific significance and future directions

- HDO ice is now robustly detectable in star-forming regions with JWST. Similarities between ice and gas water D/H ratios measured toward protostars and the gas water D/H measured toward protoplanetary disks suggest interstellar ice inheritance between protostellar envelopes and protoplanetary disks.

- Comparisons between water D/H values in protostellar ices and cometary comae suggest either some level of gas-phase water reprocessing in the protoplanetary disk *or* or an environmentally-driven diversity in prestellar water ice D/H values across different star-forming regions in our galaxy.

- Up to $\sim$20% of the sulfur in dense star-forming regions like molecular clouds and protostellar envelopes may be locked up in salts like $NH_4SH$, potentially resolving the decades-long puzzle of why $H_2S$ is not detected in interstellar ices despite predictions from chemical models.

- Given their higher desorption temperatures relative to their neutral acid-base counterparts, salts like $NH_4SH$ may have facilitated the transport of the volatile elements N and S into the inner solar system, where they could eventually be accreted by volatile-rich bodies like carbonaceous asteroids.

- Even with JWST, it may not be possible to unambiguously detect the absorption features of many of the less abundant and semi-refractory complex organic molecules like formamide due to overlaps with absorptions from more abundant and volatile organics.

Looking forward, a larger sample of ice water D/H measured toward protostars spanning a variety of environments will be needed to better constrain the ice water D/H ratio that was inherited by our solar system. Furthermore, a large fraction of the interstellar sulfur still remains missing. If it is in minerals or allotropes, chances for direct detections of such species are not promising. But wherever this missing sulfur may be, it is time for an updated sulfur ice survey with JWST data to update previous constraints. The laboratory data presented in this thesis enable such surveys. And finally, observationally targeting lines of sight with low ice-to-dust ratios but high dust columns (*i.e.*, protostellar envelopes that are still dense but have been highly thermally or energetically processed) may provide better opportunities for identifying more refractory trace ice species whose absorptions are typically overshadowed by the strong absorptions of more abundant volatiles.