Looking for the Bricks of the Life in the Interstellar Medium: the Fascinating World of Astrochemistry

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Mankind has been observing the heavens for millennia ...

From these observations, a detailed picture of the structure and evolution of stars, galaxies and of the Universe itself was built up. The Universe is found to be a place rich in atoms, from those primordial light atoms created in the Big Bang to the many types of heavier atom ...
Mankind has been observing the heavens for millennia… The Universe is found to be a place rich in atoms…

formation of atoms
Mankind has been observing the heavens for millennia ...

The Universe is found to be a place rich in atoms ...

For many years, the interstellar medium was considered too hostile an environment for molecules. ...

However, some eighty years ago, spectroscopic observations in the visible and near ultraviolet began to show otherwise ...
CONSIDERATIONS REGARDING INTERSTELLAR MOLECULES

ABSTRACT

An attempt has been made to compute the numbers of certain molecules in interstellar space. The results obtained are unfavorable to Saha’s identification of one of Merrill’s interstellar lines with \( Na_2 \). A search for the bands of \( CH, OH, NH, CN \), and \( C_2 \) would appear to be promising.


\( \zeta \) Oph:
VIS lines at 3878.8, 3886.4, 3890.2, & 4300.3 Å
UV lines near 1271, 1368, 1369, 1370, 1549, & 1694 Å
A review of microwave and radio-frequency spectral lines which might possibly be detected by the techniques of radio astronomy is attempted here. Brief discussions of this type have already been given by several authors [1, 2, 3, 4]. However, the present treatment is somewhat more complete than previously published material, and has the advantage of more recent information about certain transition frequencies. It includes a general discussion of types of spectra which might be found, expected intensities, and some characteristics and known frequencies of the lines which may be of interest in radio astronomy.

Transitions which lie in the microwave or radio-frequency region can be expected to come from atomic or molecular hyperfine structure, from atomic or molecular fine structure, and from molecular rotational frequencies. It is of course possible that some odd circumstance or chance
Radio Observations of OH in the Interstellar Medium

In this note we wish to report the detection of 18-cm absorption lines of the hydroxyl (OH) radical in the radio absorption spectrum of Cassiopeia A, thereby providing positive evidence for the existence of OH in the interstellar medium. The microwave transitions of OH in the ground state, $^2\Pi_{3/2}$, $J = 3/2$, arise from two $\Lambda$-type doublet levels, each of which is split by hyperfine interactions with the hydrogen nucleus, so that four transitions result. The two strongest lines have been previously measured in the laboratory at 1667.34 ± 0.03 Mc/sec ($F = 2\rightarrow 2$) and 1665.46 ± 0.10 Mc/sec ($F = 1\rightarrow 1$) with relative intensities of 9 and 5, respectively;¹ these results are in agreement with theory. The
DISCOVERY OF INTERSTELLAR METHYL FORMATE

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P. D. Godfrey,* B. J. Robinson,† and J. B. Whiteoak†

Received 1974 December 31

ABSTRACT

The $1_{10}-1_{11} A$-state transition of methyl formate HCOOCH$_3$ has been detected in emission in the spectrum of Sgr B2. With a laboratory determination of 1610.249 MHz for the rest frequency of the transition, the radial velocity of the observed line is $53 \pm 6$ km s$^{-1}$. The nearby $E$-state transition at 1610.906 MHz may also have been detected. It is probable that the $1_{10}$ and $1_{11}$ levels are inverted and that the continuum emission of Sgr B2 is being amplified.
INTERSTELLAR GLYCOLALDEHYDE: THE FIRST SUGAR

