



# Interstellar Detection of Vibrationally Excited Transitions of Organic Molecules

## The Bologna Laboratory Support

L. Dore

Dipartimento di Chimica “Giacomo Ciamician”, Università di Bologna, via F. Selmi 2, I-40126, Bologna, Italy  
e-mail: luca.dore@unibo.it

**Abstract.** In the ongoing effort to detect complex organic molecules (COMs) in star-forming regions, support from laboratory spectroscopy is essential. Several COMs contribute to the observed spectra, which are fairly crowded, and additional spectral complexity may result from the vibrational excitation of the more abundant species. Therefore a comprehensive characterization of the rotational spectra is needed to allow the identification of low-abundance COMs. This work reports the cases of two interstellar organics, cyanoacetylene ( $\text{HC}_3\text{N}$ ) and aminoacetonitrile ( $\text{NH}_2\text{CH}_2\text{CN}$ ), whose accurate description of the ro-vibrational energies, obtained from FT-IR, FIR and millimeter-wave spectra recorded in the laboratory, has given a contribution to the analysis of spectral line surveys with regards to the molecules in vibrationally excited states.

**Key words.** Molecular data – Methods: laboratory: molecular – Techniques: spectroscopic – Radio lines: ISM

### 1. Introduction

Among the more than 200 molecules detected in the Interstellar Medium (ISM), those with six or more atoms are organics containing carbon: following Herbst & Van Dishoeck (2009), they are referred to as complex or COMs (Complex Organic Molecules). On the birth of a protostar, first generation COMs are formed on icy surfaces, because the mobility of the frozen species increases, due the higher temperature, and the chemistry is enhanced. Then, at the “hot core” stage, with  $T \sim 100$  K in the innermost region, second generation COMs are produced from reactants subli-

mated into the gas phase (van Dishoeck 2017; van Dishoeck & Bergin 2020). Further chemical complexity is driven by energy sources, like radiation and shocks, and “pre-biotic” species can be found in the COM inventory. Actually, there are evidences that COMs may also form in cold cores in the pre-stellar phase (Öberg & Bergin 2021).

Among her 14 challenges for astrochemistry, van Dishoeck (2017) proposes “to push detections to even higher levels of complexity including pre-biotic species like amino acids”. In order to accomplish this task, quite comprehensive laboratory spectra are needed to support identification of new

molecules (Jørgensen et al. 2020). To claim a secure detection of a COM, several transitions should be detected and the whole spectrum expected at the recovered physical conditions of the source has to be consistent with observations. Moreover, at the temperatures of hot cores, rotational levels in vibrational excited states can be populated, thus the more abundant species may have a fairly complex spectra (with the contribution of their isotopologues as well), which need to be characterized to allow the identification of low-abundance COMs.

The survey EMoCA (Exploring Molecular Complexity with ALMA) toward Sagittarius B2 (Sgr B2) (see Belloche et al. 2016) is an example of the effort to detect COMs in star-forming regions. In its Table 4 are listed several detected organic species and, noticeably, some of them could be observed in vibrationally excited states. As for the analysis of the survey spectra, Jørgensen et al. (2020) recommend “to fit a complete spectral survey with a synthetic spectrum . . . rather than rely on simple independent Gaussian fits of individual lines of a given species”: this was the procedure used by Belloche et al. (2016) to analyze the spectrum from the EMoCA survey, which, actually, requires extensive data from the laboratory. Such spectral line surveys can take advantage of the capabilities of the Atacama Large Millimeter/submillimeter Array (ALMA): Belloche et al. (2019) performed a new survey at higher angular resolution and sensitivity (ReMoCA, Re-exploring Molecular Complexity with ALMA) for a deeper study of the chemical composition of Sgr B2(N), and the low-abundant urea could be detected.

## 2. Two case studies

In the following subsections are presented two interstellar organics, whose FT-IR and millimeter-wave spectra have been recorded in laboratories of the University of Bologna, and it will be shown the contribution given to the analysis of spectral line surveys with regards to the molecules in vibrationally excited states.

### 2.1. Cyanoacetylene

Cyanoacetylene ( $\text{HC}_3\text{N}$ ), the simplest cyanopolyne, is an organic molecule abundant and ubiquitous in interstellar environments; it has been the subject of a recent, extensive spectroscopic study by Bizzocchi et al. (2017). The FT-IR spectrum was collected in Bologna (“Toso Montanari” department) in the  $450 - 1100 \text{ cm}^{-1}$  range and also part of the new millimeter-wave spectra were recorded in Bologna (“Giacomo Ciamician” department), using a frequency-modulation (FM) mm-wave spectrometer to cover selected frequency intervals between 80 and 400 GHz. With an available sample of 3400 ro-vibrational lines for 13 bands plus some 1500 pure rotational lines for 12 vibrational states, including literature data, a global fit was performed with a careful treatment of the resonance effects. The fit led to an accurate set of spectroscopic constants, which enabled the computation of a large set of ro-vibrational rest frequencies for all of the vibrational levels below  $1000 \text{ cm}^{-1}$  and for pure rotational transitions with  $J = 0 - 120$ .

