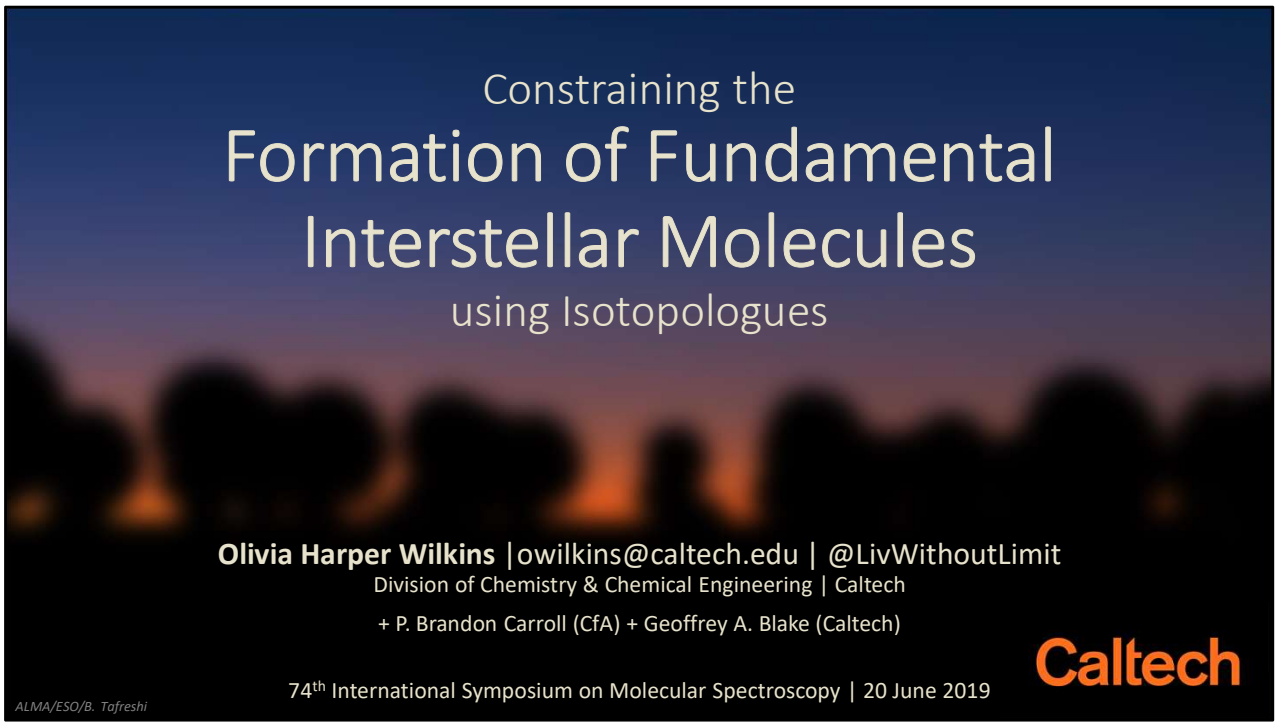
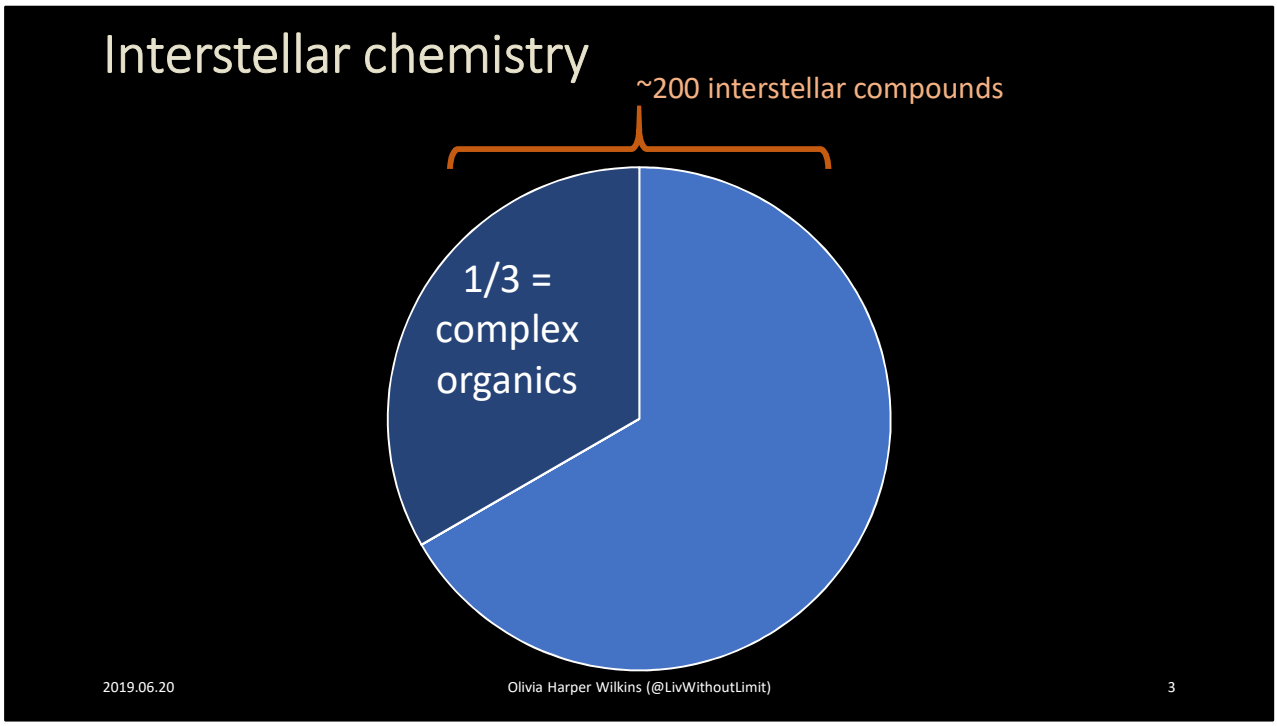


These are the slides (adjusted for ease of viewing on a PDF) for a presentation given by Olivia Harper Wilkins (Ph.D. candidate, Division of Chemistry & Chemical Engineering, Caltech) at the 74th International Symposium on Molecular Spectroscopy (ISMS).

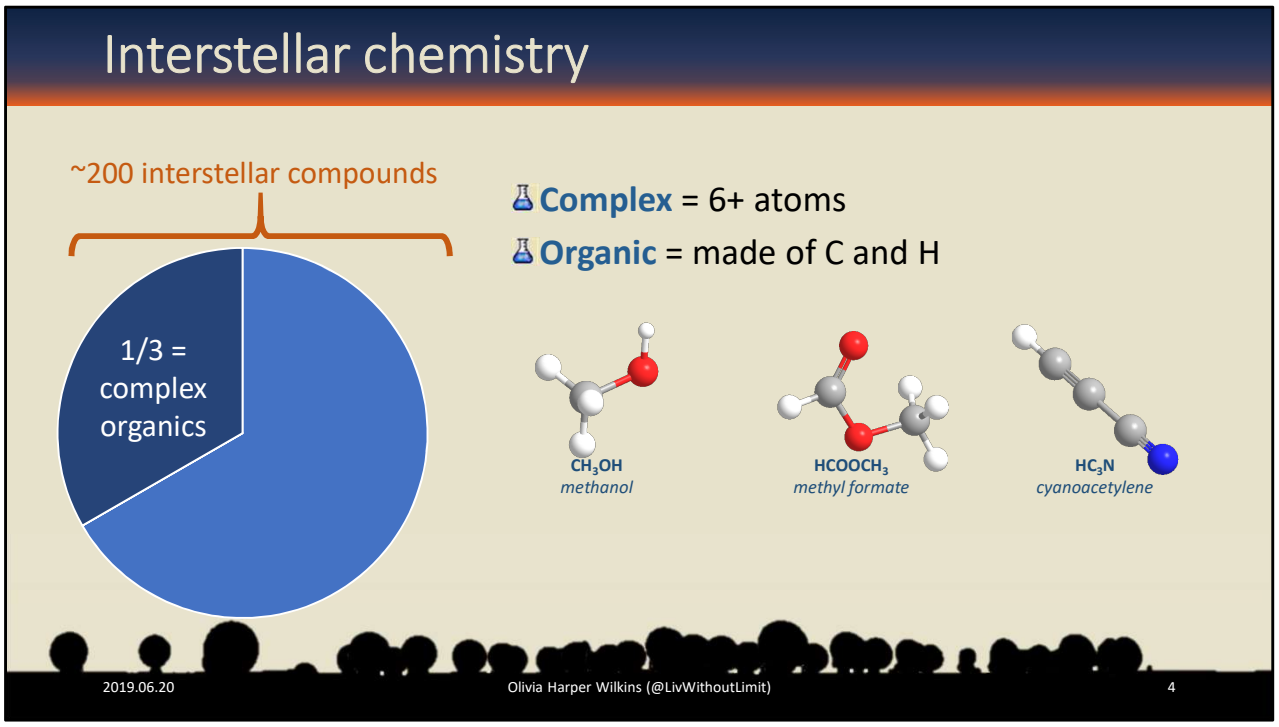
You can learn more about Olivia and her work through the following media:

email | **owilkins@caltech.edu**
website | **http://theskyisnotthelimit.org**
Twitter | **@LivWithoutLimit**
Instagram | **@LivWithoutLimit**

