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Prebiotic molecules in interstellar space: Rotational spectroscopy and quantum chemistry

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Abstract. The starting point for the development of any astrochemical model is the knowledge of whether a molecule is present in the astrophysical environment considered, with the astronomical observations of spectroscopic signatures providing the unequivocal proof of its presence. Among the goals of astrochemistry, the detection of potential prebiotic molecules in the interstellar medium and planetary atmospheres is fundamental in view of possibly understanding the origin of life. The detection of new molecules in space requires the spectroscopic signatures (mostly, rotational transition frequencies) to be accurately determined over a large frequency range. This task is more and more often the result of a synergic interplay of experiment and theory.

Keywords. Astrochemistry, ISM: molecules, molecular data, methods: laboratory

1. Introduction

As proof of a rich chemistry taking place in space, about 200 molecules have been detected in the ISM, mainly via observations of their rotational signatures, which in turn are derived from laboratory experiments effectively supported and possibly extended by quantum-chemical predictions (see, e.g., Herbst & van Dishoeck (2009), Tielens (2013), Gupta *et al.* (2013), Barone *et al.* (2015), and Puzzarini (2017)). Indeed, the astronomical observation of the spectroscopic signatures of a given molecule provides the unequivocal proof of its presence in the astrophysical environments under consideration (see, e.g. Tennyson (2005) and Yamamoto (2017)): rotational signatures can be considered the unique fingerprints of a molecule (see, e.g., Gordy & Cook (1984)). Then, the knowledge of whether a molecule is present in the astronomical environment under consideration and of its abundance is the starting point for the development of astrochemical models.

In the last decade, the formation of astronomical complex organic molecules (COMs), i.e. species showing a certain degree of complexity, has attracted considerable attention due not only to the intrinsic interest in the chemistry occurring in the harsh conditions typical of the interstellar medium (ISM), but also to their potential prebiotic role and thus their connection to the origin of life issue. Understanding how the building blocks of biological molecules were formed in abiotic environments, being either the primitive Earth or the ISM, is indeed an extremely topical issue.

Among the COMs identified in space, those containing the –CN– moiety are considered important prebiotic molecules because they are potential precursors of amino acids, thus playing a role in both theories suggested so far on the emergence of life on Earth (Chyba & Sagan (1992)), namely *exogenous delivery* and *endogenous synthesis*. In the framework of the first theory, prebiotic molecules are postulated to have come from space on comets, asteroids and meteorites. Therefore, the interest is the search of these compounds in

the ISM. According to the endogenous theory, the synthesis of simple organic molecules having a potential relation to the origin of life occurred on our planet, starting from simple inorganic molecules already present. Since Titan, the largest moon of Saturn, has been postulated to be a good model of primitive Earth, the search of prebiotic COMs has also been extended to its atmosphere.

In this contribution, an integrated experimental-theoretical strategy at the basis of the spectroscopic characterization required for guiding astronomical searches of molecular signatures in space will be presented together with its application to a significant case study. Despite the fact that state-of-the-art quantum-chemical computations (which will be discussed in the next section) are able to provide predictions for rotational transitions with an accuracy better than 0.1%, this is not sufficient for guiding astronomical searches and/or assignments, thus requiring experimental determinations of the corresponding spectroscopic parameters. To give an example, the best computed parameters can predict rotational frequencies at 100 GHz and 2 THz with an uncertainty of about 100 MHz and 3–4 GHz, respectively. However, when dealing with broadband unbiased astronomical surveys, transition frequencies require to be known with an accuracy preferably better than 100 kHz, an accuracy that can be easily obtained from experimental studies. Indeed, uncertainties in rotational frequency measurements usually range from 10 kHz to 30 kHz, with the error increasing up to 100-200 kHz only for very weak and not well resolved transitions.

