

## Complex Organic Molecules

# Exploring molecular complexity in the Galactic Center with ALMA

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**Abstract.** The search for complex organic molecules (COMs) in the ISM has revealed chemical species of ever greater complexity. This search relies heavily on the progress made in the laboratory to characterize the rotational spectra of these molecules. Observationally, the advent of ALMA with its high angular resolution and sensitivity has allowed to reduce the spectral confusion and detect low-abundance molecules that could not be probed before. We present results of the EMOCA survey conducted with ALMA toward the star-forming region Sgr B2(N). This spectral line survey aims at deciphering the molecular content of Sgr B2(N) in order to test the predictions of astrochemical models and gain insight into the chemical processes at work in the ISM. We report on the tentative detection of N-methylformamide, on deuterated COMs, and on the detection of a branched alkyl molecule. Prospects for probing molecular complexity in the ISM even further are discussed at the end.

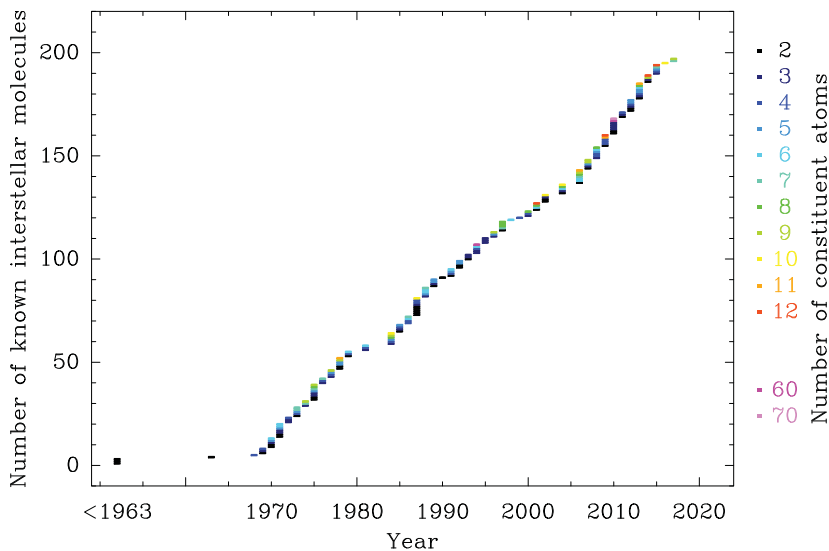
**Keywords.** ISM: molecules, astrochemistry, ISM: individual objects: Sagittarius B2(N), stars: formation

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## 1. Complex organic molecules in the interstellar medium

The in-situ exploration of comet 67P/Churyumov-Gerasimenko by the Rosetta mission has led to the detection of more than twenty organic molecules in the coma of the comet and in material excavated from the surface by the impact of Rosetta's lander Philae (Goesmann *et al.* (2015), Altwegg *et al.* (2016), Altwegg *et al.* (2017)). Most of these molecules, such as methyl cyanide, CH<sub>3</sub>CN, formamide, NH<sub>2</sub>CHO, or acetone, CH<sub>3</sub>C(O)CH<sub>3</sub>, were already known to exist in the interstellar medium (ISM) but some, like methyl isocyanate, CH<sub>3</sub>NCO, reported by Goesmann *et al.* (2015)<sup>†</sup>, were not. Shortly after, as soon as spectroscopic predictions of the rotational spectrum of the molecule became available, methyl isocyanate was detected in the ISM (Halfen *et al.* (2015), Cernicharo *et al.* (2016)). Another molecule that was not known to exist in the ISM, and has still not been found, is the amino acid glycine, NH<sub>2</sub>CH<sub>2</sub>COOH. Altwegg *et al.* (2016) reported its identification in the coma of comet 67P, confirming an earlier claim by Elsila *et al.* (2009) who analyzed samples returned from comet 81P/Wild 2 to Earth by the Stardust mission. In addition to these cometary detections, more than 80 different types of amino acids were identified in meteorites on Earth, with an isotopic composition and a racemic distribution suggesting that their presence is not due to contamination by Earth material and that they have instead a true extraterrestrial origin (see, e.g., Botta & Bada (2002)). The degree of molecular complexity found in these small solar-system bodies, in particular in meteorites, raises the following questions: is this chemical complexity a widespread outcome of interstellar chemistry in our Galaxy, and possibly even in other

<sup>†</sup> The identification of methyl isocyanate in the mass spectrum of the cometary material analyzed by Goesmann *et al.* (2015) has been recently disputed (Ligterink *et al.* (2017), Altwegg *et al.* (2017)).