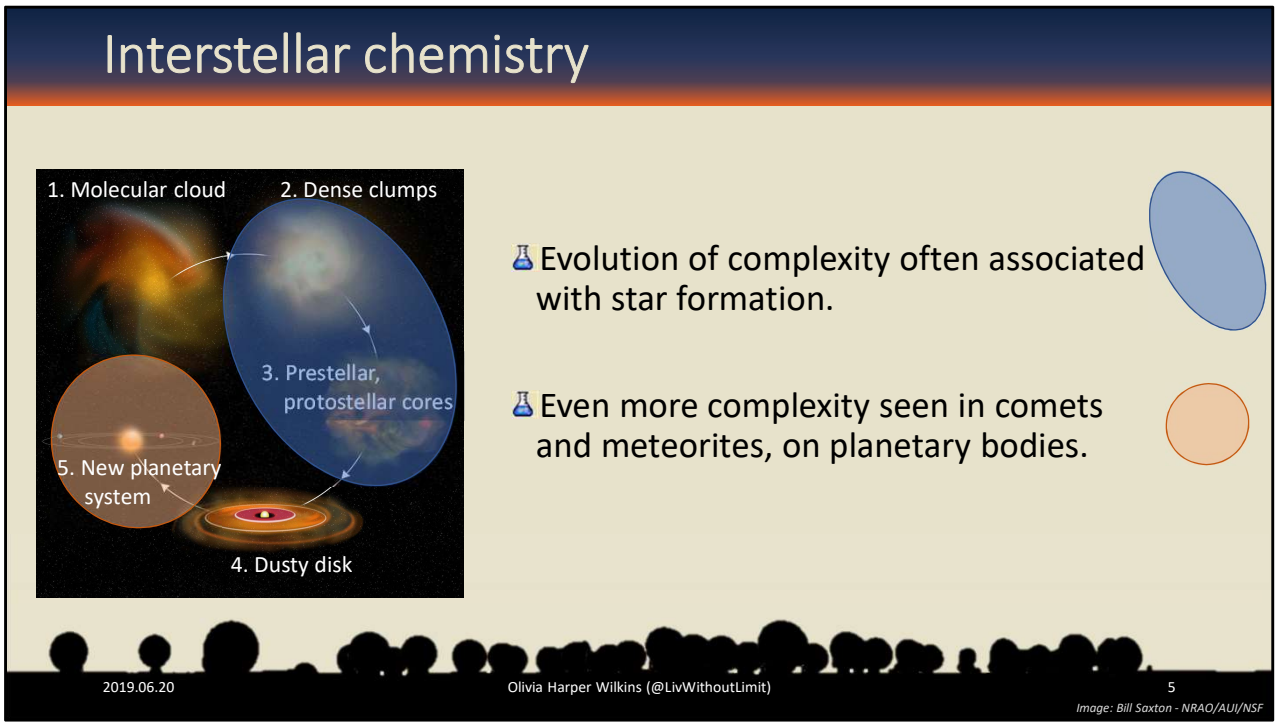
This work use ALMA Cycle 5 data and was substantially supported by a site visit to the North American ALMA Science Center (NAASC). Financial support came from the National Science Foundation (NSF) Graduate Research Fellowship Program (GRFP).



Much of what we know about interstellar chemistry is centered about the approximately 200 compounds that have been found in interstellar space and circumstellar envelopes. Of these, about a third are what we call “complex organic molecules,” or COMs.

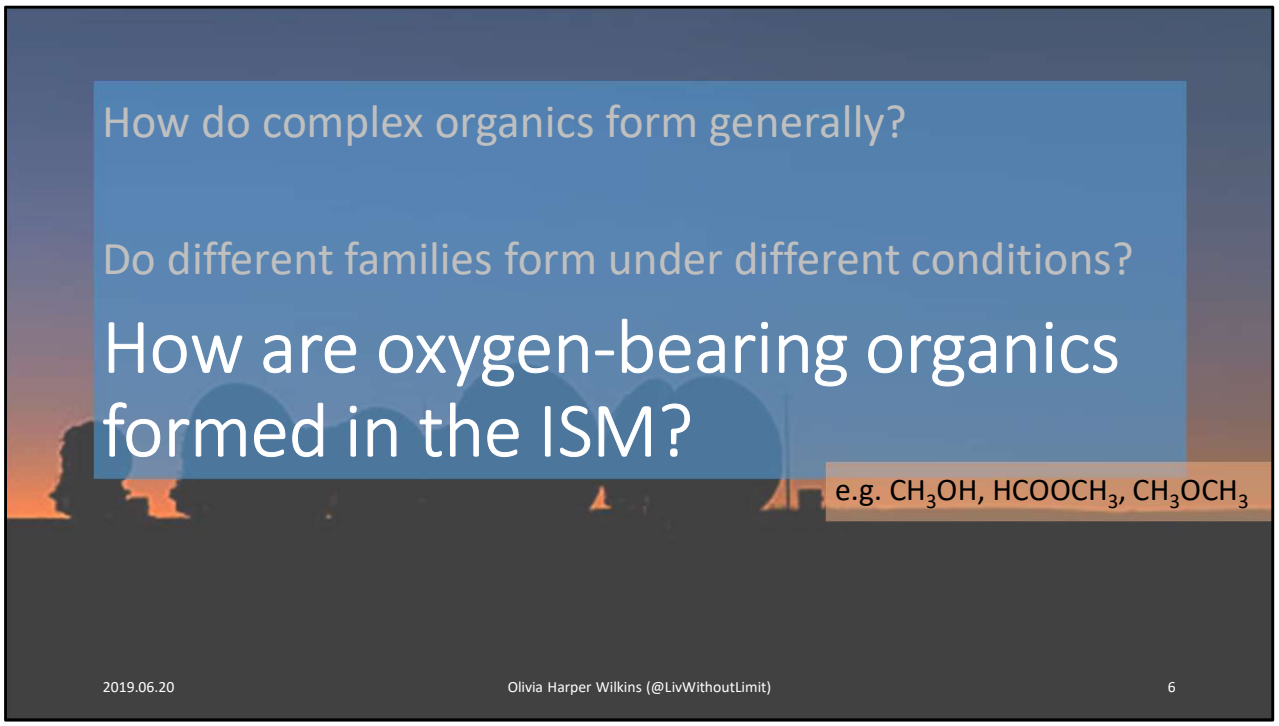


Complex organics are interstellar organic compounds – meaning they are made up of at least carbon and hydrogen – that have six or more atoms. These include compounds such as methanol (CH_3OH) and methyl formate ($HCOOCH_3$), so if you are coming at this from an organic chemistry background, this might seem funny to you because in the lab you use things like methanl to make *actual* complex molecules on Earth. Methanol and methyl formate are saturated species, but there are long, unsaturated (having relatively few hydrogens but double and triple bonds instead) carbon chains, such as cyanoacetylene (HC_3N). Note that HC_3N has only five (5) atoms so is not technically complex; however it is the simplest example of a family of these long unsaturated carbon chains that include up to $HC_{11}N$!