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ABSTRACT

Interstellar glycolaldehyde (CH$_2$OHCHO) has been detected in emission toward the Galactic center source Sagittarius B2(N) by means of millimeter-wave rotational transitions. Glycolaldehyde is an important biomarker since it is structurally the simplest member of the monosaccharide sugars that heretofore have gone undetected in interstellar clouds. There is no consensus as to how any such large complex molecules are formed in the interstellar clouds. It may be that the typical environment of dense molecular cloud cores is favorable to glycolaldehyde synthesis by means of the polymerization of formaldehyde (H$_2$CHO) on grain surfaces or in the gas phase. Alternatively, we speculate that glycolaldehyde and other simple molecules may undergo assembly from functional molecular groups on grain surfaces. Utilizing common chemical precursors, a chance process could account for the high degree of isomerism observed in complex interstellar molecules (e.g., methyl formate, acetic acid, and glycolaldehyde). This work suggests that the phenomenon of isomerism be investigated as a means of potentially constraining interstellar chemistry routes for the study of sources where the occurrence of good source-beam coupling can be achieved.
Life on Earth relies on chiral molecules—that is, species not superimposable on their mirror images. This manifests itself in the selection of a single molecular handedness, homochirality, across the biosphere. We present the astronomical detection of a chiral molecule, propylene oxide (CH$_3$CHCH$_2$O), in absorption toward the Galactic center. The presence of propylene oxide in the gas phase in a cold, extended molecular shell surrounding a cluster of star clusters in the Sagittarius B2 star-forming region. This supports the notion of the earliest stage of solar system evolution in which a chiral molecule could have formed.
CHIRALITY

LIFE = HOMOCHIRALITY
Molecules in the Interstellar Medium or Circumstellar Shells (as of 05/2018)

<table>
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<tr>
<th>2 atoms</th>
<th>3 atoms</th>
<th>4 atoms</th>
<th>5 atoms</th>
<th>6 atoms</th>
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<td>C_6H</td>
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<td>C_3NCH_2CHO</td>
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</table>

Most of the molecules known to be present in space have been detected thanks to their rotational transitions
Magellanic Cloud
ALMA

(Atacama Large Millimeter/submillimeter Array):

66 antennas - range: 84-950 GHz
With the observation that molecules pervade interstellar space came the desire to understand their formation … So how are such molecules formed?

The science of ASTROCHEMISTRY was born from within this environment …
Quantum Chemistry Meets Spectroscopy for Astrochemistry: Increasing Complexity toward Prebiotic Molecules

The STARTING POINT for the development of astrochemical models is the knowledge of whether a particular molecule is present in the astronomical environment and, if so, its abundance.
SPECTROSCOPIC SIGNATURES provide the UNEQUIVOCAL PROOF of the PRESENCE of CHEMICAL SPECIES, which is the starting point for the development of astrochemical and astrophysical models.
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WHY?

CHIRALITY ISSUE ...
\[ \nu = 2B(J + 1) - 4D(J + 1)^3 \]

\[ B = \frac{\hbar^2}{2I} \]

\[ I = \sum_{K} m_K \left( \mathbf{1} R_K^2 - \mathbf{R}_K \mathbf{R}_K^T \right) \]

Inertia Tensor

Rotational constant

Rotational spectrum of carbon monoxide recorded in emission from planetary nebula NGC 7027 using the SPIRE Fourier Transform Spectrometer on the Herschel Space Observatory [Adapted from R Wesson et al, Astron. Astrophys., 518, L144 (2010)].

\[ \nu = 2B(J + 1) - 4D(J + 1)^3 \]

Different molecules

\[ I = \sum_K m_K \left( \mathbf{1} R_K^2 - \mathbf{R}_K \mathbf{R}_K^T \right) \]
\[ \nu = 2B(J + 1) - 4D(J + 1)^3 \]

Different molecules \(\rightarrow\) Very different rotational spectra

\[ I = \sum_K m_K (1 R_K^2 - R_K R_K^T) \]

**Inertia Tensor**

Fig. 11.3 Rotational spectrum of carbon monoxide recorded in emission from planetary nebula NGC 7027 using the SPIRE Fourier Transform Spectrometer on the Herschel Space Observatory. [Adapted from R. Wesson et al., *Astron. Astrophys.*, 518, L144 (2010)].