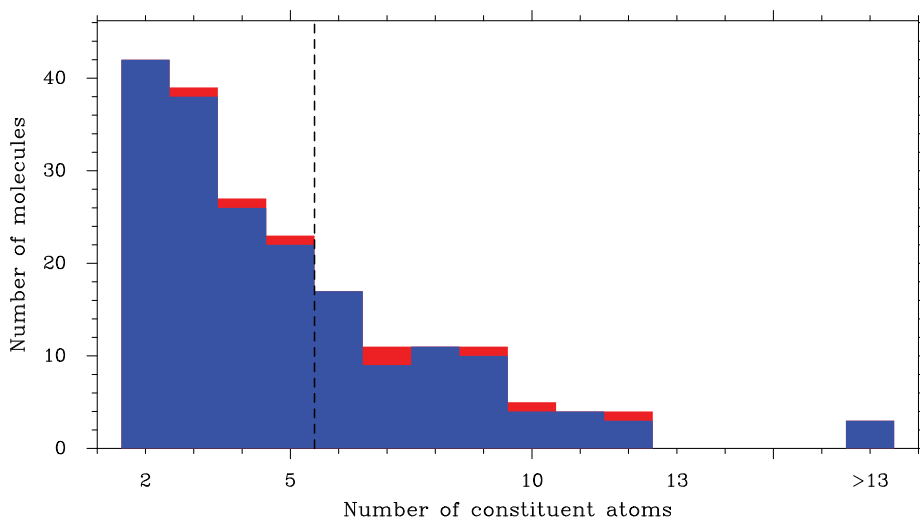


**Figure 1.** Number of known interstellar molecules as a function of time as of July 2017. The three molecules identified before 1963 are indicated on the left. The number of atoms each molecule contains is color-coded following the color scheme shown on the right. This diagram uses the information provided by H. S. P. Müller in the Cologne Database for Molecular Spectroscopy (CDMS, <http://www.astro.uni-koeln.de/cdms/molecules>).

galaxies? What degree of complexity is interstellar chemistry capable of achieving, in particular in star (and planet) forming regions?

As of today, 197 molecules have been identified in the interstellar medium or in circumstellar envelopes of evolved stars. This number does not include isotopologs, that is molecules containing less abundant isotopes such as D,  $^{13}\text{C}$ ,  $^{18}\text{O}$ ,  $^{34}\text{S}$ , or  $^{15}\text{N}$ . The first identifications of interstellar molecules, CH,  $\text{CH}^+$ , and CN, go back nearly eight decades ago and were made in absorption in the UV domain (McKellar (1940), Adams (1941), Douglas & Herzberg (1941)). However, the search for molecules in the ISM started to become efficient more than two decades later, with the advent of radio astronomy. Figure 1 shows the number of known interstellar molecules as a function of time, with the number of their constituent atoms color-coded. Since the first detection of a molecule in the radio domain, the hydroxyl radical OH by Weinreb *et al.* (1963), about seven molecules have been newly identified in the ISM every two years on average. While the rate of detection has been to first order constant over the past five decades, it is worth mentioning that the detection rate over the past decade ( $\sim 5$  new molecules per year) exceeds the rate achieved during the first decade when radio astronomy started to flourish ( $\sim 4$  new molecules per year between 1968 and 1977). This shows the current vitality of this field of research and suggests that the inventory of interstellar molecules should continue to grow significantly in the near future.

Following the review by Herbst & van Dishoeck (2009), it has become common in the astrochemical community to define a molecule as complex when it contains six atoms or more. With this definition, about one third of the known interstellar molecules are complex (Fig. 2). All these complex molecules contain at least one carbon atom and they are thus called complex organic molecules (COMs). The presence of such complex interstellar molecules raises the question of their origin. What are the chemical processes that lead to chemical complexity in the ISM? What are the respective roles of gas-phase and grain-surface/mantles processes? What are the relevant reactions? What



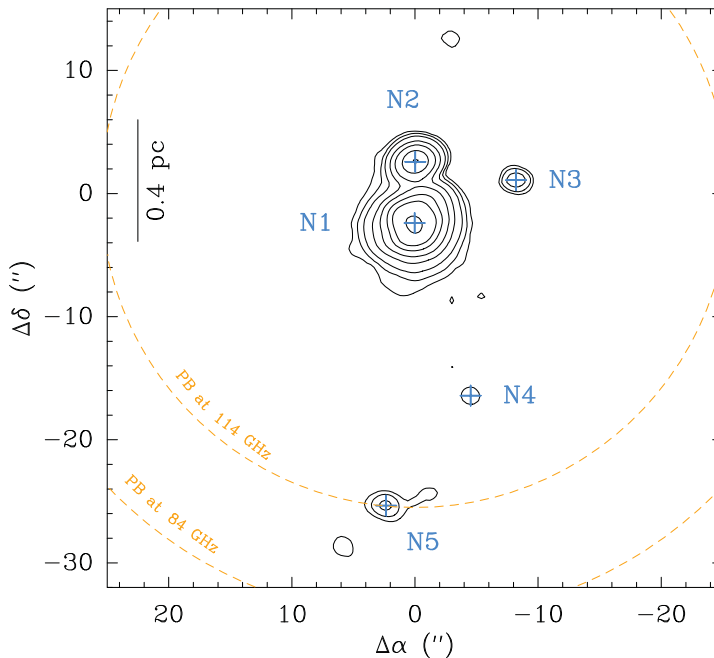
**Figure 2.** Number of known interstellar molecules as a function of the number of their constituent atoms as of July 2017. Detections published in 2015–2017 are emphasized in red. The dashed line indicates the threshold above which a molecule is defined as complex.

are their reaction rates and branching ratios? To answer all these questions, a close interplay between laboratory experiments, theoretical calculations, numerical simulations, and observations is necessary (see, e.g., Herbst & van Dishoeck (2009), Garrod & Widicus Weaver (2013), Öberg (2016)). Here, we focus on the latter with the aim of confronting results of observations to predictions of astrochemical models.

