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COMPLEX ORGANIC MOLECULES TOWARD LOW-MASS AND HIGH-MASS STAR FORMING REGIONS

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Abstract. One of the most important questions in molecular astrophysics is how, when, and where complex organic molecules, COMs ($\geq$ 6 atoms) are formed. In the Interstellar-Earth connection context, could this have a bearing on the origin of life on Earth? Formation mechanisms of COMs, which include potentially prebiotic molecules, are still debated and may include grain-mantle and/or gas–phase chemistry. Understanding the mechanisms that lead to the interstellar molecular complexification, along with the involved physicochemical processes, is mandatory to answer the above questions. In that context, active researches are ongoing in theory, laboratory experiment, chemical modeling and observations. Thanks to recent progress in radioastronomy instrumentation for both single-dish and millimeter array (e.g. Herschel, NOEMA, ALMA), new results have been obtained. I will review some notable results on the detection of COMs, including prebiotic molecules, towards star forming regions.

Keywords: astrochemistry, ISM: molecules, Submillimeter: ISM

1 Introduction

Of the over 180 molecules that have been detected toward the interstellar and circumstellar media*, about 63 are complex species (i.e. that contain 5-6 or more atoms including carbon Herbst & van Dishoeck 2009). It is noticeable that both simple and complex molecules are present during each phase of the star and planet formation: from the molecular cloud to the planetary system including embedded protostar and circumstellar disk. However, one the major question of astrochemistry is how, when and where complex organic molecules, including the so-called prebiotic molecules, are formed? This leads one to ask *i)* which are the physicochemical processes that are involved in their production/destruction? and *ii)*, whether grain surface processes or gas phase reactions prevail in their formation. In order to get strong insight into the understanding of their production, it is necessary – from an astronomical point of view – to perform systematic surveys of both simple and complex molecules toward a large sample of low-mass and high-mass star forming regions. Nonetheless, to get a full overview, it is necessary to couple astronomical observations to chemical modeling, theory, spectroscopy and laboratory experiments on interstellar ice analogs. In this proceeding, a brief review on the observed interstellar complexity will be given in Section 2. Observational limitations and advances will be discussed together with notable results in Section 3. In Section 4, we will discuss the necessity of a direct interaction between the different scientific communities for the study of the astrochemistry.

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2 The interstellar molecular complexity

Complex organic molecules (hereafter COMs), such as methyl formate ($HCOOCH_3$) and dimethyl ether $(CH_3)_2O$, are present toward both high-mass and low-mass star forming regions, including in prestellar cores (e.g. Turner 1989, 1991; Ziurys & McGonagle 1993; Nummelin et al. 2000; Remijan et al. 2002, 2003, 2004; Bottinelli et al. 2007; Schilke et al. 2001; Beuther et al. 2005; Jørgensen et al. 2005, 2011; Bisschop et al. 2008; Favre et al. 2011a,b, 2014; Bacmann et al. 2012; Pineda et al. 2012; Tercero et al. 2012, 2013; Peng et al. 2013; Brouillet et al. 2013, 2015; Vastel et al. 2014; López-Sepulcre et al. 2015; Taquet et al. 2015, etc). Of the over 63 complex species detected in the interstellar and circumstellar media (Herbst & van Dishoeck 2009), the so-called prebiotic molecules are of particular interest, especially in the context of an exogenous delivery of organic matter that might have made possible the appearance of life on Earth. Such molecules, can either be *i)* biological molecules, that are molecules used by life on Earth (such as the glycine, which is the simplest amino acid) and/or *ii)* precursors molecules that, in the network of reactions, can lead to truly biotic molecules such as sugars and amino acids, known to be found in meteorites originating from the very early Solar System (e.g. Caselli & Ceccarelli 2012; Pizzarello et al. 2006). In that context, Glycolaldehyde (CH_2OHCHO) is considered as a species of prebiotic interest since via a formose reaction involving formaldehyde (H_2CO) it will lead to 3-carbon sugars [$C_3H_6O_3$] such as glyceraldehyde. Then, a second reaction involving both glycolaldehyde and a 3C-sugar will give rise to ribose ($C_5H_{10}O_5$, 5C-sugar), the backbone of RNA. This molecule has been detected toward the hot core sources, such as Sgr B2(N) (e.g. Beltrán et al. 2009; Hollis et al. 2000, 2001) and, recently around a solar-type young star through the use of ALMA observations (Jørgensen et al. 2012, 2016). Regarding amino-acids, Belloche et al. (2008) have reported the detection of the amino acetonitrile (NH_2CH_2CN) toward the high mass-star forming region SGRB2(N). This molecule can lead to the formation of the biological molecule glycine. This latter has been detected in the Murchison meteorite (Pizzarello et al. 2006; Kvenvolden et al. 1970) and in the Wild 2 and Tchouri comets by Sandford et al. (2006) and Altwegg et al. (2016), respectively but not in the ISM. Incidentally, at the present time 4 complex species have been detected toward circumstellar disks: HC_3N, c-C_3H_2, CH_3CN and CH_3OH (Chapillon et al. 2012; Qi et al. 2013; Öberg et al. 2015; Walsh et al. 2016), implying that chemistry leading to complex organic molecules likely takes place in those objects.

