

# Intentional Seminars on Molecular Spectroscopy

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## 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)

## Time table



# Contents

<b>Session 1: Monday, June 22</b>	<b>4 PM UTC</b>	<b>7</b>
Aromaticity in metallaborocycles (G. STEPHEN KOCHERIL) . . . . .		7
Microwave spectroscopy study supported by quantum chemistry calculations of limonaketone, a key oxidation product of limonene (NOUREDDIN OSSEIRAN) . . . . .		8
Laboratory gas-phase vibrational spectra of $[C_3H_3]^+$ isomers and isotopologues by IRPD spectroscopy (ARAVINDH NIVAS MARIMUTHU) . . . .		9
Millimeter- to millimeter-wave double resonance spectroscopy (OLIVER ZINGSHEIM) . . . . .		10
<b>Session 2: Tuesday, June 23</b>	<b>4 PM UTC</b>	<b>11</b>
A new experiment for the study and control of chiral molecules using high resolution electronic and microwave spectroscopy (JOHANNES BISCHOFF)		11
The pure rotational spectrum of the hydroxymethyl radical reinvestigated to enable its interstellar detection (OLIVIA CHITARRA) . . . . .		12
Spectroscopic Characterization of Intermediates in the Abiotic Formation of Biomolecules (ANDRÉ K. ECKHARDT) . . . . .		13
Optical pumping and rovibrational energy transfer in the $C_{60}$ fullerene (BRYAN CHANGALA) . . . . .		14
<b>Session 3: Tuesday, June 23</b>	<b>10 PM UTC</b>	<b>15</b>
The Chemical Pathways of $O(^1D)$ Insertion into Methylamine ( $CH_3NH_2$ ) (HAYLEY BUNN) . . . . .		15
Rotational Spectroscopy of 2-cyano-1,3-butadiene: a Molecule of Astrochemical Relevance (MARIA ZDANOVSKAIA) . . . . .		16
Re-Examination of the Rotational Spectrum of Methyl tert-Butyl Ether (J. H. WESTERFIELD) . . . . .		17
Spectroscopic investigation of the phenalenyl radical (ZACHARIAH LEVEY) .		18
<b>Session 4: Wednesday, June 24</b>	<b>4 PM UTC</b>	<b>19</b>
High-Resolution Double Resonance Action Spectroscopy in Ion Traps: Vibrational and Rotational Spectroscopy of $CH_2NH_2^+$ (CHARLES R. MARKUS)		19
Far-infrared laboratory spectroscopy of aminoacetonitrile and first interstellar detection of its vibrationally excited transitions (MATTIA MELOSSO) .		20
Dissociation of the simplest ketohydroperoxide under the ozonolysis of ethylene: theory and experiment hand-in-hand (NADAV GENOSSAR) . . . .		21
High-resolution photo-fragmentation spectroscopy of $N_2O^+$ (ANTHONY ROUCOU)		22

<b>Session 5: Thursday, June 25</b>	<b>10 AM UTC</b>	<b>23</b>
Exploring the Dissociation of C <sub>2</sub> (JASMIN BORSOVSZKY) . . . . .		23
Isolated 1,4-Naphthoquinone and its step-wise microsolvation in the gas phase: structure and binding by rotational spectroscopy (SHEFALI SAXENA) .		24
Rotational spectroscopy with cold gas flows for kinetics studies (THOMAS S. HEARNE) . . . . .		25
High-temperature hypersonic Laval nozzle for non-LTE cavity ringdown spec- troscopy (ESZTER DUDAS) . . . . .		26
<b>Session 6: Friday, June 26</b>	<b>4 PM UTC</b>	<b>27</b>
Role of primary and secondary non-covalent interactions in the monohydrated complexes of small heterocycles such as trimethylene oxide and sulfide (WESLEY G. D. P. SILVA) . . . . .		27
Laser stabilization for accurate cavity ring down spectroscopy: application to molecular isotopic ratio (JUSTIN CHAILLOT) . . . . .		28
Electronic Spectroscopy of <i>cis</i> - and <i>trans-meta</i> -Vinylbenzyl Radicals (SEDERRA D. ROSS) . . . . .		29
The GACELA set up: a different approach to construct a broadband Fourier transform millimeterwave spectrometer (CELINA BERMUDEZ) . . . . .		30

# Session 1: Monday, June 22 4 PM UTC

22 Jun  
4:00 PM UTC

## Aromaticity in metallaborocycles

G. Stephen Kocheril<sup>a</sup>, Ling Fung Cheung<sup>a</sup>, Joseph Czekner<sup>a</sup>, Lai-Sheng Wang<sup>a</sup>

*Brown University, USA*

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.

