Origins: From the Protosun to the First Steps of Life
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The ALMA-PILS Survey: New insights into the complex chemistry of young stars

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Abstract. Understanding how, when and where complex organic and potentially prebiotic molecules are formed is a fundamental goal of astrochemistry. Since its beginning the Atacama Large Millimeter/submillimeter Array (ALMA) has demonstrated its capabilities for studies of the chemistry of solar-type stars. Its high sensitivity and fine spectral and angular resolution makes it possible to study the chemistry of young stars on Solar System scales. We here present an unbiased spectral survey, *Protostellar Interferometric Line Survey (PILS)*, of the astrochemical template source and Class 0 protostellar binary IRAS 16293-2422 using ALMA. The high quality ALMA data have allowed us to detect a wealth of species previously undetected toward solar-type protostars as well as the interstellar medium in general. Also, the data show the presence of numerous rare isotopologues of complex organic molecules and other species: the exact measurements of the abundances of the complex organic molecules and their isotopologues shed new light onto the formation of these species and provide a chemical link between the embedded protostellar stages and the early Solar System.

Keywords. astrochemistry, stars: formation, stars: protostars, ISM: molecules, ISM: individual (IRAS 16293−2422), Submillimeter: ISM

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1. Introduction: astrochemistry in the ALMA era

One of the important tasks of astrochemistry is to address how, when and where complex organic and potentially prebiotic molecules are formed in the environments of young stars. A particularly interesting question in this context is what is the chemical composition of material as it is accreted onto the circumstellar disks and, in particular, whether the rich chemistry of the early stages can be transferred to the later planet-forming stages. The Atacama Large Millimeter/submillimeter Array (ALMA) has already significantly changed the field of astrochemistry – in particular, through its capabilities for studies of the organic content in star forming regions. The key features of ALMA for this include its:

Large frequency coverage: allowing secure assignments of complex and rare species through identifications of a large number of lines.

High spectral resolution: which limits confusion and makes it possible to push deeper toward sources with narrow lines.

High sensitivity: making (fast) unbiased surveys of large spectral ranges possible.

Excellent calibration: providing consistent relative line intensities over large frequency ranges, critical for extracting physical conditions from the spectra.

High spatial resolution: making it possible to zoom in on Solar System scales toward young stars in nearby star forming regions and study the spatial coincidence of different lines and species, providing important information about the links between the physics and chemistry there.

2. The ALMA Protostellar Interferometric Line Survey (PILS)

One of the prime targets for studies of the astrochemistry of solar-type protostars is the nearby protostellar binary IRAS 16293-2422 (IRAS16293 in the following). IRAS16293 has a rich spectrum with bright line emission on different scales (e.g., Blake *et al.* 1994, Bisschop *et al.* 2008, Caux *et al.* 2011, Jørgensen *et al.* 2011) and is the place where most of the first detections of complex organics toward solar-type protostars have been made (e.g., van Dishoeck *et al.* 1995, Cazaux *et al.* 2003, Bottinelli *et al.* 2004, Kuan *et al.* 2004, Jørgensen *et al.* 2012, Kahane *et al.* 2013). IRAS16293 was therefore also a natural target for early Science Verification (SV) observations with ALMA through which the first discovery of the prebiotic molecule glycolaldehyde ("a simple sugar-like molecule") toward a low-mass protostar was made (Jørgensen *et al.* 2012).

Building on that discovery we initiated a large unbiased survey of IRAS16293 with ALMA, the *"Protostellar Interferometric Line Survey (PILS)"*, covering one of the important atmospheric windows at submillimeter wavelengths (Jørgensen *et al.* 2016). The observations cover the spectral range from 329 to 363 GHz (ALMA's Band 7) with 0.2 km s^{-1} spectral resolution and $0.5''$ angular resolution (≈ 70 AU). The survey is 1–2 orders of magnitude deeper than previous single-dish surveys and furthermore produce resolved maps of the line emission across the entire structure of the protostellar binary.

