Predicting potentially relevant molecules in astrochemistry with quantum chemical methods

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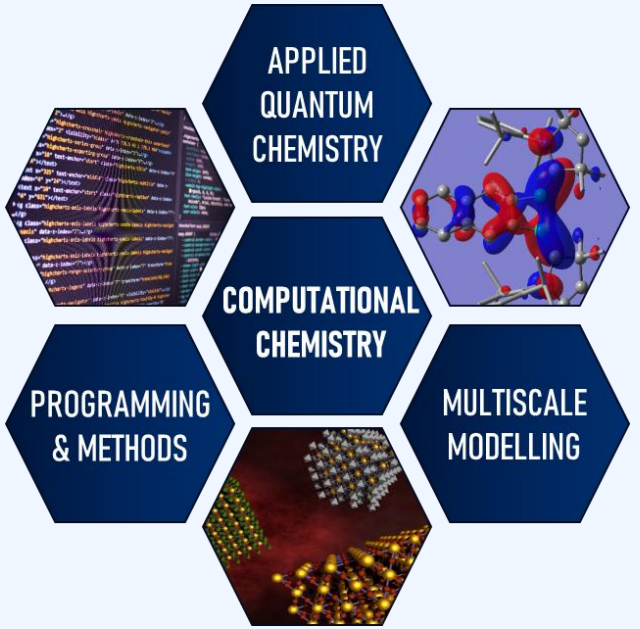
28/02/2024

ECT* Inaugural Workshop on
Nuclear Astrochemistry 2024

Computational & Theoretical Chemistry @ Kent

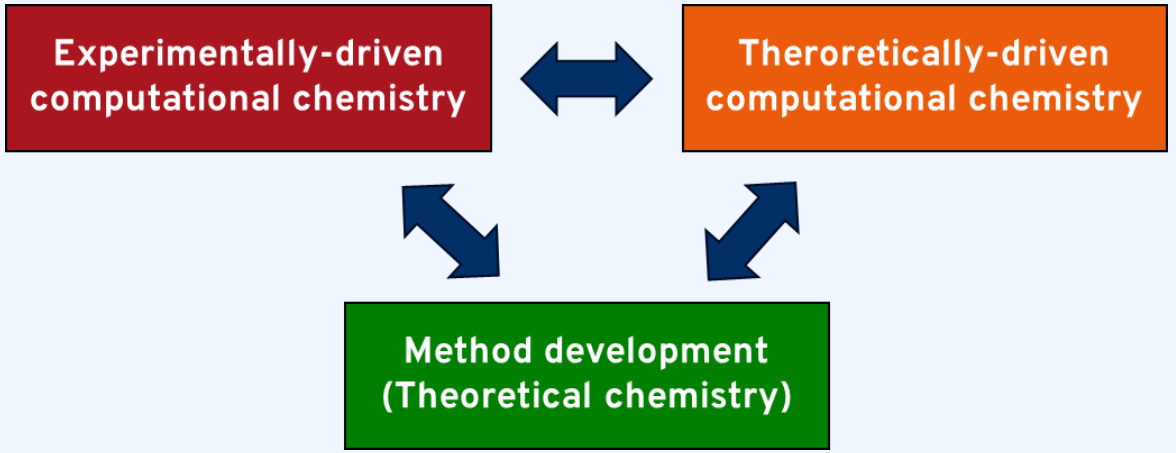
Goals

- **Apply** and **develop** computational chemistry methods (quantum chemistry; molecular dynamics) aiming at investigating:
  - **Electronic structure and photochemistry**
  - **Bonding situation**
  - **Mechanistic and reactivity aspects**



Motivation

- **Fundamentals** (**foundation**)
- **Applications** in distinct fields, such as: metal and metal-free catalysis; small-molecule activation, renewable energy; bioinorganic chemistry and biomimetic compounds; materials science and optoelectronic devices; and astrochemistry.



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Main-Group and Transition-Metal Chemistry

JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

JACS **2022**, *144*, 21363–21370.

pubs.acs.org/JACS Article

Highly Strained Arene-Fused 1,2-Diborete Biradicaloid

Annalena Gärtner, Lukas Meier, Merle Arrowsmith, Maximilian Dietz, Ivo Krummenacher, Rüdiger Bertermann, Felipe Fantuzzi,* and Holger Braunschweig*

Chemical Science

Chem. Sci. **2023**, *14*, 4589-4596

ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE View Article Online View Journal

Check for updates

Catalyst-free diboration and silaboration of alkenes and alkynes using bis(9-heterofluorenyl)s†

Cite this: DOI: 10.1039/d3sc01395b

All publication charges for this article have been paid for by the Royal Society of Chemistry

Jannik Gilmer,[ab] Timo Trageser,[a] Luis Čaić,[a] Alexander Virovets,[a] Michael Bolte,[a] Hans-Wolfram Lerner,[a] Felipe Fantuzzi[*b] and Matthias Wagner[*a]

Chemical Science

Chem. Sci. **2023**, *14*, 2215–2228.

ROYAL SOCIETY OF CHEMISTRY

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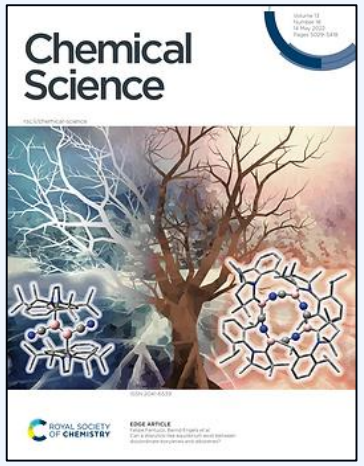
Check for updates

Nickel boryl complexes and nickel-catalyzed alkyne borylation†

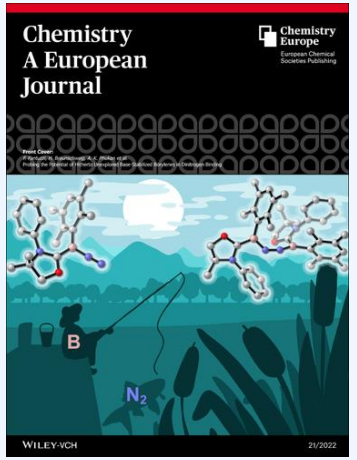
Cite this: *Chem. Sci.*, 2023, **14**, 2215

All publication charges for this article have been paid for by the Royal Society

Lukas Tendera,‡[a] Felipe Fantuzzi,‡[b] Todd B. Marder[ac] and Udo Radius[*a]



boraWanzlick equilibrium
Chem. Sci. **2022**, *13*, 5118.



N_2 activation and fixation at B
Chem. Eur J. **2022**, *28*, e202200832.

Boron-based biradicals
Chem. Eur. J. **2021**, *27*, 5160.

Multiple H_2 activation at Nb_2
Dalton Trans. **2021**, *50*, 840.

Computational & Theoretical Chemistry @ Kent

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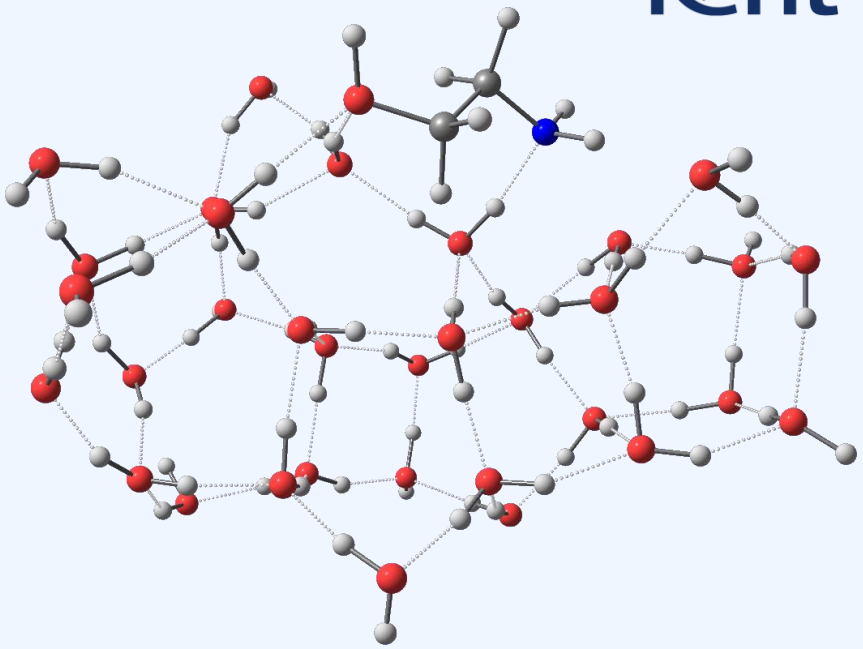
Astrochemistry & Astrobiology

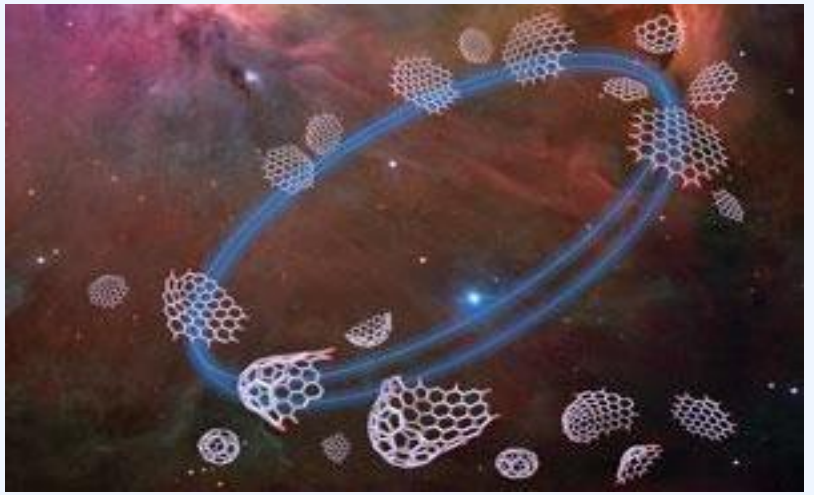
STRUCTURE AND **STABILITY** OF **ASTROCHEMICALLY-RELEVANT** MOLECULES AND IONS



MECHANISTIC INSIGHTS INTO **ASTROCHEMICAL** AND **PREBIOTIC REACTIONS**

SPECTROSCOPIC BIOSIGNATURES OF **PHOTOPROTECTIVE PIGMENTS**

MATERIALS DESIGN FOR **SPACE SCIENCE**



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UFRJ UNIVERSIDADE FEDERAL DO RIO DE JANEIRO

AARHUS UNIVERSITET

atomki DEBRECEN

LA VERDAD OS HARA LIBRES UNIVERSIDAD DE GUANAJUATO

MBN Research Center

europlanet SOCIETY

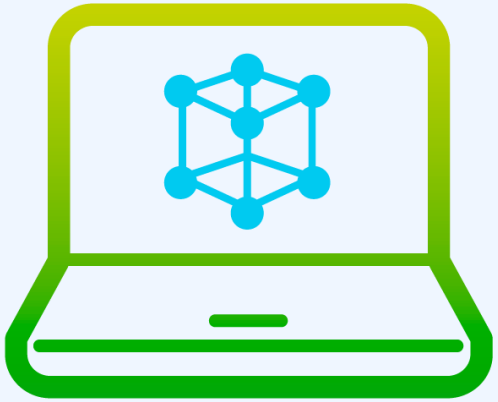
Computational Chemistry

Experiments can be **costly**

Experiments can be **dangerous**

Experiments can be **prohibited**

Solution:



Chemistry:

- Science dealing with **construction**, **transformation** and **properties** of **molecules**.

Theoretical Chemistry:

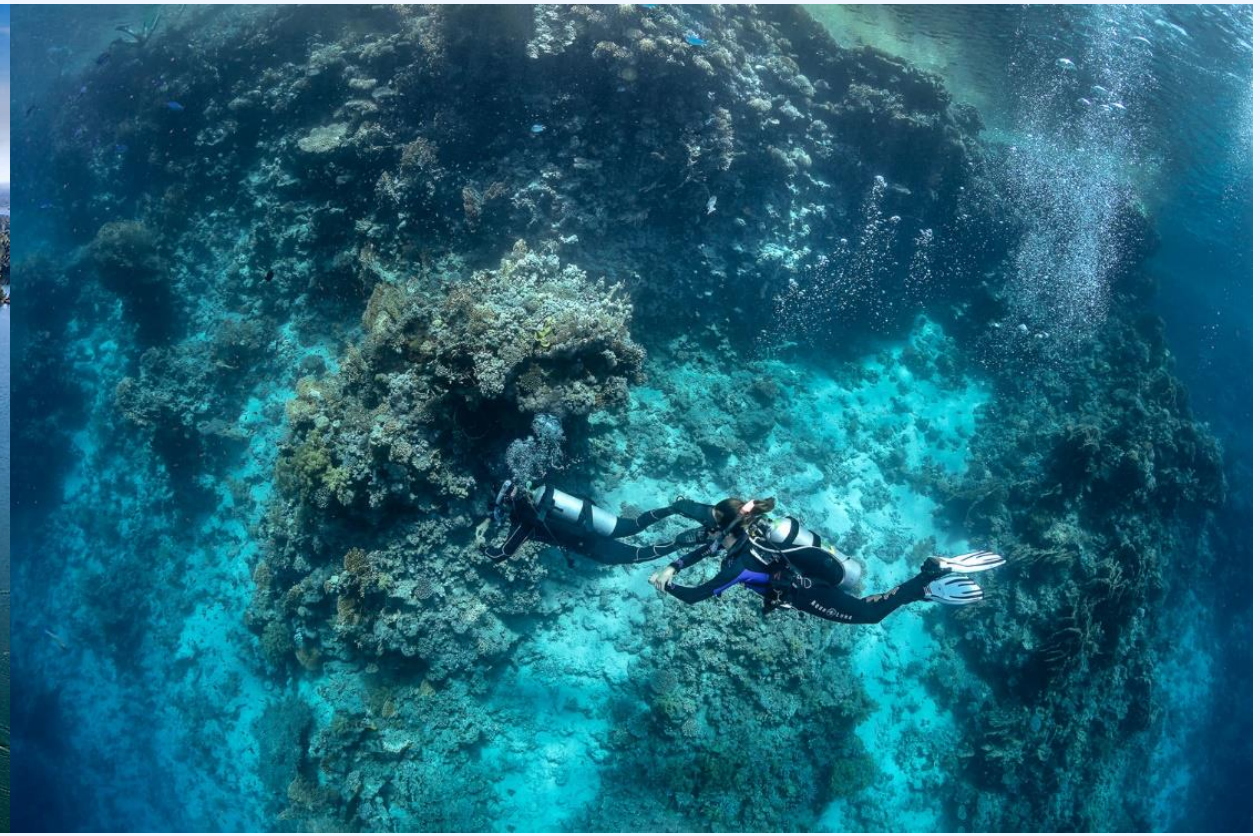
- **Mathematical methods** are combined with fundamental laws of **(chemical) physics** to study processes of **chemical relevance**.

