

High-resolution rotational spectroscopy of 3-Methylbutyronitrile – a molecule of astrophysical interest

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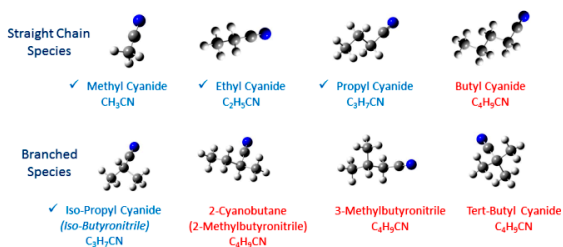
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We present high-resolution rotational spectra of the two conformers of 3-methylbutyronitrile (C_4H_9CN), i.e., the gauche and anti-conformer.

The molecule is one of the structural isomers of butyl cyanide (C_4H_9CN). Smaller straight-chain species, such as methyl cyanide, ethyl cyanide and propyl cyanide, as well as the branched-chain species iso-propyl cyanide, have already been identified in space successfully. However, despite the fact that laboratory spectra of the straight-chain n-butyl cyanide conformers have been analysed, the molecule has not been detected in space up to now (Ordu et al. 2012). More recent simulations predict the abundance of n-butyl cyanide just short of the detection limit of previous ALMA observations. The abundances of 3-methylbutyronitrile (and 2-cyanobutane, another structural isomer) discussed here are predicted to be higher than the abundance of n-butyl cyanide (Garrod et al. 2017).

Here, we present spectra between 2 and 24 GHz that were obtained by means of Fourier transform microwave spectroscopy. Spectra between 36 and 403 GHz were recorded by means of frequency modulated (FM) absorption spectroscopy. The analysis yields precise rotational constants and higher order distortion constants, as well as a set of ^{14}N nuclear electric quadrupole coupling parameters for each of the two conformers. In addition, quantum chemical calculations were performed in order to assist the assignments. Frequency calculations yield insight into the vibrational energy structure, from which partition functions and vibrational correction factors are determined. These factors are used to determine experimentally and computationally the energy difference between the two conformers, which is revealed to be negligible.

Overall, this study provides precise spectroscopic constants for the search of 3-methylbutyronitrile in the interstellar medium. In particular, this molecule is a perfect test case for our knowledge of branched molecule formation in space.



In blue: Molecules which were identified in space. Most molecules are straight-chain species, besides iso-propyl cyanide. In red: Molecules which are currently searched for in ALMA spectra.

Garrod, R.T., Belloche, A., Müller, H.S.P., and Menten, K.M., Exploring molecular complexity with ALMA (EMoCA): Simulations of branched carbon-chain chemistry in Sgr B2(N), A&A 601 (2017)

Ordu, M.H., Müller, H.S.P., Walters, A., Nunez, M., Lewen, F., Belloche, A., Menten, K.-M., and Schlemmer, S., The quest for complex molecules in space: laboratory spectroscopy of n-butyl cyanide, n-C₄H₉CN, in the millimeter wave region and its astronomical search in Sagittarius B2(N), A&A 541 (2012)

Solving discrepancies between theory and experiment: Methyl Jasmonate and Zingerone

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Modern structural studies of biologically relevant molecules require an exhaustive interplay between experiment and theory. In this work, we will present two examples where a poor choice of the theoretical method led to a misinterpretation of experimental results. We do that by performing a rotational spectroscopy study on two flexible and moderate-large sized biomolecules: Methyl jasmonate and Zingerone. The spectra for those two molecules were recorded in the 6–18 GHz frequency region was collected in the CP-FTMW spectrometer available at the University of the Basque Country (UPV/EHU).[1] The internal rotation splitting due to the potential barrier were analyzed and fit using the XIAM code[2] and the BELGI-C₁[3]. Two conformers were observed for methyl-jasmonate and one conformer for zingerone. Clearly, not every theoretical method is able to predict correctly the conformers observed. Only methods taking into account the dispersion effects and the balance between weak hydrogen bonds can achieve that goal. The results shown in this work prove thus the key role of rotational spectroscopy as a benchmark to evaluate the performance of theoretical methods.

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Polyalcohols as artificial sweeteners: signs of a sweetness–structure connection

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Since early last century, abundant research has addressed the link between sweetness and the structure of sweeteners. None of these theories has been able to offer a unified explanation regarding the sweetness–structure relation until Shallenberger and Acree's proposal.^{1,2} They observed that the sweetness depends on the strength of two H-bonds by which the sweetener is bound to the sweet receptor. They established that one of the two electronegative atoms might act as a proton donor (AH) in the hydrogen bond interaction and the other as acceptor (B). These two groups form what is called the *glucophore*, which refers to the part of the sweetener that interacts with the sweet receptor. Microwave spectroscopy studies of some molecules belonging to the polyalcohol family (sorbitol, dulcitol, mannitol, erythritol, etc.) have been carried out by means of broadband microwave spectroscopy techniques³ in combination with a laser ablation technique for vaporize the sample.⁴ The structural characterization in isolation conditions of these molecules gives us valuable information to contrast with the postulated theories about the sweet taste, deepening in the origin of the sweet properties of these molecules.