## 2. Sgr B2 and the EMOCA survey

One of the most prominent star-forming regions in our Galaxy is the giant molecular cloud Sagittarius (Sgr) B2, with a mass of  $\sim 10^7 M_{\odot}$  in a diameter of  $\sim 40$  pc (Lis & Goldsmith (1990)). Sgr B2 is located about 100 pc from the Galactic Center in projection, at a distance of 8.3 kpc from the Sun (Reid *et al.* (2014)). It contains two main sites of on-going formation of high-mass stars, Sgr B2(N) and Sgr B2(M), that both host clusters of ultra-compact H II regions (see, e.g., Gaume *et al.* (1995), Schmiedeke *et al.* (2016)). Sgr B2(N), in particular, contains several hot molecular cores (Fig. 3). The main ones, Sgr B2(N1) and Sgr B2(N2), have been known for a long time (e.g., Snyder *et al.* (1994), Belloche *et al.* (2008), Qin *et al.* (2011), Belloche *et al.* (2016)), but several new, fainter ones were recently detected with the Atacama Large Millimeter/submillimeter Array (ALMA) (Bonfand *et al.* (2017), Sánchez-Monge *et al.* (2017)). The  $H_2$  column densities of these hot cores are so high ( $10^{24}$ – $10^{25}$   $\text{cm}^{-2}$  over few arcsec) that the detection of molecules with low abundances in Sgr B2 is easier than toward other sources. This has been a key advantage for the detection of new COMs in the past few decades. Indeed, many COMs were first detected toward Sgr B2.

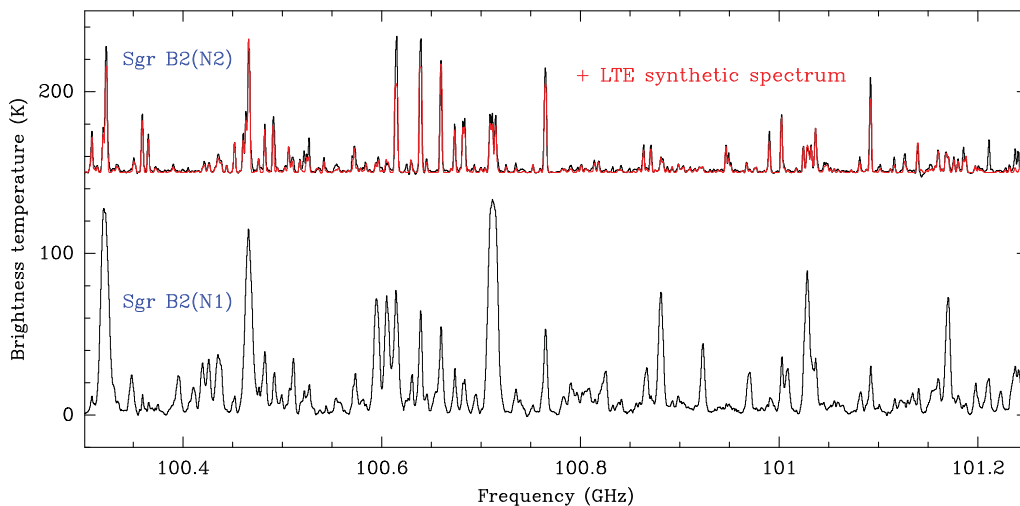
Following up a spectral line survey of Sgr B2(N) and Sgr B2(M) carried out with the IRAM 30 m single-dish telescope a decade ago, which led to the detection of several new COMs (Belloche *et al.* (2008), Belloche *et al.* (2009), Belloche *et al.* (2013)), we performed the EMOCA project with ALMA in Cycles 0 and 1. EMOCA stands for Exploring Molecular Complexity with ALMA. This interferometric project is a spectral line survey of Sgr B2(N) that covers the 3 mm atmospheric window between 84.1 GHz and 114.4 GHz, at an angular resolution of  $\sim 1.6''$  and a spectral resolution of 488 kHz,



**Figure 3.** Contour map of Sgr B2(N) representing the number of channels between 84.1 GHz and 114.4 GHz with emission detected above the  $7\sigma$  level in the continuum-subtracted spectra of the EMoCA survey. The contour levels are 500, 1000, 2000, 5000, 10000, and then increase by steps of 10000. The dashed circles represent the primary beam of the ALMA 12 m antennas at 84 GHz and 114 GHz. The equatorial offsets are given with respect to the phase center located at  $(\alpha, \delta)_{J2000} = (17^{\text{h}}47^{\text{m}}19.87^{\text{s}}, -28^{\circ}22'16'')$ . Sources identified as hot cores by Bonfand *et al.* (2017) are indicated with blue crosses and labels. Figure adapted from Bonfand *et al.* (2017).

that is a velocity resolution between 1.3 and 1.7 km s<sup>-1</sup>. We achieved a sensitivity of  $\sim 3$  mJy beam<sup>-1</sup> ( $1\sigma$ ), that is  $\sim 0.15$  K in brightness temperature scale. EMoCA aims at detecting new COMs in the ISM and, thereby, testing the predictions delivered by numerical simulations of interstellar chemistry.