\( \nu = 2B(J + 1) - 4D(J + 1)^3 \)

Different isotopologues

\[ I = \sum_{K} m_K \left( 1 R_K^2 - R_K R_T^T \right) \]

**INERTIA TENSOR**

Fig. 11.3  Rotational spectrum of carbon monoxide recorded in emission from planetary nebula NGC 7027 using the SPIRE Fourier Transform Spectrometer on the Herschel Space Observatory [Adapted from R Wesson et al, Astron. Astrophys., 518, L144 (2010)].
\[ \nu = 2B(J + 1) - 4D(J + 1)^3 \]

Different isotopologues \( \rightarrow \) Different rotational spectra

\[ I = \sum_K m_K \left( \mathbf{1} R_K^2 - \mathbf{R}_K \mathbf{R}_K^T \right) \]

INERTIA TENSOR

Fig. 11.3 Rotational spectrum of carbon monoxide recorded in emission from planetary nebula NGC 7027 using the SPIRE Fourier Transform Spectrometer on the Herschel Space Observatory [Adapted from R Wesson et al, Astron. Astrophys., 518, L144 (2010)].

\[ \nu = 2B(J + 1) - 4D(J + 1)^3 \]

Different enantiomers

\[ \mathbf{I} = \sum_{K} m_K \left( \mathbf{1} R_K^2 - \mathbf{R}_K \mathbf{R}_K^T \right) \]

**Inertia Tensor**

**Rotational Constant**

---

Fig. 11.3  Rotational spectrum of carbon monoxide recorded in emission from planetary nebula NGC 7027 using the SPIRE Fourier Transform Spectrometer on the Herschel Space Observatory [Adapted from R Wesson et al, Astron. Astrophys., 518, L144 (2010)].

\[ \nu = 2B(J + 1) - 4D(J + 1)^3 \]

Different enantiomers \( \rightarrow \) Same rotational spectra

\[
\mathbf{I} = \sum_{K} m_K \left( \mathbf{1} R_{K}^2 - \mathbf{R}_{K} \mathbf{R}_{K}^T \right)
\]

Inertia Tensor

Fig. 11.3 Rotational spectrum of carbon monoxide recorded in emission from planetary nebula NGC 7027 using the SPIRE Fourier Transform Spectrometer on the Herschel Space Observatory [Adapted from R Wesson et al, Astron. Astrophys., 518, L144 (2010)].

How to make use of rotational spectroscopy measurements & quantum-chemical computations to shed light on key questions in Astrochemistry???
How life originated?

This is one of the key questions that Astrochemistry is trying to answer.
How life originated?

Endogenous synthesis or Exogenous delivery??
Miller-Urey experiment: first attempt to synthetize biogenic or prebiotic monomers from simple gases using spark discharge experiments, i.e. to simulate the conditions to be present on the early Earth.
Endogenous synthesis

... however a pot is not a good approximation of a planetary atmosphere .... But ... ... Titan: a primordial Earth ... ...
CASSINI-HUYGENS MISSION

TITAN - the largest moon of Saturn
The second largest moon in our solar system.
The most recent measurements by instruments onboard the Cassini spacecraft revealed that Titan’s upper atmosphere harbors the richest organic chemistry in the solar system.

Cassini plasma spectrometers (CAPS) & ion neutral mass spectrometer (INMS)
Large carbocations & large carbanions!

Cassini plasma spectrometers (CAPS) & ion neutral mass spectrometer (INMS)
The most recent measurements by instruments onboard the Cassini spacecraft revealed that Titan’s upper atmosphere harbors the richest organic chemistry in the solar system.

Cassini plasma spectrometers (CAPS) & ion neutral mass spectrometer (INMS)

Large carbocations & large carbanions!

Simple molecules in the gas phase do evolve into organic macromolecules characterized by the structural complexity typical of pre-biological molecules.

Olah’s carbocations
Phenalenyl cation/anion

 JWST

(0.6-29 \, \mu m)

Phenalenyl cation/anion

B3LYP/6-31+G(d, p)

Conclusion: it is demonstrated that simple molecules in the gas phase do evolve into organic macromolecules characterized by the structural complexity typical of pre-biological molecules.

