

Intentional Seminars on Molecular Spectroscopy

Program

June 22–26, 2020

Foreword

We, the organizers, would like to thank you for participating in the inaugural Not Intentional Seminars on Molecular Spectroscopy hosted on Zoom. This seminar series seeks to fill the void left by what would have been the 75th ISMS, where large scale celebrations were expected to be held where the “Firehaus” once stood.

The molecules shown in the logo are believed to represent the frontier of molecular spectroscopy; the very essence of this meeting: 2,000 quanta of the bending mode in acetylene forces the molecule to adopt the familiar “N” geometry. Similarly, ammonia experiencing mild perturbations along the asymmetric stretching coordinate yields “T”. There is nothing special about benzene. We hope that the quality of science that will be presented over this conference will embody the spirit and tenacity of these highly excited, unrealistically meta-stable states.

We look forward to the enlightening discussions and cutting edge research that will be presented over the next few days.

Sincerely yours,
The Executive, Scientific, and Disciplinary Committee

Stephen Kocheril (Brown University)
Kelvin Lee (Center for Astrophysics | Harvard & Smithsonian)
Marie-Aline Martin-Drumel (University of Paris-Saclay/CNRS)

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Session 1: Monday, June 22 4 PM UTC

22 Jun
4:00 PM UTC

Aromaticity in metallaborocycles

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Metallabenzes are a class of molecules in which a CH unit in benzene is replaced by a functionalized transition metal atom. While, all-boron-analogues of aromatic and antiaromatic hydrocarbons are well-known, there have not been any metallaboron analogues. We have produced and investigated a series of metallaboron analogues using high-resolution photoelectron imaging and quantum chemical calculations. Vibrationally resolved photoelectron spectra have been obtained and compared with theoretical results, determining their structures. Through chemical bonding analyses, we have identified unique aromatic characters in these metallaboron clusters.

22 Jun
4:17 PM UTC

Microwave spectroscopy study supported by quantum chemistry
calculations of Limonaketone, a key oxidation product of limonene

Noureddin Osseiran^a,
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22 Jun
4:34 PM UTC

Laboratory gas-phase vibrational spectra of $[\text{C}_3\text{H}_3]^+$ isomers and isotopologues by IRPD spectroscopy

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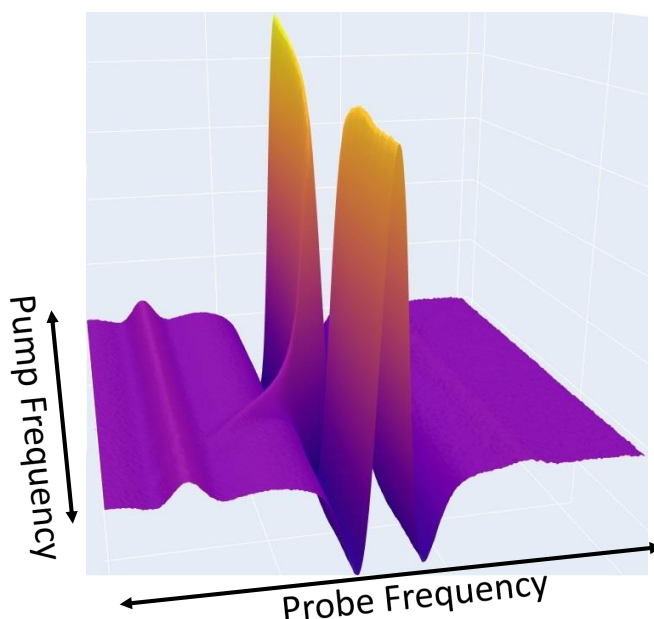
Millimeter- to millimeter-wave double resonance spectroscopy

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Complex organic molecules show regularly rich spectra, sometimes close to the confusion limit. The plethora of lines often originate from the presence of different conformers or low-lying vibrational states. The analyzes of spectra are considerably further complicated by vibration-rotation or other interactions. However, accurate spectroscopic predictions in the millimeter-wave region are essential for identifying molecules in space. The double resonance technique can help to solve these challenges.