In addition to delivering maps of thousands of spectral lines, the EMoCA survey represents an improvement by more than one order of magnitude both in angular resolution and sensitivity compared to our previous single-dish survey. In particular, its angular resolution of 1.6'' (13000 au in projection) is sufficient to separate the two main hot cores, Sgr B2(N1) and Sgr B2(N2), that are separated by  $\sim 5''$  in the north-south direction. A nice surprise of this survey is that the emission lines of the northern hot core, Sgr B2(N2), have widths (FWHM) of 5 km s<sup>-1</sup> only, which reduces considerably the level of line confusion compared to previous single-dish data. As shown in Fig. 4, the lines detected toward the main hot core, Sgr B2(N1), are broader ( $\sim 7$  km s<sup>-1</sup>) and some of them have stronger wings. With the aim to look for weak lines of low-abundance species, we have focused our analysis on Sgr B2(N2) so far. We model its emission spectrum using Weeds (Maret *et al.* (2011)) under the assumption of local thermodynamic equilibrium (LTE), which is reasonable given the high densities probed with ALMA. Our spectroscopic database, which is needed to model the spectra, contains all entries available in the JPL and CDMS databases (Pickett *et al.* (1998), Müller *et al.* (2001), Endres *et al.* (2016)), as well as additional predictions sent to us by spectroscopists. Our current model of the emission spectrum of Sgr B2(N2) is shown in red in Fig. 4. In the next three



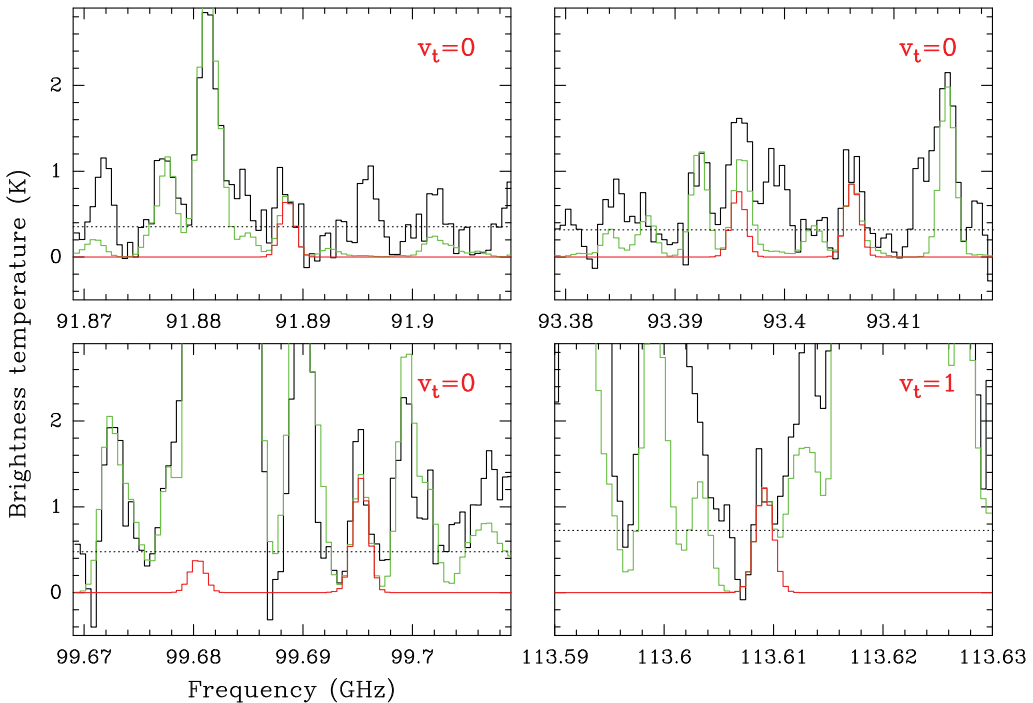
**Figure 4.** Short portion of the EMOCA spectrum observed toward the hot molecular cores Sgr B2(N1) and Sgr B2(N2) with ALMA at an angular resolution of  $\sim 1.6''$ . The red spectrum shows the LTE model that contains the contribution of all the molecules identified so far toward Sgr B2(N2).

sections, we report on some of the results obtained with the EMOCA survey based on this model.

### 3. Tentative detection of N-methylformamide

N-methylformamide,  $\text{CH}_3\text{NHCHO}$ , is a structural isomer of the known interstellar molecule acetamide,  $\text{CH}_3\text{C}(\text{O})\text{NH}_2$ , that was detected in Sgr B2(N) by Hollis *et al.* (2006) (see also Halfen *et al.* (2011)). Both molecules contain a peptide bond which is the characteristic chemical bond linking amino acids in proteins. N-methylformamide can also be seen as a partially hydrogenated form of methyl isocyanate,  $\text{CH}_3\text{NCO}$ , which was recently detected in the ISM as mentioned in Sect. 1. Given that both acetamide and methyl isocyanate were known interstellar molecules, N-methylformamide appeared as a good candidate for an interstellar detection. New measurements of the rotational spectrum of the *trans* conformer of this molecule were performed in Lille (France) and Kharkiv (Ukraine) over the frequency range 45–630 GHz, and accurate spectroscopic predictions were then obtained with the RAM36 program (Ilyushin *et al.* (2010)) for its ground state and its first two torsionally excited states (Belloche *et al.* (2017)).

