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Molecular complexity in the interstellar medium

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Abstract. The search for complex organic molecules in the interstellar medium (ISM) has revealed species of ever greater complexity. This search relies on the progress made in the laboratory to characterize their rotational spectra. Our understanding of the processes that lead to molecular complexity in the ISM builds on numerical simulations that use chemical networks fed by laboratory and theoretical studies. The advent of ALMA and NOEMA has opened a new door to explore molecular complexity in the ISM. Their high angular resolution reduces the spectral confusion of star-forming cores and their increased sensitivity allows the detection of low-abundance molecules that could not be probed before. The complexity of the recently-detected molecules manifests itself not only in terms of number of atoms but also in their molecular structure. We discuss these developments and report on ReMoCA, a new spectral line survey performed with ALMA toward the high-mass star-forming region Sgr B2(N).

Keywords. ISM: molecules, astrochemistry, stars: formation, ISM: abundances

1. Growing complexity of interstellar molecules

A complex organic molecule (COM), that is, an organic molecule with six atoms or more according to the definition currently adopted in astrochemistry (Herbst & van Dishoeck 2009), was among the first ten molecules identified in the ISM: methanol, CH_3OH, was detected the same year as carbon monoxide, CO (Ball *et al.* 1970; Wilson *et al.* 1970). Since then, with the continuous developments of radio astronomy and the progress made in the laboratory to characterize the rotational spectra of molecules, 74 COMs have been identified in the ISM as of June 2019 (see, e.g., "Molecules in Space" in the Cologne Database for Molecular Spectroscopy†, and McGuire 2018). They represent about one third of the total number of known interstellar molecules (212). Excluding the fullerenes, the largest molecule identified in the ISM so far, *c*-C_6H_5CN (see Sect. 1.2), has 13 atoms. However, much larger molecules have been identified in meteorites, with for instance more than 80 different amino acids (see, e.g., Botta & Bada 2002). The recent in-situ chemical inventory of comet 67P/Churyumov-Gerasimenko by the *Rosetta* mission has also revealed molecules such as glycine that have not been detected in the ISM yet (Altwegg *et al.* 2016, 2017). This gives us good reasons to believe that the number of molecules present in the ISM is much larger than what we know today.

One of the goals of astrochemistry is to explore the degree of chemical complexity that can be reached in the ISM. Beyond the mere identification of molecules, astrochemists want to understand the processes that lead to the formation of COMs in the ISM. It is also important to investigate how chemical complexity is passed over (or not) from one stage of star formation to the next one. This will tell us if the molecular complexity of meteorites and comets in our solar system is a widespread outcome of interstellar chemistry in

† https://cdms.astro.uni-koeln.de/classic/molecules

our Galaxy. To make progress, a close interplay between observations, astrochemical modelling, and experiments is necessary. We discuss below a few recent results that illustrate the growing complexity of interstellar molecules in terms of molecular structure. Sections 2 and 3 present a new ALMA spectral survey and one of its first results.

1.1. *Chiral molecules*

Life on Earth is based on homochirality, with amino acids being left-handed and sugars being right-handed. The origin of this homochirality might be extraterrestrial (Bonner *et al.* 1999). Several unsuccessful searches for chiral molecules in the ISM were reported in the past: Jones *et al.* (2007) and Cunningham *et al.* (2007) did not detect propylene oxide, *c*-$CH(CH_3)CH_2O$, toward Sgr B2(N) and Orion-KL with the Australia Telescope Compact Array and the Mopra telescope, respectively; Møllendal *et al.* (2012) failed to detect 2-aminopropionitrile, $CH_3CH(NH_2)CN$, toward Sgr B2(N) with the IRAM 30 m telescope, and Richard *et al.* (2018) did not succeed with ALMA either. Some progress was made with ALMA by Belloche *et al.* (2016) with a tentative detection toward Sgr B2(N) of deuterated ethyl cyanide, CH_3CHDCN, which is chiral through the deuterium substitution. The first secure detection of a chiral molecule in the ISM came shortly after, with three transitions of propylene oxide detected in absorption toward Sgr B2(N) by McGuire *et al.* (2016) with the Green Bank Telescope (GBT) and the Parkes telescope. Although the number of detected lines is small for the identification of such a complex molecule, the low spectral confusion in the cm range gives confidence in the assignment. This radio detection does not tell if propylene oxide has an enantiomeric excess, but McGuire *et al.* (2016) discuss in detail the prospects of such a measurement using circular dichroism. The recent identification of two chiral derivatives of propylene oxide by Pizzarello & Yarnes (2018) in the Murchison meteorite, both with an enantiomeric excess, suggests that an enantiomeric excess in interstellar propylene oxide is plausible.