This accurate description of the ro-vibrational energies, including interactions between states which induce local perturbation in the spectra, proved essential, in a new analysis of the  $\text{HC}_3\text{N}$  emission in the EMoCA spectrum of Sgr B2(N2) (Belloche et al. 2016), for the explanation of some inconsistencies at 92.1 and 100.4 GHz between synthetic and observed spectra (see Figures 13 and 14 of that article). In fact, an anharmonic resonance couples the  $\nu_5 = \nu_7 = 1$  and  $\nu_7 = 4$  states and, at the crossing of the respective  $0^f$  and  $2^f$  sublevels,  $J = 9, 10$  lines are displaced from their unperturbed positions. Finally, features from within the excited state  $\nu_6 = 1, \nu_7 = 2$  were found to significantly contribute around 101 GHz to the synthetic spectrum which best matches the observed one.

As a further laboratory study, a new global ro-vibrational fit including the far infrared bands from 190 to  $450 \text{ cm}^{-1}$  and the stretching bands in the range  $2000 - 3400 \text{ cm}^{-1}$  is in progress.

## 2.2. Aminoacetonitrile

Aminoacetonitrile ( $\text{NH}_2\text{CH}_2\text{CN}$ ) may form on interstellar ices in the second step of the Strecker synthesis, with methanimine ( $\text{CH}_2\text{NH}$ ) and hydrogencyanide ( $\text{HCN}$ ) as precursors (Danger et al. 2011); the following hydrolysis could lead to the formation of glycine, the smallest amino acid. However, Garrod (2013) studied the formation of glycine using a three-phase chemical model, and he found that  $\text{NH}_2\text{CH}_2\text{CN}$  is mainly formed within and upon the ice mantles by radical-radical addition.

This COM was first detected by Belloche et al. (2008) in Sgr B2(N) and only ground-state features were observed. However, at 100 K there is a significant contribution of the excited states to the partition function, which was estimated to be about 7% by Braakman et al. (2010). This is mainly due to the three lowest energy vibrational modes at  $216\text{ cm}^{-1}$  ( $\nu_{11}$ , C–C $\equiv$ N bend),  $247\text{ cm}^{-1}$  ( $\nu_{18}$ , –NH<sub>2</sub> torsion), and  $370\text{ cm}^{-1}$  ( $\nu_{17}$ , NH<sub>2</sub>–CH<sub>2</sub> torsion). Millimeter- and submillimeter-wave spectra in the three states were then investigated by Degli Esposti et al. (2017) in a joint effort between Bologna and the laboratory of Toho University in Japan. It turned out that  $\nu_{11}$  and  $\nu_{18}$  fundamentals are coupled by a Coriolis interaction, which was accounted for in the analysis of the spectra. Thus, accurate predictions of rotational transitions in the three lowest vibrational states of aminoacetonitrile became available, but they remained undetected in the ISM.

The three vibrational states are expected to be populated in Sgr B2(N1), the main hot core of Sgr B2(N), and their accurate energies are needed to evaluate the vibration-rotation partition function and the line strengths of the pertinent rotational transitions. To recover the energies, the FIR spectrum of aminoacetonitrile was recorded in the range  $100 - 500\text{ cm}^{-1}$  on the AILES 1 beamline of the SOLEIL synchrotron facility and the three fundamentals  $\nu_{11}$ ,  $\nu_{18}$ , and  $\nu_{17}$  were analyzed in Bologna (Melosso et al. 2020). Rotational energy levels with  $J$  up to 80 and  $K_a$  up to 25 were probed, allowing an extensive centrifugal

distortion analysis of the spectra to obtain a reliable set of spectroscopic constants.

The main result expected from the investigation was the determination of the vibrational energies: actually, their values are now known with a relative uncertainty as low as  $2 \times 10^{-8}$ . Then, from the experimental spectroscopic parameters the temperature dependence of the ro-vibrational partition function ( $Q$ ) of aminoacetonitrile was computed (*i*) including only the ground state rotational levels and (*ii*) including all the vibrational states below  $400\text{ cm}^{-1}$ . At 75 K the contribution of the excited states is 2.7%, which increases to 25.7% at 150 K. A further refinement was accomplished by counting the excited states up to  $1600\text{ cm}^{-1}$ , relying on the harmonic approximation or low-resolution data: at 150 K there is an additional increase of  $Q$  by 6.4%.