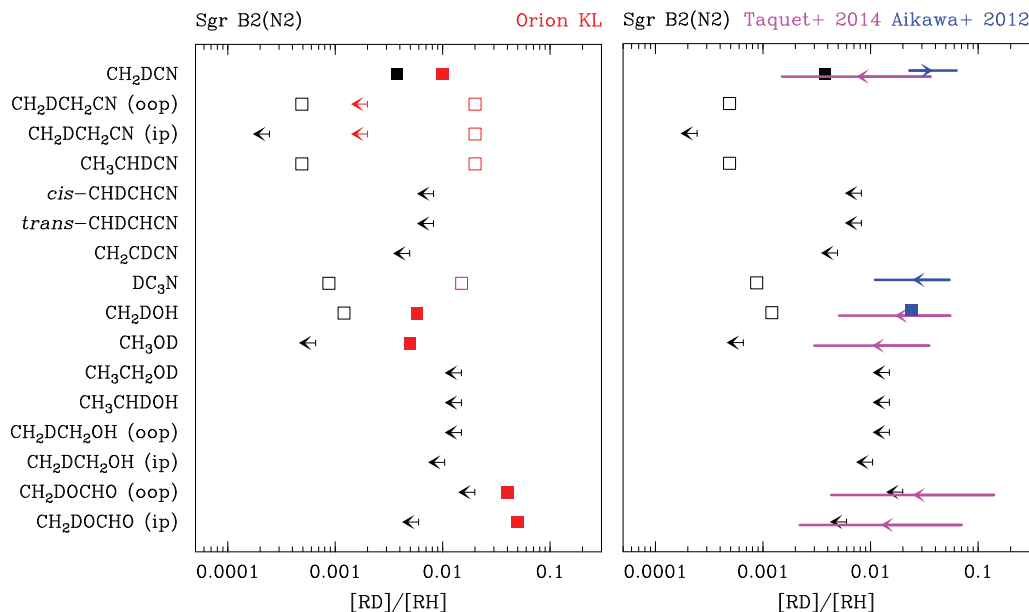
With these spectroscopic predictions, we searched for emission of N-methylformamide in the EMOCA spectrum of Sgr B2(N2). Five of the lines that we assigned to  $\text{CH}_3\text{NHCHO}$  suffer little from contamination by emission lines of other species. Four of these five lines are shown in Fig. 5. Given that our full model of Sgr B2(N2) includes the contribution of all species identified so far (red spectrum in Fig. 4 and green spectrum in Fig. 5), we selected seven additional lines of N-methylformamide that could be “decontaminated” with the full model and we used them together with the five well detected lines to build a population diagram for this molecule. A fit to this diagram yields a temperature of  $\sim 150$  K, which is typical of the rotational temperatures derived for other COMs in Sgr B2(N2). Since only five lines are detected without contamination, the detection of  $\text{CH}_3\text{NHCHO}$  is considered as tentative only (Belloche *et al.* (2017)). However, the fact that our model takes into account the emission of all species identified so far and that



**Figure 5.** Spectra of Sgr B2(N2) showing four of the five transitions of N-methylformamide that do not suffer much from contamination by emission lines of other species in the EMOCA survey (Belloche *et al.* (2017)). In each panel, the observed ALMA spectrum is shown in black, the synthetic spectrum of N-methylformamide in red, and the model containing the contributions of all molecules identified so far in green. The dotted line indicates the  $3\sigma$  detection level. The line in the bottom right panel belongs to the first torsionally excited state of N-methylformamide, while the other ones are ground-state lines.

the derived rotational temperature of N-methylformamide is typical of COM emission in Sgr B2(N2), we are confident that the identification of this molecule in this source is correct.

We used the EMOCA survey to compare the abundance of N-methylformamide to the ones of related species.  $\text{CH}_3\text{NHCHO}$  is, within a factor of two, nearly as abundant as  $\text{CH}_3\text{NCO}$  and  $\text{CH}_3\text{C}(\text{O})\text{NH}_2$ , and more than one order of magnitude less abundant than formamide,  $\text{NH}_2\text{CHO}$ , and isocyanic acid,  $\text{HNCO}$ . We compared these abundance ratios to predictions obtained with the chemical kinetics model MAGICKAL (Garrod (2013)), the network of which was expanded to include N-methylformamide as well as related species. The first conclusion of this comparison is that an efficient formation of  $\text{HNCO}$  via  $\text{NH}+\text{CO}$  on grains with an activation energy below 1500 K is necessary to achieve the observed abundance of  $\text{CH}_3\text{NCO}$ . The second conclusion is that the production of  $\text{CH}_3\text{NHCHO}$  on grain surfaces is plausible via two formation routes: the successive addition of H to  $\text{CH}_3\text{NCO}$  and radical-radical reactions ( $\text{CH}_3+\text{HNCHO}$  or  $\text{HCO}+\text{HNCH}_3$ ) (Belloche *et al.* (2017)). The good match between the predicted and measured abundance ratios is an additional support to our identification of N-methylformamide in the EMOCA spectrum of Sgr B2(N2). However, the chemical model produces an overabundance of acetamide, which should be investigated in more details in the future.