Computational Chemistry:

- **Computers** use theoretical chemistry models as an **"experimental" tool**, probing molecules.
- Focus on obtaining **results** relevant to **chemical problems**.
- Which problems? **Limit** is your **imagination**!

Computational Chemistry in action!

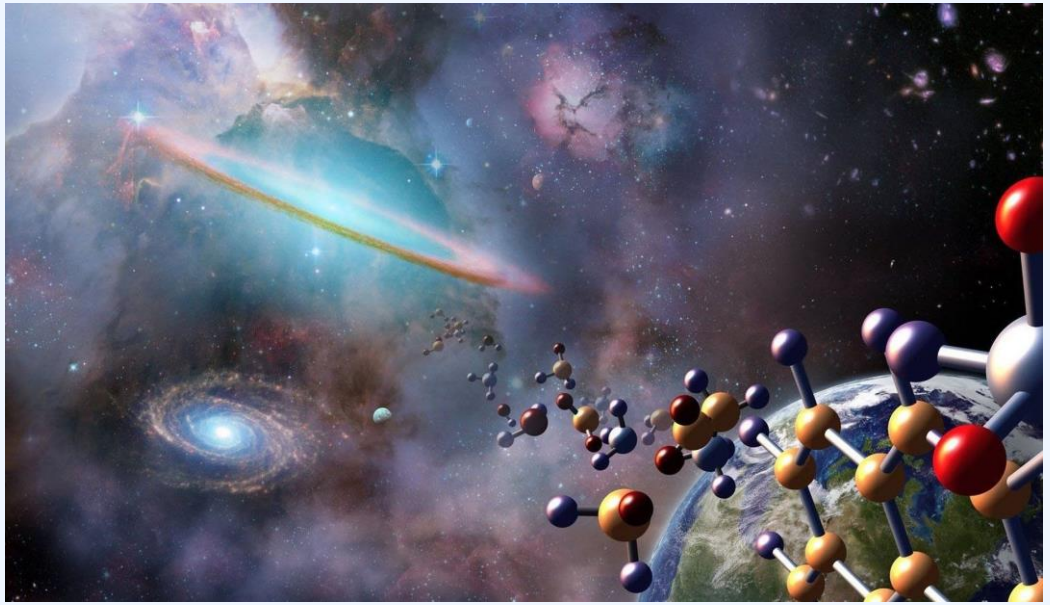
To boldly go where no experiment has gone before



Outline

Case studies of the investigation of astrophysically-relevant systems using quantum chemical models

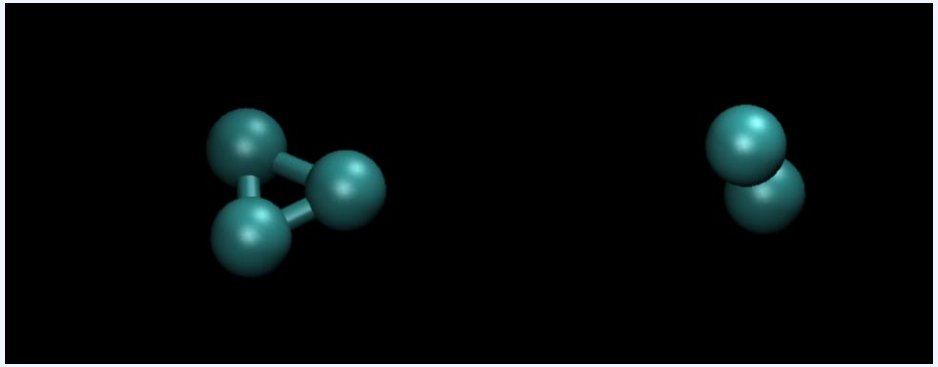
- Astrophysical **molecular ions**
  - **$C_2H_4O_2$** molecular ions
  - The **benzene** dication
  - Unusual systems featuring **C–Cl multiple bonds**
  - **$HNCO^{2+}$**
  - Multiply charged **naphthalene** and its isomers
  - **Noble-gas** molecular cations
- Simulation of electronic spectra of **amorphous ices** (H_2S)
- **Fullerenes** and hydrogenated fullerenes
- **Magnesium-bearing** carbon chains
- An interstellar **boron** carrier?

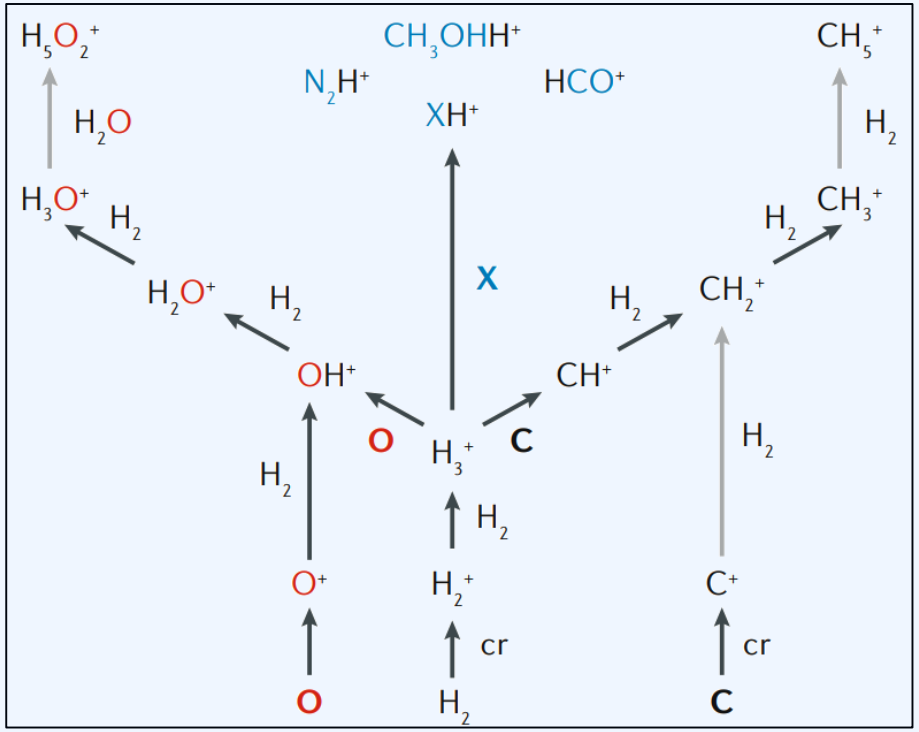


Astrophysical Molecular Ions

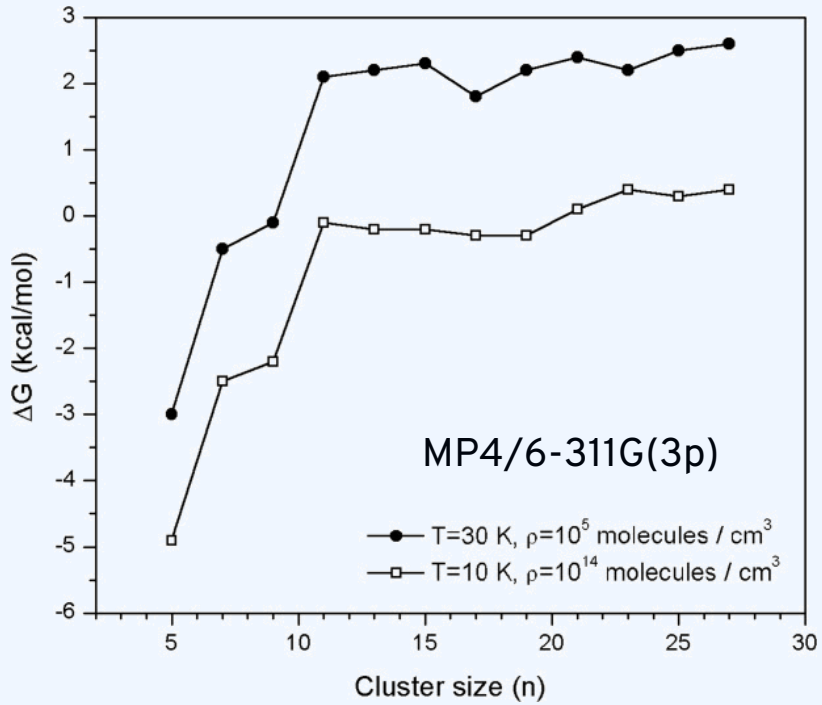
Molecular ions have a key role in **driving interstellar chemistry.**

- **Ion-molecule** reactions are usually **exothermic.**
- **Attractive potentials** increase **reaction rates.**
- More than **30 different ions** in interstellar environments.





B. A. McGuire, O. Asvany, S. Brünken, S. Schlemmer. *Nat. Rev. Phys.* **2020**, *2*, 402.

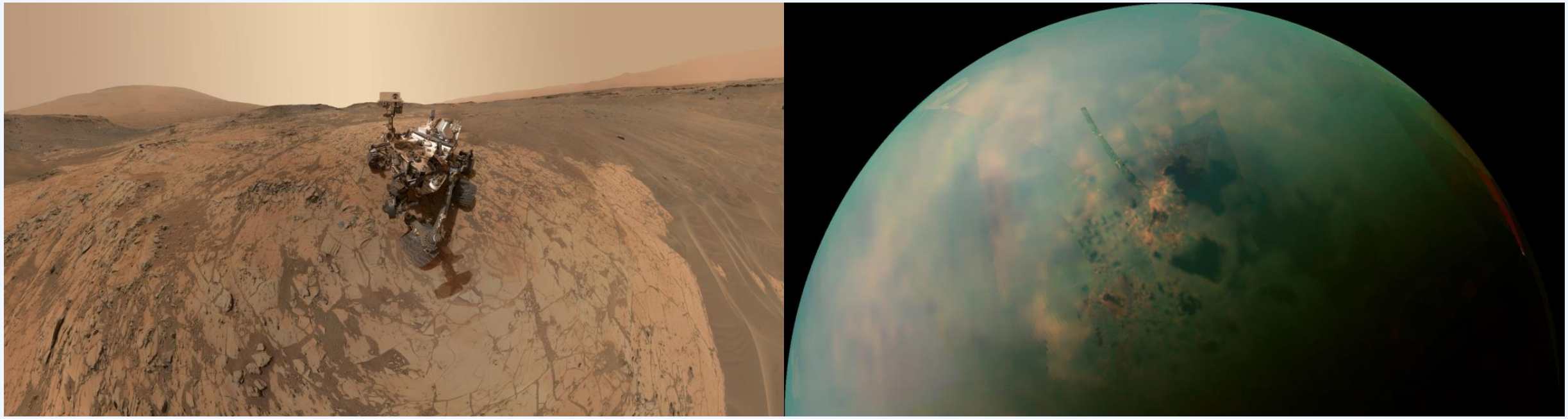


M. Barbatti, M. A. C. Nascimento. *Int. J. Quantum Chem.* **2012**, 112, 3169.

Astrophysical Molecular Ions

Molecular dications are also present in the **Solar System.**

- Layer of CO_2^{2+} in the **ionosphere of Mars** (155-160 km of altitude).
- Formation of N_2^{2+} in the **upper atmosphere of Titan** (1110-1200 km of altitude).



R. Thissen, O. Witasse, O. Dutuit, C. S. Wedlund, G. Gronoff, J. Lilensten. *PCCP* **2011**, *13*, 18264.

J. F. Lockyear, C. L. Ricketts, M. A. Parkes, S. D. Price. *Chem. Sci.* **2011**, *2*, 150

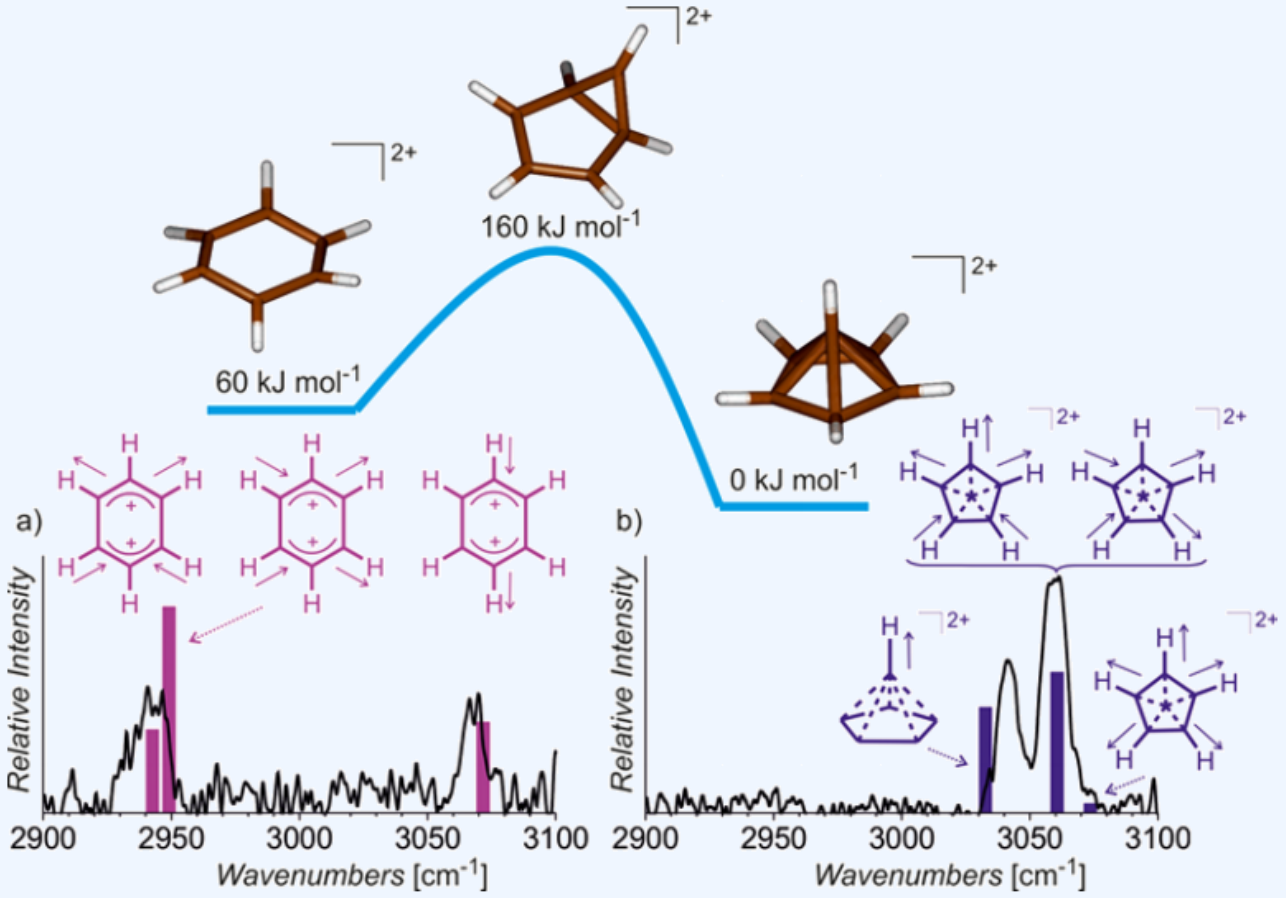
S. Falcinelli, F. Pirani, M. Alagia, L. Schio, R. Richter, S. Stranges, N. Balucani, F. Vecchiocattivi.. *Atmosphere* **2016**, *7*, 112.