WHAT NeXT?
Detection of the aromatic molecule benzonitrile (c-C₆H₅CN) in the interstellar medium

Brett A. McGuire,¹,²* Andrew M. Burkhardt,³ Sergei Kalenskii, Christopher N. Shingledecker,⁵ Anthony J. Remijan,¹ Eric Herbst,³,⁵ Michael C. McCarthy²,⁶


“Polycyclic aromatic hydrocarbons and polycyclic aromatic nitrogen heterocycles are thought to be widespread throughout the universe...”
Detection of **prebiotic species** would thus confirm that the organic chemistry on Titan is a model of the prebiotic atmosphere of early Earth.

Prebiotic molecules = precursors of biological molecules (=> precursors of the origin of life)
ASTROBIOLOGY

ALMA detection and astrobiological potential of vinyl cyanide on Titan

Maureen Y. Palmer,1,2,3* Martin A. Cordine,1,3 Conor A. Nixon,1 Steven B. Charnley,1 Nicholas A. Teanby,4 Zbigniew Kisiel,5 Patrick G. J. Irwin,6 Michael J. Mumma1

Recent simulations have indicated that vinyl cyanide is the best candidate molecule for the formation of cell membranes/vesicle structures in Titan’s hydrocarbon-rich lakes and seas. Although the existence of vinyl cyanide (C2H3CN) on Titan was previously inferred using Cassini mass spectrometry, a definitive detection has been lacking until now. We report the first spectroscopic detection of vinyl cyanide in Titan’s atmosphere, obtained using archival data from the Atacama Large Millimeter/submillimeter Array (ALMA), collected from February to May 2018. We detect the three strongest rotational lines of C2H3CN in the frequency range of 230 to 232 GHz, each with high confidence. Radiative transfer modeling suggests that most of the C2H3CN emission originates at altitudes below 5 km, in agreement with recent photochemical models. The vertical column densities implied by our best-fitting models are in the range of 3.7 × 10^13 to 1.4 × 10^14 cm^-2. The corresponding production rate of vinyl cyanide and its contribution to the formation mole fraction imply the availability of sufficient dissolved material to form ~10^7 cell membranes/cm^2 in Titan’s sea Ligeia Mare.
Synergism between Molecular (laboratory) Spectroscopy and Radioastronomy

MW/mm/submm spectroscopy

Radioastronomy
Synergism between Molecular (exp & comp) Spectroscopy and Radioastronomy

\[ \hat{H}\psi = E\psi \]

MW/mm/submm spectroscopy

Radioastronomy

QUANTUM CHEMISTRY
Synergism between Molecular (exp & comp) Spectroscopy and Radioastronomy

Virtual Multi-frequency Spectrometer
Virtual Multi-frequency Spectrometer

Preprocessing

Raw Data

Inputs Creation

Jobs Management

Data Importer

Postprocessing

Spectra Processing

Analysis Tools

Comparison Tools

Computations

Anharmonic Vibrational Spectroscopy

Vibrationally resolved Electronic Spectroscopy

NMR

SPFIT SPCAT

Big Data Tools
ROTATIONAL AND INFRARED SPECTROSCOPY OF ETHANIMINE: A ROUTE TOWARDS ITS ASTROPHYSICAL AND PLANETARY DETECTION

Alessio Melli,¹ Mattia Melosso,¹ Nicola Tasinato,² Giulio Bosi,¹ Lorenzo Spada,¹,² Julien Bloino,²,³ Marco Mendolicchio,² Luca Dore,¹ Vincenzo Barone,² and Cristina Puzzarini¹

The ethanimine isomers can serve as precursors of the alanine amino acid and may play important roles in forming biological molecules in the interstellar medium.
THE DETECTION OF INTERSTELLAR ETHANIMINE (CH₃CHNH) FROM OBSERVATIONS TAKEN DURING THE GBT PRIMOS SURVEY

