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Accurate Rotational Spectroscopy for Astrophysical Investigations: the Challenge of Chiral and Flexible Molecules and Molecular Complexes

Summary – In this short review we analyze some results and the challenges related to the analysis of molecular spectra of Complex Organic Molecules (COMs) in the microwave and millimeter frequency range including the detection of their chirality. These analyses are essential for the detection of new molecules of increasing complexity in the huge amount of astronomical data and rich surveys collected by the most recent and advanced radiotelescopes and *in-situ* measurements..

Key words: Molecular Spectroscopy; Rotational Spectroscopy, Complex Organic Molecules; Chirality; Astrochemistry.

The investigation of phenomena related to the chemistry of the Cosmos, in particular regarding the evolution of stars, is strongly based on the identification and quantification of molecules by spectroscopic methods, that is by their emission of light. Spectroscopic lines, in addition to telling us what molecules are present, and their abundance (concentration), are excellent tracers of the physical conditions. For example, temperature (more strictly, rotational temperature) can be measured by comparison of intensities for different rotational lines of the same molecule, gas density can be derived from the collisional excitation of these lines, and radial motion of the cloud; e.g., collapse, can be obtained from the Doppler effect [1]. Already more than 200 molecules have been detected in the gas phase of interstellar clouds

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(see for example refs. [1] and [2]) mainly by their rotational spectra and include cations, anions, radicals, small hydrides, oxides, sulfides and halogens but also larger (up to 10 heavy atoms) neutral molecules; the latter, known as Complex Organic Molecules (COMs). Many more complex organic species are expected to be detected thanks to new telescopes: submillimeter observatories such as the Atacama Large Millimeter Array (ALMA), the Stratospheric Observatory for Infrared Astronomy (SOFIA), and the recent Herschel Space Observatory (HSO) which have been and will be providing observational data with unprecedented spectral sensitivity, signal-to-noise ratio and spatial resolution, thus laboratory work is essential to provide the community with the spectral features needed to analyze the cosmological surveys.

The analysis of high resolution spectra of COMs including chiral ones, is sometimes a formidable task because of their high degree of flexibility. The same flexibility belongs to weakly bound molecular complexes (molecules held together by non-covalent interactions) which have been studied in relation to the determination of collision rates which are of vital importance in reactions schemes [3] and are thought to play a role in the chemistry of dense and molecular clouds and in planetary atmospheres [4]. For all of these systems, the presence of several low energy conformations and the presence of large amplitude motions on shallow potential energy surfaces are typical giving rise to complex rotational spectra, which represent a challenge for spectroscopic and computational methods. Therefore a great effort is needed to provide the astronomers with reliable and accurate data for their search of molecules in space.

Usual experimental and theoretical strategies for recording and analyzing the rotational spectra of flexible organic molecules include the use of the cold and isolated conditions of a free jet expansion and heated sources for the non-volatile systems, coupled to absorption or Fourier Transform spectrometers [5, 6] which show an extremely high accuracy, resolution and sensitivity. The introduction of three wave mixing techniques by Patterson *et al.* [7] has expanded applications of microwave spectroscopy into the field of chiral analysis [8-10].

The experimental work is strongly supported and complemented by theoretical modeling and calculations with the aim of assigning the observed spectra and to obtain information on the molecular dynamics which involve, for example, conformational rearrangements [11], tautomeric equilibria [12], large amplitude motions [13], vibro-rotational coupling [14] and the prediction of vibrational spectra [15], see for example the conformational/tautomeric equilibrium of 2-mercaptopyridine [12], represented in figure 1.

Radioastronomical observations encode a huge amount of information. In order to facilitate their decryption, public, on line databases have been built. For instance several different single dish surveys are available through the Spectral Line Search Engine (SLISE at https://www.cv.nrao.edu/~aremijan/PRIMOS/). Atacama Large Millimeter/submillimeter Array data are available at ALMA archive (http://almascience.eso.org/aq/). The analysis of interferometric data is not straightforward, and the reduction of raw data to final spectra requires specific and advanced knowledges.

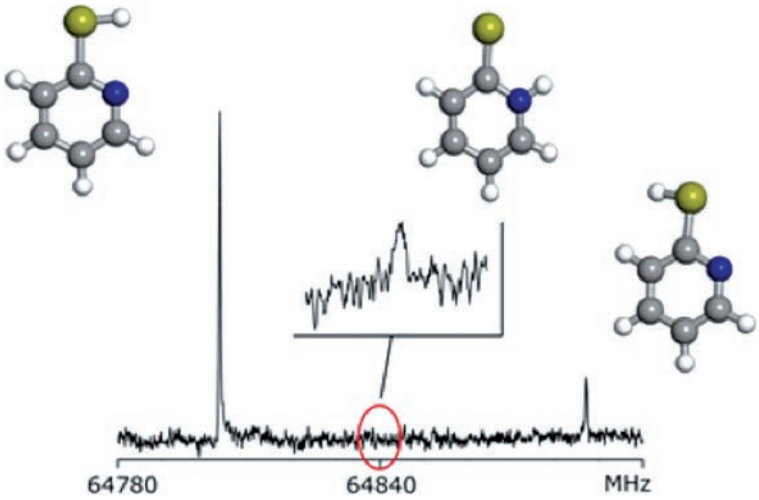

Fig. 1. The precise information on the conformational/tautomeric equilibrium of 2-mercaptopyridine given by millimeter wave free jet absorption spectroscopy.