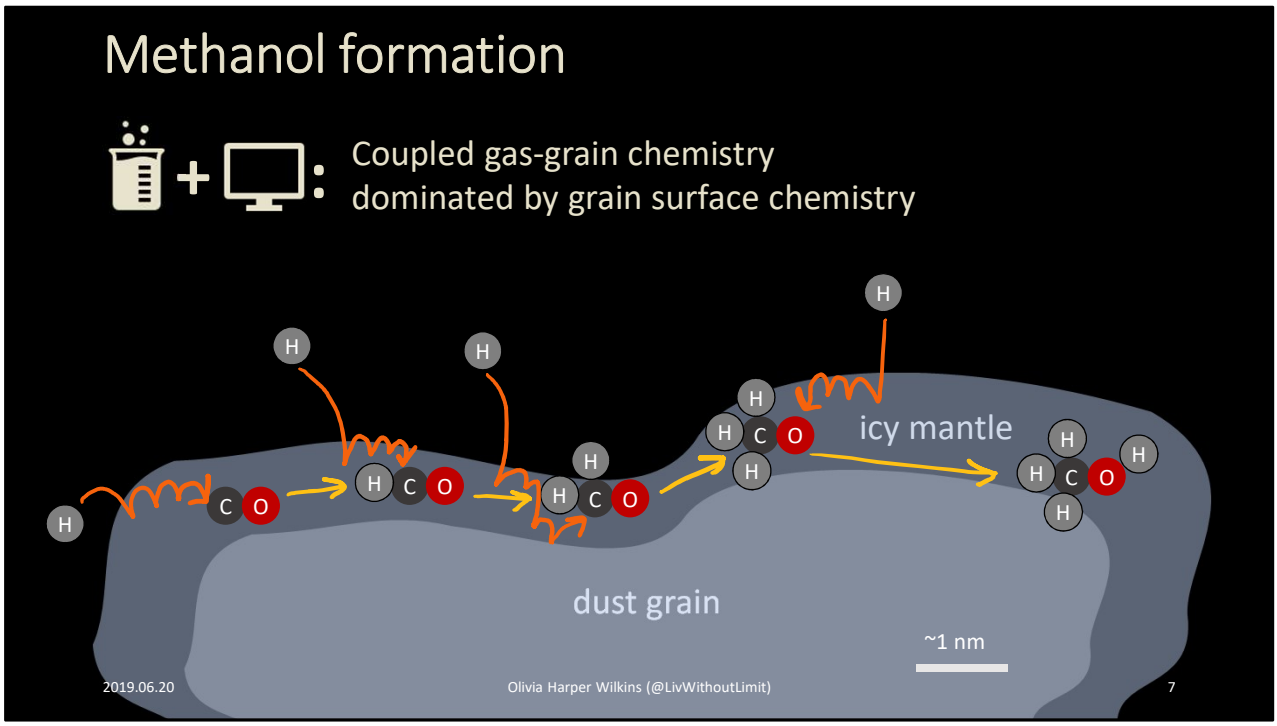


Much of the complex organic chemistry we are interested in takes place in the earliest stages of star formation. The basic schematic of star formation is this: we start with a molecular cloud (1 in the graphic on the left) in which dense clumps begin to form (2). As these clumps accrue more mass and collapse under gravity, we have the formation of prestellar and protostellar cores (3). After a million years or so, these cores become dusty protoplanetary disks (4) that are formed by angular momentum throwing the mass surrounding the young star out into a flattened disk as it spins (think of throwing up a ball of pizza dough and spinning it as it gradually flattens out into a pizza crust). It is here where new planets form, resulting in planetary systems (5) such as our own solar system.

While we don't have a full understanding of the evolution of complex chemistry in the interstellar medium, the rich abundance of complex organics in the earliest stages of star formation (2 and 3) result in the evolution of complexity often being associated with star formation. Even more complexity – including prebiotic molecules such as amino acids – is seen in objects such as comets and meteorites, which likely delivered material to the early Earth, as well as on planetary bodies. Thus understanding this chemical evolution could provide insight into the chemical evolution of planetary systems, providing hints in understanding how life emerges.

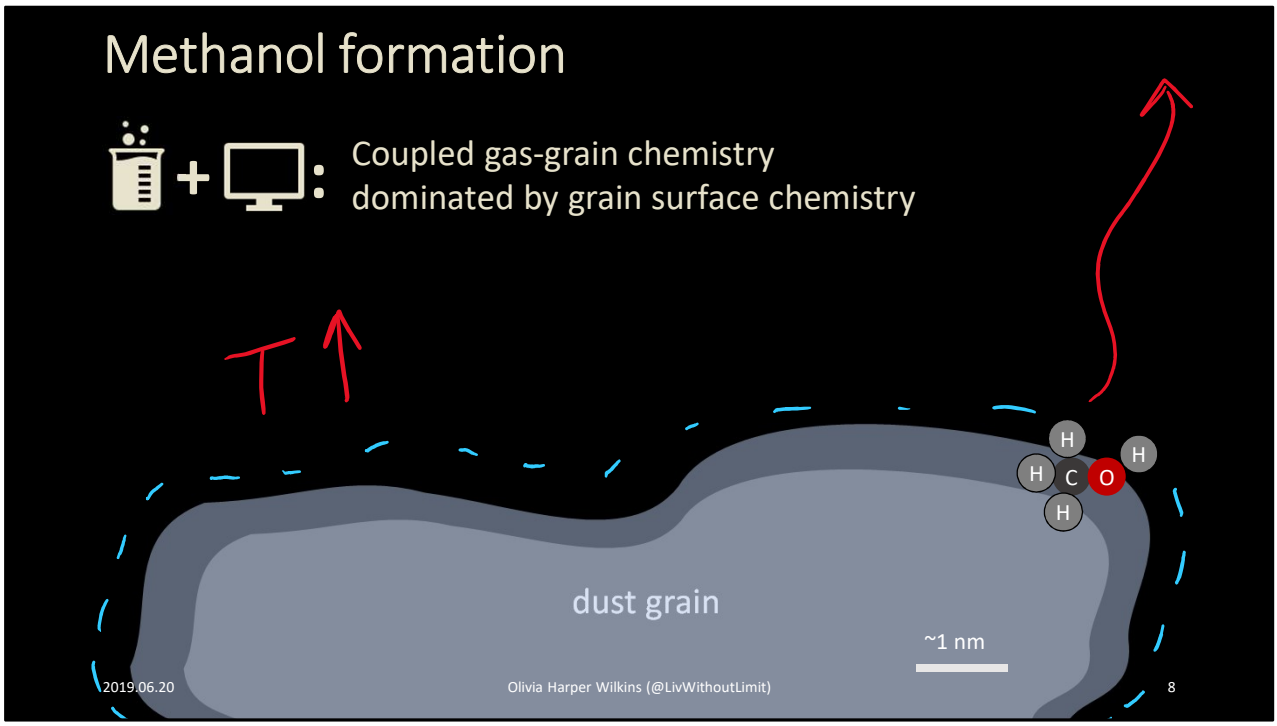


As an astrochemist, I am interested in several questions. On a broad scale, I am interested in investigating how complex organics form generally. If we go a bit narrower, another question we can ask is whether different families of complex organics form under different conditions. (When I say different families, I'm talking about categories such as oxygen-bearing, nitrogen-bearing, sulphur-bearing, and pure hydrocarbons.) Narrower still, the specific question I'm interested in answering is, "How are oxygen-bearing organics formed in the interstellar medium (ISM)?" Here I'm focusing on methanol (CH_3OH), but I'm also interested in methyl formate ($HCOOCH_3$) and dimethyl ether (CH_3OCH_3).