2. Methodology

The integrated experiment-theory approach employed in our laboratory is illustrated in Figure 1: state-of-the-art quantum-chemical calculations are performed in order to obtain accurate predictions of the rotational spectroscopy parameters that are subsequently used to plan the experimental measurements, to support the spectral assignment, and –if the case– to complement experiment with missing information. To exploit this interplay of experiment and theory, we rely on the VMS-ROT software (Licari *et al.* 2017), developed in the framework of the Virtual Multi-frequency Spectrometer project (see Barone 2016). VMS-ROT is composed of four independent modules: (1) the computational one which is in charge of the quantum-chemical calculations of the spectroscopic parameters, (2) the prediction-fitting module, which makes use of Pickett SPFIT/SPCAT program (Pickett 1991) for predicting the rotational spectrum and, once the experimental spectrum is available, for assigning the recorded transitions and thus refine the starting computed constants, (3) the graphical user interface (GUI) module that offers a powerful set of tools for a *vis-á-vis* comparison of experimental and simulated spectra, and (4) the assignment tool for assigning the experimental transitions in terms of quantum numbers upon comparison with the predicted ones. One important feature of VMS-ROT is the possibility of simulating rotational spectra at a given temperature, thus allowing the user to figure out the frequency regions where the most intense lines are expected according to the astrophysical object of interest.

In order to effectively guide and support measurements, accurate predictions of the spectroscopic parameters are mandatory (see, e.g., Puzzarini *et al.* 2010). For this reason, equilibrium geometries, which straightforwardly provide the corresponding equilibrium rotational constants, are obtained by means of composite schemes. These are approaches where the most important contributions for reducing as much as possible the errors associated to quantum-chemical calculations are computed at the highest possible level and then combined together resorting on the additivity approximation (the reader in referred, for example, to Puzzarini *et al.* (2008) and Puzzarini *et al.* (2010) for a detailed account). Then, equilibrium rotational constants are corrected for vibrational contributions evaluated at a lower level of theory (see, e.g., Barone *et al.* 2015). This requires

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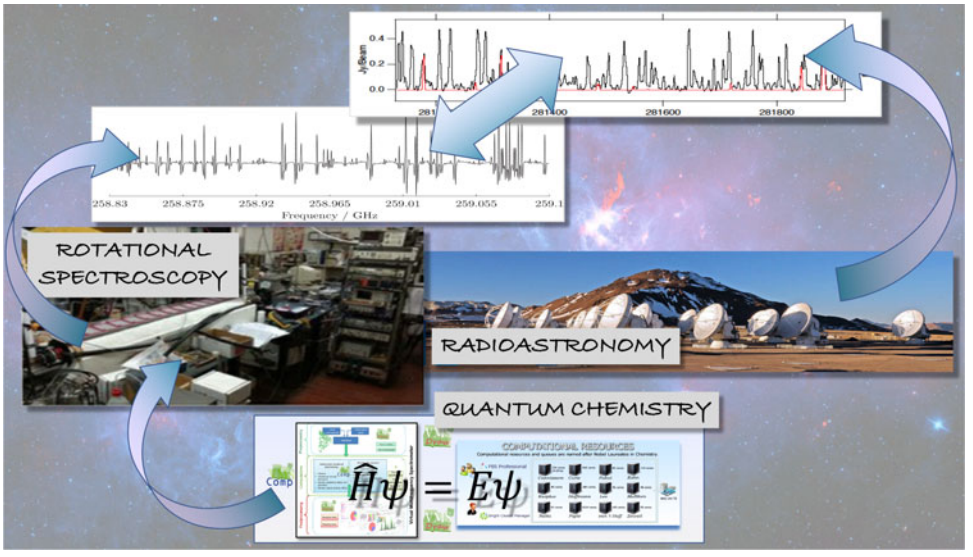

Figure 1. Synergism of laboratory (experimental and computational) spectroscopy and astronomical observations.