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22 Jun  
4:17 PM UTC

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

Noureddin Osseiran<sup>a</sup>,  
<sup>a</sup> *Université Lille, PhLAM, France*

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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

Aravindh Nivas Marimuthu<sup>a</sup>,  
<sup>a</sup> *Radboud University, the Netherlands*

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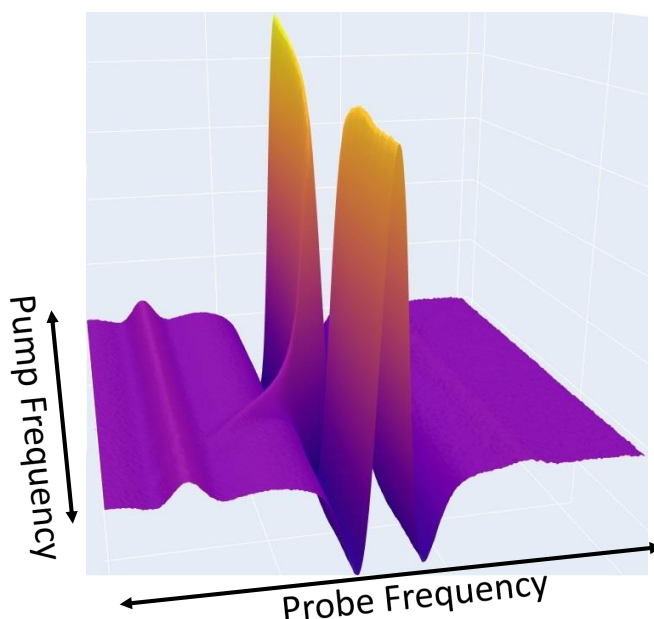
# Millimeter- to millimeter-wave double resonance spectroscopy

Oliver Zingsheim<sup>a</sup>, L. Bonah<sup>a</sup>, H.S.P. Müller<sup>a</sup>, F. Lewen<sup>a</sup>,  
S. Thorwirth<sup>a</sup>, S. Schlemmer

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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

Johannes Bischoff<sup>a</sup>, A. O. Hernandez-Castillo<sup>a</sup>, Ju Hyeon Lee<sup>a</sup>, Marco De Pas<sup>a</sup>,  
Henrik Haak<sup>a</sup>, Gerard Meijer<sup>a</sup>, and Sandra Eibenberger-Arias<sup>a</sup>

<sup>a</sup> *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4, 14195 Berlin, Germany*

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

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

Olivia Chitarra<sup>a</sup>, Marie-Aline Martin-Drumel<sup>a</sup>, Olivier Pirali<sup>a</sup>,  
Silvia Spezzano<sup>b</sup>, Valerio Lattanzi<sup>b</sup>, Holger S. P. Müller<sup>c</sup>, J.-C. Loison<sup>d</sup>

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<sup>b</sup> *Center for Astrochemical Studies, Max-Planck-Institut für extraterrestrische Physik,  
Garching, Germany*

<sup>c</sup> *I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*

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The hydroxymethyl ( $\text{CH}_2\text{OH}$ ) and methoxy ( $\text{CH}_3\text{O}$ ) radicals, products of  $\text{CH}_3\text{OH}$  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  $\text{CH}_2\text{OH}$  pure rotational spectrum and while this isomer is the most thermodynamically stable, only  $\text{CH}_3\text{O}$  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  $\text{CH}_2\text{OH}$  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  $\text{CH}_3\text{OH}$  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  $\text{CH}_2\text{OH}$  in cold interstellar environments.

# Spectroscopic Characterization of Intermediates in the Abiotic Formation of Biomolecules

André K. Eckhardt<sup>a</sup>,

<sup>a</sup> *Center for Astrophysics | Harvard & Smithsonian, Cambridge, MA, USA*

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 C<sub>60</sub> fullerene

Bryan Changala<sup>a</sup>, Marissa L. Weichman<sup>a</sup>, Jutta Toscano<sup>a</sup>, Qizhong Liang<sup>a</sup>, Jun Ye<sup>a</sup>

<sup>a</sup> *JILA/University of Colorado, Boulder, USA*

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# Session 3: Tuesday, June 23

## 10 PM UTC

23 Jun  
11:00 PM UTC

### The Chemical Pathways of O(<sup>1</sup>D) Insertion into Methylamine (CH<sub>3</sub>NH<sub>2</sub>)

Hayley Bunn<sup>a</sup>, Chase P. Shultz<sup>a</sup>, Susanna L. Widicus-Weaver<sup>a</sup>