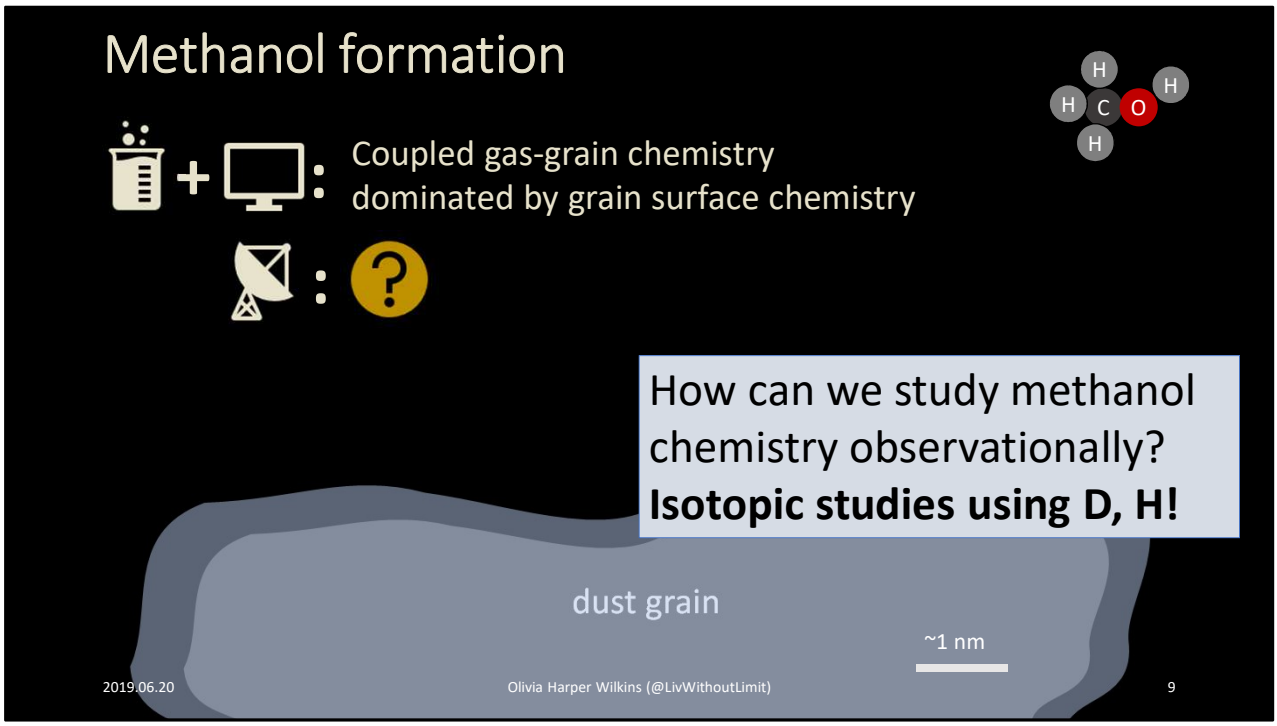


Much of what we know about how methanol forms is from laboratory experiments and computational modeling. Much of the literature points toward a coupled gas-grain chemistry in which methanol formation is dominated by grain surface chemistry. Interstellar dust grains typically have diameters on submicron scales. In colder environments, like those in the early stages of star formation, these dust grains are surrounded by an icy mantle made up of simple compounds, including carbon monoxide (CO) and carbon dioxide (CO_2). Our current understanding of methanol formation is that it happens primarily through *successive hydrogenation of CO*, in which hydrogen atoms arrive at the dust grain and hop around until they find CO and add one at a time to CO embedded in the icy mantles of these dust grains: CO → HCO → H_2CO → H_3CO → CH_3OH.

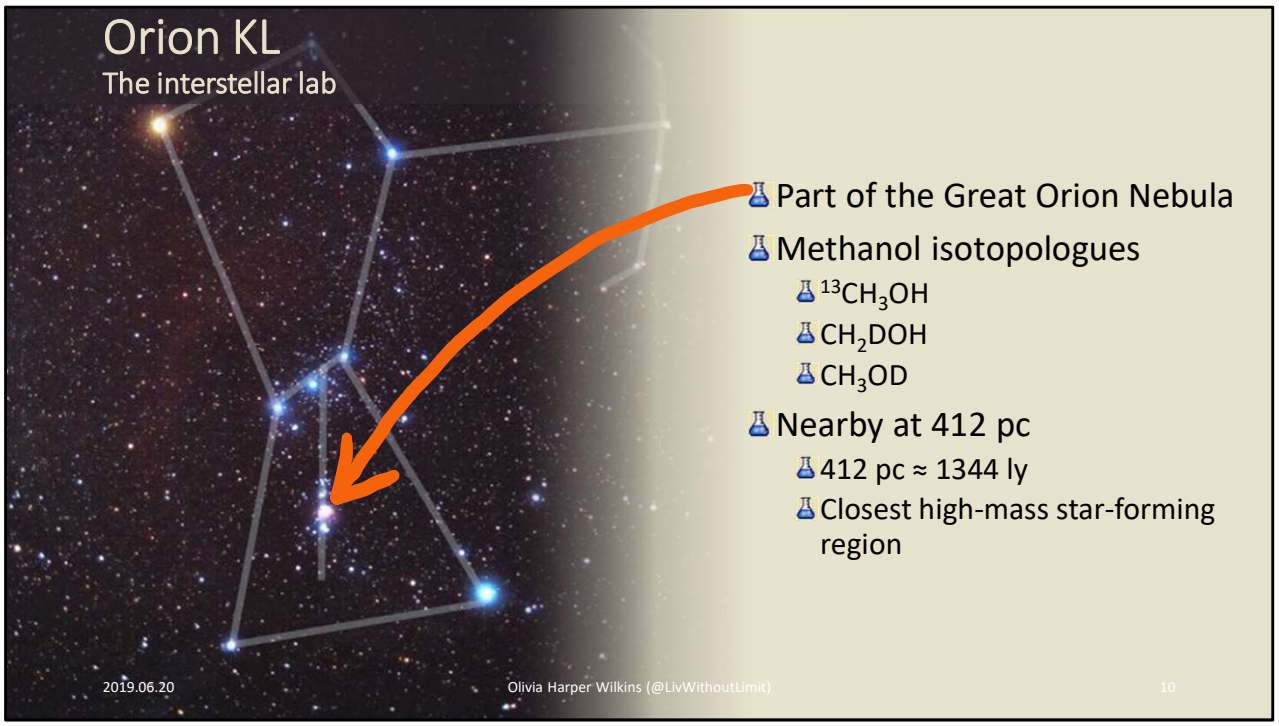
In the schematic above, the addition of individual hydrogen atoms are shown by **orange** arrows. The **yellow** reaction arrows show the progression between steps with the product of each step to the right of the respective arrow. *In the original presentation, this was animated instead of drawn.*



As a protostar evolves, the temperature in the envelope begin to increase and the icy mantles begin to sublimate (go from solid-phase to gas-phase). Once temperatures are high enough (80-95 Kelvin, depending on factors like grain size, as reported by Green et al. 2009, MNRAS), the methanol desorbs from the icy grains into the gas phase where we can observe it with radio telescopes like ALMA.