We present first millimeter- to millimeter-wave double resonance (DR) spectra to unambiguously assign new lines of propanal. As already shown in chirped pulse Fourier transform microwave (CP-FTMW) experiments [1], the Autler-Townes splitting allows for distinguishing between regressive or progressive energy level schemes. The Autler-Townes splitting is clearly visible in our 2D spectra, see figure. Furthermore, implementation of a double modulation technique (pulse modulation of pump and frequency modulation of probe source) allows for confusion- and baseline-free spectra containing only the line(s) of interest. We discuss details of the observed Autler-Townes splitting and possible future applications, such as automation and incarnations of DR spectroscopy in chirped pulse experiments.



[1] Schmitz et al., *J. Phys. Chem. Lett.* **6** (2015) 1493-1498.

Session 2: Tuesday, June 23 4 PM UTC

23 Jun
4:00 PM UTC

A new experiment for the study and control of chiral molecules using high resolution electronic and microwave spectroscopy

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Chiral molecules are important in nature and exist in one of two mirror-image versions (enantiomers) that cannot be transformed into each other by mere rotation or translation. Opposite enantiomers can have very different effects when interacting with other chiral species, leading, for example, to differences in sensory perception or—in the case of pharmaceuticals—desirable or detrimental outcomes. Nonetheless, most physical properties of enantiomers are identical. This makes chiral analysis challenging.

Recently, a method that can selectively populate or depopulate a rotational level of an enantiomer was developed. The enantiomer-specific state transfer method [1] builds on microwave three-wave mixing [2], a previously established method that uses microwave spectroscopy to distinguish between enantiomers. Our group has designed, built, and characterized a compact spectrometer capable of performing chirped-pulse Fourier transform microwave and electronic spectroscopy. By combining laser-induced fluorescence with microwave spectroscopy, we seek to maximize the state-specific enantiomeric enrichment. Recent experimental results and details on the new spectrometer will be discussed.

[1] Eibenberger, S. et al. *Phys. Rev. Lett.* 2017, 118, 123002

[2] Patterson, D. et al. *Nature* 2013, 497, 475-477

The pure rotational spectrum of the hydroxymethyl radical reinvestigated to enable its interstellar detection

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The hydroxymethyl (CH_2OH) and methoxy (CH_3O) radicals, products of CH_3OH photodissociation, are considered key reactive intermediates in the interstellar medium (ISM), and their recombination with other fragments is postulated to lead to the formation of commonly observed complex organic molecules (COMs) as glycolaldehyde, ethanol, ethylene glycol, and dimethyl ether. Determination of the $\text{CH}_3\text{O}/\text{CH}_2\text{OH}$ ratio should enable to differentiate between gas and grain surface formation scenario for the radicals and therefore for the COMs that form from them. Interestingly, despite the recent first laboratory detection of CH_2OH pure rotational spectrum and while this isomer is the most thermodynamically stable, only CH_3O has so far been detected in the ISM. A plausible explanation to this lack of interstellar detection is the non-observation in the laboratory of the most intense transitions at low temperature.

We have re-investigated the pure rotational spectrum of CH_2OH at room temperature in the millimeter-wave domain, using a frequency multiplication chain spectrometer, with emphasized searches for the fundamental b -type transitions and those intense at low temperature. The radical was produced by H abstraction from CH_3OH using F atoms produced by a microwave discharge. A combined fit of the infrared and millimeter-wave lines from the literature and our new measurements using a rigid-rotor Hamiltonian yielded a large improvement in the spectroscopic parameters values allowing now confident searches of CH_2OH in cold interstellar environments.

Spectroscopic Characterization of Intermediates in the Abiotic Formation of Biomolecules

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Simple biorelevant molecules like the simplest sugar glycolaldehyde and the simplest amino acid glycine have been detected in interstellar media or in the coma of comets. The route of formation of these key species is still a riddle today. Carbenes are powerful reagents in organic chemistry and some of them have shown to exist in interstellar media. The spectroscopic characterization of simple carbenes in their possible role in the formation of carbohydrates and amino acids will be discussed. [1, 2]



[1] A. K. Eckhardt, P. R. Schreiner, *Angew. Chem. Int. Ed.* 2018, 57, 5248-5252.