**Figure 6.** *Left panel:* Level of deuterium fractionation measured for a sample of (complex) organic molecules toward Sgr B2(N2) (Belloche *et al.* (2016)). Filled and empty squares indicate robust and tentative detections, respectively. Upper limits are indicated with arrows. The symbols in red show the level of deuteration reported for Orion KL by Gerin *et al.* (1992), Margulès *et al.* (2009), Daly *et al.* (2013), Esplugues *et al.* (2013), Neill *et al.* (2013), and Coudert *et al.* (2013). *Right panel:* Same measurements toward Sgr B2(N2) compared to predictions of chemical models of collapsing protostellar envelopes. The purple bars and arrows show the evolution of the level of deuterium fractionation as a function of time during the main accretion phase in the model of Taquet *et al.* (2014) while the blue ones and the blue square show the model predictions of Aikawa *et al.* (2012).

#### 4. Deuterated complex organic molecules

The cosmic abundance of deuterium with respect to hydrogen is low ( $\sim 1.5 \times 10^{-5}$ , Linsky (2003)). Still, molecules in star-forming regions are often found to be enriched in deuterium (e.g., Parise *et al.* (2006)). This mainly results from the exothermicity of the reaction of  $H_3^+$  with HD, the reservoir of deuterium in molecular clouds, that produces  $H_2D^+$ , and the depletion of CO, the main destroyer of  $H_3^+$ , onto the surface of dust grains that occurs in the dense and cold regions of molecular clouds. Given these properties, the degree of deuterium fractionation of molecules in star-forming regions is a powerful tool to trace the history of their cold prestellar phase (see, e.g., Caselli & Ceccarelli (2012), Ceccarelli *et al.* (2014)). Although the level of deuteration is known to be low in the Galactic Center region (e.g., Gerin *et al.* (1992)), we took advantage of the high sensitivity of the EMOCA survey to search for deuterated COMs in Sgr B2(N2).

We firmly detected CH<sub>2</sub>DCN and could also report tentative detections of CH<sub>2</sub>DCH<sub>2</sub>CN, CH<sub>3</sub>CHDCN, DC<sub>3</sub>N, and CH<sub>2</sub>DOH (Belloche *et al.* (2016)). The level of deuteration measured for these species, as well as upper limits derived for other deuterated COMs, are summarized in the left panel of Fig. 6, along with measurements or upper limits reported in the literature for Orion KL. Overall, the degree of deuteration of COMs in Sgr B2(N2) is on the order of 0.1%, a factor three to ten lower than in Orion KL. The right panel of Fig. 6 compares the Sgr B2(N2) results to predictions of chemical models of (low-mass) protostellar envelopes (Aikawa *et al.* (2012), Taquet *et al.* (2014)). Apart for a possible



agreement for CH<sub>2</sub>DCN in one model, the models produce overabundances of deuterated COMs by at least a factor of four.

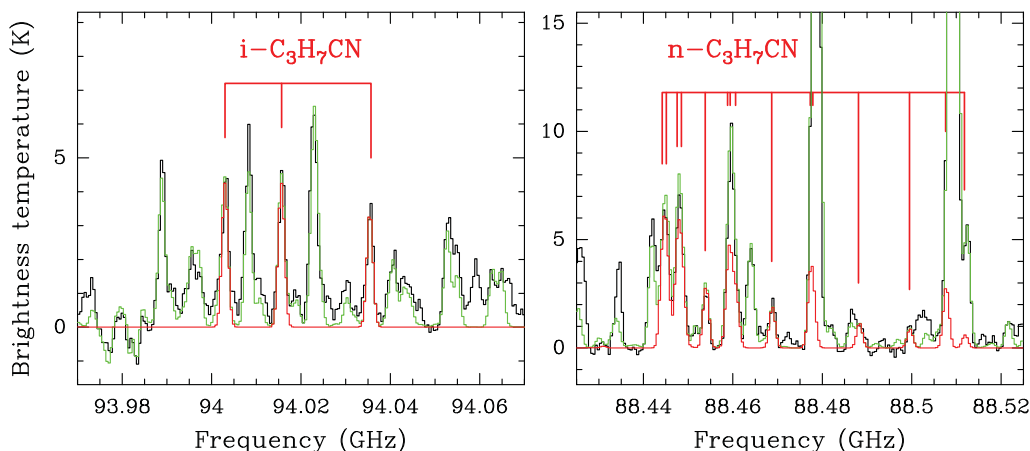
The low level of deuteration of COMs in Sgr B2(N2) has at least two possible origins. First, it may reflect a lower elemental abundance of deuterium in the Galactic Center region compared to the local ISM, owing to stellar processing of previous generations of stars, as has been claimed, albeit with large uncertainties, by previous studies that were based on small molecules (Jacq *et al.* (1999), Lubowich *et al.* (2000), Polehampton *et al.* (2002)). A second possibility could be the thermal history of star formation in Sgr B2. Both the gas kinetic temperature (30–50 K, Ott *et al.* (2014)) and the dust temperatures (20–28 K, Guzmán *et al.* (2015)) are higher in Sgr B2 than in nearby star forming regions. In the model of Taquet *et al.* (2014), the level of deuteration of methanol is reduced by a factor three at the end of the prestellar phase when the initial dust temperature is increased by 3 K only, from 17 K to 20 K. The deuteration of COMs is thus very sensitive to the temperature during the prestellar phase, and the higher temperatures prevailing in the Galactic Center region could have contributed to the low level of COM deuteration found in Sgr B2(N2). In addition, it is worth mentioning that the factor five difference found in Sgr B2(N2) between the deuteration level of methyl cyanide, CH<sub>3</sub>CN, and ethyl cyanide, C<sub>2</sub>H<sub>5</sub>CN, may point to different formation pathways, in the gas phase for the former and in the ice mantles for the latter. Dedicated numerical simulations of deuteration designed for Sgr B2 will be needed in the future to investigate its thermal history and the chemical pathways of its deuterium chemistry in detail.