Ryan A. Loomis¹, Daniel P. Zaleski¹, Amanda L. Steber¹, Justin L. Neill¹, Matthew T. Muckle¹, Brent J. Harris¹, Jan M. Hollis², Philip R. Jewell³, Valerio Lattanzio⁴,⁵, Frank J. Lovas⁶, Oscar Martinez, Jr.⁴,⁵, Michael C. McCarthy⁴,⁵, Anthony J. Remijan³, Brooks H. Pate¹, and Joanna F. Corby⁷

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² NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA
³ National Radio Astronomy Observatory, 520 Edgemont Road, Charlottesville, VA 22904–2475, USA
⁴ Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, USA
⁵ School of Engineering & Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, MA 02138, USA
⁶ National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
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Abstract

We have performed reaction product screening measurements using broadband rotational spectroscopy to identify rotational transition matches between laboratory spectra and the Green Bank Telescope PRIMOS radio astronomy survey spectra in Sagittarius B2 North (Sgr B2(N)). The broadband rotational spectrum of molecules created in an electrical discharge of CH₃CN and H₂S contained several frequency matches to unidentified features in the PRIMOS survey that did not have molecular assignments based on standard radio astronomy spectral catalogs. Several of these transitions are assigned to the E- and Z-isomers of ethanimine. Global fits of the rotational spectra of these isomers in the range of 8–130 GHz have been performed for both isomers using previously published mm-wave spectroscopy measurements and the microwave measurements of the current study. Possible interstellar chemistry formation routes for E-ethanimine and Z-ethanimine are discussed. The detection of ethanimine is significant because of its possible role in the formation of alanine—one of the twenty amino acids in the genetic code.
Values in cm$^{-1}$

Relative energy/cm$^{-1}$

Reaction coordinate

$E$ $Z$

$TS_{E-Z}$

- 9677.2
- 10351.2

Values in cm$^{-1}$

VMS-Rot: the NEW rotational spectroscoppy module

VMS-ROT program structure

D. Licari, N. Tasinato, L. Spada, C. Puzzarini, V. Barone

VMS-Rot: the NEW rotational spectroscopy module

(E) - Ethanimine

$|\mu_a| = 0.8 \text{ D}$

$|\mu_b| = 1.8 \text{ D}$
(Z) - Ethanimine

$|\mu_a| = 2.4 \text{ D}$

$|\mu_b| = 0.4 \text{ D}$
THE DETECTION OF INTERSTELLAR ETHANIMINE (CH$_3$CHNH) FROM OBSERVATIONS TAKEN DURING THE GBT PRIMOS SURVEY

RYAN A. LOOMIS$^1$, DANIEL P. ZALESKI$^1$, AMANDA L. STEBER$^1$, JUSTIN L. NEILL$^1$, MATTHEW T. MUCKLE$^1$, BRENT J. HARRIS$^1$, JAN M. HOLLIS$^2$, PHILIP R. JEWELL$^3$, VALERIO LATTANZI$^4,5$, FRANK J. LOVAS$^6$, OSCAR MARTINEZ, JR.$^4,5$, MICHAEL C. MCCARTHY$^4,5$, ANTHONY J. REMJAN$^3$, BROOKS H. PATE$^1$, AND JOANNA F. CORBY$^7$

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New measurements …

\[ \sim 92 \text{ GHz} \& 250-302 \text{ GHz} \]

Ethanimine is an unstable molecule that was produced through pyrolysis of a commercial sample of isopropylamine, \((\text{CH}_3)_2\text{CHNH}_2\)
New Global FIT: predictions
Exogenous delivery

Delivery of key prebiotic molecules formed beyond the Earth by asteroids, comets, meteorites, and interplanetary dust particles …
Exogenous delivery

... search for key prebiotic molecules in the Interstellar Medium ... need to understand how they are formed ...
In search of prebiotic molecules signatures ... 
In search of the "holy grail" ... 
In search of glycine ... & "BEYOND"
The challenge of the conformational equilibrium

- Observation/creation of elusive conformers?
- Accurate
  - structure ($R_e$)
  - thermodynamic ($\Delta H$, $\Delta G$)
  - spectroscopic parameters
  - $B_0$, $D_{JK}$, IR, Raman ..