To overcome this difficulty, a feasibility study to re-image ALMA archival data is currently underway (ALMA Re-I project). ESASky is an open science discovery portal providing full access to the entire sky as observed with Space astronomy missions, as of February 2017 (http://open.esa.int/esasky/), it includes both ESA and international partners data mission.

Once spectral surveys are obtained, the challenge lies in the assignment of the thousands of interstellar molecular lines that are present. This is made easier by the existence of spectral databases for rotational transitions, such as the Splatalogue Database for Astronomical Spectroscopy (http://www.splatalogue.net/), containing the quantal assignments, frequencies, and intensities of both measured and predicted rotational lines for many species.

As an example, we report the analysis of the spectral profile of the Class 0 protostar IRAS 16293-2422 B. The astronomical observations are part of the ALMA project 2012.1.00712.S, aimed to the search of pre-biotic molecules in low-mass protostars. These observations were carried out with 31 antennas of the 12-m main array. They covered four spectral windows: 89.49-89.72, 92.78-93.01, 102.49-102.72 and 103.18-103.41 GHz, each of which with a 0.23 GHz bandwidth and 3840 channels, resulting in a 60 kHz channel spacing corresponding to a velocity resolution of 0.2 km/s. In collaboration with the ALMA Italian Regional Center, we reduced the data according to the standard recipes in the Common Astronomical Software Applications package (v4.2.1) and we extracted the spectrum of the source within one 1”×1” synthesized beam size, centered on the 102.690 GHz peak (RA=16^{h} 32^{m} $22.^{s}612$; Dec=-24°28’32”.588). Then, exploiting the already mentioned Splatalogue data base, we could assign the molecular lines of several species. An excerpt of the

spectra is reported in Figure 2, within the assignment of methylacetylene, ethylene glycol, acetone, glycolaldheyde, ethanol, methylformate. The unassigned lines are indicated with a question mark.

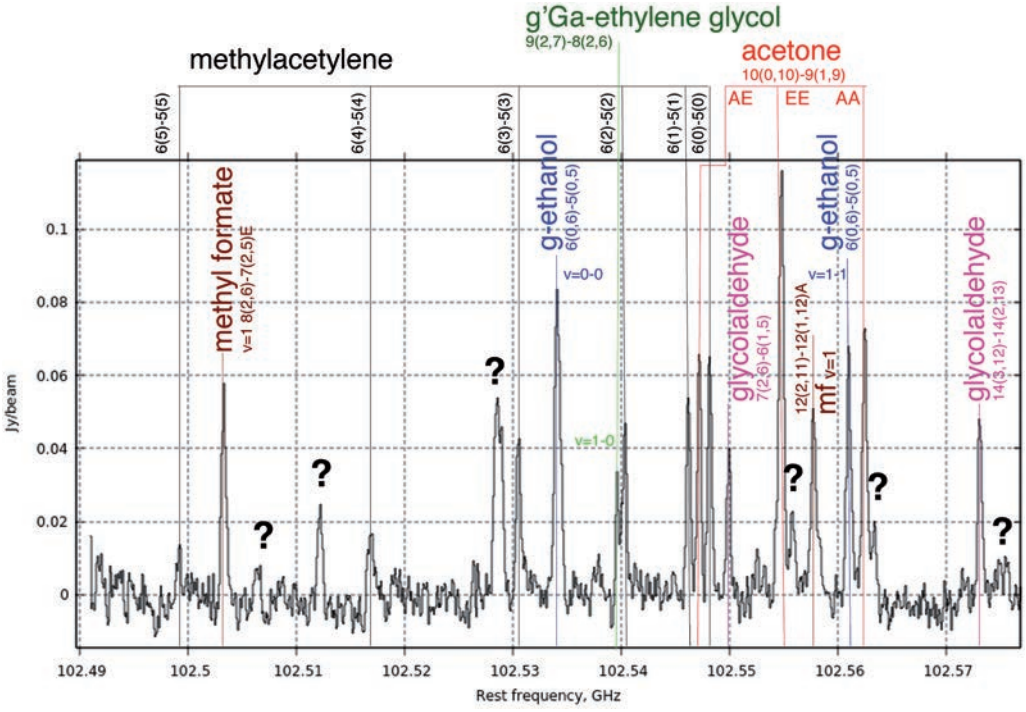

Fig. 2. Line survey and assignment of the protostar IRAS 16293-2422 B (ALMA, band 3).

As regards classical chiral molecules (not taking into account transient chirality, such as in ethyl alcohol or hydrogen peroxide), only propylene oxide has been detected in space [16] but laboratory data exist for many other chiral species such as sugars (see Figure 3) [17, 18] or aminoacids [19].