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O(<sup>1</sup>D) 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(<sup>1</sup>D) 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

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23 Jun  
11:17 PM UTC

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

Maria Zdanovskaia<sup>a</sup>,

<sup>a</sup> *University of Wisconsin, Madison, USA*

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23 Jun  
11:34 PM UTC

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

J. H. Westerfield<sup>a</sup>, Sommer L. Johansen<sup>a</sup>, Kelly S. Meyer<sup>a</sup>, Kyle N. Crabtree<sup>a</sup>

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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

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# Spectroscopic investigation of the phenalenyl radical

Zachariah Levey<sup>a</sup>, Klaas Nauta<sup>a</sup>, Timothy W. Schmidt<sup>a</sup>

<sup>a</sup> *University of New South Wales, Australia*

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 $\text{CH}_2\text{NH}_2^+$

Charles R. Markus<sup>a</sup>, Sven Thorwirth<sup>a</sup>, Oskar Asvany<sup>a</sup>, Stephan Schlemmer<sup>a</sup>

<sup>a</sup> *I. Physikalisches Institut, Universität zu Köln, Germany*

Applying various action spectroscopic techniques in a 4 K cryogenic ion trap instrument, protonated methanimine,  $\text{CH}_2\text{NH}_2^+$ , 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  $\nu_2$  symmetric C-H stretch were measured around  $3026\text{ cm}^{-1}$ , which were used to predict pure rotational transition frequencies of  $\text{CH}_2\text{NH}_2^+$  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  $\text{CH}_2\text{NH}_2^+$ -He complexes formed in the 4 K He bath of the trap.

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

Mattia Melosso<sup>a</sup>, Arnaud Belloche<sup>b</sup>, Luca Dore, Fillipo Tamassia<sup>c</sup>, Marie-Aline Martin-Drumel<sup>d</sup>, Olivier Pirali<sup>d</sup>, Cristina Puzzarini

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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<sup>-1</sup>. 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.

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

Nadav Genossar<sup>a</sup>, Joshua H. Baraban<sup>b</sup>, Jessica P. Porterfield<sup>c</sup>

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<sup>c</sup> *Center for Astrophysics | Harvard & Smithsonian, Cambridge, MA, USA*

Hydroperoxides from the ozonolysis of alkenes, in addition to Criegee intermediates, have been proposed as an atmospheric source of OH radical in the absence of sunlight, but have remained largely elusive due to their reactivity. The simplest alkene, ethylene, is released into the atmosphere by plants and thus may react with atmospheric ozone to form a 5-membered ring,  $c\text{-C}_2\text{H}_4\text{O}_3$ . This, in turn, dissociates to form  $\text{CH}_2=\text{O}$  &  $\text{CH}_2=\text{OO}$ , which subsequently fragments to H, OH, and CO. A different possible path involves ring opening followed by H atom migration to produce  $\text{CHO}-\text{CH}_2-\text{OOH}$ , hydroperoxy-acetaldehyde (HPA), the simplest keto-hydroperoxide (KHP), which is lower in energy by 100 kcal/mol from the starting materials [1]. We predicted the rotational spectrum of the lowest lying conformer of HPA with high accuracy *abinitio* calculations. The geometry optimizations of the two lowest lying conformers were performed at the all-electron CCSD(T)/cc-pCVQZ level of theory, and anharmonic effects were incorporated through VPT2 calculations using the frozen core CCSD(T)/ANO0 level of theory. Although this species was recently claimed to be initially observed in a stirred jet system using VUV photoionization mass spectrometry [2], we have not yet been able to detect HPA by chirped-pulse microwave spectroscopy [3], though it is one of the most stable species in this reaction scheme. We thereby suggest a dissociation path through OH elimination and a subsequent  $\beta$ -scission towards the formation of the dipole-less glyoxal which cannot be detected through microwave spectroscopy. This path is supported by thermochemical calculations on HPA, glyoxal, and a suggested intermediate according to the mHEAT protocol [4]. We encourage the search for glyoxal using complementary spectroscopic techniques.

[1] Pfeifle et. al., J. Chem. Phys., 148, 174306, 2018.

[2] Roussio et. al., J. Phys. Chem. A, 122, 8674-8685, 2018.

[3] Porterfield et. al., Phys. Chem. Chem. Phys, 21, 18065–18070, 2019.

[4] Thorpe et. al. J. Chem. Phys., 150, 224102, 2019.