1.2. *Aromatic molecules*

Polycyclic aromatic hydrocarbons (PAHs) are thought to be the carriers of the unidentified infrared bands (Tielens 2008), but none has been firmly identified so far. After the uncertain detection of benzene by Cernicharo *et al.* (2001), which relied on only one weak mid-infrared absorption feature in its ν_4 bending mode, the recent GBT detection of the aromatic molecule benzonitrile, *c*-C_6H_5CN, toward the cold dense core TMC-1 by McGuire *et al.* (2018) may represent a key step to understand the formation of polycyclic aromatic molecules in the ISM. Eight rotational transitions were detected in emission, some of them even with their hyperfine structure resolved, yielding a robust identification. McGuire *et al.* (2018) proposed two possible formation routes for benzene and/or benzonitrile, one involving electron irradiation of acetylene, in the gas phase or in the icy mantles of dust grains (Field 1964; Zhou *et al.* 2010), and the other one via a cyclization process of large cyanopolyynes HC_nN (Loomis *et al.* 2016). Benzonitrile may also form from the addition of CN to benzene, which makes it an interesting tracer of benzene, a molecule from which PAHs are expected to form (Joblin & Cernicharo 2018).

1.3. *Branched molecules*

Our earlier spectral survey of Sgr B2(N) with the IRAM 30 m telescope (Belloche *et al.* 2013) led to the detection of several new COMs, in particular *normal*-propyl cyanide, *n*-C_3H_7CN (Belloche *et al.* 2009). With the advent of ALMA, we started a project to

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explore the molecular complexity of Sgr B2(N) at higher angular resolution. We made significant progress with the first survey called EMoCA (Exploring Molecular Complexity with ALMA) at an angular resolution of 1.5", which allowed us to obtain individual spectra of the main hot cores, N1 and N2, that were blended in the single-dish beam. Sgr B2(N2) was found to have narrow linewidths (5 km s^{-1}), which means a reduced spectral confusion. Among other results, EMoCA led to the first detection of a branched alkyl molecule, *iso*-propyl cyanide, *i*-C_3H_7CN, a structural isomer of *n*-C_3H_7CN (Belloche *et al.* 2014). The detection of a branched molecule opens a new domain in the structures available to the chemistry of star-forming regions. It also establishes a further link between interstellar chemistry and the chemical composition of meteorites, where branched molecules even dominate over straight chain ones (Cronin & Pizzarello 1983).

2. The ReMoCA survey

The chemical models presented in Belloche *et al.* (2014), using the astrochemical code MAGICKAL (Garrod 2013), reproduce the abundance ratio i/n of 0.4 measured for propyl cyanide, and further simulations by Garrod *et al.* (2017) predict that for butyl cyanide, C_4H_9CN, one of the branched isomers should even dominate over the straight chain form. These predictions and the rotational spectroscopy work performed on these isomers in parallel (Müller *et al.* 2017; Wehres *et al.* 2018) motivated us to search for the isomers of butyl cyanide and perform the ReMoCA survey (Re-exploring Molecular Complexity with ALMA) toward Sgr B2(N) during ALMA's Cycle 4, improving by a factor of three both the angular resolution and the sensitivity compared to EMoCA. The high angular resolution of 0.5" was key to resolve the emission around the main hot core Sgr B2(N1). While the peak position of Sgr B2(N1) is affected by the high optical depth of the dust emission, the high angular resolution allowed us to spot slightly offset positions with narrow linewidths (5 km s^{-1}). We thus now have the possibility to characterize the chemical composition of Sgr B2(N1) at unprecedented sensitivity.

3. Detection of urea

One of the first results of the ReMoCA survey is the detection of urea, $NH_2C(O)NH_2$, toward Sgr B2(N1) (Belloche *et al.* 2020). Urea was discovered in the 18th century as an *organic* (that is, in the paradigm of that epoch, produced by living organisms) molecule. It was synthetized by Wöhler (1828) from *inorganic* compounds, which was a key experiment now regarded as the start of modern organic chemistry. Urea was detected in meteorites by Hayatsu *et al.* (1975) but two inconclusive searches for it in the ISM were reported (Raunier *et al.* 2004; Remijan *et al.* 2014). The ReMoCA identification of urea relies on nine lines clearly detected toward Sgr B2(N1), in its ground and first vibrational states. The recent rotational spectroscopy characterization of its vibrational states by Thomas *et al.* (2014) and Kisiel *et al.* (2014) was essential to secure the detection. We find that urea is one and two orders of magnitude less abundant than acetamide, $CH_3C(O)NH_2$, and formamide, NH_2CHO, respectively. Surprisingly, it is at least one order of magnitude less abundant in Sgr B2(N2) than in Sgr B2(N1), relative to formamide. The reasons for this difference between the two sources will have to be explored.

4. Conclusions

The recent advances in the search for COMs in the ISM have revealed that interstellar chemistry is capable of producing chiral, aromatic, and branched molecules. These molecules are still relatively simple (less than 13 atoms), but their molecular structures are reminiscent of the structures that characterize more complex molecules in meteorites.

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Astronomers have thus probably probed only a small fraction of the molecules present in the ISM. The large partition functions of more complex species may ultimately hamper their detection, but the molecules detected so far, with their variety of molecular structures, already allow us to identify with numerical simulations which chemical processes are key to produce these structures. On the observational side, ALMA and NOEMA have only started to deliver the chemical composition of star-forming regions and we can expect further progress in the coming decade. On a longer term, ngVLA and SKA may also contribute to push the limits of chemical complexity in the ISM even further.

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