In 2013, Patterson *et al.* [7] have experimentally demonstrated how to distinguish a pair of enantiomers by microwave spectroscopy using a new three-wave mixing method. The method is based on the fact that for the enantiomers the product of the three electric dipole moments in the principal axis system has opposite sign. Using a special cycle of transitions which needs to have a-, b-, and c-type transitions it is possible to generate a coherent emission signal that is proportional to the product of the three-dipole moment components. The phase of the free induction decay signal is opposite (in the time domain) for different enantiomers. To observe the signal an additional requirement is that the electric fields of the three waves have to be mutually orthogonal. As a result, the signal amplitude is also proportional to the enantiomeric excess.

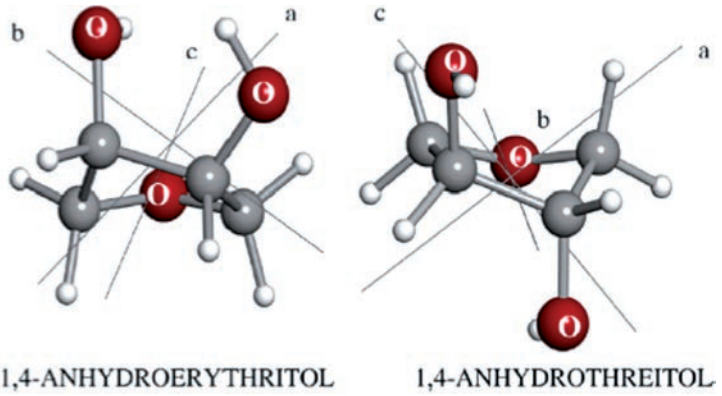

Fig. 3. Sketch of the two most stable conformers of the two isomeric anhydrosugars 1,4-anhydroerythritol and 1,4-anhydrothreitol (AT) and of their principal axes systems (from ref 17b).

Despite several challenges for which the research is still ongoing (such as phase calibration, phase-matching or off-resonant excitation) which has recently been well presented elsewhere [20] and go beyond the aims of this report, it is interesting to highlight a new project for the construction of the first millimeter-wave chirality spectrometer [21, 22]. The success of this project will advance the technologies for the chiral detection and can be applicable to space mission in areas such as Enceladus, Europa, Titan, and Mars. Organic molecules on the planets can be in-situ characterized. This could be the first step for the search of life.

In conclusion, we have discussed how the data obtained from laboratory spectroscopy in the microwave and millimeter wave range are essential for the analysis of the huge amount of data collected and the extremely rich surveys performed by telescopes and especially by the Atacama Large Millimeter Array (ALMA). One of the objectives is the detection of new molecules of increasing complexity and possibly the measurement of their chirality with *in-situ* techniques. All of this represent a challenge from the spectroscopic point of view and for this reason a strong interplay between the laboratory spectroscopists and observational astronomers is required.

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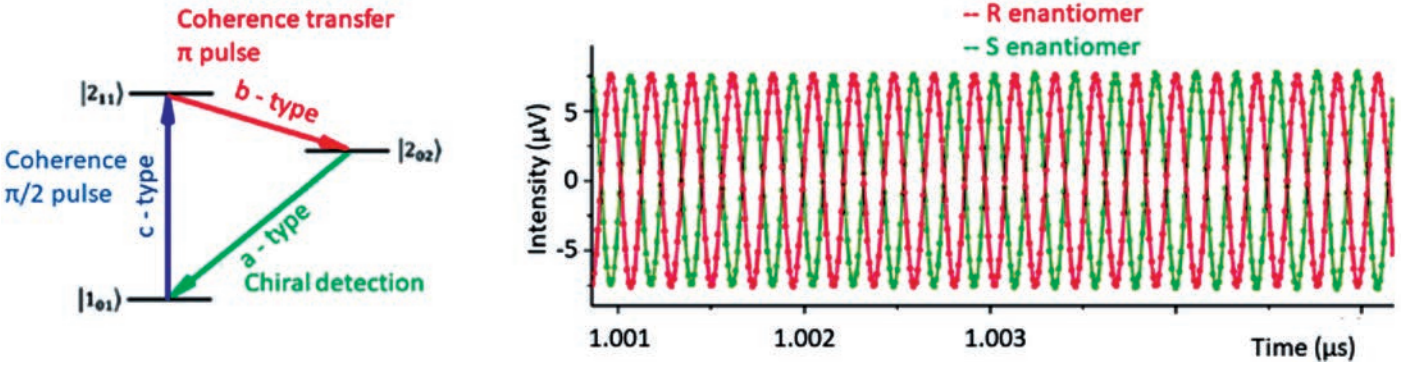

Fig. 4. On the left, the three-wave mixing scheme is shown. The two excitation pulse are applied and the chiral signal (FID) can be measured. On the right it is shown a small interval of the filtered chiral signal obtained using the three-wave mixing experiment. The two enantiomers have opposite phase.

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