Spectroscopy of new Imine astrophysics target: Methylimino-acetonitrile (CH_3N=CHCN)

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There are to date about 200 molecules that have been detected in the interstellar medium or circumstellar shells. Among these molecules, several tens are the methylated derivatives of compounds previously detected.

For several years, we have been studying molecules belonging to the imine family. Following the detection of the dimer of HCN, the cynaoethanimine, its methylated derivative appears as a privileged fiber. This molecule is methylimino-acetonitrile: CH_3N=CHCN. There are two isomers E and Z, the most stable isomer is the E whose energy is 124.4 cm^{-1}) (1.49 kJ/mol) lower than that of Z. There was no spectrosocpic data allowing detection without ambiguity of this molecules in the interstellar medium. We recorded and analyzed spectra up to 660 GHz.

This compound is not stable in laboratory conditions, it was produced in-situ by pyrolisis and introduced in a 1m long pyrex cell in a flow mode.

With regard to the E isomer, this is also an interesting case on spectroscopic point of view. Even if the internal rotation barrier is quite high 714 $cmcm^{-1}$, some A-E doublets due to the methyl top internal torsion were observed. This is due to quite high ρ value: 0.274, just slightly smaller than the acetaldehyde value of 0.329.

The analysis is performed using the RAM36 code (Ilyushin, V.V. et al; J. Mol. Spectrosc., 259, 26, 2010). The spectroscopic results will be presented.

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Imidazole rotation spectrum investigation for astrophysical search

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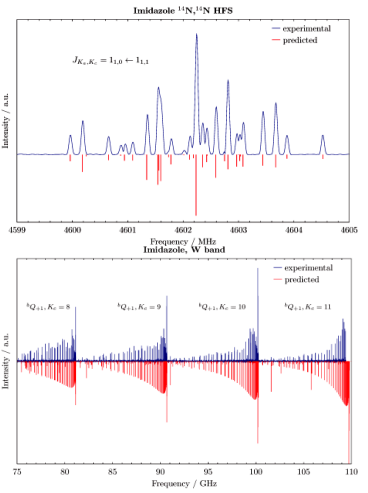
Many of the around 200 known interstellar molecules have been proposed as precursors in various synthetic networks which would yield higher organics in primordial environments (e.g. Strecker synthesis and Michael addition [1]).
Besides simple and ubiquitous interstellar species (e.g., H_2O, NH_3, HCN, H_2CO, etc.), more complex compounds may have been crucial in building up the molecular complexity on early-stage planetary bodies.
In particular, organic ring compounds play a key role in terrestrial biochemistry and, most likely, they were also pivotal ingredients in Earth\'s prebiotic chemistry.
Apart from the noteworthy large fullerenic structures, relatively few organic ring molecules have been unambiguously detected in the interstellar medium.
Among those detected are c-C_3H_2 (cyclopropenylidene), c-C_2H_4O (ethylene oxide), benzene (c-C_6H_6), and cyanobenzene (c-C_6H_5-CN).
The recent tentative detection of 2H-azirine (c-C_2H_3N) and aziridine (c-C_2H_5N) have also been reported [2,3].
Larger N-bearing heterocycles, such as purines, pyrimidines and quinoline structures, have been identified in meteoritic organic matter (e.g. [4]).
The five-membered ring imidazole c-$C_3N_2H_4$ is a substructure of fundamental biological molecules such as purines and the amino acid histidine.
This species has been suggested as a possible candidate for detection in the interstellar medium due to its large dipole moment (μ_a ~ 3.7D) and for its favourable partition function (no spin statistics).
An unsuccessful search in a sample of cold core clouds and massive star forming regions was performed almost 40 years ago [5].
During the last few decades, the performances of the millimeter telescopes have witnessed an impressive improvement in terms of sensitivity, spectral coverage, and resolution, considerably increasing the chance of new molecular detections.
Unfortunately, the only rotational studies of imidazole present in literature are limited to the cm-wave region [6,7], and the precision of the rest frequencies in the millimetre regime (the wavelength range best exploited by a state-or-the-art observing facility like ALMA) is not adequate.
Here we present a comprehensive investigation of the rotational spectrum of imidazole from 2 to 295 GHz. The 2-8 and 75-110 GHz frequency regions, were covered using the laboratory facility developed in the Schnell group at DESY (Hamburg). The spectrum in the 260-295 GHz region was taken in Pate's laboratory at the University of Virginia (Charlottesville).