S. Falcinelli, M. Rosi. *Molecules*, **2020**, *25*, 4157.

Astrophysical Molecular Ions

Interstellar complex organic molecular ions

- Can be formed by photon, electron, proton, or heavy particle **collision processes on molecules**.
- **Polyatomic systems**: several ways to stabilise the charge.
- Ionisation can trigger **isomerisation reactions**.
- Most stable **ionic structures** are different than those of the corresponding **neutral species**.
- Different structures lead to **different properties**.



Jašík, Gerlich, J. Roithová. *J. Am. Chem. Soc.* **2014**, *136*, 2960.

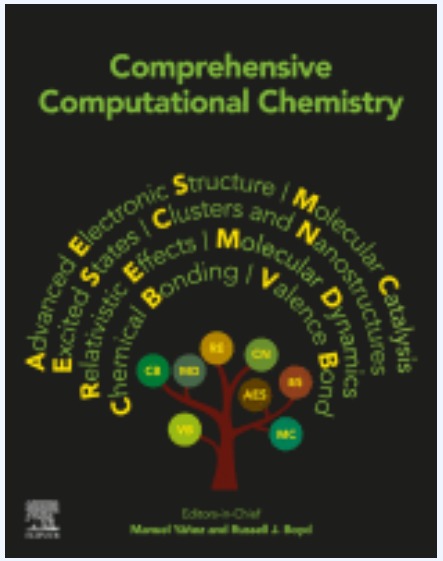
Astrophysical Molecular Ions

How to investigate molecular ions?

- **Challenging** to study **experimentally**.
- **Highly reactive** and difficult to produce in **large quantities**.
- **Computational chemistry** can map the most stable **structures** and investigate their **bonding situation**.

Computational protocol

- **Potential energy surface** exploration.
  - If automatic, Cluster; Automaton; Glomos.
- **Density Functional Theory** (DFT), **coupled-cluster** or **multireference** levels for geometry optimisations and vibrational frequencies.
- If DFT, single-point energies at the **coupled-cluster** or **multireference** levels (consider also **benchmark**).
- Investigation of the **bonding situation** of selected species.
  - Canonical Kohn-Sham Molecular Orbitals (KS-MOs)
  - Natural Bond Orbital (NBO)
  - Intrinsic Bond Orbital (IBO)
  - Natural Orbitals for Chemical Valence (NOCV)
  - Spin-Coupled Generalised Valence Bond (SCGVB)
  - **Interference Energy Analysis** (IEA)

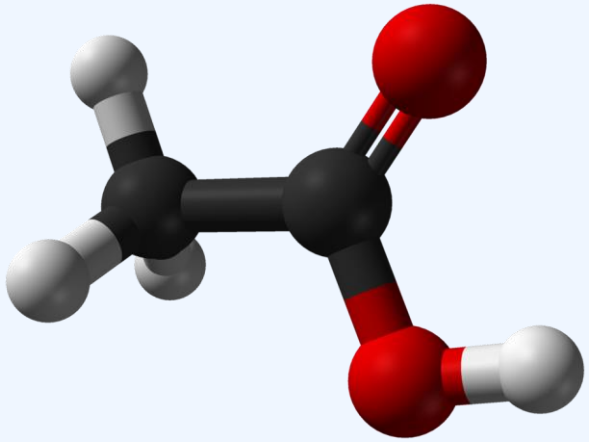


T. M. Cardozo, D. W. O. de Sousa, **F. Fantuzzi**, M. A. C. Nascimento, Comprehensive Computational Chemistry, **2024**, *1*, 552-588; **2024**, *1*, 589-604.

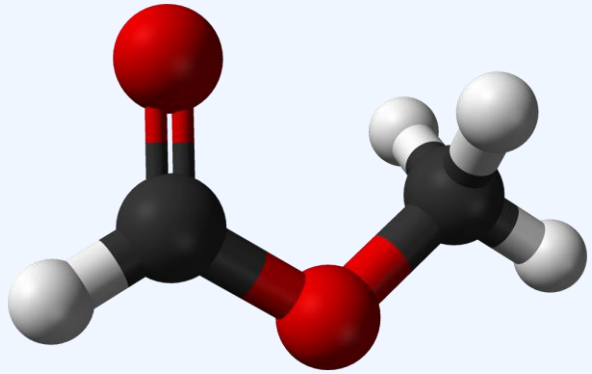
$C_2H_4O_2$ Molecular Ions

$C_2H_4O_2$: The first interstellar isomeric triad

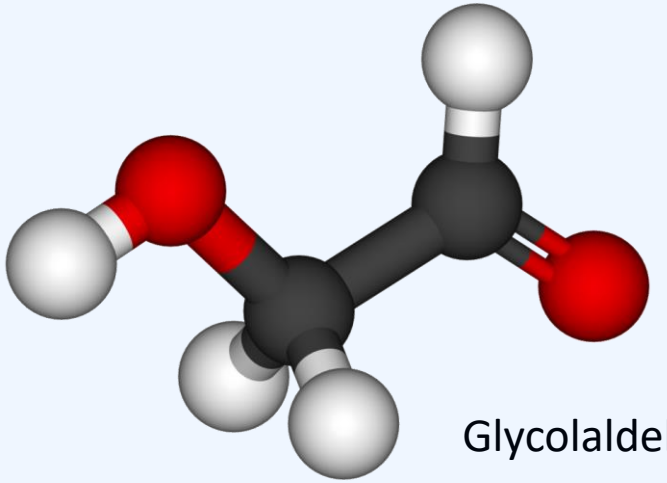
- Important group of **complex organic molecules** (COMs).
- Detected in an increasingly **wide range** of **astrophysical environments**.
- Important in **interstellar chemistry** and may also have a role as **prebiotic species**.
- **Glycolaldehyde**: simplest of the monosaccharide **sugars**.
- Are these structures **resistant** enough towards **single** and **double** ionisation?
- What are the **most stable structures** of the **$C_2H_4O_2$+** and **$C_2H_4O_2^{2+}$** systems?



Acetic acid (CH_3COOH)



Methyl formate ($HCOOCH_3$)



Glycolaldehyde (CH_2OHCHO)

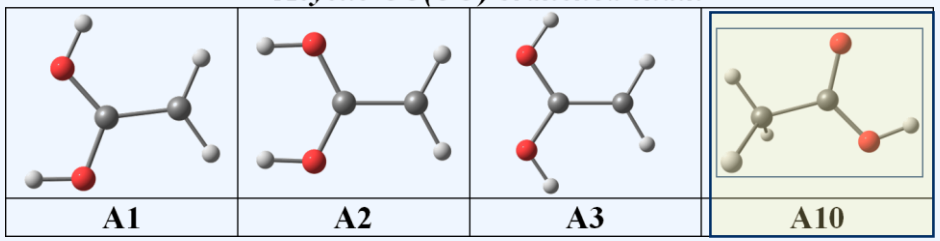
S. J. El-Abd, C. L. Brogan, T. R. Hunter, E. R. Willis, R. T. Garrod, B. A. McGuire. *ApJ* **2019**, *883*, 129.

$C_2H_4O_2$ Molecular Ions

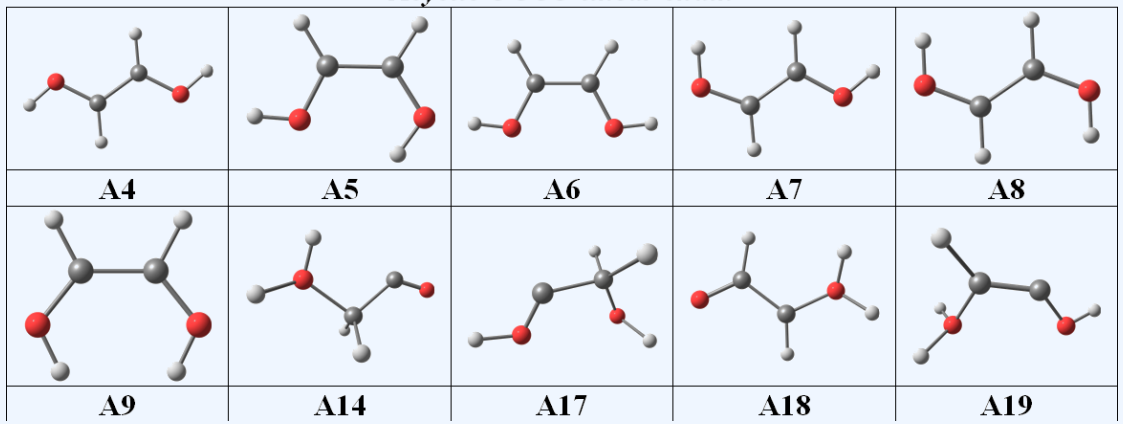
$C_2H_4O_2^+$

- Most stable $C_2H_4O_2^+$ species are **enolic.**
- **1,1-enols** more stable than 1,2-enols.
- **A10** (acetic acid: 17.4 kcal/mol); **A15** (methyl formate: 38.5 kcal/mol).

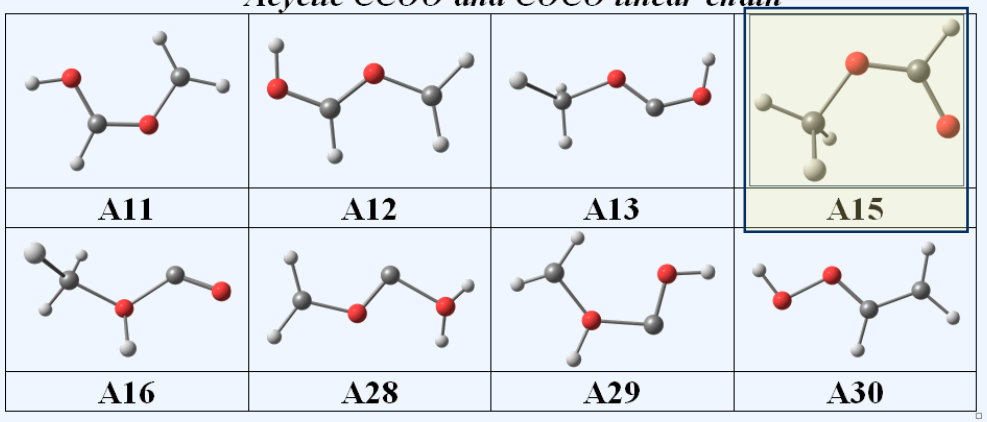
Acyclic CC(OO) branched chain



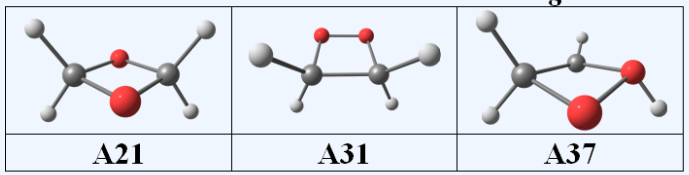
Acyclic OCCO linear chain



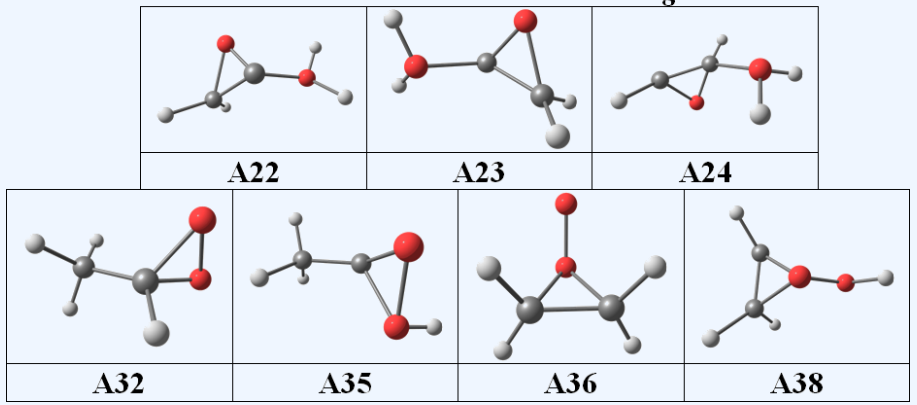
Acyclic CCOO and COCO linear chain



CCOO or COCO 4-membered ring



OCC or OOC 3-membered ring

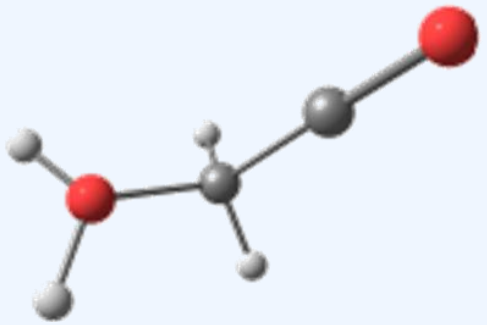


F. Fantuzzi, S. Pilling, A. C. F. Santos, L. Baptista, A. B. Rocha, H. M. Boechat-Roberty. *MNRAS* **2011**, *417*, 2631.
F. Fantuzzi, L. Baptista, A. B. Rocha, H. M. Boechat-Robery. *Int. J. Quantum Chem.* **2012**, *112*, 3303.