Flexible Building blocks of biomolecules: glycine

Thermodynamic properties

CC/DFT conformational energies (kJ mol\(^{-1}\)) wrt most stable Ip, T=410 K
- CCSD(T)/CBS+CV conformational energies, harmonic frequencies,
- B3LYP/SNSD anharmonic contributions computed by means of the HDCPT2[2] model, in conjunction with simple perturbation theory (SPT)[3].

<table>
<thead>
<tr>
<th>Conformer</th>
<th>(\Delta E_{\text{ele}})</th>
<th>(\Delta E_{\text{ZPVE}})</th>
<th>(\Delta H (T=410 \text{ K}))</th>
<th>(\Delta G (T=410 \text{ K}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\text{RRHO}^*)</td>
<td>(\text{HRAO}^{**})</td>
<td>\text{Exp.}</td>
<td>(\text{RRHO}^*)</td>
</tr>
<tr>
<td>IIn/ccc</td>
<td>2.29</td>
<td>3.73</td>
<td>2.80</td>
<td>2.45</td>
</tr>
<tr>
<td>IVn/gtt</td>
<td>4.87</td>
<td>4.74</td>
<td>4.59</td>
<td>4.62</td>
</tr>
<tr>
<td>IIIp/tct</td>
<td>7.44</td>
<td>7.94</td>
<td>7.61</td>
<td>6.62</td>
</tr>
<tr>
<td>Vn/gct</td>
<td>10.88</td>
<td>11.21</td>
<td>10.87</td>
<td>11.21</td>
</tr>
<tr>
<td>VIp/ttc</td>
<td>20.32</td>
<td>19.80</td>
<td>20.02</td>
<td>20.24</td>
</tr>
</tbody>
</table>

- Accurate computations of entropy contributions require the proper treatment of low-frequency torsional motions and anharmonic effects.

* Harmonic Oscillator Rigid Rotor
** Anharmonic Oscillator Hindered Rotor

In search of prebiotic molecules signatures …

Let’s take a step back …
In search of prebiotic molecules signatures …

Let’s take a step back …

Two research lines to be pursued:

>> Search of smaller prebiotic molecules

>> Formation routes
In search of prebiotic molecules signatures …

Let’s take a step back …

Two research lines to be pursued:

>> Search of smaller prebiotic molecules

>> Formation routes
In search of prebiotic molecules signatures ...

“One of the most important open issues in astrochemistry and astrobiology is the detection in space of complex organic molecules (COMs), in particular those related to the formation of biomolecule building blocks .... Among the various chemical species, the compounds containing the −CN− moiety are considered important prebiotic molecules as potential precursors of amino acids. ....”
“... roughly half of the 170 molecules that have been detected in space were first detected toward the Sgr B2(N) region. One puzzling result is that many of the large molecules identified in this source are found to have cold rotational temperatures (∼10 K) despite the fact that most models of complex molecule formation require high-temperature (100–200 K) processing of interstellar ices. ...”
Z− & E−C-cyanomethanimine: the rotational spectra were experimentally investigated only below 100 GHz
Rotational spectrum extended: 100 – 420 GHz
E-isomer

Z-isomer

Asai IRAM 30-m dataset: NO detection (from starless regions to the more evolved hot-corinos associated with both Class 0 and Class I objects)
## UPPER LIMITS

- $1 \times 10^{11} \text{ cm}^{-2}$ (L1544; 26'');
- $2 \times 10^{11} \text{ cm}^{-2}$ (Barnard 1; 26'');
- $1 \times 10^{12} \text{ cm}^{-2}$ (L1157-B1; 12'');
- $2 \times 10^{12} \text{ cm}^{-2}$ (L1157-mm, L1448-R2; 12'');
- $3 \times 10^{12} \text{ cm}^{-2}$ (IRAS4A, L1527, SVS13-A; 12'').