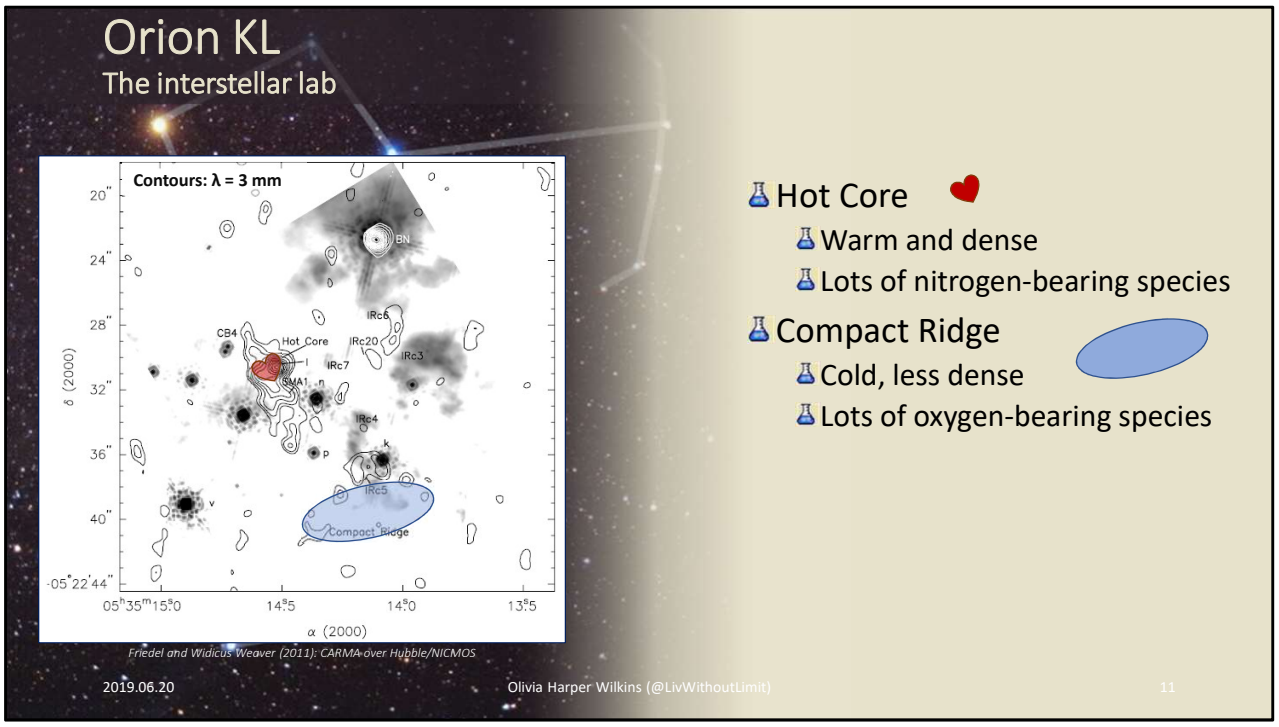


When it comes to our observational understanding of methanol chemistry, however, we are left with a lot of questions. Methanol chemistry has been studied observationally using isotopic studies incorporating the deuterium (D) versus hydrogen (H) chemistry, but previous work has been inconclusive. In this work, we are trying to close the gaps in our observational knowledge of interstellar methanol chemistry.



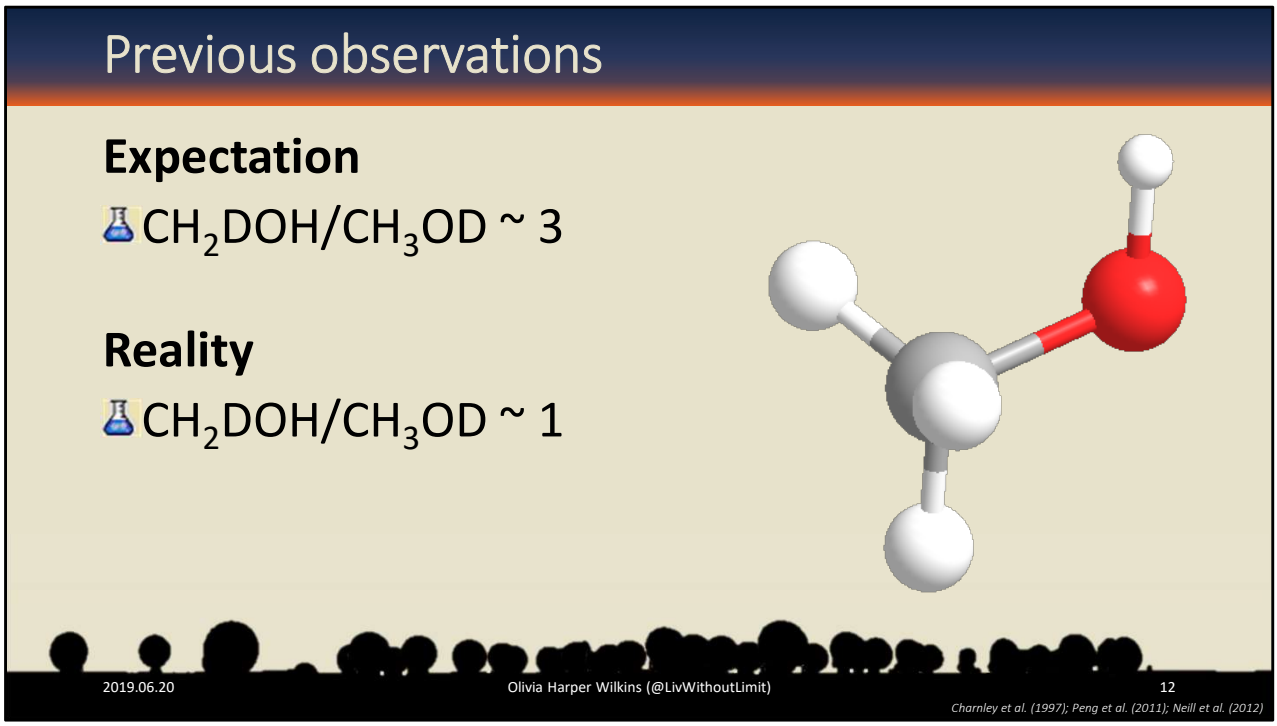
The laboratory where much of the isotopic studies of methanol have taken place is the Orion Kleinmann-Low Nebula, or Orion KL. Orion KL is part of the Great Orion Nebula, which is the reddish blog below the middle star of the belt of the constellation Orion. It is the ideal chemistry laboratory for this work for several reasons, the first being that it is a fully stocked laboratory in that it has all of the isotopolgues* we hope to see. In addition to the primary isotopologue $^{12}CH_3OH$, we see $^{13}CH_3OH$, CH_2DOH, and CH_3OD. Orion KL is also an ideal laboratory for this work because it is the closest region of massive star formation to the solar system at about 412 parsecs, or 1344 lightyears, away. Because it is so close, we can resolve structures within the nebula.

*Isotopes are chemically identical atoms that have the same number of protons but different numbers of neutrons (e.g. ^{12}C and ^{13}C; H and D). That is, besides having different masses, isotopes are identical. Isotopologues are molecules that are chemically identical but have different isotopes (e.g. $^{12}CH_3OH$ and $^{13}CH_3OH$; CH_3OH and CH_3OD). Isotopomers are molecules that have the same isotopic abundances but these isotopes are located at different positions within the molecule (e.g. CH_2DOH and CH_3OD).