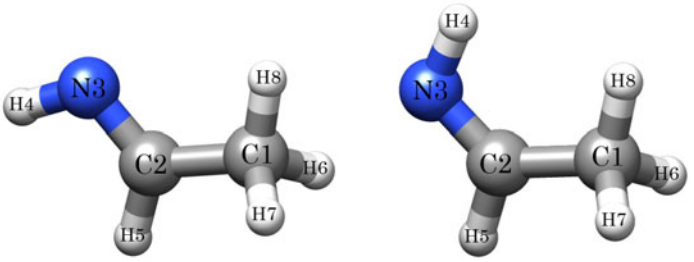

Figure 2. Isomers of ethanimine: the most stable E form is displayed on the left, the Z isomer on the right. They are separated by an energy barrier computed to be 115.7 kJ mol^{-1}.

to perform anharmonic force field calculations, which also provide, as a byproduct, centrifugal distortion parameters (see, e.g. Puzzarini *et al.* 2010).

If the molecular species under investigation has never been studied before (i.e. experimental data are entirely missing), the experimental work is first of all carried out at low frequency, i.e. in the centimeter-wave region, using a Fourier Transform Microwave (FTMW) spectrometer and then the study is extended in the millimeter/submillimeter-wave frequency range (Puzzarini *et al.* 2012; Degli Esposti *et al.* 2017). The final outcome will be the accurate knowledge of the rotational spectrum in all, or most of, working range of the Atacama Large Millimeter/submillimeter Array of radiotelescopes (ALMA).

3. Results: the ethanimine case study

The very first application of the VMS-ROT software, thus exploiting the integrated protocol briefly addressed in the previous section, is ethanimine (CH_3CHNH), which exists in two isomeric forms (see Figure 2). The astrochemical importance of this molecule is related to its prebiotic potential as possible precursor of amino acids by reaction with HCN and H_2O, or with formic acid (see, e.g. Woon 2002; Elsila *et al.* 2007; Loomis *et al.* 2013; Quan *et al.* 2016). Therefore, it provides an important piece of information in the framework of the exogenous delivery theory. Furthermore, based on the computational

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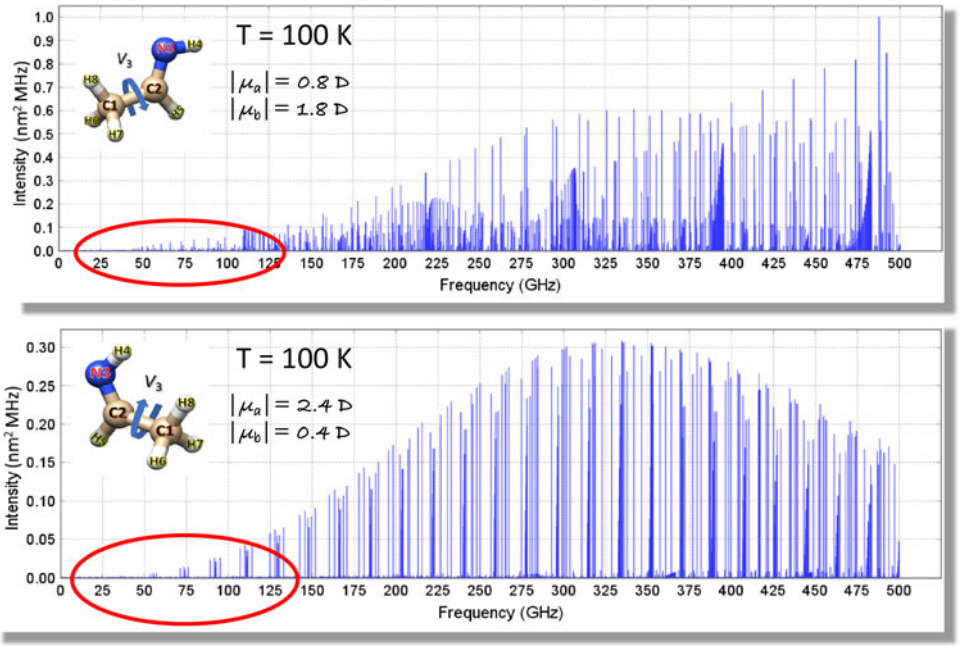

