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Challenges in Astrochemistry:
the spectroscopic point of view.
Comment on “Prebiotic chemistry and origins of life
research with atomistic computer simulations”
by A. Pérez-Villa, F. Pietrucci, and A. M. Saitta

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Heavy atoms (i.e. heavier than hydrogen and helium), dust and molecules can be considered as “cosmic chemical clocks” which mark the stages of life development during the evolution of the Universe. Understanding how atoms and simple molecules assembled into more complex ones, also including prebiotic species and biochemical building blocks, up to the emergence of life in a primitive Earth and whether this might be happened elsewhere in the Universe is one of the greatest challenges in contemporary science. The origin of life can be modeled as a sequence of so-called “emergent” events, each of which added new structure and chemical complexity to the prebiotic Earth. The overarching issue in studying life’s origins is that even the simplest known lifeform is vastly more complex than any non-living components that might have contributed to it. The challenge is to establish a progressive hierarchy of emergent steps that leads from prebiotic molecules to functional clusters of molecules perhaps self-assembled or arrayed on a mineral surface, to self-replicating molecular systems

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15 that copied themselves, to encapsulation, and to eventually cellular life. In
this progressive series of emergent events, the first vital step can be envisaged
in the synthesis and accumulation of abundant carbon-based biomolecules, the
simplest molecular building blocks, including amino acids, sugars, and bases:
anywhere energy and simple carbon-rich molecules are found together, a suite
20 of interesting organic molecules is sure to emerge. Subsequent steps are then
characterized by the assembly of the right combination of small molecules into
much larger collections, “macromolecules” with specific functions.

Saitta and coworkers in their review [1] have pointed out that interpreting
the fundamental prebiotic chemical reactions in terms of thermodynamics and
25 kinetics, with particular focus on reactions in solution, is a crucial step in under-
standing the emergence of life. They have also demonstrated that simulations
are very effective in the determination of free energy landscapes based on reac-
tion coordinates built from the structural topological properties of the reactants
and the products, showing that the most advanced methods in computational
30 physics and chemistry can play a particularly useful role in the modeling and
simulating chemical reactions. However, taking some steps back, the starting
point for the development of any astrochemical model is the knowledge whether
the (prebiotic) molecule of interest is present in the astronomical environment
considered and, if so, its abundance. In this scenario, molecular spectroscopy,
35 and in particular –above all techniques– rotational spectroscopy, plays a crucial
role since the astronomical observation of spectroscopic signatures provides the
unequivocal proof of the presence of the chemical species under investigation
[2]. Focusing on the interstellar medium (ISM), currently, the census of the
interstellar molecular species detected exceeds two hundred [3], and the rate of
40 discovery continues at a rapid pace.

In this comment, we present how rotational spectroscopy can give its con-
tribution to the giant puzzle of the origin of life. To this aim, we rely on an in-
tegrated experimental-theoretical strategy in order to provide the astronomical
community with the spectroscopic characterization required for guiding astro-
45 nomical searches of molecular signatures in space. Despite the fact that state-

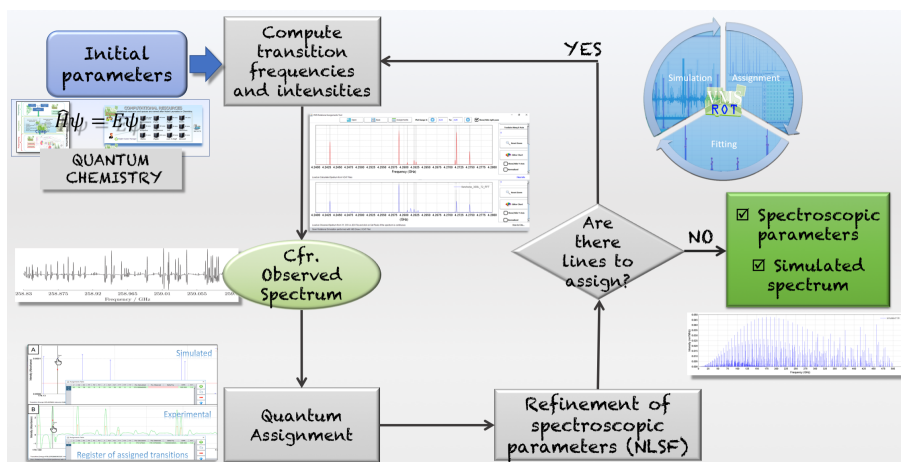


Figure 1: Synergism of laboratory experimental and computational rotational spectroscopy.

of-the-art quantum-chemical computations 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, since uncertainties in rotational frequency measurements usually range from 1 kHz to 30 kHz, with the errors that may increase up to 100-200 kHz only for very weak or non-resolved transitions.

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

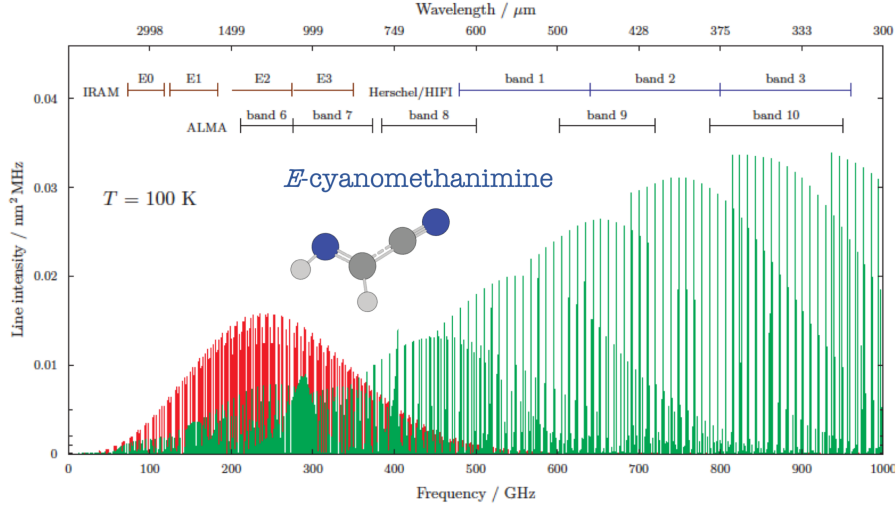


Figure 2: Rotational spectrum of *E*-cyanomethanimine at $T = 100$ K.

rely on the VMS-ROT software [4], developed in the framework of the Virtual
 65 Multi-frequency Spectrometer project (see ref. [5]). 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
 [6] for predicting the rotational spectrum and, once the experimental spectrum
 70 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-à-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
 75 important feature of VMS-ROT is the possibility of simulating rotational spec-
 tra 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.

To effectively guide and support measurements, accurate predictions of the
 80 spectroscopic parameters are mandatory (see, e.g., refs. [7]). For this rea-

son, composite schemes are exploited; 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 [8, 7, 9, 10, 11]. 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 [12]. 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). An example is provided in Figure 2 for the rotational spectrum of *E*-cyanomethanimine at 100 K [13].

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