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Laboratory rotational spectroscopy of isotopic species of Methyl Mercaptan, $CH_3{}^{34}SH$ and CH_3SD, and search for them in ISM

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Methyl mercaptan (also known as Methanethiol), CH3SH, has been found in the warm and dense parts of high as well as low mass star-forming regions.[1,2] Laboratory spectroscopy of its ^{34}S and D isotopologues and detecting them will enable astrophysicists to determine the $^{32}S/^{34}S$ as well as the respective H/D abundance ratios and relate those to the observed astrophysical environment. The molecule is also of fundamental interest because of the large amplitude internal rotation of the CH_3 group against its framework SH. The ^{34}S isotopic species of CH_3SH has been measured in natural abundance in the frequency ranges of 49–510 GHz and 1.1–1.5 THz.[3] The spectrum of CH_3SD has been recorded in the range 150–510 GHz. The analysis of the spectra has been performed up to the second excited torsional state. For the ^{34}S isotopologue extensive assignments of $\Delta K = 0$ transitions in $v_t = 0$ to 2 have been done. Numerous assignments of $\Delta K = \pm 1$ transitions have been made in $v_t = 0$ and to a lesser extent in the two higher torsional states. The results of modeling these data with the RAM36 program and of searches for these isotopologues in our ALMA data of the 3 mm wavelength range will be presented.

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Accurate millimetre and submillimetre rest frequencies for cis- and trans-dithioformic acid, HCSSH

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To better understand the sulphur chemistry of the Interstellar Medium (ISM), new S-bearing molecules must be studied in the laboratory, obtaining accurate rest frequencies for an astronomical search. Recently, many new S-bearing compounds have been detected for the first time in the ISM and chemical models have been improved through inclusion of these and other species, too. Notwithstanding this progress, some molecules are still not considered in the current picture of sulphur chemistry. We focus on the two isomers of dithioformic acid, trans- and cis-HCSSH, which is the sulphur analogue of formic acid.

We studied the species in the laboratory using the frequency modulation sub-millimetre absorption spectrometer at the Center for Astrochemical Studies (CAS) in Garching. The molecules were produced directly within a free-space cell by glow discharge of a gas mixture. We measured lines belonging to the electronic ground state up to 478 GHz, leading to a comprehensive centrifugal distortion analysis. Hence, the new dataset provided by this study can be used for astronomical search. In particular trans-HCSSH, the lowest-energy conformer, is the best candidate for a potential detection.

The nanocosmos gas Cell: A broadband Fourier transform millimeterwave spectrometer based on radio astronomy receivers

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A Gas Cell reactor for the study of the chemical composition and evolution in different astronomical environments has been built as a part of the NANOCOSMOS project. It employs the same detection system as those present in radio-telescopes, constituting a novel and state-of-the-art approach to do rotational spectroscopy with kHz resolution. In particular, it has been implemented with Q-band (31.5-50 GHz) and W-band (72-116 GHz) receivers analogous to those built for the 40 meters telescope of Yebes Observatory (CNTRAG-IGN, Spain). These receivers are sensitive to the rotational emission of the molecules present in a one meter Gas Cell (no external polarization needed). The technique provides large instantaneous bandwidth, spectral purity, and a linear dependence of the signals with the partial pressure. Some pictures of the instrument are presented in Figure 1. The full description of the previous prototype cell can be found in *I. Tanarro, et al. A&A 2018.* In the initial experiments of the Gas Cell as a rotational spectrometer, we recorded the spectrum of CH_3CN in the Q and W-bands. After an integration time of 11 minutes, we could observe its vibrational excited states up to ~1000 cm^{-1} and its isotopologues in natural abundance, including ^{15}N with a spectral resolution of ~38 kHz and an estimated detection limit of 10^{-6} mbar.

The Gas Cell is also equipped with a quadrupole mass spectrometer, a UV-Visible spectrometer, a cold plasma generator (inductively coupled RF discharge) and UV-lamps. All these components make of the Gas Cell a versatile instrument that allows a full characterization of gas mixtures directly introduced in the chamber and also of the reaction products formed in cold plasmas or by UV radiation of the mixtures. In the present communication, we report the results of our investigation about the UV and plasma effects on several gas mixtures that mimic different scenarios such as the interstellar medium, the stratosphere of Titan (CH_4, N_2), or the prebiotic terrestrial atmosphere (CH_4, NH_3, H_2O).

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Figure 1: Pictures of Nanocosmos Gas Cell