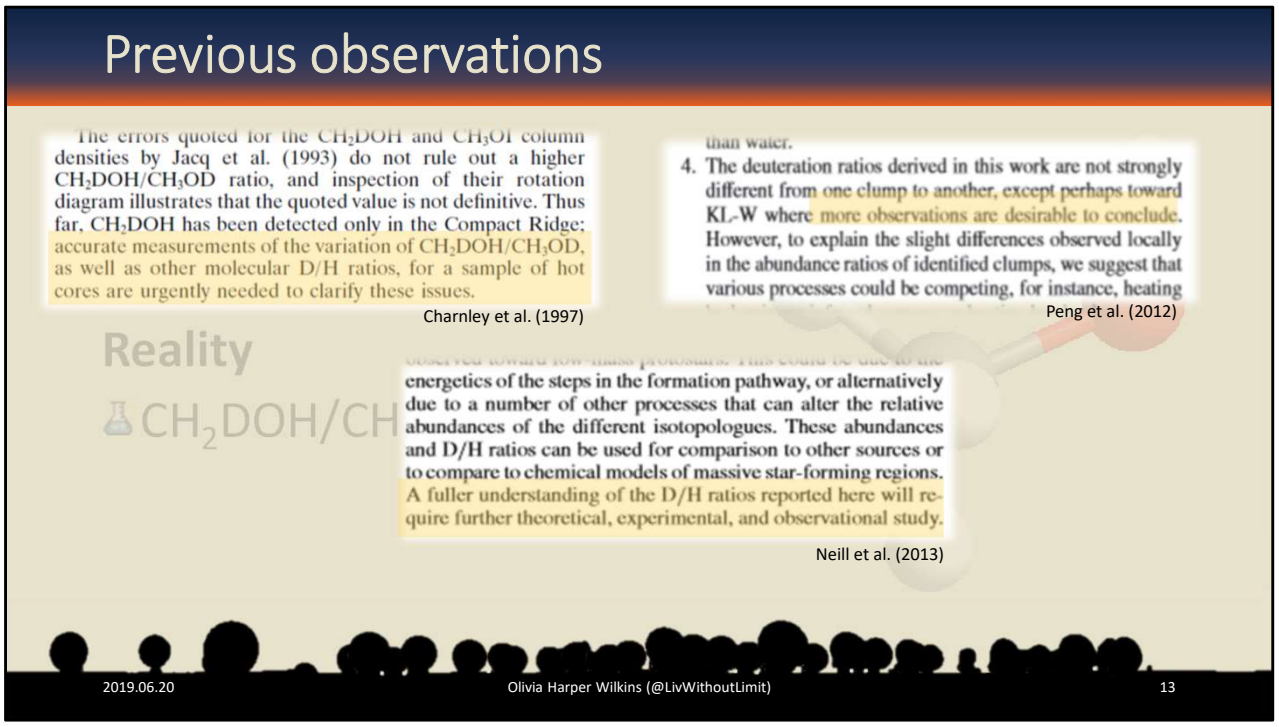


Within the Orion KL nebula, there is a lot of structure that we can resolve with ALMA. The above image shows contours of the 3-millimeter continuum (dust emission) toward Orion KL taken with another interferometer (radio telescope array) – CARMA – with Hubble/NICMOS image at 2 microns in grayscale. The so-called **hot core** is shown by the red heart (this region is actually heart-shaped in ALMA continuum data). This region is relatively warm and dense and harbors a lot of nitrogen-bearing chemistry. To the southwest* is the colder and less dense compact ridge, indicated by a blue oval. In this region, we see a lot of oxygen-bearing species. While methanol is everywhere throughout the Orion KL nebula, other oxygen-bearing complex organics – like methyl formate and dimethyl ether – are tied to the complex ridge.

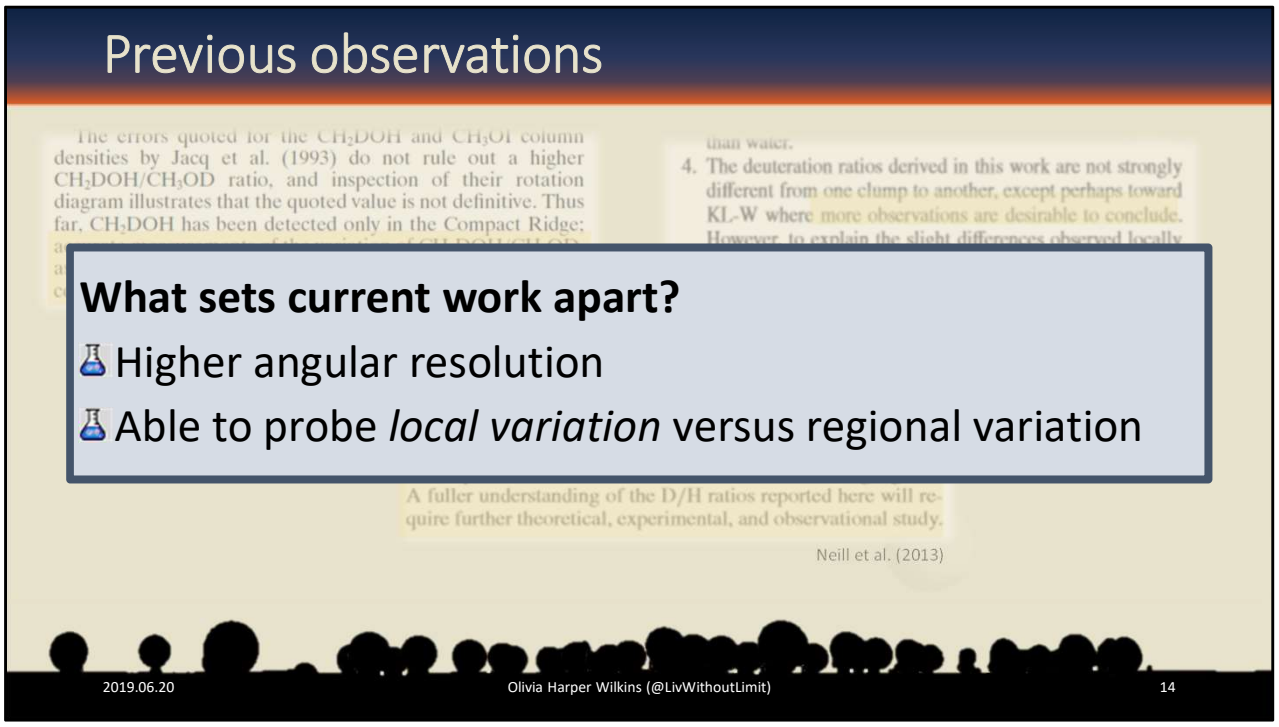
In astronomy, west and east are opposite, as if we are on the inside of a globe, on which the wider universe is projected, looking out towards the heavens.



When observing the methanol chemistry in Orion KL, we would expect a ratio between the carbon-deuterated (CH_2DOH) and oxygen-deuterated (CH_3OD) methanol isotopomers to be about three (3) because there are three hydrogens at the carbon site versus just one bonded to oxygen. However, previous observations of methanol toward Orion KL show a ratio closer to about one (1), from <1 to about 1.5. This is surprising and is indicative that the chemistry we observe in Orion KL is doing something other than what we would expect.



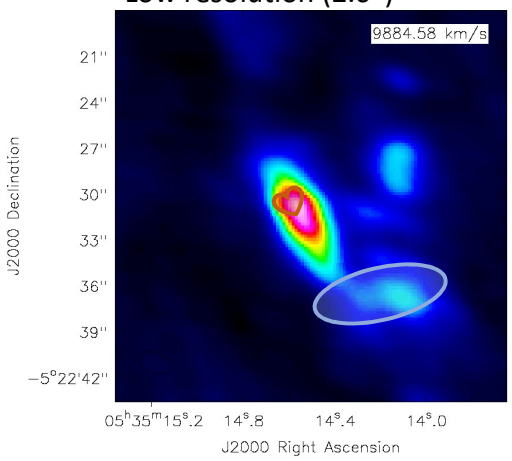
In the previous work, the unexpected isotopomer ratio has been acknowledged. Charnley et al. (1997) conclude their findings by saying that "accurate measurements of the variation of CH_2OH/CH_3OD… for a sample of hot cores is urgently needed to clarify these issues." Similarly, Peng et al. (2012) says that "more observations are desirable to conclude," and Neill et al. (2013) end with "A fuller understanding of the D/H ratios reported here will require further theoretical, experimental, and observational study."



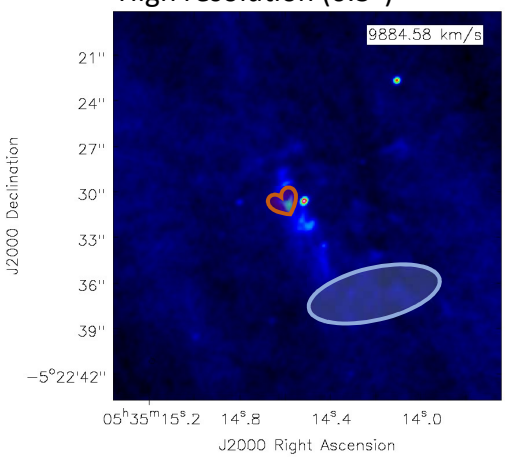
If isotopic studies of methanol, specifically using deuterium, have been carried out toward Orion KL and have been inconclusive, then what are doing that sets our current work apart from the previous work. The biggest difference between the previous work and current work is that we use higher angular (spatial) resolution. That is, we are probing the *local* variation whereas the previous work looked at *regional* variations within the nebula.