By assuming that HNCHCN and H$_2$ are tracing the same material and comparing the corresponding column densities, we derived $X_{\text{HNCHCN}}$ (cyanomethanimine abundance):

- $\leq 4 \times 10^{10}$ for starless and hot-corinos
- $\leq 5 \times 10^9$ for shocks.
**Laboratory measurements and astronomical search for cyanomethanimine** *

M. Melosso¹, A. Melli¹, C. Puzzarini¹,²,*, C. Codella², L. Spada¹,³, L. Dore¹, C. Degli Esposti¹, B. Lefloch⁴, R. Bachiller⁵, C. Ceccarelli⁴,², J. Cernicharo⁶, and V. Barone³

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³ Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa, Italy  
⁴ Univ. Grenoble Alpes, CNRS, Institut de Planétologie et d’Astrophysique de Grenoble (IPAG), 38000 Grenoble, France  
⁵ IGN, Observatorio Astronómico Nacional, Calle Alfonso XII, 28004 Madrid, Spain  
⁶ Grupo de Astrofísica Molecular. Instituto de CC. de Materiales de Madrid (ICMM-CSIC). Sor Juana Inés de la Cruz 3, Cantoblanco, 28049 Madrid, Spain

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Rotational spectrum extended: 100 – 420 GHz
In search of prebiotic molecules signatures …

Let’s take a step back …

Two research lines to be pursued:

>> Search of smaller prebiotic molecules

>> Formation routes
How are prebiotic molecules formed in the interstellar medium?

>> Gas-phase chemistry

>> Surface (grain) chemistry
Synergism between Molecular (laboratory) Spectroscopy and Quantum Chemistry

MW/mm/submm spectroscopy

\[ \hat{H}\psi = E\psi \]
How are prebiotic molecules formed in the interstellar medium?

>> Gas-phase chemistry

1) Precursors
2) Reaction path
Let me show an example: Formamide formation route in cold interstellar clouds.
For a given formation pathway

>> **Intermediates & Transition states:**
structure, energetic & vibrational features

>> **Kinetics**

Vazart, Calderini, Puzzarini, Skouteris, Barone, JCTC 12, 5385 (2016)
Relative Energies (kJ/mol)

<table>
<thead>
<tr>
<th>Method</th>
<th>Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B2PLYP-D3/m-augVTZ</td>
<td>0.67</td>
</tr>
<tr>
<td>CCSD(T)/m-augVTZ</td>
<td>7.65</td>
</tr>
<tr>
<td>CCSD(T)/CBS+CV</td>
<td>3.77</td>
</tr>
<tr>
<td>CCSD(T)/CBS+CV+fT</td>
<td>2.05</td>
</tr>
<tr>
<td>CCSD(T)/CBS+CV+fT+fQ</td>
<td>1.67</td>
</tr>
</tbody>
</table>

Formaldehyde + NH₂ → TS5

TS5

495 cm⁻¹

ΔG° = 0.67 kJ/mol
Relative Energies (kJ/mol)

TS5

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>B2PLYP-D3/m-augVTZ</td>
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</tr>
</tbody>
</table>

Reaction Coordinates
<table>
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<tr>
<th>Method</th>
<th>kJ / mol</th>
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<tr>
<td>B2PLYP-D3/m-augVTZ</td>
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<td>1.67</td>
</tr>
</tbody>
</table>

**Relative Energies (kJ/mol)**

- Precursors: formaldehyde + NH2
- TS5: i495 cm⁻¹
- RI0b: 3.6
- RI3: -74.5
Relative Energies (kJ/mol)

<table>
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<tr>
<th>TS5</th>
<th>kJ / mol</th>
</tr>
</thead>
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Vazart, Calderini, Puzzarini, Skouteris, Barone, JCTC **12**, 5385 (2016)
Less refined calculations led to a lower barrier to formamide, the corresponding rate constants being consequently higher.


Vazart, Calderini, Puzzarini, Skouteris, Barone, JCTC 12, 5385 (2016)
Gas phase formation of Deuterated Formamide

The gas-phase formation mechanism proposed for formamide can also be used to predict relative formation rates of deuterated formamide.

Single dish observations of deuterated formaldehyde towards IRAS16293 have shown a HDCO/H$_2$CO ratio of $\sim$0.15.

