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A song of ice and gas: the formation and evolution of complex organic molecules

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English summary

Stars are born together with molecules. Long before a young star becomes visible, its natal environment is already quietly assembling new molecular species under extreme conditions. This thesis is concerned with that hidden chemical history: how simple atoms in the interstellar medium are transformed into increasingly complex molecules as stars form and evolve.

Star formation: a physical and chemical process

Stars form within cold, dense regions of interstellar space known as **molecular clouds**. These molecular clouds are some of the quietest places in the Universe, with temperatures so low (~ 10 K, or equivalently, $< -260^\circ\text{C}$) that motion nearly freezes. However, it is exactly these calm, frigid conditions that allow both stars and molecules to form.

As gravity slowly pulls material together inside a cloud, gas becomes denser and colder. At this stage, atoms and simple molecules (e.g., H and CO) begin to stick to tiny dust grains and gradually coat them with thin layers of ice. Although invisible to the naked eye, these icy grains are crucial to the ongoing chemistry: they provide surfaces where atoms can meet, react, and grow into new molecules.

As the collapse continues, a protostar forms at the center of the cloud. While the surrounding material is gradually heated by the growing star, icy mantles on dust grains begin to warm, rearrange, and eventually evaporate into the gas phase. Regions close to the protostar become compact reservoirs of warm, molecule-rich gas. These regions, known as **hot cores** or **hot corinos**, are where astronomers observe some of the richest chemistry in space.

Complex organic molecules: a rising star in astrochemistry

Among the many molecules found in star-forming regions, astronomers are especially interested in **complex organic molecules**, or **COMs**. These are carbon-containing molecules made of at least six atoms—far simpler than DNA or proteins, but already considered “complex” by the standards of the Universe (see Fig. 1 for a sample of oxygen-bearing COMs, or O-COMs).

For a long time, scientists assumed that such molecules are mainly built upon simpler species in the gas phase after evaporated from dust grains. Over the past two decades, however, laboratory experiments and astrochemical models have revealed that this picture is incomplete. Many gas-phase reactions turn out to be too inefficient to explain the observed abundances of COMs. Observations have also shown that gas-phase COMs already exist in extremely cold regions before protostars are born, where almost nothing should be able to move. This discovery forced a rethink of how chemistry works in the early stages of star formation. As a result, more attention turned to solid-phase chemistry on grain surfaces, where atoms and small molecules can combine step by step, even at very low temperatures. Subsequent theoretical

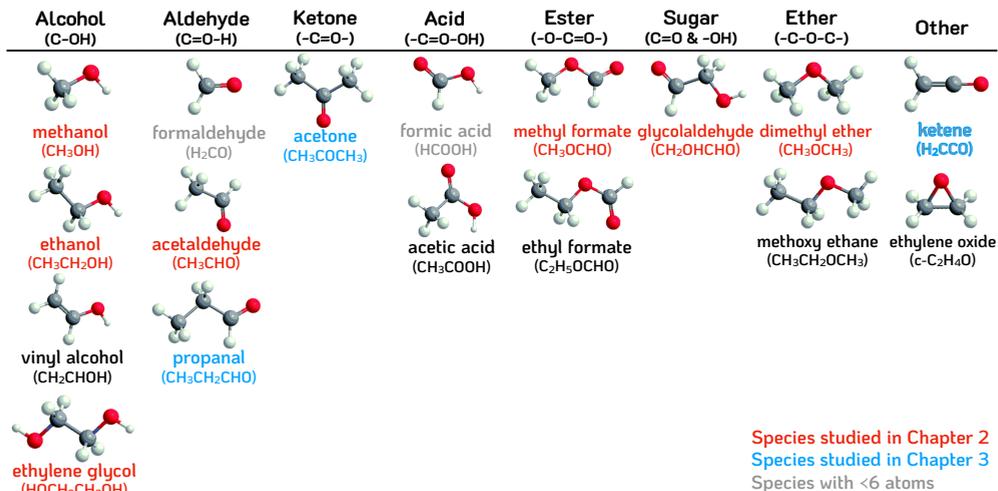


Figure 1: Summary of some commonly detected oxygen-bearing COMs (O-COMs), categorized by their functional groups. Adopted from Fig. 12 of Maity et al. (2015).

studies have gone a step further, proposing reaction pathways that do not require molecules to diffuse but instead proceed locally when reactants are created next to one another.

Today, the formation of COMs is understood as a combination of processes taking place in cold ices, during gradual warm-up, and later in the gas. The question now is no longer whether grain-surface chemistry matters, but how different chemical mechanisms work together over time.