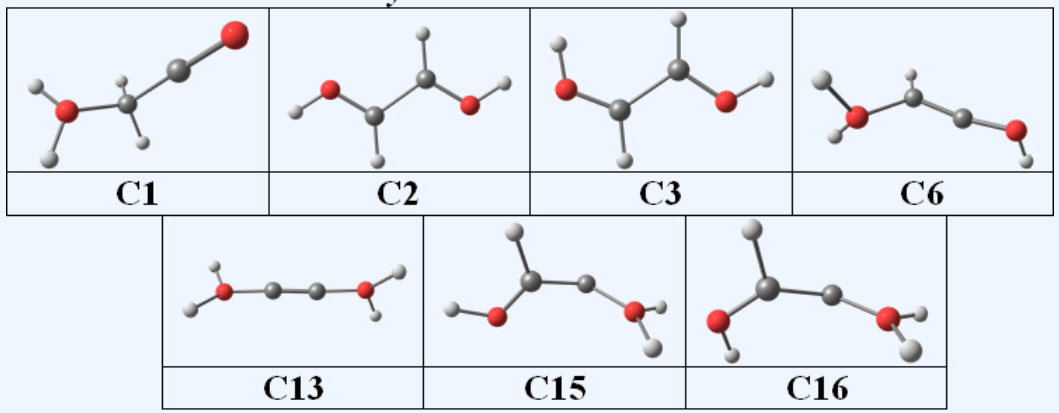
$C_2H_4O_2$ Molecular Ions

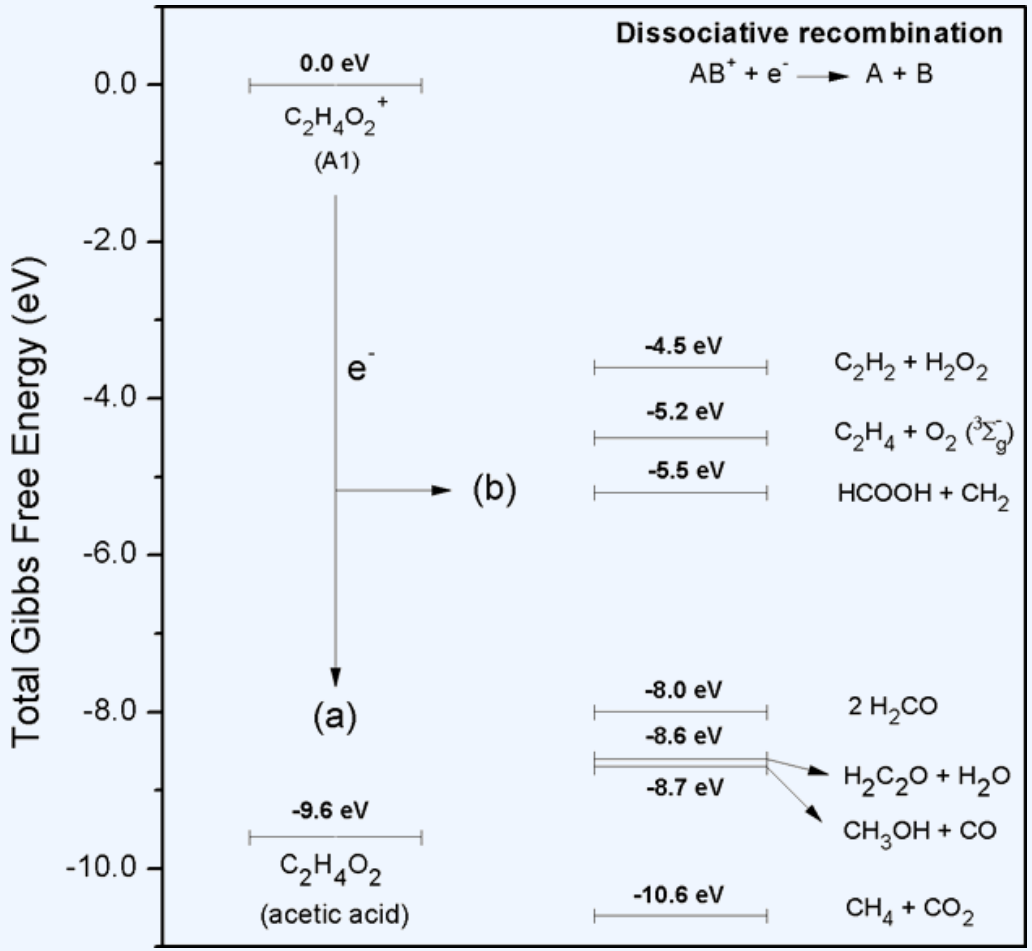
$C_2H_4O_2^{2+}$

- Most stable $C_2H_4O_2^{2+}$: **no neutral analogue.**
- H_2O^+ and $C{\equiv}O^+$ terminals.



Acyclic OCCO linear chain





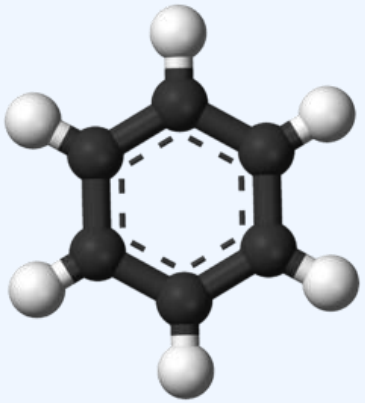
Preferential formation of $CH_4 + CO_2$ by **dissociative recombination**.

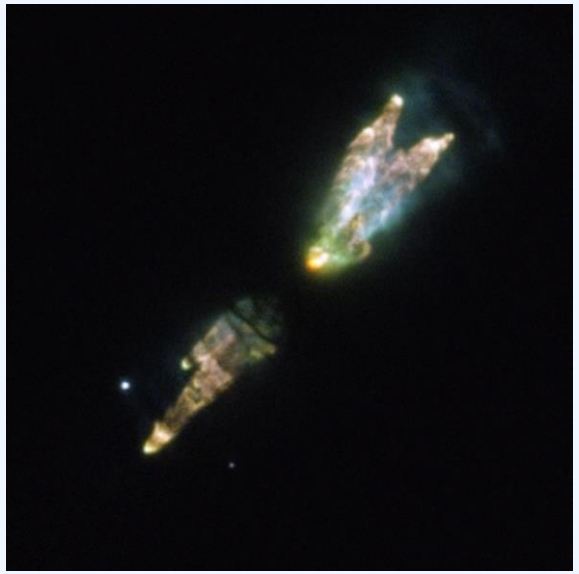
F. Fantuzzi, S. Pilling, A. C. F. Santos, L. Baptista, A. B. Rocha, H. M. Boechat-Roberty. *MNRAS* **2011**, *417*, 2631.
F. Fantuzzi, L. Baptista, A. B. Rocha, H. M. Boechat-Robery. *Int. J. Quantum Chem.* **2012**, *112*, 3303.

The Benzene Dication

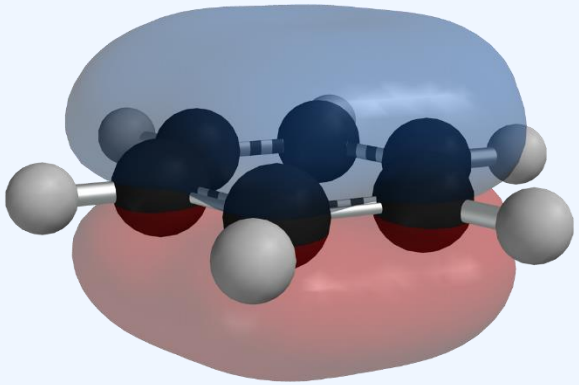
Benzene (C_6H_6)

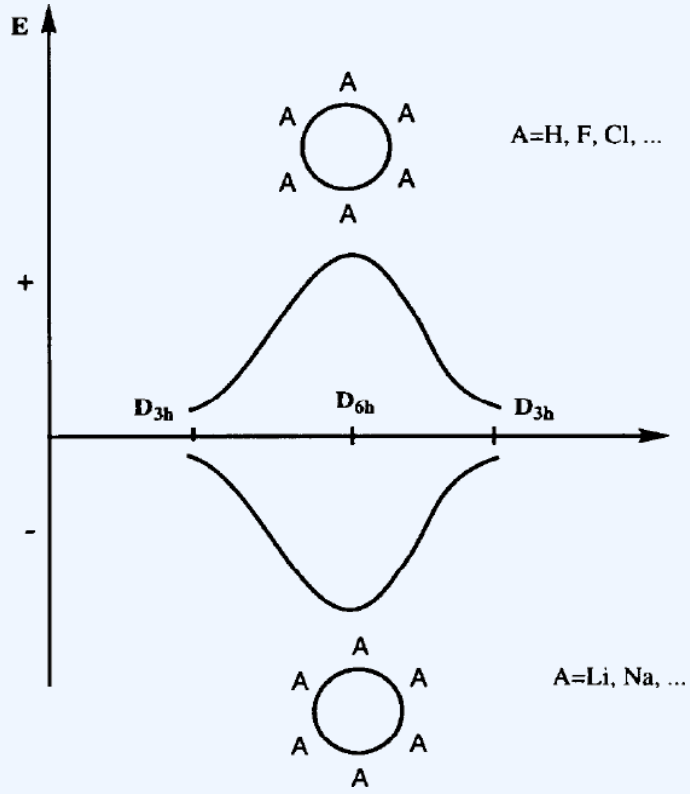
- Basic unit of **polycyclic aromatic hydrocarbons** (PAHs).
- **Cyclic** structure of **D_{6h} symmetry**.
- No **permanent electric dipole moment**.
- Nature of the chemical bond in benzene is **still a matter of debate**.
- First detection by Cernicharo in the PNe **CRL 618** using **infrared** (ISO).





J. Cernicharo, A. M. Heras, A. G. G. M. Tielens, J. R. Pardo, F. Herpin, M. Guélin, L. B. F. M. Waters. *ApJ*, **2001**, *546*, L123.

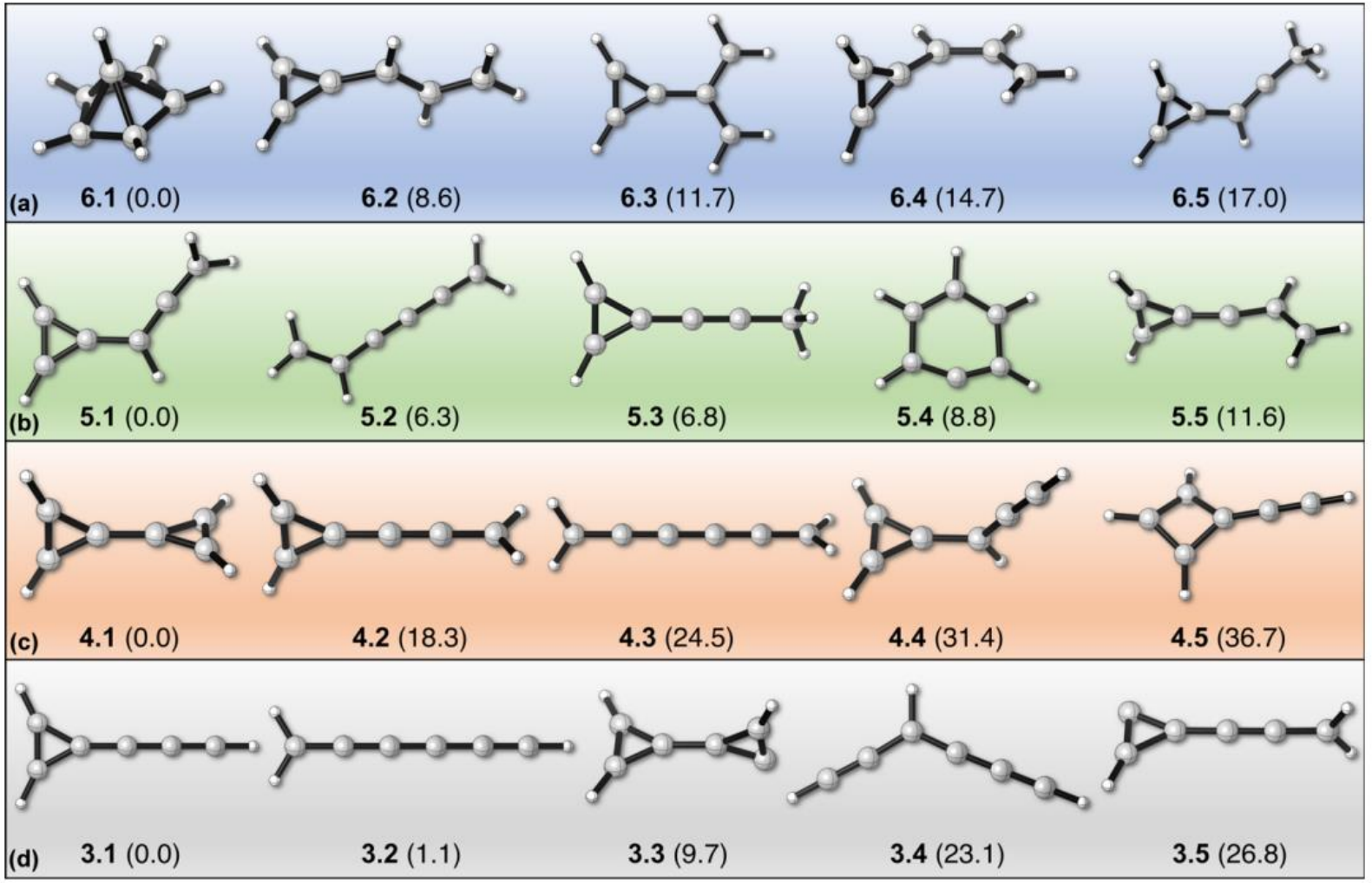




S. Shaik, A. Shurki, D. Danovich, P. C. Hiberty. *J. Mol. Struc.* **1997**, *398*, 155-167.
S. Shaik, A. Shurki, D. Danovich, P. C. Hiberty. *Chem. Rev.* **2001**, *101*, 1501-1539.
T. M. Cardozo, **F. Fantuzzi**, M. A. C. Nascimento. *Phys. Chem. Chem. Phys.* **2014**, *16*, 11024-11030.