3. Selected results concerning the origin of complex organics

Fig. 1 illustrates the richness of the data with spectra extracted toward each of the two components of the binary: IRAS16293A, which appears elongated in the dust continuum maps and with wide lines corresponding to an "edge-on structure", and IRAS16293B, which appears more circular in the dust continuum maps and show narrow lines (FWHM ≈ 1 km s^{-1}) consistent with a more face-on morphology. Toward IRAS16293B more than 10,000 lines can be seen corresponding to approximately one line per 3 km s^{-1}, i.e. close to the line confusion limit across significant parts of the spectrum (Jørgensen *et al.* 2016).

Through LTE modeling and careful evaluation of the spectroscopy, so-far more than 100 species (including isotopologues) have been assigned toward IRAS16293B of which 27 species have not previously been seen toward solar-type protostars and 16 species represent new detections in the interstellar medium altogether.

One example of a first detection toward a solar-type protostar with PILS was the of identification of methyl isocyanate, CH_3NCO, reported by Ligterink *et al.* (2017) and independently by Martín-Doménech *et al.* (2017). Methyl isocyanate is an interesting organic molecule with a peptide-bond characteristic of amino-acids. Its origin has been debated but through UHV experiments with irradiation of CH_4:HNCO ice mixtures, Ligterink *et al.* demonstrated that it could be formed via CH_3 and (H)NCO recombinations in the solid-state (see also Chuang *et al.* 2017, Ligterink *et al.* 2018).

Another example was the first discovery of an organohalogen methyl chloride or chloromethane, CH_3Cl, in the interstellar medium reported in Fayolle *et al.* (2017). The identification of CH_3Cl in the PILS data triggered a search for this species in data from the ROSINA instrument on the Rosetta mission toward Comet 67P/C-G also reported in Fayolle *et al.* (2017). The main implication of this discovery is the direct link between protostellar chemistry and the constituents observed in icy bodies in our own Solar System prompting further comparisons between the protostellar and cometary inventories (Drozdovskaya *et al.* 2018 and M. Drozdovskaya *et al.* in prep.).

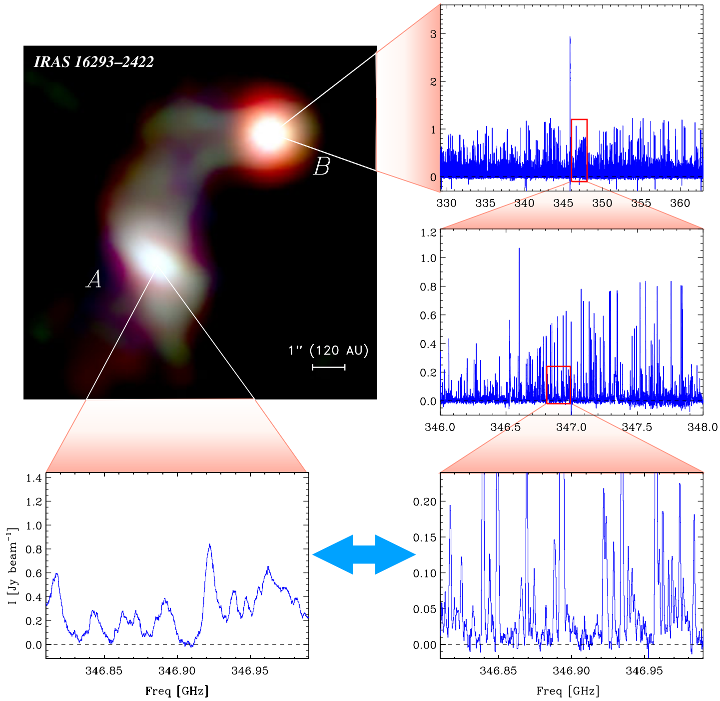

Figure 1. Example of the ALMA-PILS data for IRAS 16293-2422: the panel in the top left corner shows a false color image of the dust continuum radiation (blue: 0.8 mm; green: 1.3 mm and red 3.0 mm) toward the protostellar binary. The panels in the righthand column shows the spectra toward IRAS16293B zooming-in from the full ≈ 33 GHz spectral range to a small (180 MHz) window illustrating the richness of the data. The panel in the lower left shows the same zoomed-in spectrum toward IRAS16293A where the significantly broader line are visible.