[2] A. K. Eckhardt, M. M. Linden, R. C. Wende, B. Bernhardt, P. R. Schreiner, *Nat. Chem.* 2018, 10, 1141-1147.

23 Jun
4:51 PM UTC

Optical pumping and rovibrational energy transfer in the C₆₀ fullerene

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Session 3: Tuesday, June 23

10 PM UTC

23 Jun
11:00 PM UTC

The Chemical Pathways of O(¹D) Insertion into Methylamine (CH₃NH₂)

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O(¹D) is well known to undergo insertion reactions primarily between C-H bonds and, under certain circumstances, can be used as a tool for the formation of unstable alcohol species for collection of their rotational spectrum [1]. Aminomethanol, predicted to form via insertion into methylamine [2,3], is an important prebiotic precursor to the amino acid glycine but due to its instability under terrestrial conditions it still evades spectral detection. Here we present the efforts towards disentangling the complex chemistry resulting from the reaction of O(¹D) with methylamine, where the high exothermicity results in a complex mixture of primary, secondary, and tertiary reaction products, complicating spectral assignment. Molecular signals due to both known and assigned molecules are observed along with signals that are unassignable with reference to the Splatalogue database. Could these unknown molecular signals be due to aminomethanol?

[1] B. M. Hays, N. Wehres, B. Alligood DePrince, A. A.M. Roy, J. C. Laas, S. L. Widicus Weaver, *Chem. Phys. Lett.*, 630, 18 (2015)

[2] B. M. Hays, S. L. Widicus Weaver, *J. Phys. Chem. A*, 117, 32, 7142–7148 (2013)

[3] M. E. Wolf, P. R. Hoobler, J. M. Turney, H. F. Schaefer III, *Phys. Chem. Chem. Phys.*, 2019,21, 24194–24205

23 Jun
11:17 PM UTC

Rotational Spectroscopy of 2-cyano-1,3-butadiene: a Molecule of Astrochemical Relevance

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23 Jun
11:34 PM UTC

Re-Examination of the Rotational Spectrum of Methyl tert-Butyl Ether

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Methyl tert-butyl ether is a gasoline additive and a water pollutant. Its rotational spectrum was measured from 26.5–40 GHz using Chirped-Pulse Fourier Transform Microwave Spectroscopy. Measurements were conducted at low temperature via supersonic expansion and room temperature via static cell. The molecule was previously reported in Ref. [1] in a range of 9–18.6 GHz. This work expands that fit and converts it to the Rho Axis Method utilizing the program RAM36. The improved ground torsional state measurements as well as the room temperature data allowed for tentative assignments of torsionally excited transitions.

[1] Suenram et. al 1997

Spectroscopic investigation of the phenalenyl radical

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The phenalenyl radical is a polycyclic aromatic hydrocarbon (PAH) open-shell radical containing three six-membered rings fused together by a central carbon atom. It contains an uneven number of carbon atoms and electrons, resulting in a neutral radical. Phenalenyl and similar 'open-shell graphene fragments' have been recently garnering interest due to their intriguing electronic structure and, consequentially, a possible application in quantum molecular and spin electronics. [1–3] As a resonance-stabilised hydrocarbon radical, phenalenyl may also be present as a reaction intermediate in combustion, the atmosphere and interstellar space. [4] Previously, the first electronic excited state of the phenalenyl radical has been recorded which uncovered a complex vibronic spectrum including pseudo-Jahn-Teller and Herzberg-Teller coupling effects with a higher excited state. [5] In this work, the higher excited electronic states of jet-cooled phenalenyl radical in-vacuo are recorded using laser spectroscopic techniques to further investigate and eventually understand the electronic structure of this neutral radical.