These findings lead one to ask which degree of complexity can be reached in the ISM. In that context, the detection of a branched molecule iso-propyl cyanide (i-C_3H_7CN), which is not a straight-chain carbon molecule has been reported by Belloche et al. (2014). More recently, the propylene oxide (CH_3CHCH_2O), a chiral molecule (see Marloie et al. 2010, for chiral molecules that can likely be searched for in the ISM together with spectroscopic characterization), has been detected in the ISM by McGuire et al. (2016). As a consequence, observations of the chemical complexity and the diversity that offer star-forming regions make possible to access the physico-chemical conditions in which simple and complex molecules form and evolve.

3 Search for complex organic molecules and spectral confusion

In this section, we just focus on the spectral analysis on observational data of COMs and, in particular, on the problem of spectral confusion in line surveys and how to reduce it. For further details on the detection of complex molecules, we refer to the full review on complex molecules by Herbst & van Dishoeck (2009). COMs harbor a multitude of rotational lines in the (sub)millimeter windows, that leads to spectral confusion in the data: some transitions appear to be blended and/or partially blended with the emission from another molecule for example. In addition, this also results in a forest of weak lines in astronomical surveys. This latter point is illustrated in the Figure 4 of Tercero et al. (2010). To clearly assign a bunch of transitions to a given molecule (so to partially reduce the confusion) and accurately derive a reliable abundance, accurate spectroscopy is obviously needed as pointed out by Favre et al. (2014) and Vastel et al. (2015). Nonetheless, recent progress in radioastronomy instrumentation for both single-dish and millimeter array (e.g. Herschel, NOEMA, ALMA, IRAM-30m) help to lower the confusion level as described below.

3.1 High angular and spectral resolution

High-resolution observations help to reduce spectral confusion. It is actually evident that the use of high spectral resolution help to separate the emission arising from different molecules in a spectrum. Regarding observations performed with high angular resolution, the use of the spatial information together with the synthesized beam (may) allow the observer to spatially isolate where the molecule is emitting from and thus, to spatially and spectrally lower the confusion level. Indeed, the spectrum resulting from single-dish observations gives the average signal integrated over a large beam area that may include the emission from different species. Alternatively, the spectrum that results from interferometric observations gives the average signal integrated over a smaller integrated area that may exclude the spatial contamination from another molecule.

3.2 Spectral Surveys

The use of actual published line surveys likely help to lower the spectral confusion level. For example, the sensitive broadband observations of the Orion-KL star-forming region acquired with the Heterodyne Instrument for the Far-Infrared (HIFI) instrument on the Herschel Space Observatory as part of the HEXOS key program (Bergin et al. 2010) is among the most completed molecular line surveys of this region. Indeed, the high spectral resolution (1.1 MHz) and the wide frequency range covered by these observations (480 GHz to 1907 GHz) have allowed us to identify ∼13,000 features and model a total of 39 molecules (79 isotopologues) toward Orion-KL (see Crockett et al. 2014) and, the HIFI spectral fit of these simple and complex molecules are available to the community. The observer can thus use these fit template model spectra to make reliable line identifications and to appreciate where potential line blends may exist.

3.3 High sensitivity

The search for COMs, including prebiotic molecules, is difficult because of their relatively low abundance and line intensity. Especially, in very rich molecular sources such as Orion-KL, high spectral confusion makes it difficult to detect the weakest lines. Regarding the detection of these weak lines, high sensitivity is key. Indeed, the high sensitivity that is available in the radioastronomy instruments (IRAM-30m, ALMA) has allowed new salient detection, such that as follows:

- **PO and PN**. Phosphorus is one of the main biogenic elements (it is part of the adenosine triphosphate, ATP) and one of the major question is to know whether PO is the main gas phase reservoir of phosphorus in molecular clouds (Thorne et al. 1984). Until recently, P-bearing molecules have been detected in some objects of the Solar System (e.g. Altwegg et al. 2016), in evolved stars: HCP, PH_3, CP, CCP, PO, PN (e.g. Agúndez et al. 2007) and, towards high-mass star forming regions: PN (Ziurys 1987; Fontani et al. 2016) and PO (Rivilla et al. 2016). Recently, as part of the Large Program dedicated to Astrochemical Surveys At IRAM (ASAI; Lefloch & Bachiller, in preparation) and thanks to the high sensitivity of the IRAM 30-m telescope, Lefloch et al. (2016) have reported the first detection of PO and PN in the direction of L1157, a solar-type star forming region.