Figure 3. Simulation of the rotational spectra of *E*- (top panel) and *Z*-CH_3CHNH (bottom panel) at T = 100 K obtained with VMS-ROT. The absolute values of the dipole moment components are also reported. The red circles highlight the frequency ranges for which measurements were available prior to the investigation by Melli *et al.* (2018).

work reported by Balucani *et al.* (2010), ethanimine is expected to be formed in Titan's atmosphere from the reaction between ethane, C_2H_6, and excited nitrogen atoms, $N(^2D)$.

Both isomers of ethanimine have been identified in Sagittarius B2 North, SgrB2(N), using the Green Bank Telescope (GBT) (see Loomis *et al.* 2013). However, the previous experimental works on ethanimine rotational spectrum were limited to low frequencies, i.e. below 140 GHz (see Brown *et al.* 1980; Lovas *et al.* 1980; Loomis *et al.* 2013). Since extrapolations from low-frequency laboratory measurements usually provide inaccurate predictions for higher frequencies and, in view of the extended astronomical observatory facilities provided by ALMA (working frequency range: ∼80-950 GHz), the extension of the investigation of the rotational spectra for the isomers of ethanimine is warranted.

To extend the spectroscopic characterization of both isomeric forms of CH_3CHNH, an accurate computational study of the energetics as well as structural and spectroscopic parameters has been first of all performed. A composite scheme that combines coupled-cluster techniques with extrapolation to the complete basis-set limit and consideration of core-correlation contributions has been employed to provide accurate equilibrium parameters (see Heckert *et al.* 2006 and Puzzarini *et al.* 2010). The latter have then been augmented by vibrational corrections evaluated by means of density functional theory (see, e.g., Puzzarini *et al.* 2019). As mentioned above, quantum-chemical calculations have been carried out through the computational module of VMS-ROT. In order to improve the prediction of the rotational spectrum, the computed rotational constants were replaced by those available from Lovas *et al.* (1980). The resulting simulated spectra for the two isomers at 100 K are shown in Figure 3, also highlighting the frequency region covered by previous experimental works. From Figure 3 it is clear that the most intense transitions are expected to lie above 300 GHz.

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Table 1. Computed and experimental rotational parameters (values in MHz) of ethanimine.

	***E*-ethanimine**		***Z*-ethanimine**	
	Theory[a]	**Experiment**[b]	**Theory**[a]	**Experiment**[b]
A_0	53178.26	53120.561(30)	50002.63	49964.87(93)
B_0	9780.14	9782.7720(47)	9831.98	9832.4823(96)
C_0	8702.82	8697.0263(46)	8652.81	8646.0305(94)
Δ_J	6.48×10^{-3}	$6.4641(49)\times10^{-3}$	6.99×10^{-3}	$6.938(13)\times10^{-3}$
Δ_K	0.568	0.5763(34)	0.468	0.468[c]
Δ_{JK}	−0.0165	−0.01403(21)	−0.0163	−0.01219(23)
δ_J	1.09×10^{-3}	$1.1033(19)\times10^{-3}$	1.25×10^{-3}	$1.2657(65)\times10^{-3}$
δ_K	-0.0535	−0.06709(59)	−0.0522	−0.0642(19)
χ_{aa}	1.03	0.62(11)	−3.62	−3.688(13)
χ_{ab}	−0.46	−0.46[c]	1.75	1.75[c]
χ_{bb}	−4.05	−3.78(12)	0.57	0.548(39)
χ_{cc}	3.02	3.16(12)	3.05	3.140(39)
V_3[d]	563.1	566.37(20)	523.3	517.41(33)
Rel. energy[a,d]	0	–	231.5	–

Notes: [a]Equilibrium CCSD(T)/CBS+CV rotational constants and energies augmented by vibrational corrections at the B2PLYP-D3BJ/maug-cc-pVTZ-*d*H level. Quartic centrifugal distortion constants at the CCSD(T)/cc-pCVQZ level. Nuclear quadrupole coupling constants at the CCSD(T)/cc-pCVQZ level augmented by vibrational corrections at the B2PLYP-D3BJ/maug-cc-pVTZ-*d*H level. For details, see Melli *et al.* (2018).
[b]Watson A-reduction. Values in parenthesis denote one standard deviation and apply to the last digits of the constants.
[c]Fixed at the theoretical value.
[d]V_3 values in cm^{-1}.