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Microwave spectroscopic and quantum chemical investigations on 2-Acetylthiophene

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The torsional barrier of the acetyl methyl group strongly depends on the substituent attached to the other side of the carbonyl group, especially if double bonds or π conjugated systems are present. Although several molecules of this type have been investigated, no apparent trends for the torsional barrier of the acetyl methyl group have been found. In allyl acetone the barrier height is 224.95(120) cm^{-1} [1], while completely different values were found for *syn*- and *anti*-methyl vinyl ketone (376.6(2) cm^{-1} and 433.8(1) cm^{-1}) [2] or the *cis* and *trans* conformers of 2-acetyl-5-methylfuran (212.71(30) cm^{-1} and 307.78(59) cm^{-1}) [3]. In this work the influence of thiophene, a sulfur-containing five membered aromatic ring, on the internal rotation barrier will be presented.

The microwave spectrum of 2acetylthiophene was recorded using a pulsed molecular jet Fourier transform microwave spectrometer operating in the frequency range from 2 to 26.5 GHz. The assignment of the transitions is currently in progress. Conformational analysis was carried out at the MP2/6-311++G(d,p) level of theory and yielded two stable conformers (*cis* and *trans*), whereby *cis*-2acetylthiophene is the energetically more stable conformer. The calculated torsional barrier at different levels of theory varies from 191 to 318 cm^{-1} and 160 to 284 cm^{-1} for the *cis* and the *trans* conformer, respectively. Coupled with the internal rotation, an oscillation of the acetyl group occurs with an amplitude of 5° for the *cis* and 10° for the *trans* conformer.

Calculations on several derivatives were also performed to compare the results of 2-acetylthiophene. We found that like 2-acetylthiophene all derivatives have two stable conformers. The comparison with 2-acetyl-furan and 2-acetylpyrrole has shown, that the relative stability of the *cis* or *trans* conformer depends on the hetero atom in the ring. Further comparisons with the aldehyde derivatives 3-methyl-2-thiophenecarboxaldehyde, 3-methyl-2-furaldehyde and 3-methylpyrrole-2-carboxaldehyde have been drawn.

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Structure and rotational spectral features of *N*-Butyraldehyde oxime: a study using MB-FTMW

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n-Butyraldehyde oxime ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{NOH}$) has two geometrical forms with respect to the C=N bond, (*E*)- and (*Z*)-isomers. Values of C-C=N-O dihedral angle are 180 and 0 degree for (*E*)- and (*Z*)-isomers, respectively. Furthermore, this molecule has the possibility to exist in various rotational conformations in the gas phase, because of having a long flexible carbon chain with three C-C single bonds.

We have been observed the microwave spectra of *n*-butyraldehyde oxime from 26–40 GHz. Four rotational conformers were found to exist in the gas phase by Stark-modulated microwave spectroscopy (Stark-MW). They are the E_a and E_b conformers of (*E*)-isomers; the Z_a , and Z_b conformers of (*E*)-isomers. Rotational constants were determined for E_a , Z_a , and Z_b conformers. However, the data fitting was not succeeded for the E_b conformer due to the lack of experimental spectral lines.

Molecular structure and conformations of the (*Z*)-isomer of *n*-butyraldehyde oxime by gas-phase electron diffraction (GED). We have the results of the two types of data analysis. One is the GED+MW joint analysis, a combination of the GED data and two sets of rotational constants for the Z_a , and Z_b conformer. Another is the GED data analysis in the 2D large-amplitude motions for C-C the bonds.

In this work, we observed the rotational spectrum *n*-butyraldehyde oxime by molecular-beam Fourier transform microwave spectrometer. Our interests are: 1) determination of the rotational constants by high-resolution spectrum; 2) hyperfine splittings due to the ^{14}N atom; 3) search for the fourth conformer, the E_b conformer; 4) spectral assignments of the isotopomers; and 5) splitting lines due to the large-amplitude vibrational motion of the molecule. In the lower spectral range, 5–24 GHz, we could easily observe the spectral lines for the E_a , Z_a , and Z_b conformers which were resolved to three components in each a-type R-branch transition. Now we are focusing our third agenda, identification of the fourth conformer.