The $C_6H_n^{2+}$ systems

CCSD(T)/def2-QZVPP//PBE0/def2-TZVPP

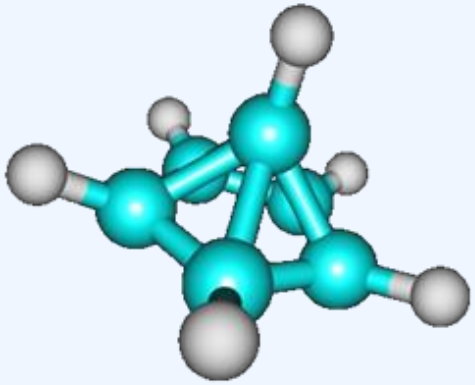


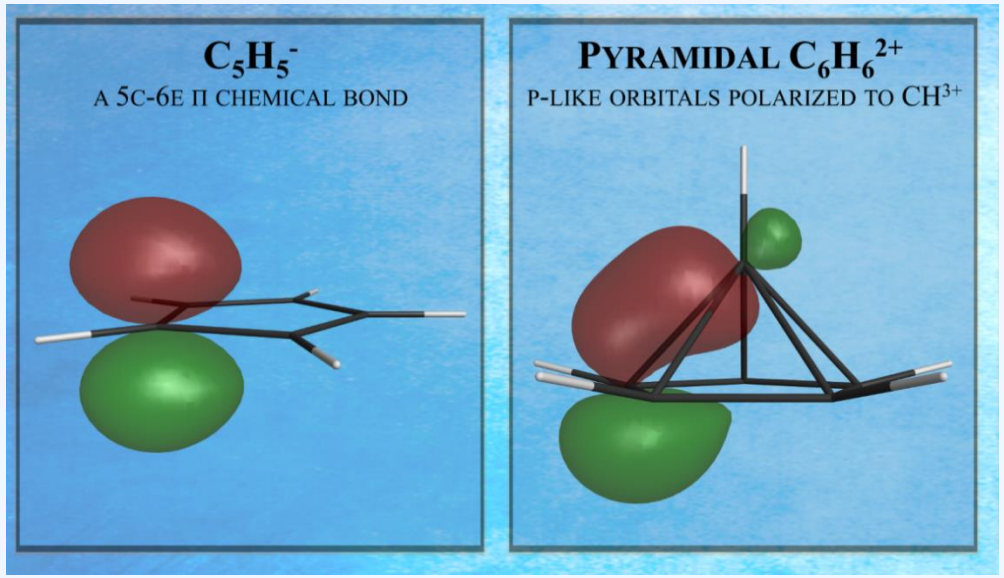
W. Wolff, A. Perlin, R. R. Oliveira, **F. Fantuzzi**, L. H. Coutinho, F. A. Ribeiro, G. Hilgers. *J. Phys. Chem A* **2020**, *124*, 9261.

The Benzene Dication

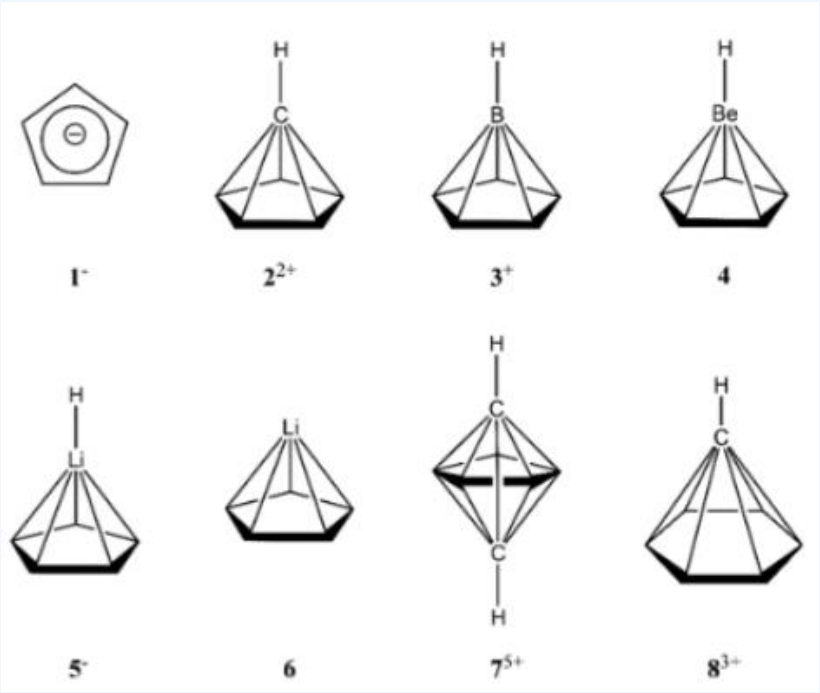
Chemical bond in $C_6H_6^{2+}$

- Global minimum: **pentagonal-pyramidal structure.**
- Bonding situation analogous to that of **cyclopentadienyl.**
- Replacement of CH^{3+} cap leads to structures with **similar bonding situation.**





SCGVB calculations



F. Fantuzzi, D. W. O. de Sousa, M. A. C. Nascimento. *Comp. Theor. Chem.* **2017**, *1116*, 225.

Astrochemical C–Cl Bonds

University of Kent

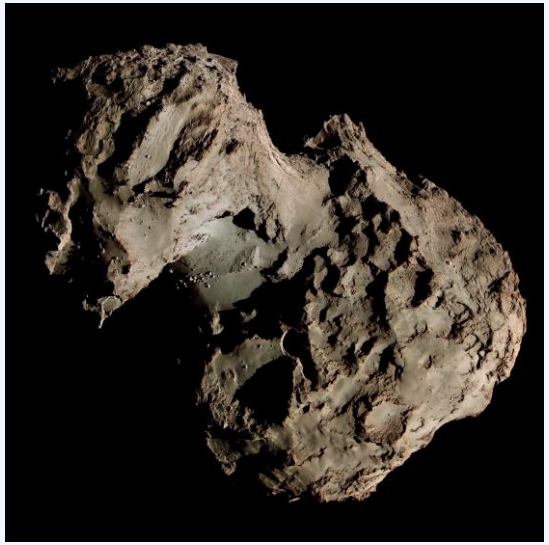
Organohalogens

- Molecules that contain at least **one halogen atom bonded to carbon**.
- Abundant on the Earth, mainly produced through **industrial** and **biological** processes.
  - Proposed as **biomarkers** in the search for life on **exoplanets**.
- **2017**: Interstellar **detection** of two isotopologues of CH_3Cl in the low-mass protostar **IRAS 16293–2422**.
  - Same work: **detection** of CH_3Cl in the coma of the comet **67P/Churyumov–Gerasimenko**.
  - Cometary impacts may deliver organohalogens to young planets.
    - **Potential abiotical production**.

nature astronomy
LETTERS
DOI: 10.1038/s41550-017-0237-7

Protostellar and cometary detections of organohalogens

Edith C. Fayolle[1*], Karin I. Öberg[1], Jes K. Jørgensen[2], Kathrin Altwegg[3,4], Hannah Calcutt[2], Holger S. P. Müller[5], Martin Rubin[3], Matthijs H. D. van der Wiel[6], Per Bjerkeli[7], Tyler L. Bourke[8], Audrey Coutens[9], Ewine F. van Dishoeck[10,11], Maria N. Drozdovskaya[4], Robin T. Garrod[12], Niels F. W. Ligterink[10,13], Magnus V. Persson[7], Susanne F. Wampfler[4] and the ROSINA team[14]

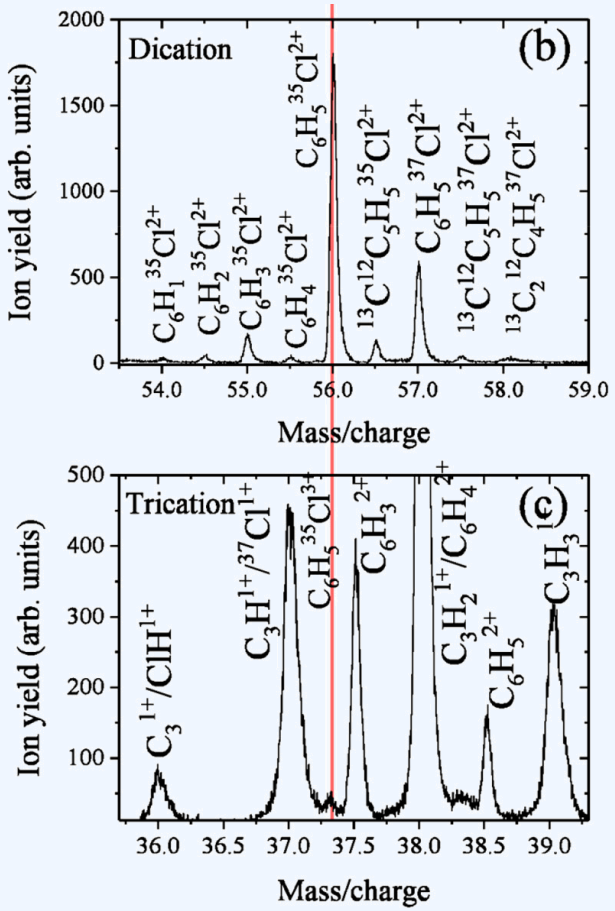


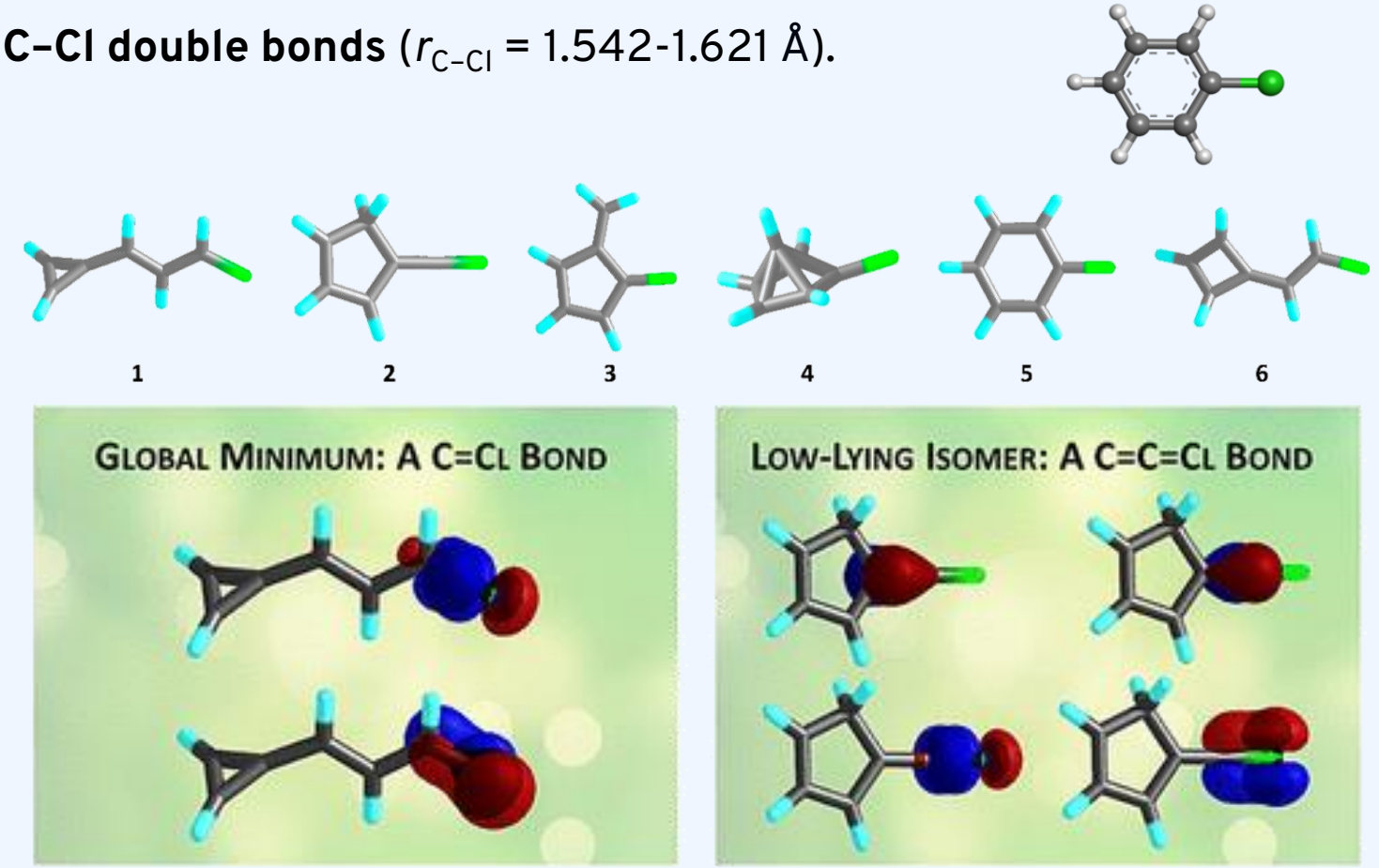
E. C. Fayolle et al. *Nat. Astron.* **2017**, *1*, 703–708.

Unusual C–Cl Multiple Bonds

Chlorobenzene (C_6H_5Cl) and its multiply charged isomers

- C_6H_5Cl **dication** and **trication** species were observed **in proton impact** experiments on **chlorobenzene**.
- Most stable structures: **unusual C–Cl double bonds** (r_{C-Cl} = 1.542-1.621 Å).





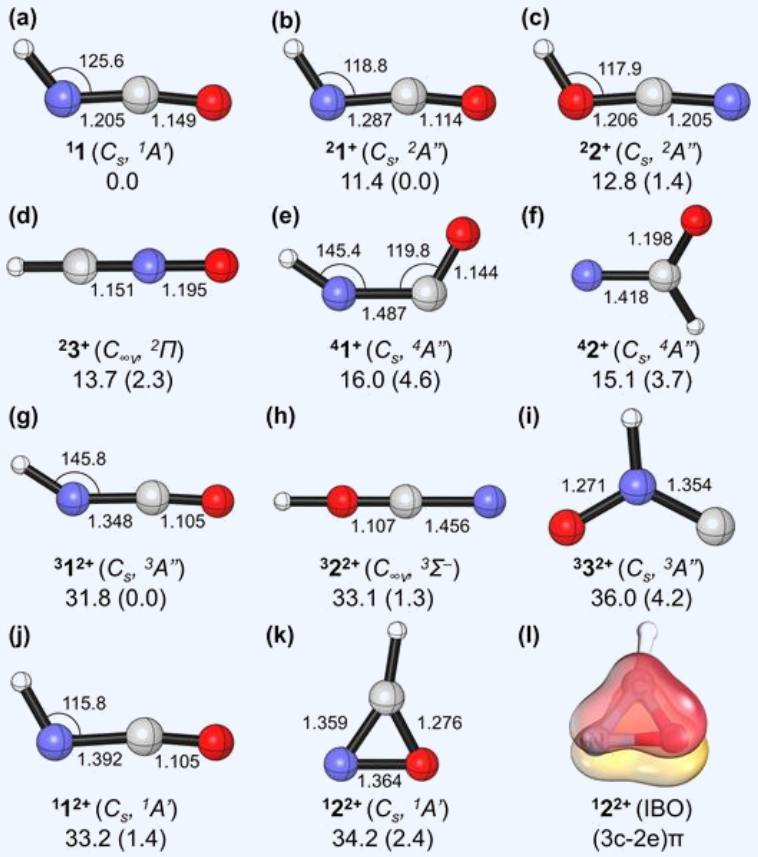
F. Fantuzzi, B. Rudek, W. Wolff, M. A. C. Nascimento. *J. Am. Chem. Soc.* **2018**, *140*, 4288-4292.