- **Glycolaldehyde and its isotopologues**. The high sensitivity and angular resolution that offers ALMA, allowed us to observe and measure the emission from species with low abundances with respect to methanol for example. In that context, using ALMA observations as part as the the ALMA Protostellar Interferometric Line Survey (PILS), Jørgensen et al. (2012) and Jørgensen et al. (2016) have reported the first discovery of this precusor of sugar, together with its ^{13}C- and deuterated flavors, towards IRAS 16293-2422, a solar-type protostar.

4 Astrochemistry: astronomical observations, chemical modeling, theory, spectroscopy and laboratory experiments

The direct interaction between the different scientific communities is key for the study of the astrochemistry. Indeed, to get a complete overview and understand the physicochemical processes that are involved in the production and/or destruction of interstellar molecules, it is necessary to couple observations to chemical modeling and laboratory experiments on interstellar ice analogs.

4.1 The gas phase vs grain surface chemistry controversy

Formation mechanisms of complex molecules are the subject of active debate. Indeed, they could be formed on ice grain mantles via radical-radical surface reactions (e.g. the Langmuir-Hinshelwood mechanism, see Hasegawa et al. 1992; Garrod & Herbst 2006) and/or in the gas-phase. In that context, formation of methyl formate ($HCOOCH_3$) and dimethyl ether (CH_3OCH_3) is still subject to controverse. Indeed, both of these species are detected in the ISM: in cold (≤20K) and warm (∼100K) sources. A notable result is that their abundances are about the same over a large range of abundances and sources. This correlation between methyl formate and dimethyl ether in ISM objects is pointed by Jaber et al. (2014). This findings suggests that either these molecules present a common precursor or that they have a mother–daugther relation. Nonetheless, chemical models are unable to reproduce the observed abundances (Taquet et al. 2012). Indeed, different routes can lead to their formation: *i)* they could be formed on ice grain mantles through the following successive processes: hydrogenation of CO, CR-induced photo-dissociation and finally warm-up (Garrod & Herbst 2006; Garrod et al. 2008; Öberg et al. 2009; Kalvāns 2015) and/or *ii)* they can be produced through gas-phase reactions involving the radical methoxy CH_3O (see Balucani et al. 2015). At the present time, the following question is still unresolved : are dimethyl ether and methyl formate synthesized through gas phase chemistry and/or at the icy surface of grain mantle? To reply the above question it is necessary to couple observations with chemical models and Laboratory experiments in order to investigate *i)* which pathway may dominate in their production and that, according to the physical conditions of the environment in which they are observed and *ii)* to measure the rate coefficient of the different routes to reproduce, via the use of chemical model, the observed abundances.

4.2 Systematic surveys

From an astronomical point of view, understanding the mechanisms that lead to the interstellar molecular complexification implies to perform systematic surveys of simple and complex species toward a large sample of sources. This is crucial to *i)* investigate the different possible formation/destruction pathways and, *ii)* to understand the influence of the environmental conditions.

In that light, there is the ongoing NOEMA Large Program Seeds Of Life In Space (SOLIS[†], C. Ceccarelli & P. Caselli, in preparation). This large NOEMA program aims to understand how, when and where complex organic molecules form during the early stages of solar-type stars formation. To answer the above questions, this program intends to perform systematic surveys with NOEMA of a bunch of COMs (and many other molecules) toward a sample of low–mass and intermediate–mass objects. It is important to note that the SOLIS project involves an international team composed of specialists in astrophysical observations, modeling, laboratory experiments and theoretical chemistry calculations.

5 Conclusions

Complex molecules, including those of prebiotic interest, are present toward high and low mass star-forming regions. From an astronomical point of view, molecular line surveys are key to get an overview and to access considerable insight into the physicochemical processes that are involved in their production/destruction. In that light, ALMA and NOEMA are 2 key interferometers for astronomical studies because they both provide high sensitivity together with high angular resolution. Nonetheless, it is important to note that understanding the mechanisms that lead to the interstellar molecular complexification requires to couple astronomical observations to chemical modeling, theory, spectroscopy and laboratory experiments on interstellar ice analogs.

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