Resolving more structure

Low resolution (2.0”)



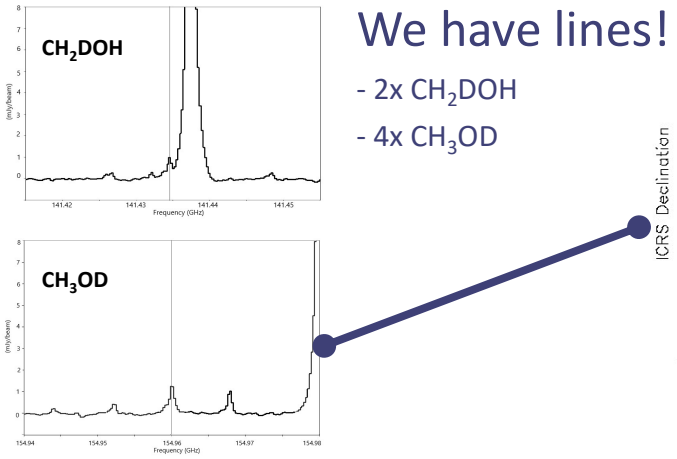
High resolution (0.3”)



2019.06.20 Olivia Harper Wilkins (@LivWithoutLimit) 15

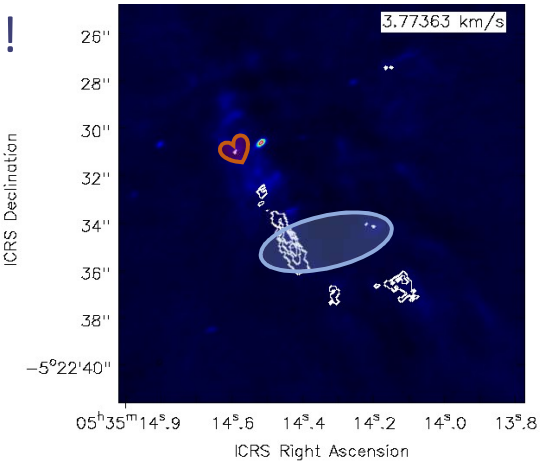
Visually, resolving more structure looks like this. To the left, we have an example of relatively low resolution (2.0”) that is similar to what was used in the previous work. The hot core (red heart) and compact ridge (blue oval) are highlighted. As can be seen, the hot core is smeared out into a larger region of emission. Everything is rather blobby and, because the emission is clumped together at this lower resolution, these clumps are rather bright. On the right is the same image but at high resolution (0.3”), which we are using in this work, again with the hot core (red heart) and compact ridge (blue oval) being highlighted. If you squint, you can see the heart-shaped emission in cyan of the hot core. You can also see a lot more substructure surrounding the hot core in the right image than what you can resolve in the right. While the compact ridge isn’t as bright, a lot more substructure can be picked out. Similarly, in the right image you can see two bright point sources (rainbow circles): BN (northwest) and I (about the center). In the left image, these point sources are smeared out into the surrounding nebula.

Preliminary results



We have lines!

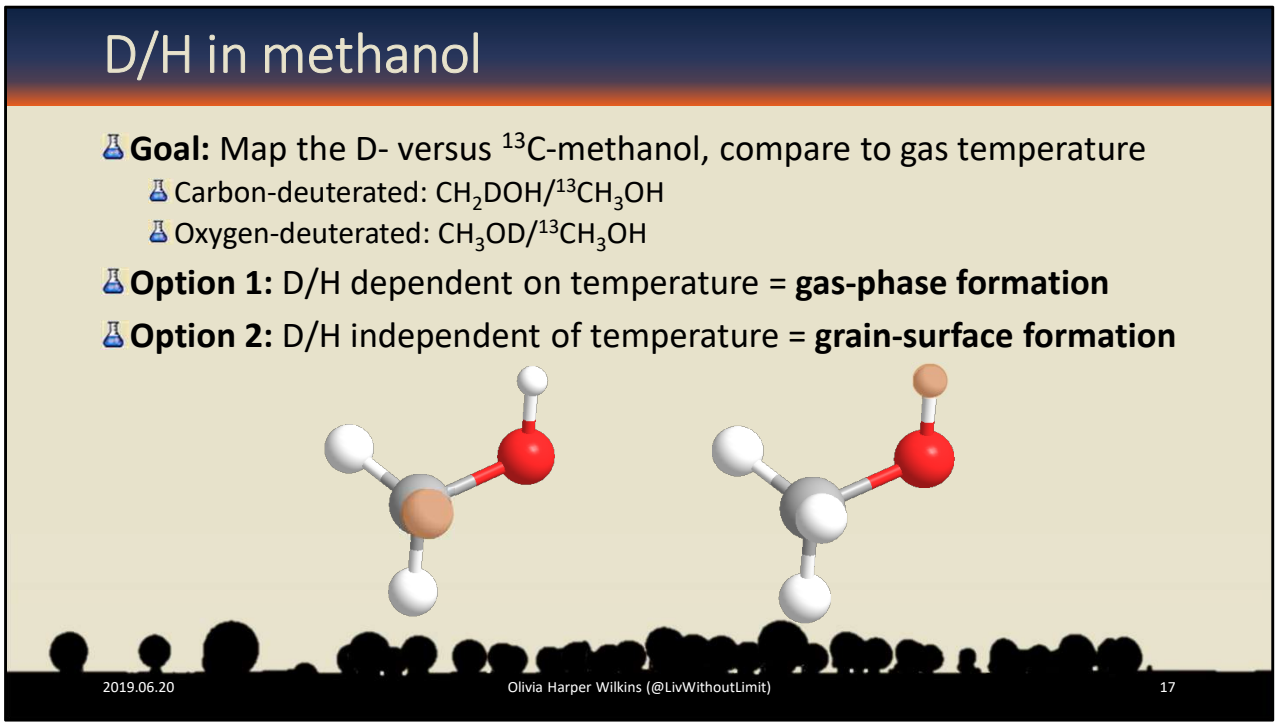
- 2x CH_2DOH
- 4x CH_3OD



2019.06.20 Olivia Harper Wilkins (@LivWithoutLimit) 16

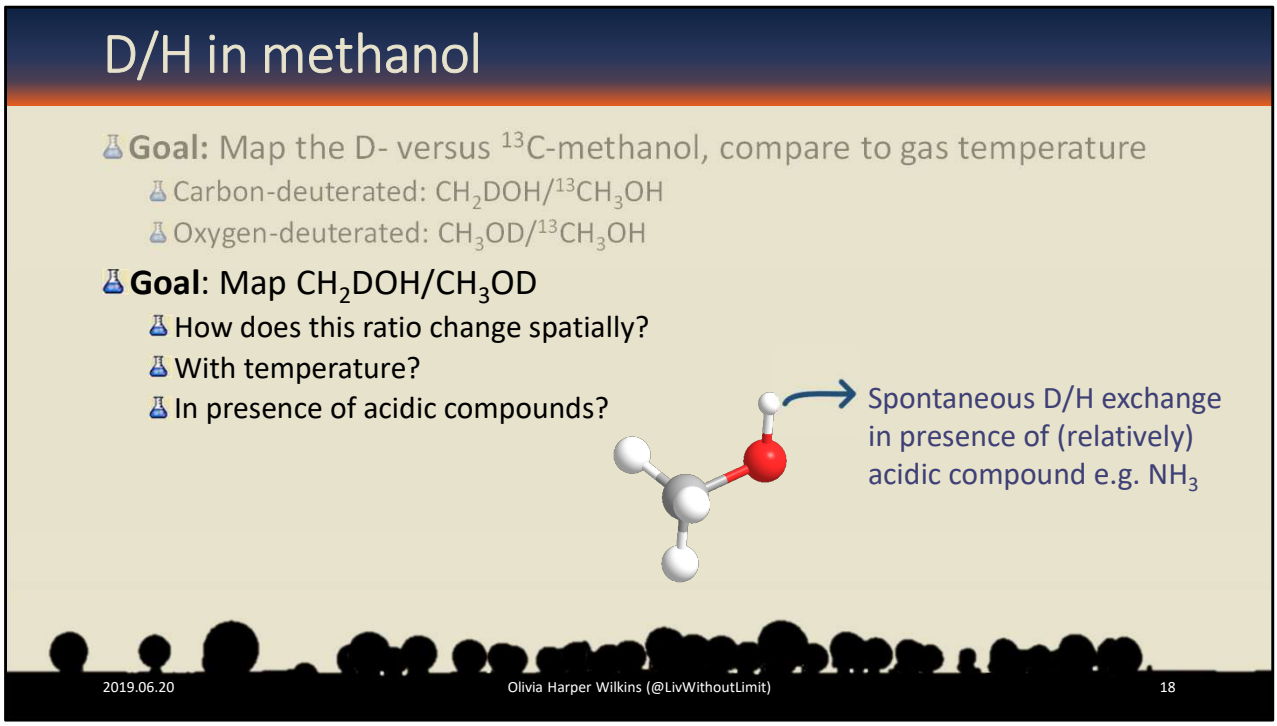
At a first glance at our cycle 5 data, we have lines! On the left are example spectra for CH_2DOH (top) and CH_3OD (bottom). Overall, we have 2 lines of CH_2DOH and 4 lines of CH_3OD. For these spectral line data to be useful, we need their emission to overlap within the nebula so that we can rigorously constrain their (relative) abundances.