## High-resolution photo-fragmentation spectroscopy of $\text{N}_2\text{O}^+$

Anthony Roucou<sup>a</sup>, Raghed Bejjani<sup>a</sup>, Xavier Urbain<sup>a</sup>, Guilhem Vanlancker<sup>a</sup>, Clément Lauzin<sup>a</sup>

<sup>a</sup> *Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Belgium*

The photodissociation spectra of  $\text{N}_2\text{O}^+$  have been studied in the UV range using the new STARGATE instrument (Spectroscopy of Transient Anions and Radicals by Gated and Accelerated Time-of-flight Experiment) developed in UCLouvain. This talk will first present the instrument and then results obtained on the  $\tilde{A}^2\Sigma^+(200) \leftarrow \tilde{X}^2\Pi_{3/2}(000)$  transition of  $\text{N}_2\text{O}^+$  in the UV. The spectrometer combines a Time-Of-Flight (TOF) spectrometer, nanosecond pulsed dye laser, pulsed deflection and an energy selector. This combination allows to achieve background free photodissociation spectroscopy of mass-selected ions having a tunable rotational temperature ranging from 50 to 550 K.

The performances of this spectrometer are used to study the photodissociation of  $\text{N}_2\text{O}^+(\tilde{A}^2\Sigma^+)$  in  $\text{NO}^+(X^1\Sigma^+)$  and  $\text{N}(^2\text{D})$  in the 30500–32500  $\text{cm}^{-1}$  range (307–327 nm). The analysis of the observed rovibronic overtones and combination bands measured will be discussed.

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# Session 5: Thursday, June 25

## 10 AM UTC

25 Jun  
10:00 AM UTC

### Exploring the Dissociation of C<sub>2</sub>

Jasmin Borsovszky<sup>a</sup>,

<sup>a</sup> *University of New South Wales, Australia*

Diatomic Carbon is potentially the most common carbon-carbon bond in the universe, having been detected in the photospheres of carbon cycle stars, the interstellar medium, and most notably, is responsible for the blue-green emission bands in the spectra of comets. Alongside its universal prevalence, C<sub>2</sub> is also one of the fundamental homonuclear diatomics, however its dissociation energy has never been directly measured, and is known to an accuracy almost an order of magnitude worse than that of its counterparts N<sub>2</sub> and O<sub>2</sub> [1]. The mechanism by which it dissociates is also not well known. While previous work has observed a lack of fluorescence from  $v = 12$  of the  $e\ ^3\Pi_g$  state, suggesting the presence of a predissociative mechanism, [2] it has never been directly observed. There is significant interest in modelling the dissociation of C<sub>2</sub>, as predissociation is expected to resolve the discrepancies in rotational temperature between observed and modelled cometary spectra of C<sub>2</sub>. [3,4] This project seeks to provide the first observation of predissociation in C<sub>2</sub>, using velocity-mapped imaging. C<sub>2</sub> will be produced by photolysing C<sub>2</sub>Cl<sub>4</sub>, then excited through  $v = 12$  of the Fox Herzberg bands to dissociate into carbon atoms. These atoms will be ionised using a 2+1 REMPI scheme, and the dissociation energy calculated from the velocity distribution of the carbon atom dissociation products. The correlation between the spin-resolved states of the molecule and resulting atoms will also be investigated. If successful, this will be the first direct measurement of the strength of one of the most fundamental diatomic bonds, allowing improved modelling of cometary spectra and deepening our understanding of the universe at large.

[1] Ruscic, B.; Feller, D.; Peterson, K. *Theor. Chem. Acc.* 2014, 133 (1).

[2] Welsh, B.; Krechkivska, O.; Nauta, K.; Bacskey, G.; Kable, S.; Schmidt, T. *J Chem. Phys.* 2017, 147 (2), 024305.

[3] Herzberg, G. *ApJ.*, 1939, 89, p. 290.

[4] Welsh, B. *The  $e\ ^3\Pi_g$  State of Dicarbon: First Evidence of Pre-dissociation*. Honours Thesis, The University of New South Wales, 2017

# 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 <sup>18</sup>O 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.

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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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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  $\mu\text{m}$  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 ( $\text{CH}_4$ ), were used as test molecules. Vibrational ( $T_{\text{vib}}$ ) and rotational ( $T_{\text{rot}}$ ) 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  $30 \pm 3$  K was measured for  $\text{CH}_4$ , 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.

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# 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.

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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 GACELA<sup>1</sup> (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 (CH<sub>3</sub>CN, OCS, SO<sub>2</sub>...). High accuracy measurements of the frequencies ( $\sim 38$  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.

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<sup>1</sup>Cernicharo, *et al.* 2019, A&A 626, A34.