- [1] Morita, Y.; Suzuki, S.; Sato, K.; Takui, T., *Nat. Chem.* 2011, 3 (3), 197-204.
 - [2] Trinquier, G.; Malrieu, J.-P., *Phys. Chem. Chem. Phys.* 2017, 19 (40), 27623-27642.
 - [3] Starikov, A. G.; Starikova, A. A.; Minyaev, R. M.; Minkin, V. I.; Boldyrev, A. I., *Chem. Phys. Lett.* 2020, 740, 137073.
 - [4] Schmidt, T. W., *Int. Rev. Phys. Chem.* 2016, 35 (2), 209-242.
 - [5] O'Connor, G. D.; Troy, T. P.; Roberts, D. A.; Chalyavi, N.; Fückel, B.; Crossley, M. J.; Nauta, K.; Stanton, J. F.; Schmidt, T. W., *J. Am. Chem. Soc.* 2011, 133 (37), 14554
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Session 4: Wednesday, June 24 4 PM UTC

24 Jun
4:00 PM UTC

High-Resolution Double Resonance Action Spectroscopy in Ion Traps: Vibrational and Rotational Spectroscopy of CH_2NH_2^+

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Applying various action spectroscopic techniques in a 4 K cryogenic ion trap instrument, protonated methanimine, CH_2NH_2^+ , has been investigated by high-resolution rovibrational and pure rotational spectroscopy for the first time. In total, 39 rovibrational transitions within the fundamental band of the ν_2 symmetric C-H stretch were measured around 3026 cm^{-1} , which were used to predict pure rotational transition frequencies of CH_2NH_2^+ in the ground vibrational state. Based on these predictions, nine rotational transitions were observed between 109 and 283 GHz using a novel double resonance method. This method consists of rotational excitation followed by vibrational excitation, which is finally detected as a dip in the number of CH_2NH_2^+ -He complexes formed in the 4 K He bath of the trap.

Far-infrared laboratory spectroscopy of aminoacetonitrile and first interstellar detection of its vibrationally excited transitions

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Aminoacetonitrile, a molecule detected in the interstellar medium only towards Sagittarius B2 (Sgr B2), is considered an important prebiotic species as well as a possible precursor of the simplest amino acid glycine. So far, observations were limited to ground state emission lines, whereas transitions from within vibrationally excited states remained undetected. Establishing the energies of the low-lying vibrational states of aminoacetonitrile, which are expected to be populated in Sgr B2(N1), the main hot core of Sgr B2(N), is fundamental in order to properly evaluate the vibration-rotation partition function of aminoacetonitrile as well as the line strengths of the rotational transitions of its vibrationally excited states. This is necessary to derive accurate column densities and secure the identification of these transitions in astronomical spectra.

The ro-vibrational spectrum of aminoacetonitrile has been recorded in the far-infrared region using the bright-synchrotron radiation. Three bands, that correspond to the lowest vibrational modes of aminoacetonitrile, were observed in the frequency region below 500 cm⁻¹. The combined analysis of ro-vibrational and pure rotational data allowed us to prepare new spectral line catalogs for all the states under investigation. We used the imaging spectral line survey ReMoCA performed with ALMA to search for vibrationally excited aminoacetonitrile toward Sgr B2(N1). The astronomical spectra were analyzed under the local thermodynamic equilibrium (LTE) approximation. Results. Almost 11000 lines have been assigned during the analysis of the laboratory spectrum of aminoacetonitrile, thanks to which the vibrational energies of the $v_{11} = 1$, $v_{18} = 1$, and $v_{17} = 1$ states have been determined. The whole dataset, that includes high J and K transitions, is well-reproduced within the experimental accuracy. Reliable spectral predictions of pure rotational lines can now be produced up to the THz region. On the basis of these spectroscopic predictions, we report the interstellar detection of aminoacetonitrile in its $v_{11} = 1$ and $v_{18} = 1$ vibrational states toward Sgr B2(N1) in addition to emission in its vibrational ground state. The intensities of the identified $v_{11} = 1$ and $v_{18} = 1$ lines are consistent with the detected $v = 0$ lines under LTE at a temperature of 200 K.