The image on the right shows an integrated intensity map (also called a moment-0 map) of CH_3OD, again with the hot core shown by the red heart region and the compact ridge shown by a blue oval. As can be seen by the white contours, the CH_3OD shows up mostly toward the compact ridge, which is to be expected since the colder compact ridge is home to oxygen-bearing chemistry whereas the warmer hot core is populated by nitrogen-bearing species. Furthermore, deuterium chemistry is considered a tracer of cold formation chemistry. Even though the primary isotopologue of methanol is seen everywhere in the nebula, we would expect to see the deuterated-methanol only toward the compact ridge. Thus, we are confident that what we are looking at is in fact deuterated methanol.



Using the isotopologue data from this ALMA Cycle 5 data, we have two goals toward understanding the methanol chemistry within Orion KL. The first is to map the deuterated methanol versus ^{13}C-methanol and compare this to the profile of the gas temperature. We use $^{13}CH_3OH$ as a proxy for $^{12}CH_3OH$, which is generally optically thick, making its abundance difficult to accurately constrain. We will map both the carbon-deuterated and oxygen-deuterated species versus $^{13}CH_3OH$ and will be looking for one of two trends. First, if the D/H ratio is dependent on the temperature, we are likely looking at a chemistry in which the deuteration of methanol is intimately tied to the gas-phase, perhaps as far back as its formation chemistry itself. On the other hand, if D/H is independent of gas temperature, this would provide support for the hypothesis that methanol formation is in fact dominated by grain-surface formation. This latter scenario is what we expect to see.

A future goal of this work is to also look at multiply-deuterated methanol to get an idea of reaction rates and formation times within Orion KL.



The second goal of this work is to map the ratio between the two isotopomers of deuterated-methanol. We are interested in this because the hydroxyl (-OH) hydrogen can under go spontaneous D/H exchange in the presence of relatively acidic compounds, of which there is an abundance in Orion KL, which would alter the relative abundance of CH_3OD. We expect that the CH_2DOH/CH_3OD ratio will *not* be constant across Orion KL because of the possibility for spontaneous D/H exchange, thereby increasing or decreasing the amount of CH_3OD while the abundance of CH_2DOH remains relatively static. Additional questions to consider if we observe this trend include:

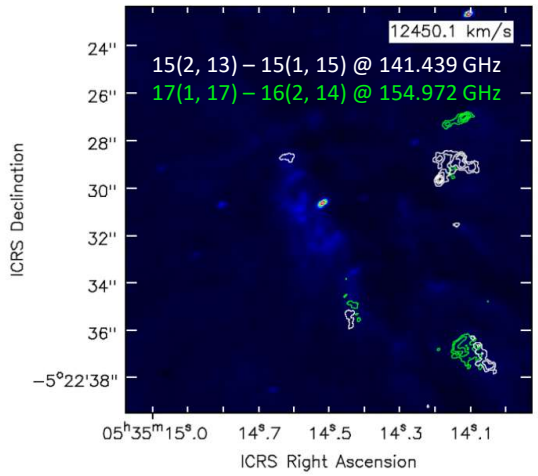
- How does this ratio change spatially? (Are some regions more susceptible to spontaneous D/H exchange?)
- How does this ratio change with temperature? (Does gas temperature drive this exchange?)
- How does this ratio change in the presence of acidic compounds? (Which relatively acidic compounds are most likely to interact with methanol once it has formed?)

This goal allows us to look at the methanol chemistry *after* methanol has already formed.

Moment 0 maps

* Integrated value of spectrum for specific lines

Carbon-deuterated (CH_2DOH) lines
little spatial overlap



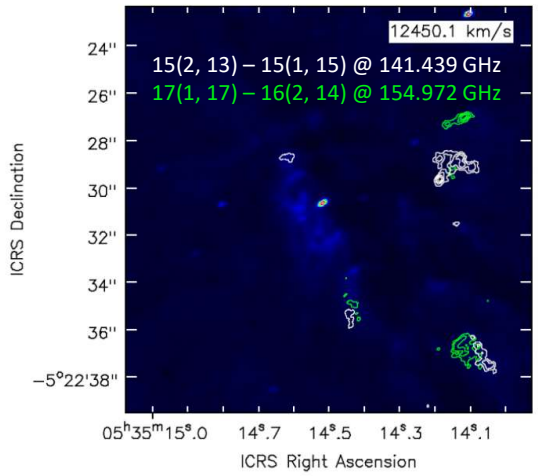
2019.06.20 Olivia Harper Wilkins (@LivWithoutLimit) 19

Recall that in order to do the proposed analysis robustly, we need to have the emission of multiple lines of a given isotopologue overlapping. However, if we look at the integrated intensity (moment 0) map of the carbon-deuterated methanol, we see that the lines have very little overlap. While these spectra could be smoothed out, this would result in regional studies of the CH_2DOH, which has already been done in the previously published literature.

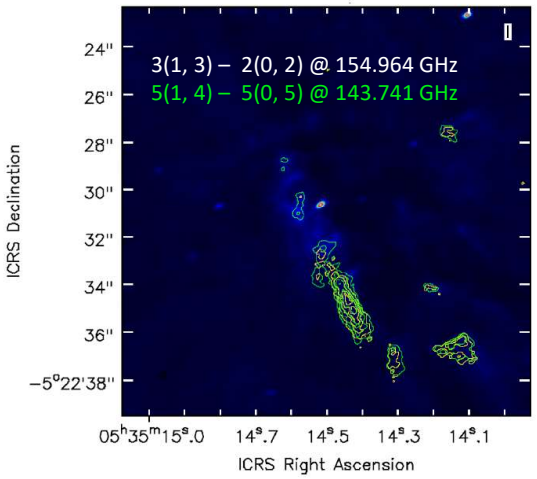
Moment 0 maps

* Integrated value of spectrum for specific lines

Carbon-deuterated (CH_2DOH) lines
little spatial overlap



Oxygen-deuterated (CH_3OD) lines
ideal overlap



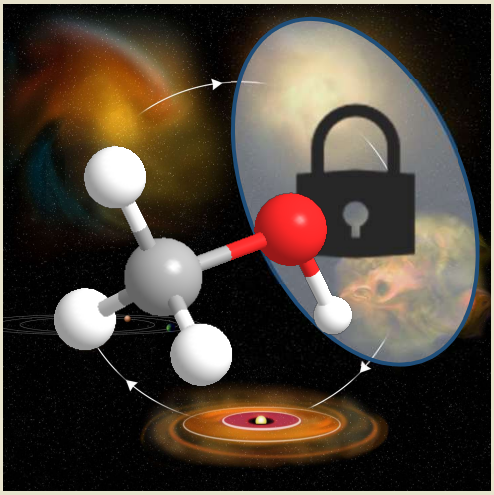
2019.06.20 Olivia Harper Wilkins (@LivWithoutLimit) 20

Fortunately, the oxygen-deuterated lines have ideal overlap, so we can certainly proceed with looking at the oxygen-deuterated chemistry in the Orion KL nebula. We hope to acquire more data toward lower-energy CH_2DOH lines more on par with that of the CH_3OD lines, which could perhaps account for the little spatial overlap. Additional investigations into this, perhaps including reprocessing our data, are required to understand why the CH_2DOH emission is so spread out.

Summary

- Complex organic chemistry is often linked to star formation.
- Methanol chemistry isn't well-understood, but it may be the key to understanding more complex chemistry.
- Previous studies use (relatively) low spatial resolution; this work looks to probe local structure.

Olivia Harper Wilkins | owilkins@caltech.edu
http://theskyisnotthelimit.org | @LivWithoutlimit



To summarize, the key concepts I would like you to takeaway are that:
- Complex organic chemistry is often linked to star formation.
- Methanol chemistry isn't well-understood, but it may be the key to understanding more complex chemistry.
- Previous studies use (relatively) low spatial resolution; this work looks to probe local structure.

If you'd like to follow along or if you have questions/thoughts/ideas, you can reach me via:
email | **owilkins@caltech.edu**
website | **http://theskyisnotthelimit.org**
Twitter | **@LivWithoutLimit**
Instagram | **@LivWithoutLimit**