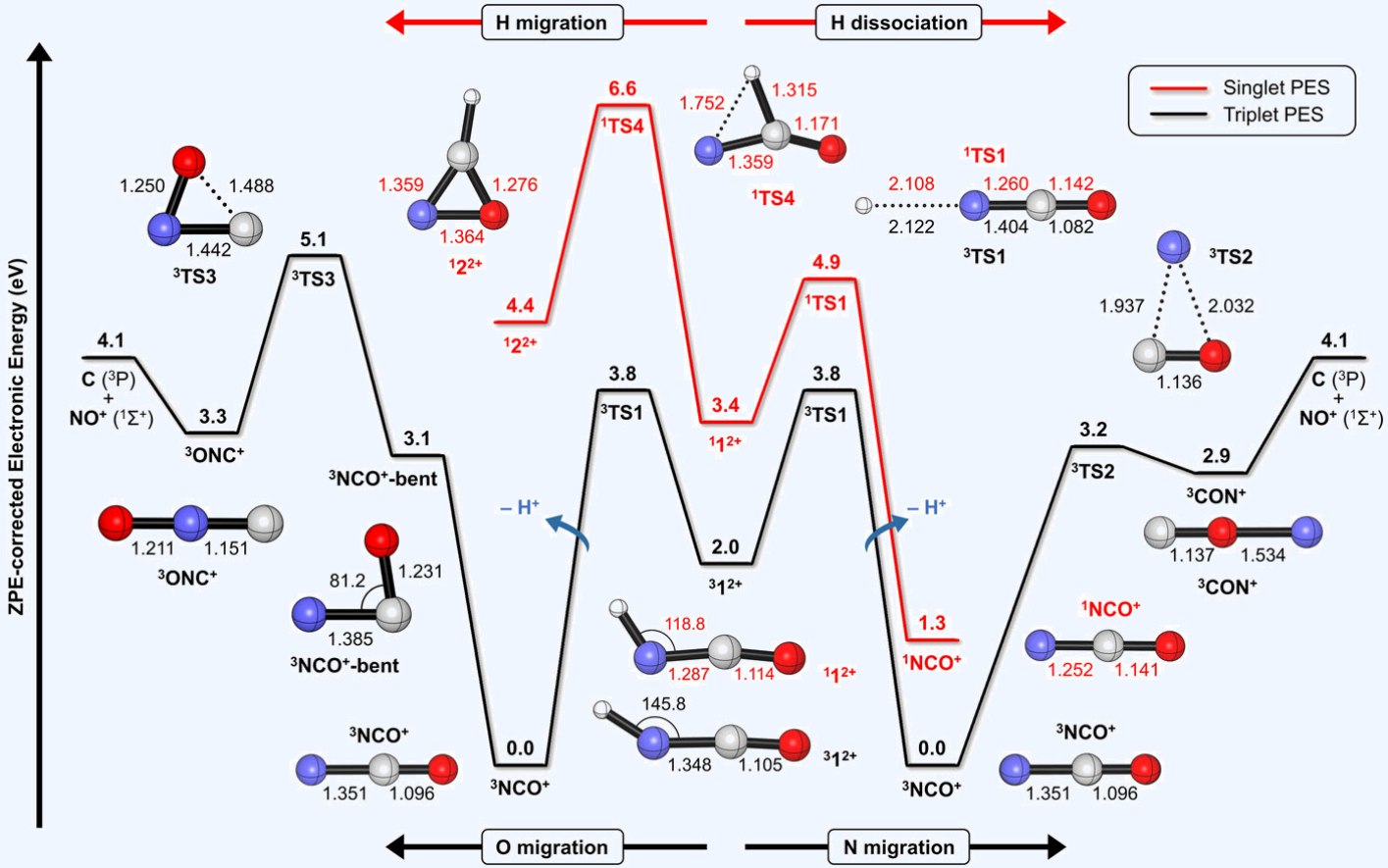
$HNCO^{2+}$

- HNCO: firstly detected in **Sgr B2** (1972).
  - Contains the **four most important elements** of **organic life**.
  - May play a key **astrobiological role**.
  - **Bent** molecule.
- **$HNCO^{2+}$**: Electronic structure? Fragmentation pathways?

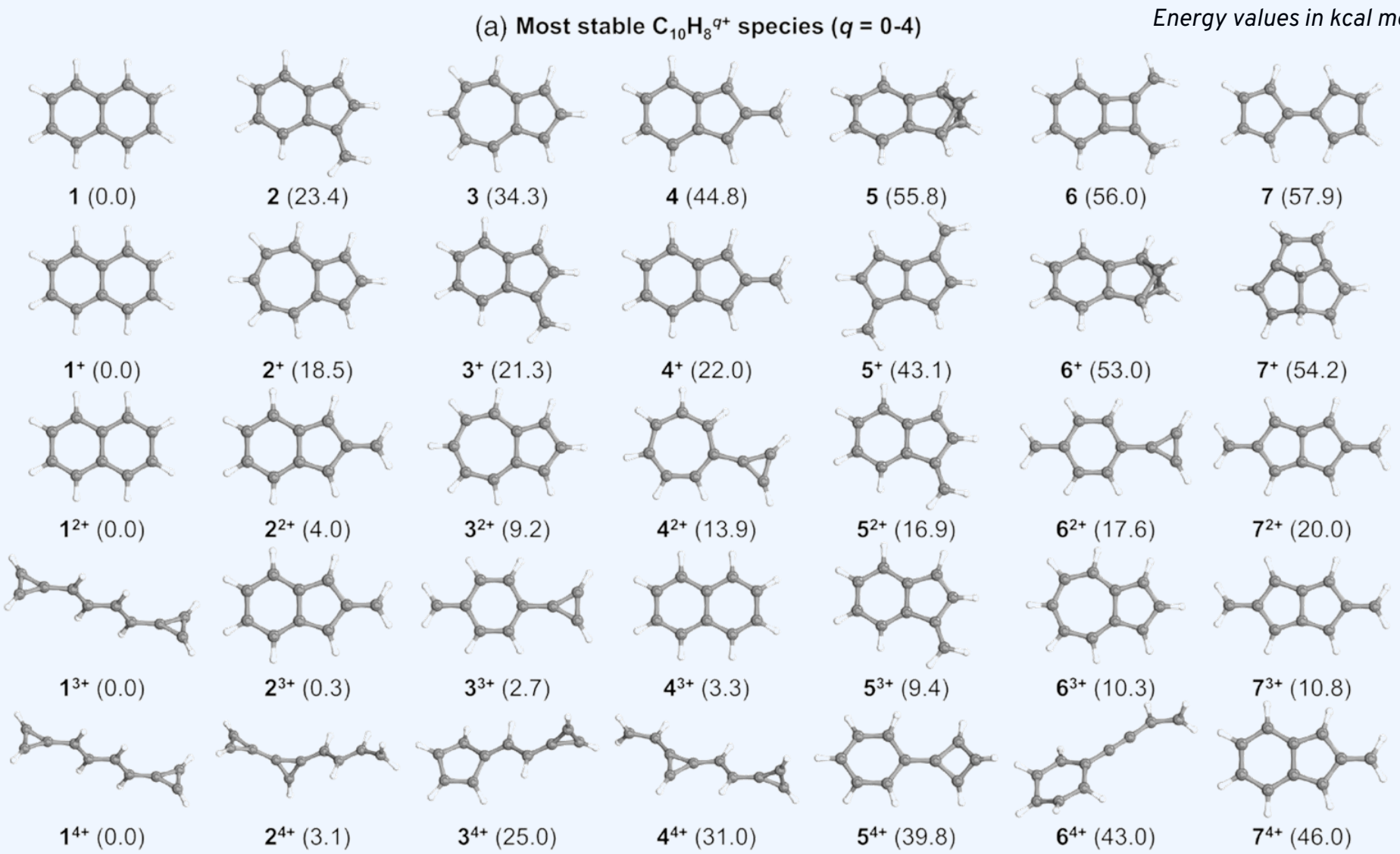
M. Gerlach, **F. Fantuzzi**, L. Wohlfart, K. Kopp. B. Engels, J. Bozek, C. Nicolas, D. Mayer, M. Gühr, F. Holzmeier, I. Fischer. *J. Chem. Phys.* **2021**, 154, 114302.

MRCI/CASSCF(14,12)/def2-QZVPP
Exp. NCO^+/NO^+ shift: 4-5 eV

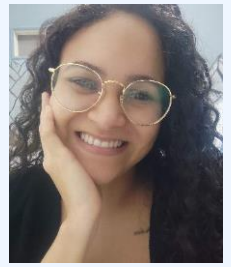




Multiply charged naphthalene and its isomers



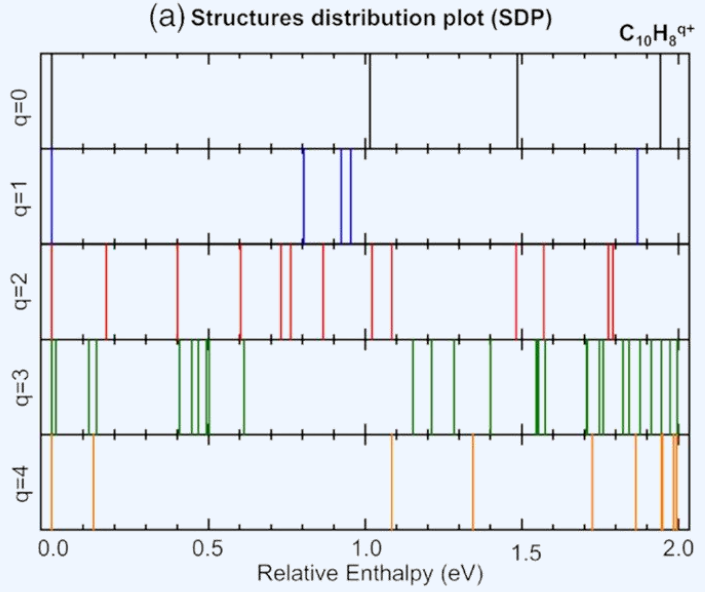
Julia Santos

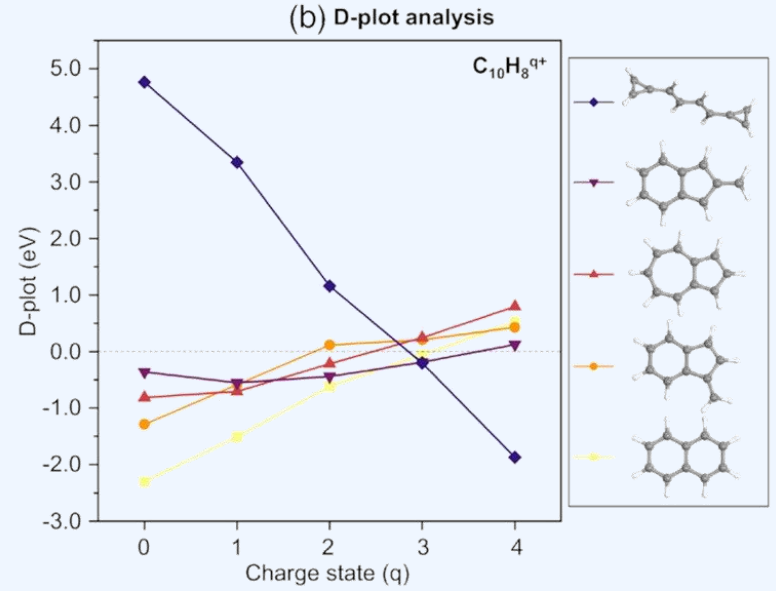


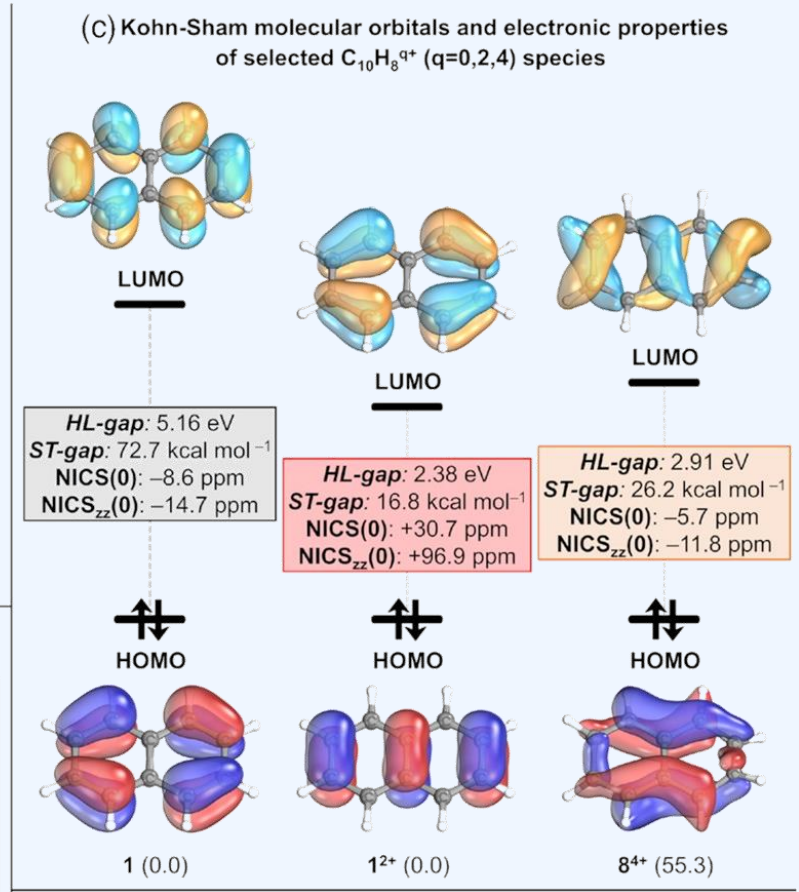
Yanna Martins-Franco

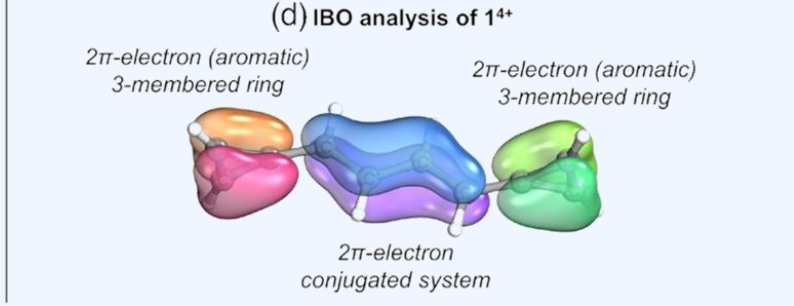
J. C. Santos, **F. Fantuzzi**, H. M. Quitián-Lara, Y. Martins-Franco, K. Menéndez-Delmestre, H. M. Boechat-Roberty, R. R. Oliveira. *MNRAS* **2022**, *512*, 4669.