24 Jun
4:34 PM UTC

Dissociation of the simplest ketohydroperoxide under the ozonolysis of ethylene: theory and experiment hand-in-hand

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24 Jun
4:51 PM UTC

High-resolution photo-fragmentation spectroscopy of N_2O^+

Anthony Roucou^a,
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Session 5: Thursday, June 25

10 AM UTC

25 Jun
10:00 AM UTC

Exploring the Dissociation of C₂

Jasmin Borsovszky^a,

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Isolated 1,4-Naphthoquinone and its step-wise microsolvation in the gas phase: structure and binding by rotational spectroscopy

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1,4-Naphthoquinone (NTQ) is an important product of naphthalene oxidation and it also appears as a motif in many biologically active compounds. NTQ is introduced into the atmosphere by direct emissions from combustion of organic matter, and as a result of reactions of polycyclic aromatic hydrocarbons in the troposphere. Here we present a study of NTQ and its interactions with water using broadband rotational spectroscopy. Bare NTQ and its complexes with one, two and three water molecules have been detected. Their structures and relative arrangements have been determined by using ¹⁸O isotopic data aided by theoretical calculations. Water molecules have been found to adapt their arrangement with respect to NTQ to maximise primary and secondary interactions, with more efficient competition between in-plane and above-plane complex configurations as the number of water molecules increase.

25 Jun
10:34 AM UTC

Rotational spectroscopy with cold gas flows for kinetics studies

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High-temperature hypersonic Laval nozzle for non-LTE cavity ringdown spectroscopy

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Abemassad Benidar^a, Samir Kassi^d, Christine Charles^e, Robert Georges^a

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^b *Department of Chemistry, University of Missouri, Columbia, MO, USA* ^c *Department of Mechanical Engineering, Indian Institute of Technology Guwahati, Guwahati, India*

^d *LIPhy, Université Grenoble Alpes/CNRS, Saint Martin d'Hères, France*

^e *Research School of Physics, Australian National University, Canberra, ACT, Australia*

A small dimension Laval nozzle connected to a compact high enthalpy source equipped with cavity ringdown spectroscopy (CRDS) is used to produce vibrationally hot and rotationally cold high-resolution infrared spectra of polyatomic molecules in the 1.67 μm region. The nozzle was designed to operate with argon heated up to 2000 K and to produce a quasi-unidirectional flow to reduce the Doppler Effect responsible for line broadening. The hypersonic flow was characterized using computational fluid dynamics simulations, Pitot measurements and CRDS. Two different gases, carbon monoxide (CO) and methane (CH_4), were used as test molecules. Vibrational (T_{vib}) and rotational (T_{rot}) temperatures were extracted from the recorded infrared spectrum leading to $T_{\text{vib}} = 1346 \pm 52$ K and $T_{\text{rot}} = 12 \pm 1$ K for CO. A rotational temperature of 30 ± 3 K was measured for CH_4 , while two vibrational temperatures were necessary to reproduce the observed intensities. The population distribution between vibrational polyads was correctly described with $T_{\text{vib}}^I = 894 \pm 47$ K, while the population distribution within a given polyad (namely the dyad or the pentad) was modeled correctly by $T_{\text{vib}}^{II} = 54 \pm 4$ K, testifying to a more rapid vibrational relaxation between the vibrational energy levels constituting a polyad.

Session 6: Friday, June 26

4 PM UTC

Role of primary and secondary non-covalent interactions in the monohydrated complexes of small heterocycles such as trimethylene oxide and sulfide

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26 Jun
4:00 PM UTC

The monohydrated complexes of trimethylene oxide and sulfide were investigated in the gas phase using Fourier transform microwave spectroscopy (8-18 GHz) aided by quantum mechanical calculations. In the assigned trimethylene oxide-water complex, the water sub-unit binds exclusively to the oxygen atom of the ring via a $\text{OH} \cdots \text{O}$ hydrogen bond (HB). In the sulfur containing complex, in addition to the primary $\text{OH} \cdots \text{S}$ HB, a secondary $\text{CH} \cdots \text{O}$ interaction is observed. The experimental results for the sulfur analog are consistent with the predictions from both *ab initio* and density functional theory (DFT) calculations with the aug-cc-pVTZ basis set whereas for the oxygen analog, both planar and puckered ring configurations are possible depending on the level of theory. Our experimental data aligns better with the results from DFT calculations which predict the trimethylene oxide ring to adopt a planar configuration in the complex. The nature and strength of the HBs are studied in detail using topological and energy decomposition analyses. Comparisons are also made computationally with the selenium analog to evaluate the characteristics of the HB along the chalcogen series. The results show that the HBs formed by these rings with water are mostly electrostatic and dispersive in nature and that the HB strength decreases from oxygen to selenium.