Observing COMs in the gas: the path so far

Molecules can move in different ways. Besides moving as a whole, they can also rotate and vibrate, producing radiation of specific energies. When this radiation is measured across different wavelengths (which represent energies), it forms what astronomers call a **spectrum**. By analyzing an observed spectrum, astronomers can identify which molecules are present and measure their physical properties such as abundance and temperature.

For decades, astronomers have primarily observed interstellar molecules in the gas phase, since their rotational motions produce signals at millimeter and submillimeter (also known as “radio”) wavelengths that are relatively easy to observe with radio telescopes. Gas-phase observations are especially powerful in hot core regions close to protostars, where icy mantles have evaporated from dust grains. Surveys of these regions reveal an extraordinary richness of molecules, often with dozens of lines packed into small frequency ranges (as shown in Fig. 2). In particular, the Atacama Large Millimeter/submillimeter Array (ALMA) has been revolutionary in the field, offering both the sensitivity needed to detect rare molecules and the spatial resolution needed to isolate compact chemical regions.

Observations of gas-phase COMs show both similarities and differences in their abundances among protostellar sources. The abundances of some COMs (e.g., CH₃OCH₃

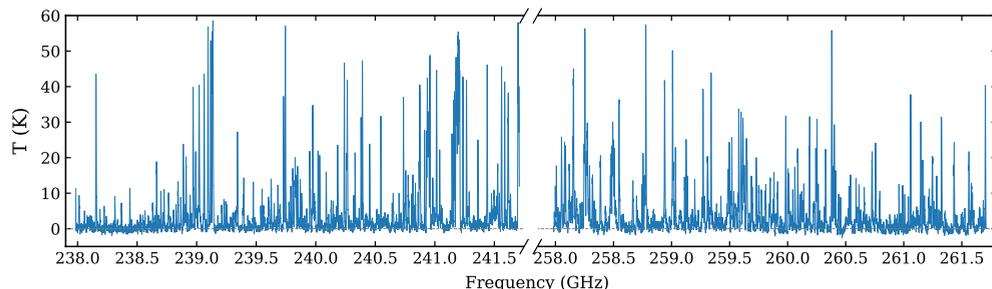


Figure 2: ALMA spectrum of G19.88-0.53, one of the high-mass hot cores studied in Chapters 2 & 3. Most of the displayed lines are emitted by gas-phase COMs.

and CH_3OCHO) remain consistent across sources with different masses, while those of others (e.g., CH_3CHO and $\text{C}_2\text{H}_5\text{OH}$) vary more significantly. Such patterns hint at similar formation environments that are more likely realized in the very beginning of star formation, but also suggest additional processing after molecules sublime into the gas phase. However, gas-phase observations alone cannot tell us what happened before evaporation—a limitation that becomes critical when trying to understand the full formation and evolutionary history of COMs.

Observing COMs in ices: the missing half of the picture

While gas-phase observations are powerful, they reveal only part of the chemical inventory. In the earliest stages of star formation, most molecules are locked up in icy mantles on dust grains. These ices are not able to rotate and emit radio waves like their gaseous counterparts, but instead they can absorb infrared (IR) light through various vibrations such as bending and stretching.

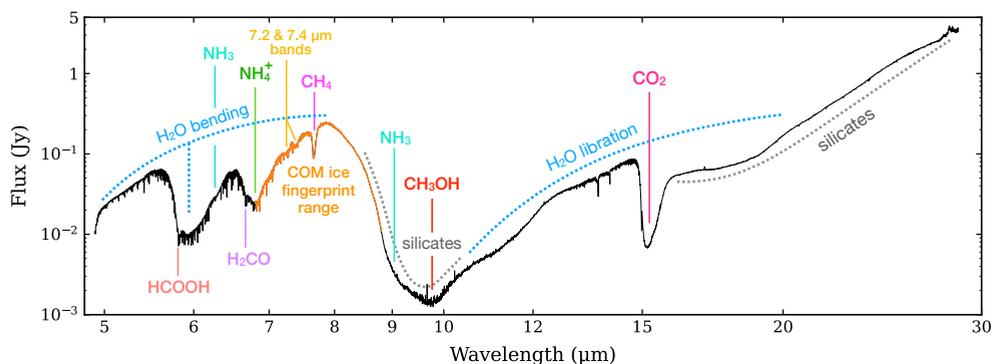


Figure 3: JWST spectrum of B1-c, a famous low-mass protostar studied in Chapter 4. The absorption features of major interstellar ices and the fingerprint range of COM ices (6.8–8.8 μm) are labeled in different colors.