## 5. Branched molecules in the interstellar medium

One of the first results of the EMOCA survey was the interstellar detection of a branched alkyl molecule (Belloche *et al.* (2014)). The rotational spectrum of this molecule, *iso*-propyl cyanide, *i*-C<sub>3</sub>H<sub>7</sub>CN, was studied in the laboratory by Müller *et al.* (2011). It is a structural isomer of the straight-chain form *normal*-propyl cyanide, *n*-C<sub>3</sub>H<sub>7</sub>CN, that we detected earlier in our single-dish survey of Sgr B2(N) (Belloche *et al.* (2009)). Both isomers are clearly detected in the EMOCA spectrum, with about 50 transitions for the branched form and 120 transitions for the chain-like form (Fig. 7). The population diagram of *n*-C<sub>3</sub>H<sub>7</sub>CN yields a well constrained rotational temperature of ~150 K, typical of the COM emission in Sgr B2(N2). From the LTE modelling, we derived a surprisingly high abundance ratio [*i*-C<sub>3</sub>H<sub>7</sub>CN]/[*n*-C<sub>3</sub>H<sub>7</sub>CN] of 0.4, with the branched form nearly as abundant as the chain-like one.

We compared the measured abundance ratio of the two isomers of propyl cyanide again to predictions of the chemical kinetics model MAGICKAL (Garrod (2013)). The reaction network of this model was expanded to include, for the first time, the formation of branched molecules (Garrod *et al.* (2017), Belloche *et al.* (2014)). The measured abundance ratio of the two isomers of propyl cyanide is well reproduced by the model. The model indicates that both molecules can be formed on grain surfaces, but via different formation routes. The dominant routes for *n*-C<sub>3</sub>H<sub>7</sub>CN are the addition reactions CH<sub>3</sub>ĊH<sub>2</sub>+ĊH<sub>2</sub>CN and ĊN+CH<sub>2</sub>=CHCH<sub>3</sub> while the formation of *i*-C<sub>3</sub>H<sub>7</sub>CN is dominated by the radical-radical reaction ĊH<sub>3</sub>+CH<sub>3</sub>ĊHCN. In the model, the key parameter influencing the *i/n* ratio is the barrier of the ĊN addition to C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> (Garrod *et al.* (2017)).

As mentioned in Sect. 1, amino acids of extraterrestrial origin were detected in meteorites on Earth. Both branched and chain-like isomers of these amino acids were identified, and the branched isomers were even found to dominate over the chain-like ones (e.g., Cronin & Pizzarello (1983)). The detection of a branched alkyl molecule in the



**Figure 7.** *Left panel:* Example of transitions of *iso*-propyl cyanide detected toward Sgr B2(N2) with ALMA (Belloche *et al.* (2014)). The observed spectrum is shown in black, the synthetic spectrum of *iso*-propyl cyanide in red, and the model containing the contributions of all molecules identified so far in green. *Right panel:* Example of transitions of *normal*-propyl cyanide detected toward Sgr B2(N2) with ALMA. The red spectrum is the synthetic spectrum of *normal*-propyl cyanide.

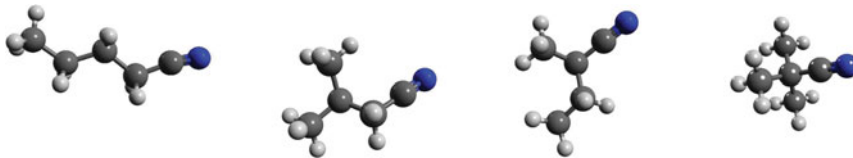
ISM thus establishes a further link between the chemical composition of meteorites and interstellar chemistry.

## 6. Outlook

The EMOCA project is just one example illustrating the new window opened by ALMA in terms of angular resolution and sensitivity to probe the complexity of interstellar chemistry and confront the derived chemical composition of astronomical sources to the predictions of astrochemical models. While Sgr B2 is a place of choice to detect molecules of low abundance thanks to its high column densities, spectral line surveys of other sources with ALMA, such as the PILS survey toward a nearby low-mass protostar (The ALMA Protostellar Interferometric Line Survey, Jørgensen *et al.* (2016)), are exploring the outcome of interstellar chemistry in other environments and will also contribute to improving our understanding of the chemical processes at work in the ISM.