The high sensitivity of the PILS data makes it possible to further explore the degree of complexity that arises around solar-type protostars. Examples of that are the first detections of the complex organics acetone and propanal each containing three carbon atoms, previously only seen toward the Galactic Center and selected hot cores (see Lykke *et al.* 2017, and references therein). Besides serving as important tests of astrochemical models, these discoveries raise the interesting question whether there are any limitations to the "size" of these complex organics, e.g., in terms of the number of carbon-atoms.

The high sensitivity also allow more systematic characterisations of the isotopic compositions of complex organics toward IRAS16293B. The survey has yielded detections of numerous isotopologues of complex organics toward IRAS1629B, including the first detections of deuterated forms of formamide (NH_2CHO; Coutens *et al.* 2016), deuterated and ^{13}C-isotopologues of glycolaldehyde ($CH_2(OH)CHO$; Jørgensen *et al.* 2016), and other oxygen-bearing organics (Jørgensen *et al.* 2018) as well as cyanamide (NH_2CN; Coutens *et al.* 2018). In particular, the survey provides systematic estimates of the D/H and $^{12}C/^{13}C$ ratios for full sets of O- and N-bearing organics (Jørgensen *et al.* 2018, Calcutt *et al.* 2018) as well as S-species (Drozdovskaya *et al.* 2018). Interestingly, no systematic differences are found between between the D/H ratios for molecules where the deuterium is substituted in different functional groups for given molecules – but the D/H ratios do vary between, e.g., "simpler" and more "complex" organics (e.g., Jørgensen *et al.* 2018).

The data also show the detection of a number of species where more than one hydrogen atom is substituted by deuterium, for example formaldehyde (H_2CO; Persson *et al.* 2018) and methyl formate (CH_3OCHO; Manigand *et al.* 2018). Similar to the case for water (e.g., Coutens *et al.* 2014) it is found that the doubly-substituted species are more abundant relative to singly-substituted variants than the singly-substituted to non-substituted species. Both the systematic differences in the deuteration from species-to-species as well as the relation between the differently substituted molecules appear to be related to the formation times of the individual variants in the icy mantles of dust grains (e.g., Jørgensen *et al.* 2018, Persson *et al.* 2018, Manigand *et al.* 2018).

4. Summary

The results presented here are a direct illustration of how ALMA is moving studies of the chemistry of the earliest stages of star and planet formation into a new era – even though the current studies are only scratching the surface of what is achievable in terms of angular resolution, much broader surveys etc. It should be emphasised that this effort is not just purely observational, but its success depends on a tight collaboration between astronomers, spectroscopists, modelers, laboratory experimentalists and more.

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Discussion

Wandel: What is the forecast for the detection of complex molecules with higher molecular weight using ALMA in the near future?

Jørgensen: The challenge with going for larger/more complex molecules is mainly matching the available laboratory spectroscopy with the extracted spectra from the ALMA data. We can do a reasonably good job on systematically identifying molecules with two to three carbon atoms. Going much beyond that becomes challenging because of lacking laboratory spectroscopy and line confusion.

Liseau: The source is in the western part of the active star-forming cloud ρ Oph, where nowhere else the spectral line density is observed to be as high and diverse. Why is your source so special?

Jørgensen: IRAS16293 is surrounded by a massive envelope and has a high luminosity compared to other protostars in Ophiuchus. The region where the molecules sublimate is therefore relatively extended and represents a high column density. Thus, I think it is largely a sensitivity issue. In fact, when we are integrating deeper on other protostars with ALMA, many start showing lines from similar organics as IRAS16293.