Unfortunately, infrared observations are challenging and limited from the ground due to the absorption of Earth's atmosphere. Earlier infrared telescopes mainly de-

tected simple ices (e.g., H_2O , CO , and CO_2), with methanol (CH_3OH) stood out as the only COM ice that was firmly detected in space. Fortunately, the launch of the *James Webb* Space Telescope (JWST) in 2021 changed this situation dramatically. With its exceptional sensitivity and spectral resolution, JWST can detect weak absorption features produced by larger molecules (e.g., COMs larger than methanol) in the solid phase (see Fig. 3 for a JWST spectrum of a protostar).

JWST observations open a new window on chemistry in space, but also bring a lot of challenges. The fingerprints of ices, which are present in the form of “absorption bands” in infrared spectra, usually do not have isolated and predictable shapes as the “emission lines” produced by gaseous molecules. Since the band shapes of molecular ices vary irregularly with temperature and mixing conditions (i.e., which species are mixed and in what proportions), measuring their spectra in laboratories is essential for analyzing the observational data. As an emerging field in astrochemistry, the study of COM ices relies on close interplay between observations, laboratory experiments, and continued refinement of analysis strategies.

This thesis: tracing COMs from ice to gas

This thesis aims at advancing the observational studies of COMs in both gas and ice using two of the most powerful telescopes in the world—ALMA and JWST. The first part of this thesis (Chapters 2–3) extends traditional case studies of gas-phase COMs in individual sources to systematic analyses of large samples. The gas-phase observations are then connected to the newly available observations of COM ices by JWST in the second part (Chapters 4–5). The combination of ALMA and JWST observations enables us to trace a more complete ice-to-gas evolution of COMs during early stages of star formation.

The first part of this thesis focuses on ALMA observations of gas-phase COMs in the hot core of a dozen of high-mass protostars. Specifically, **Chapter 2** studies six oxygen-bearing COMs (i.e., those highlighted in red other than methanol in Fig. 1) and compares their abundances across 14 high-mass sources and five low-mass sources. By normalizing these six molecules to methanol (the simplest and most abundant COM), this chapter shows a counterintuitive result: the abundance ratios between these O-COMs and methanol seem not vary with stellar luminosity or mass. Although the abundance ratios show varying degrees of scatter for different molecules, the overall trends remain constant across stellar luminosity.

Chapter 3 extends the systematic study of gas-phase COMs in Chapter 2 to acetone (CH_3COCH_3) and propanal ($\text{C}_2\text{H}_5\text{CHO}$), two larger O-COMs with three carbon atoms that have only been studied in individual sources. In addition to measuring their physical properties, this chapter examines several possible formation pathways by checking their gas-phase abundances with respect to those of other potentially relevant molecules such as acetaldehyde (CH_3CHO) and ketene (H_2CCO). This chapter also summarizes the gas-phase abundance ratios between methanol and all the eight O-COMs studied in Chapters 2 and 3, revealing interesting results that aldehydes (those with $-\text{CHO}$ group) are overall depleted in the gas phase, while molecules with CH_3O radicals are among the most abundant O-COMs in observations. These results show the importance of systematic analysis, and also call for more attention to acetone, which is an abundant O-COM but has often been overlooked by the community.

The second part of this thesis shifts the focus from gas to ice. **Chapter 4** shows the possibility of detecting solid-phase COM larger than methanol with JWST and demonstrates the full procedure of how to quantify the COM ice abundances from the “COM ice fingerprint range” (i.e., 6.8–8.8 μm) in JWST spectra. This chapter also presents the first direct gas-to-ice comparison of COMs in the same protostellar systems. By measuring the abundances of four commonly detected O-COMs in both phases, this chapter shows that some molecules appear to keep intact during the transition from ice to gas, while others do not. The results indicate that both inheritance from ices and subsequent gas-phase reprocessing can play significant roles in shaping the COM chemistry.

Chapter 5 expands the study of the COM ice fingerprint range in Chapter 4 to a larger sample of protostellar sources, and comes up with a systematic method for isolating weak ice features from infrared spectra. By measuring the properties of absorption bands (e.g., their peak positions and widths) and comparing them with laboratory data, we can identify the most plausible ice species or mixtures responsible for these bands. This chapter provides the first systematic analysis of the COM ice fingerprint range, strengthening the case that solid-phase chemistry is widespread during early star formation.

Looking ahead: a new era of astrochemistry

We have now entered a new era of astrochemistry. While ALMA continues to provide high-quality spectra and maps of molecular gas, JWST has opened the door to systematic studies of bigger molecules in ice. Instead of inferring ice chemistry indirectly from gas-phase observations, we can now observe both reservoirs directly and compare them quantitatively. In the coming years, large observational programs will expand these studies to many more sources with different masses. At the same time, laboratory experiments and chemical models will be leveraged to enable deeper analyses of observational data. Together, these advances bring us closer to addressing broader questions about the chemical origins of planetary systems, and ultimately, the pathways that lead to life.