Finally, rotational transitions from within vibrationally excited states of  $\text{NH}_2\text{CH}_2\text{CN}$  were searched for in the ReMoCA spectrum of Sgr B2(N1S) (Belloche et al. 2019). First, transitions in the ground state with little contamination by emission of other species were identified and, using the new spectroscopic information, a best-fit LTE synthetic spectrum was obtained for  $v = 0$ . Then, a few transitions from within  $\nu_{11} = 1$  and  $\nu_{18} = 1$  were identified, and the detection was confirmed because they were well reproduced by the LTE model with the same set of parameters as the vibrational ground state.

Assuming a temperature of 200 K, the value of the column density of aminoacetonitrile derived from the LTE modeling is  $1.1 \times 10^{17}\text{ cm}^{-2}$ . The chemical model of Garrod (2013) estimates a ratio of  $\sim 1.3 \times 10^{-3}$  between the peak abundance of aminoacetonitrile and that of methanol. Because the column density of methanol is  $2.0 \times 10^{19}\text{ cm}^{-2}$  in Sgr B2(N1S) (Motiyenko et al. 2020), the observational ratio is found to be  $5.5 \times 10^{-3}$ : a result which shows that there is some consistency between model and observations.

### 3. Conclusions

In the survey EMOCA toward Sgr B2 (Belloche et al. 2016), cyanoacetylene could be observed in vibrationally excited states. Then, a more recent spectroscopic study (Bizzocchi et al. 2017) reported an accurate description of the ro-vibrational energies of HC<sub>3</sub>N, including interactions between states which induce local perturbation in the spectra. Relying on the new data, some inconsistencies in the analysis of the EMOCA spectrum were resolved, and new emissions of HC<sub>3</sub>N from within the excited state  $\nu_6 = 1, \nu_7 = 2$  were found to significantly contribute to the synthetic spectrum matching the observed one.

The first interstellar detection of vibrationally excited transitions of aminoacetonitrile was accomplished using the imaging spectral line survey ReMOCA performed with ALMA (Belloche et al. 2019) toward Sgr B2(N1). Identification of the emissions was possible thanks to the reliable spectral predictions of pure rotational lines obtained from laboratory studies (Degli Esposti et al. 2017; Melosso et al. 2020), and thanks to the accurate column densities obtained from the energies of the low-lying vibrational states of NH<sub>2</sub>CH<sub>2</sub>CN investigated in laboratory.

In conclusion, this work shows the interplay between laboratory spectroscopy and observational spectral surveys to detect complex organic molecules in space, with a specific focus on the contribution of the vibrational excitation.

*Acknowledgements.* Helpful discussions with L. Bizzocchi, M. Melosso, and F. Tamassia are gratefully acknowledged. This work has been supported by University of Bologna (RFO funds).

### References

- Belloche, A., Garrod, R. T., Müller, H. S. P., et al. 2019, *Astronomy & Astrophysics*, 628, A10
- Belloche, A., Menten, K., Comito, C., et al. 2008, *Astronomy & Astrophysics*, 492, 769
- Belloche, A., Müller, H. S. P., Garrod, R. T., & Menten, K. M. 2016, *Astronomy & Astrophysics*, 587, A91
- Bizzocchi, L., Tamassia, F., Laas, J., et al. 2017, *The Astrophysical Journal Supplement Series*, 233, 11
- Braakman, R., Belloche, A., Blake, G., & Menten, K. 2010, *The Astrophysical Journal*, 724, 994
- Danger, G., Borget, F., Chomat, M., et al. 2011, *Astronomy & Astrophysics*, 535, A47
- Degli Esposti, C., Dore, L., Melosso, M., et al. 2017, *The Astrophysical Journal Supplement Series*, 230, 26
- Garrod, R. T. 2013, *The Astrophysical Journal*, 765, 60
- Herbst, E. & Van Dishoeck, E. F. 2009, *Annual Review of Astronomy and Astrophysics*, 47, 427
- Jørgensen, J. K., Belloche, A., & Garrod, R. T. 2020, *Annual Review of Astronomy and Astrophysics*, 58, 727
- Melosso, M., Belloche, A., Martin-Drumel, M.-A., et al. 2020, *Astronomy & Astrophysics*, 641, A160
- Motiyenko, R. A., Belloche, A., Garrod, R. T., et al. 2020, *Astronomy & Astrophysics*, 642, A29
- Öberg, K. I. & Bergin, E. A. 2021, *Physics Reports*, 893, 1
- van Dishoeck, E. F. 2017, *Proceedings of the International Astronomical Union*, 13, 3
- van Dishoeck, E. F. & Bergin, E. A. 2020, arXiv preprint arXiv:2012.01472