Our study of deuterated COMs in Sgr B2(N2) has shown that a sensitive, unbiased spectral line survey at high angular resolution is an exquisite tool to measure the level of deuterium fractionation of molecules with high accuracy. This is made possible by the conditions prevailing in this hot core: the densities are so high that collisions dominate over radiative processes and the LTE approximation is valid. The spectra of COMs, which can have several dozens of lines detected, can thus be fitted with great accuracy. In this respect, Sgr B2 is an excellent laboratory to test the predictions of chemical models quantitatively. Numerical simulations of deuterium chemistry designed for Sgr B2(N) should help us in the future set valuable constraints on the D/H elemental abundance in the Galactic Center region.

After the detection of acetamide,  $\text{CH}_3\text{C}(\text{O})\text{NH}_2$ , and the tentative detection of *N*-methylformamide,  $\text{CH}_3\text{NHCHO}$  (Sect. 3), it is tempting to search for the next structural isomer of these two molecules, acetimidic acid,  $\text{CH}_3\text{C}(\text{OH})\text{NH}$ , which is the third most stable isomer in the  $\text{C}_2\text{H}_5\text{NO}$  family (Lattalais *et al.* (2010)). However, the rotational spectrum of this molecule has not been characterized in the laboratory yet, and its dipole



**Figure 8.** Ball-and-stick representations of the chain-like and branched forms of butyl cyanide. From left to right:  $n$ - $C_4H_9CN$ ,  $i$ - $C_4H_9CN$ ,  $s$ - $C_4H_9CN$ , and  $t$ - $C_4H_9CN$ . Figure adapted from Garrod *et al.* (2017), image credit: E. Willis.

moment is a factor of two smaller than the ones of acetamide and N-methylformamide (Lattalais *et al.* (2009)). Therefore, its detection in the ISM will be challenging.

The detection of a branched alkyl molecule (Sect. 5) has opened a new domain in the structures available to the chemistry of star forming regions. The next step in complexity in the alkyl cyanide family is butyl cyanide,  $C_4H_9CN$ . This molecule has one straight-chain isomer and three branched ones (Fig. 8). The straight-chain form, *normal*-butyl cyanide, was searched for in the ISM but it has not been detected so far, neither in our previous IRAM 30 m survey of Sgr B2(N) nor in the EMOCA survey (Ordu *et al.* (2012), Garrod *et al.* (2017)). The chemical model MAGICCAL predicts that one of the branched forms,  $s$ - $C_4H_9CN$ , should in fact dominate over the straight-chain form in Sgr B2(N2) and that we may have been only short of a detection with the EMOCA survey (Garrod *et al.* (2017)). This motivated us to start a follow-up survey of Sgr B2(N) at 3 mm with ALMA in its Cycle 4. This new project will represent an improvement by a factor of three both in angular resolution and sensitivity with respect to the EMOCA survey. The characterization of the rotational spectrum of  $s$ - $C_4H_9CN$  was performed in Cologne (Müller *et al.* (2017)) and the Cycle 4 observations have been completed recently.  $s$ - $C_4H_9CN$  will be one of the first molecules we will search for in this new, sensitive spectral line survey that may reveal the presence of other interesting COMs as well.

As mentioned in Sect. 2, the EMOCA survey revealed that the hot core Sgr B2(N2) has linewidths as narrow as  $5 \text{ km s}^{-1}$  at arcsecond scale. This helped reduce the spectral confusion compared to previous single-dish surveys. EMOCA has indeed not reached the confusion limit on this source yet, while the spectrum of Sgr B2(N1) is almost confusion-limited. There is thus still room for improvement on Sgr B2(N2), and also on the other fainter hot cores detected in Sgr B2(N) (Bonfand *et al.* (2017), Sánchez-Monge *et al.* (2017)), which is one of the goals of our new Cycle 4 project. However, it is likely that the confusion limit will almost be reached in this next survey and the following question will arise: how will we beat the confusion limit in order to explore even further the chemical complexity of the ISM in the future? At least two possibilities can be investigated. As spectral confusion increases with frequency in Sgr B2(N) (Belloche *et al.* (2013)), the first option is to go to lower frequencies, as has already been explored at low angular resolution with the PRIMOS spectral survey of Sgr B2(N) performed with the Green Bank Telescope (e.g., Neill *et al.* (2012)). Higher angular resolution will however be necessary to probe the hot cores in an optimal way: this will be possible with ALMA once it is equipped with receivers operating below 80 GHz (bands 1 and 2 or 2+3, Di Francesco *et al.* (2013), Fuller *et al.* (2016)), and on a longer term with the Next Generation Very Large Array (ngVLA, Hughes *et al.* (2015)). The second direction will be to perform very deep integrations with ALMA on sources that have narrower

linewidths, such as the Class 0 protostar IRAS 16293–2422 which is the target of the PILS survey (Jørgensen *et al.* (2016)).

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