Multiply charged naphthalene and its isomers

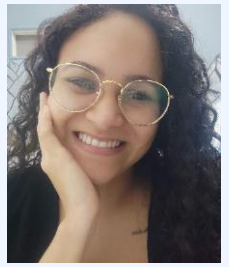








Julia Santos



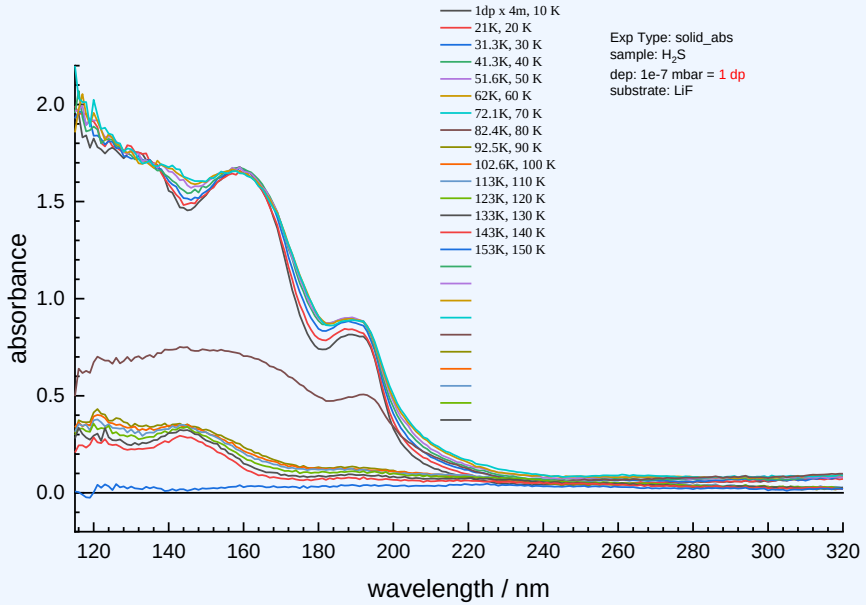
Yanna Martins-Franco

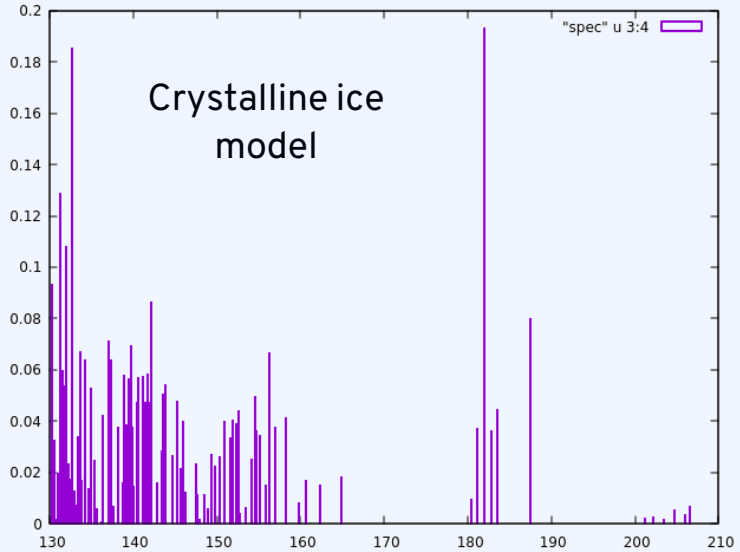
J. C. Santos, **F. Fantuzzi**, H. M. Quitián-Lara, Y. Martins-Franco, K. Menéndez-Delmestre, H. M. Boechat-Roberty, R. R. Oliveira. *MNRAS* **2022**, *512*, 4669.

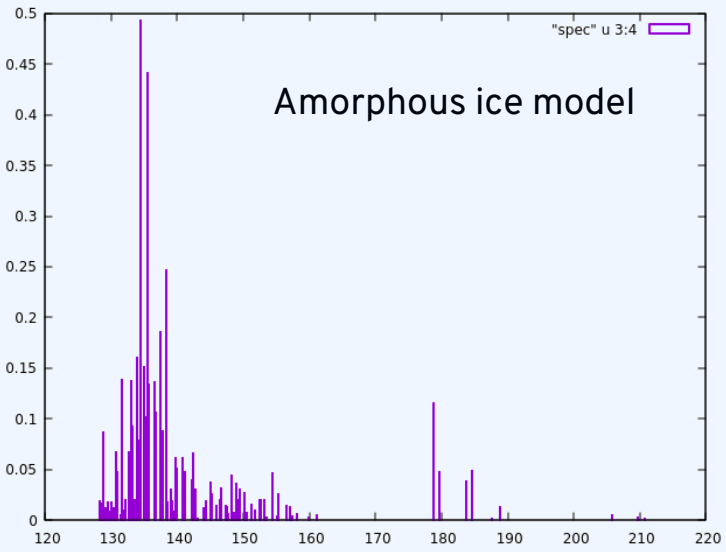
H_2S Ices

Cauê Souza

- Protocol for the prediction of **electronic absorption spectra** of **amorphous interstellar ices**
  - **TD-DFT calculations** (100 states) benchmarked against high-accurate **DLPNO-EOM-CCSD**.
  - **Amorphous ice**: $(H_2S)_n$ clusters obtained by MD simulations.
  - **Crystalline ice**: $(H_2S)_n$ cluster obtained from the crystal structure.
  - **Amorphous ice model**: spectrum describes better the features at 180–200 nm and 140–180 nm.
  - **Crystalline ice model**: describes the broader region below 150 nm.







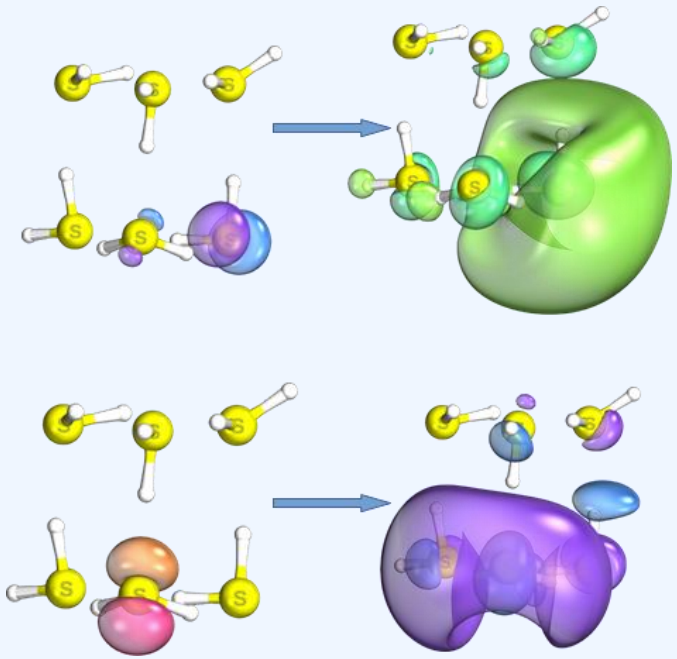
Unpublished results

Protocol adapted from D. E. Woon, Mol. Phys. **2023**, e2254419

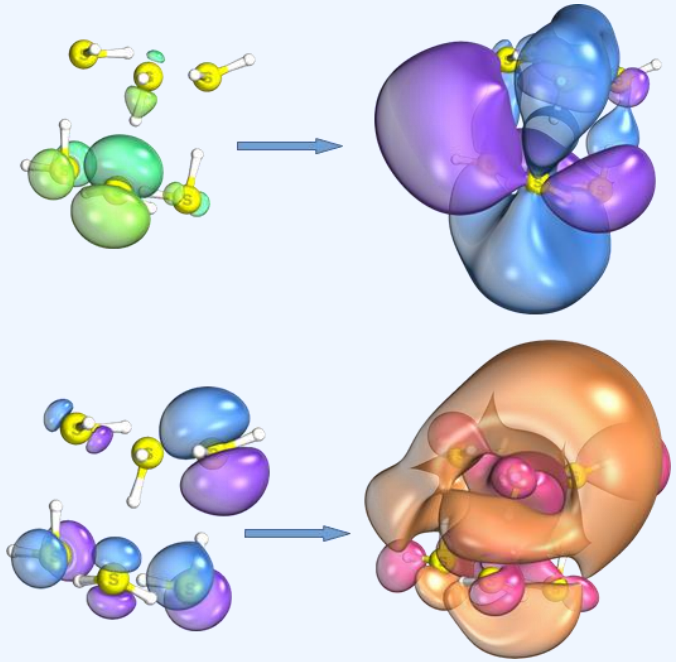
H_2S Ices

Cauê Souza

- Protocol for the prediction of **electronic absorption spectra** of **amorphous interstellar ices**
  - **Lower energy transitions** (ca. 188 nm): **charge transfer** from one H_2S to multiple molecules.
    - The starting orbitals resemble those of the isolated molecule.
  - **Higher energy transitions** (ca. 156 nm): collective character, Rydberg transitions.



188 nm



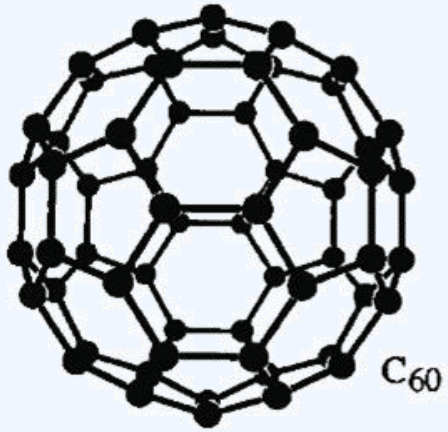
156 nm (other 2 contributions)

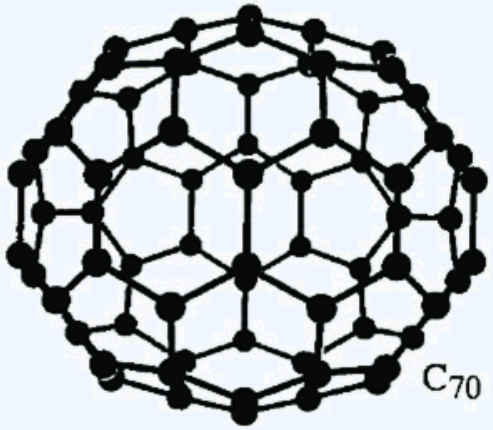
Unpublished results

Protocol adapted from D. E. Woon, Mol. Phys. **2023**, e2254419

Interstellar Fullerenes

- 2010: C_{60} and C_{70} observed in the carbon-rich planetary nebula Tc1 through its **infrared spectrum**.
- C_{60}^{+}: **carrier** of a diffuse interstellar band.





REPORTS

Detection of C_{60} and C_{70} in a Young Planetary Nebula

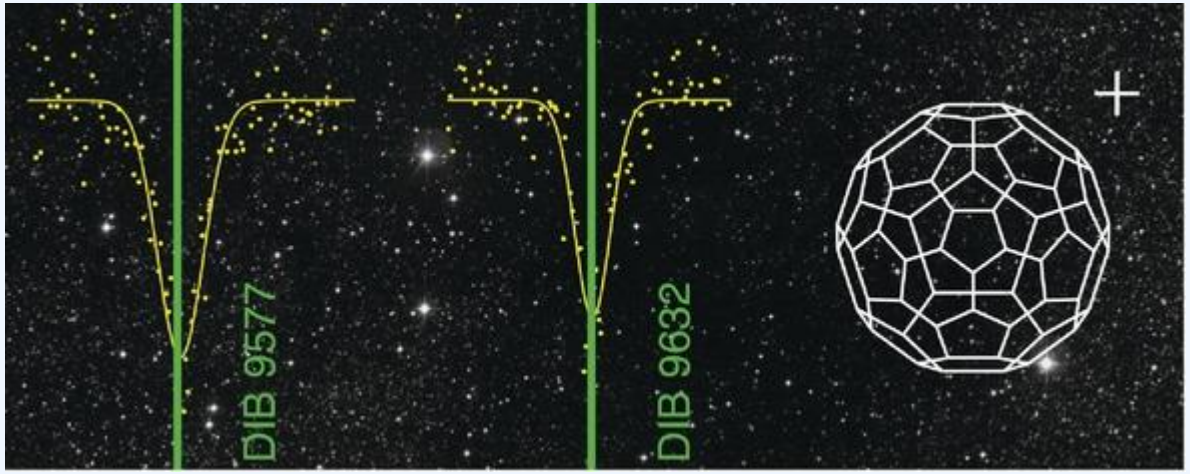
Jan Cami,[1,2]* Jeronimo Bernard-Salas,[3,4] Els Peeters,[1,2] Sarah Elizabeth Malek[1]

In recent decades, a number of molecules and diverse dust features have been identified by astronomical observations in various environments. Most of the dust that determines the physical and chemical characteristics of the interstellar medium is formed in the outflows of asymptotic giant branch stars and is further processed when these objects become planetary nebulae. We studied the environment of Tc 1, a peculiar planetary nebula whose infrared spectrum shows emission from cold and neutral C_{60} and C_{70}. The two molecules amount to a few percent of the available cosmic carbon in this region. This finding indicates that if the conditions are right, fullerenes can and do form efficiently in space.