26 Jun
4:17 PM UTC

Laser stabilization for accurate cavity ring down spectroscopy:
application to molecular isotopic ratio

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Electronic Spectroscopy of *cis*- and *trans-meta*-Vinylbenzyl Radicals

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Resonance-stabilized radical (RSR) isomers of C_9H_9 persist in complex energetic environments such as flames and plasmas derived from aromatic precursors. Of the myriad possible C_9H_9 RSRs, only 1-indanyl (the global minimum) and 1-phenylallyl have been conclusively identified spectroscopically. Electronic spectra near 600 nm, close to several DIBs, were recently reported by the group of Maier for C_9H_9 products of a heptadiyne discharge. They were tentatively ascribed to isomers of vinylbenzyl on the basis of computed transition energies and ionization potentials, the best agreement with the latter property (ca. 7.3 eV) provided by the meta isomer. To further examine this conjecture, we have undertaken surveys for the electronic spectra of o-, m-, and p-vinylbenzyl radicals in discharges of vinyltoluenes, using resonant two-color ionization and fluorescence spectroscopy. In a jet-cooled discharge of m-vinyltoluene, we have detected *cis*- and *trans*-m-vinylbenzyl radicals near 525 nm. We observe adiabatic ionization energies (ca. 7.15 eV) for both conformers that are comfortably bracketed by B3LYP (7.11 eV) and CBS-QB3 (7.22 eV) calculations, from which we conclude that the carrier of the 600 nm spectrum remains unidentified. Optical-optical hole burning spectroscopy has been used to untangle *cis* and *trans* features of m-vinylbenzyl. There is very little to distinguish the two conformers from calculations, thermochemically or spectroscopically: they are similarly stable, their ground and excited state equilibrium geometries are planar, and their electronic transition energies, AIEs, predicted rotational contours, and excited state vibrational frequencies are highly similar. The most significant point of difference is a large (for *cis*) and relatively small (for *trans*) increase in the vinyl torsion force constant upon excitation, strongly suggesting identification of the *cis* conformer from an origin dispersed fluorescence spectrum, acceptance of which identification allows several other ground-state assignments to fall into place. A considerable breakdown in mirror symmetry between excitation and emission spectra for a_0 modes is tentatively attributed to interference between Franck-Condon and Herzberg-Teller contributions to the transition moment, the low symmetry of the molecule (C_s) placing little restriction on such an interaction

The GACELA set up: a different approach to construct a broadband Fourier transform millimeterwave spectrometer

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We have constructed GACELA¹ (Gas Cell for Laboratory Astrophysics): a broadband Fourier transform millimeterwave based on a detection system analogous to those found in radio-telescopes. The spectrometer is equipped with Q-band (31.5–50 GHz) and W-band (72–116 GHz) receivers, very sensitive to the rotational emission of the molecules present in a one meter Gas Cell. The technique provides large instantaneous bandwidth, spectral purity, and a linear dependence of the signals with the partial pressure so that it is perfectly suited for high resolution emission spectroscopy of molecules of astrophysical importance.

GACELA has been initially tested with molecules whose rotational spectrum was well known (CH₃CN, OCS, SO₂...). High accuracy measurements of the frequencies (~ 38 kHz) and intensities (in K) can also be determined using our new instrument. Subsequently, GACELA experiments have been devoted to study the rotational spectra of molecules of astrochemical interest whose millimeterwave spectrum remains unknown. Among these molecules, the formamide derivatives and dinitriles are very attractive because they are candidates to be found in the space and they present low-energy excited vibrational states that can also contribute to the large number of unidentified lines in the millimeter and submillimeter wave surveys.

¹Cernicharo, *et al.* 2019, A&A 626, A34.