The DCONH$_2$/HCONH$_2$ ratio observed is 0.02–0.05, i.e. $\sim$3–8 times lower.
Goal: vis-à-vis comparison

★ Direct comparison with experiment
★ Accuracy & interpretation
★ Easy-to-use procedure + Analysis tools

References:


4. VB, JCP 122, 014108 2005,


6. JB, MB, VB JCTC, 8, 1015 2012

7. JB, VB, JCP 136, 124108 2012

From Harmonic to Full anharmonic
- Harmonic
- Harmonic Scaled
- GVPT2 Freq
  - +Harm Int
  - Full anharmonic
    - Freq+Int

B3LYP/SNSD

J. Bloino, J. Phys. Chem. A ASAP
DOI:10.1021/jp509985u
IR spectra of glycine: Interpretation and prediction

- Best-estimated MI-IR spectra for the main glycine isotopologue
  - CCSD(T)/CBS+CV //B3LYP/SNSD

- Single contribution spectra
- Simulate IR spectra recorded in the low-temperature Ar matrix
  - Relative abundancies + conformational cooling

- **ALL with respect to experiment**
- MAE < 8 cm⁻¹, |MAX| ≤ 20 cm⁻¹

- Amide I (νC=O): within 5 cm⁻¹ for ALL conformers

- Theory can predict ANY spectra

---

Chiroptical spectroscopies: ROA

ROA spectra of (+)-(R)-methyloxirane

Gas phase ROA spectra, harmonic, anharmonic vs experiment

- Vibrational frequencies
  - Harmonic: ‘best cheap’=CCSD(T)/cc-pVTZ+CBS(MP2)+CV(MP2)
  - Anharmonic: CC/B3LYP, ‘best cheap’ harmonic + anharmonic contributions
  - B3LYP/SNSD

ROA intensities: B3LYP/SNSD


Vibrational and bulk + explicit solvent effect

Contributions of various effects on the overall phenomena
- Final spectrum simulated with the methanol solution described with continuum CPCM model + 2 explicit CH$_3$OH, FC|VG, first 8 electronic states, Lorentzian, FWHM of 500 cm$^{-1}$

Specific solvent

Bulk solvent
PCM

Vibronic
Molecular vibrations
Inter-molecular
Solvent effects: VCD

Anharmonic calculations: gas phase vs pure liquid for $\alpha$-pinene$^2$ (800-1350 cm$^{-1}$)

- Computation: PCM with vibrational nonequilibrium$^1$ and local field effects, B3LYP/SNSD
Spectra Computation in Condensed Phases

- Parameterize Solvent (LRR-DE)
- Parameterize Solute (JOYCE)
- NPBC-MD (GLOB)
- Cherry-pick snapshots (Clustering)
- QM/MM (ONIOM/PMM)

Merlino workflow

Spectra (VMS)
DROP Model
Dynamics Restraining Optimized Potential

multi-layered QM/MM model
Tyrosine zwitterion in SPC

- 22 QM calculation vs 500
- Relevant accuracy loss
A new strategy..

\[ \hat{H} = \hat{H}_{EE-ONIOM} + \Delta \hat{V} \]

Quantum Centre

Perturbing environment:

**electrostatic perturbation** on the QC electronic states

S. Del Galdo, B. Chandramouli, G. Mancini and V. Barone (Submitted)
Zwitterionic Tyrosine in SPC

- 4 QM calculations
- No accuracy loss
Representation & e interaction
The AVALON Project
Advanced Virtual Astrochemistry Lab for an Ongoing Network
Experimental Laboratory: Molecular Spectroscopy, …

Quantum Chemistry, Simulation & Visualization

ASTROCHEMISTRY

Observations & Modeling

SmartLab

Virtual Reality
Mankind has been observing the heavens for millennia …

… a lot of questions are still waiting for an answer …

… the chemical evolution in space and origin-of-life issues are waiting to be solved …

… to be continued …
THANK YOU
For
YOUR ATTENTION