The predicted rotational transitions (see Figure 3) were subsequently used to guide the experimental work. The rotational spectra of ethanimine, produced by pyrolysis of a commercial sample of isopropylamine ($(CH_3)_2CHNH_2$), have been recorded around 92 GHz and in the 250-302 GHz frequency range using a millimeter/submillimeter-wave frequency-modulation spectrometer, with an estimated accuracy of 40–60 kHz. The presence of a finite V_3 barrier, due to the hindered internal rotation of the methyl group, leads to a splitting of the threefold degeneracy into two levels, a nondegenerate A level and a doubly-degenerate E level, which renders the rotational spectrum rather complicated. The reader is referred to Melli *et al.* (2018) for a detailed account.

The recorded spectra have been analyzed and assigned using the VMS-ROT software, which is able to efficiently treat the A/E splittings observed in the rotational spectra. For the final analysis, all previous measurements have also been incorporated in the fit of the spectroscopic parameters. A selection of them is collected in Table 1, which furthermore points out the accuracy of our initial computed data. Finally, VMS-ROT was used to provide the prediction of the rotational spectrum of both isomeric forms at different temperatures of relevance to astronomical observations. An example is provided by Figure 4, which shows the rotational spectrum of *E*-ethanimine, as predicted by our global fit, at T = 30 K.

To conclude, aiming to provide useful information to guide astronomical searches for ethanimine, an accurate computational spectroscopy characterization has been combined with new measurements of the rotational spectra of both isomers. The VMS-ROT software was demonstrated to be an extremely powerful tool that allows the exploitation of a synergic interplay of experiment and theory in the field of rotational spectroscopy applied to the astronomical search of prebiotic molecules in the ISM, but also in Titan's atmosphere.

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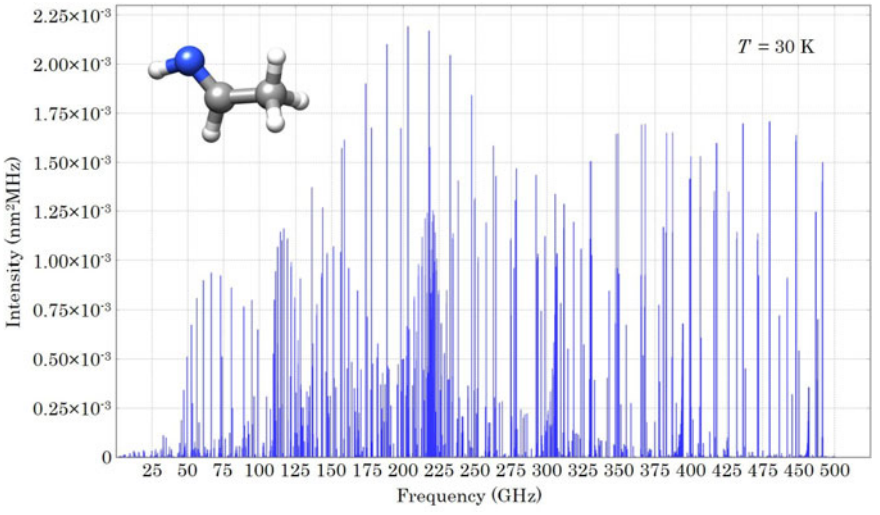

Figure 4. Simulation of the rotational spectrum of *E* ethanimine using experimental rotational parameters augmented for computed high order centrifugal distortion constants at T = 30 K.

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