Interstellar dust makes up only a small fraction of the matter in our galaxy, but it plays a crucial role in the physics and chemistry of the interstellar medium (ISM) and star-forming regions (*1*). The bulk of this dust is created in the outflows of old, low-mass asymptotic giant branch (AGB) stars; such outflows are slow (5 to 20 km/s) but massive (10^{-8} to 10^{-4} solar masses per year) (*2*–*4*). Once most of the envelope is ejected, the AGB phase ends and the stellar core—a hot white dwarf—becomes gradually more exposed. When this white dwarf ionizes the stellar ejecta, they become visible as a planetary nebula (PN).

Chemical reactions and nucleation in the AGB outflows transform the atomic gas into molecules and dust grains. For carbon-rich AGB stars (sometimes called carbon stars), this results in a large polycyclic aromatic hydrocarbons (PAHs) and fullerenes (*8*, *9*), a class of large carbonaceous molecules that were discovered in laboratory experiments aimed at understanding the chemistry in carbon stars (*10*). Fullerenes have unique physical and chemical properties, and the detection of fullerenes and the identification of their formation site are therefore considered a priority in the field of interstellar organic chemistry (*11*). However, astronomical searches for fullerenes in interstellar and circumstellar media have not resulted in conclusive evidence (*12*–*14*). The most promising case to date is the detection of two diffuse interstellar bands (DIBs) in the near-infrared (*15*) whose wavelengths are close to laboratory spectra of C_{60}^{+} in solid matrices (*16*); this finding awaits confirmation from comparison to a cold, gas-phase spectrum.

Here, we report on the detection of the fullerenes C_{60} and C_{70} in the circumstellar environment of Tc 1. Tc 1 is a young, low-excitation PN where the white dwarf is still enshrouded by the dense stellar ejecta. At optical wavelengths, Tc 1 shows Hα emission up to ~50 arc sec away from the central star, but the PN also has a much

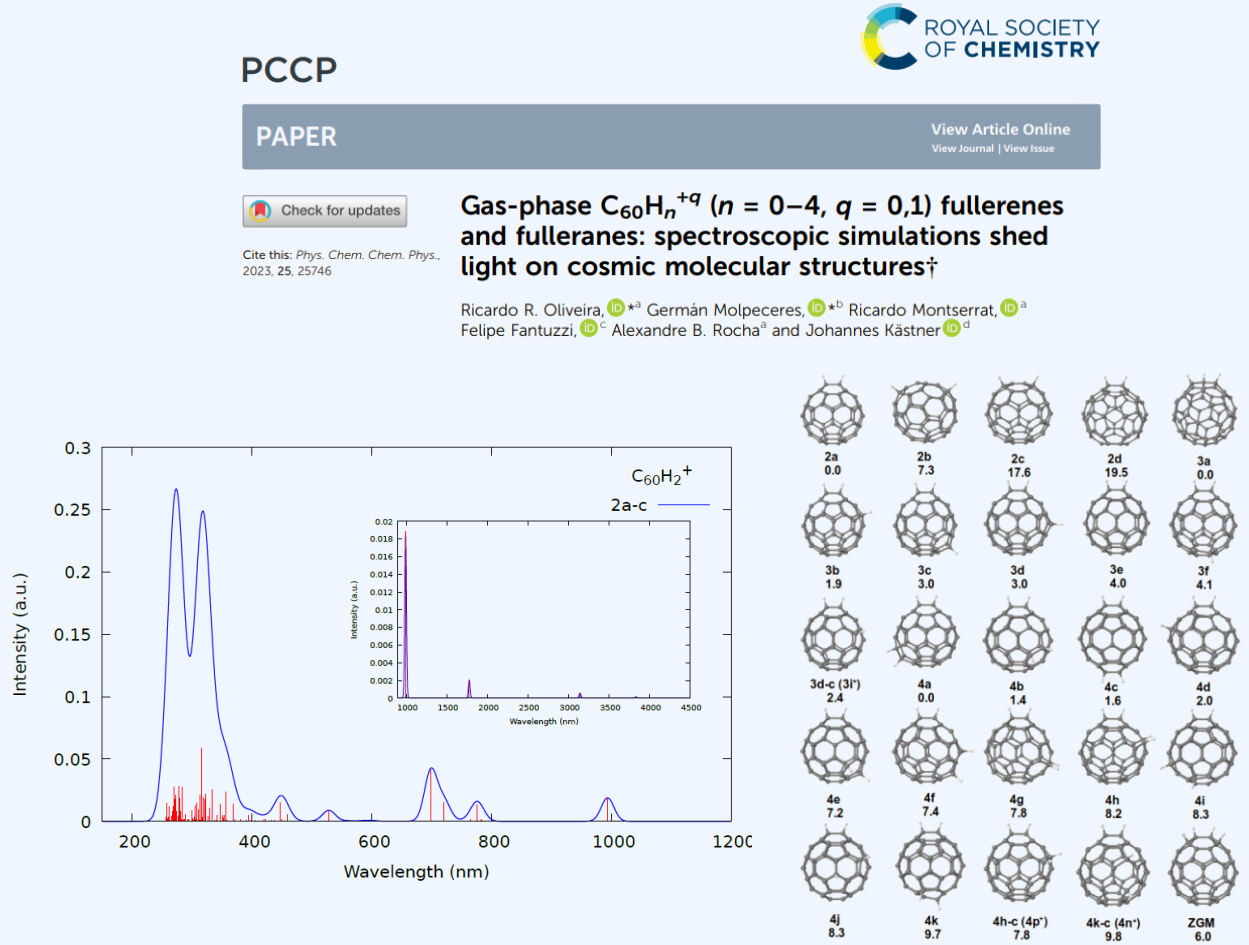


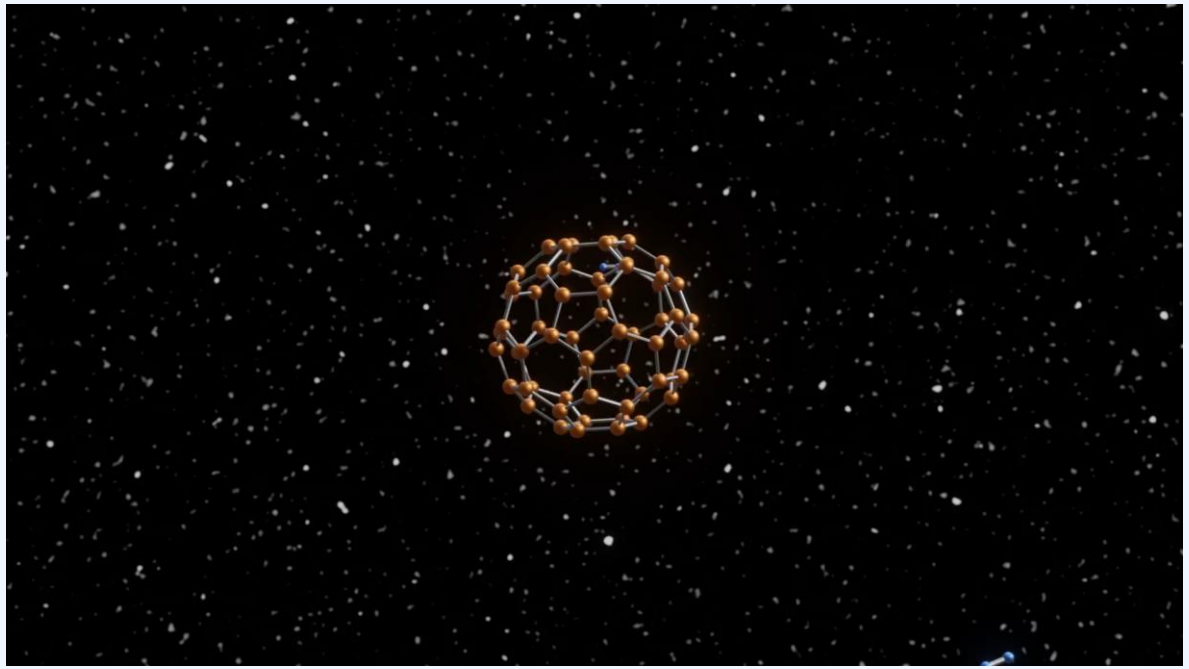
J. Cami, J. Bernard-Salas, E. Peeters, S. E. Malek. *Science* **2010**, *329*, 180-182
J. P. Maier, E. K. Campbell. *Angew. Chem. Int. Ed.* **2017**, *56*, 4920-4929.

Hydrogenated Fullerenes

Interstellar hydrogenated fullerenes?

- **Near-infrared electronic signatures** as indicators of **interstellar hydrogenated fullerenes**

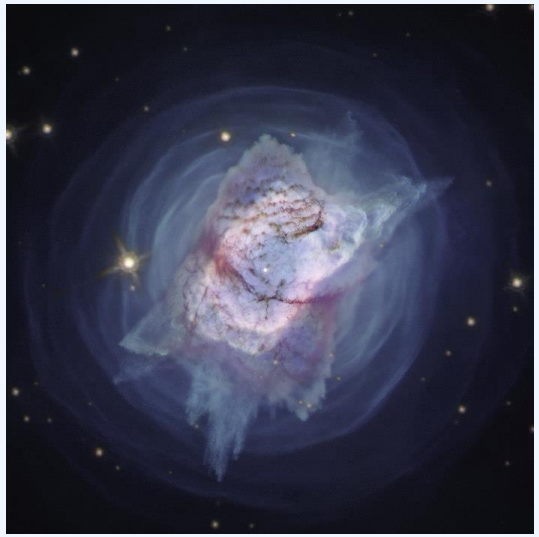




R. R. Oliveira, G. Molpeceres, R. Montserrat, **F. Fantuzzi**, A. B. Rocha, J. Kästner. *Phys. Chem. Chem. Phys. 2023, 25, 25746.*

Interstellar HeH^+

- With the temperature of the young Universe falling below 4,000 K, **ions** of the **light elements** produced in **Big Bang nucleosynthesis** recombined in reverse order of their **ionisation potential**.
- He^{2+} and He^+ were the first to combine with free electrons, forming the **first neutral atoms**.
- Neutral helium atoms formed the Universe's **first molecular bond** in HeH+.
- Despite decades of unsuccessful attempts, HeH+ was detected in **NGC 7027** in 2019.
- Detection used the upgraded version of the **German Receiver for Astronomy at Terahertz Frequencies** (upGREAT) in the **Stratospheric Observatory for Infrared Astronomy (SOFIA)**.



NGC 7027

Letter | Published: 17 April 2019

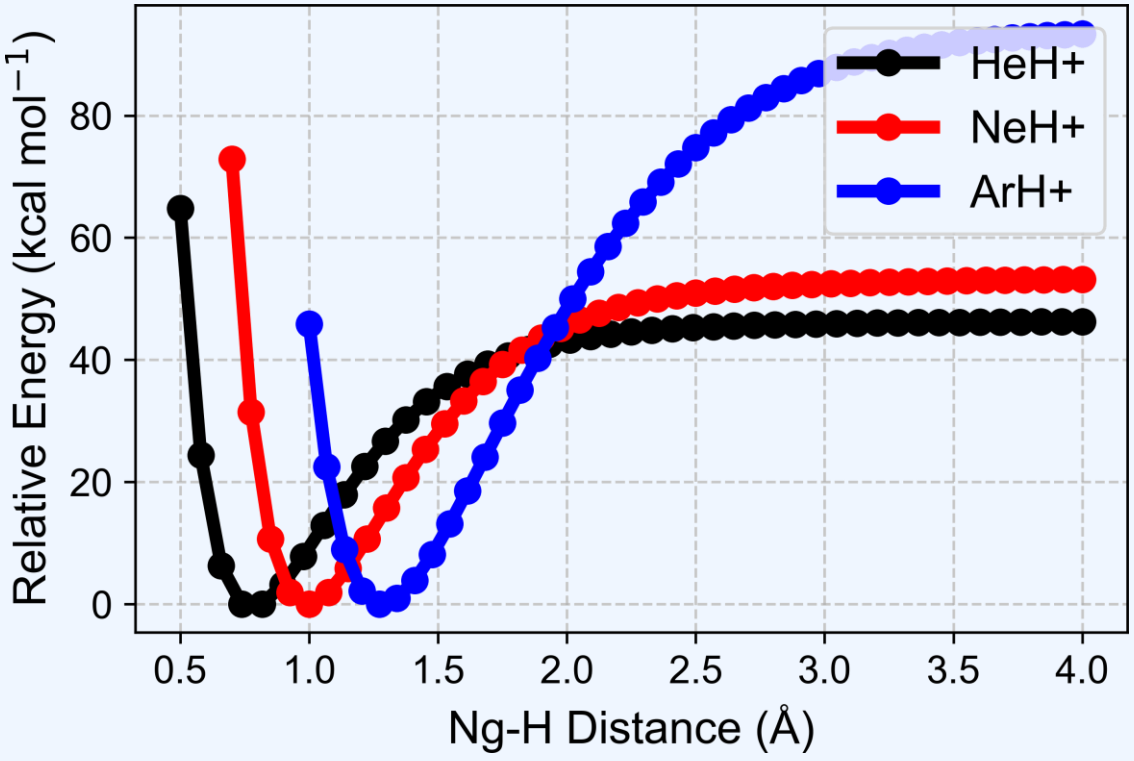
Astrophysical detection of the helium hydride ion HeH^+

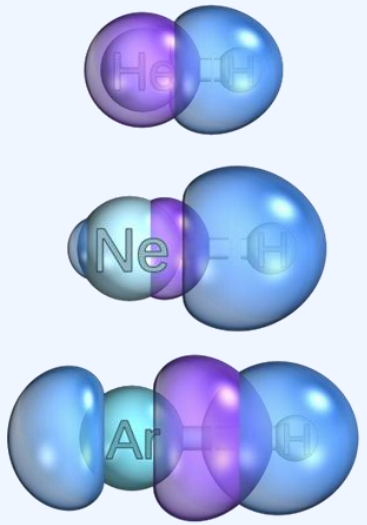
Rolf Güsten, Helmut Wiesemeyer, David Neufeld, Karl M. Menten, Urs U. Graf, Karl Jacobs, Bernd Klein, Oliver Ricken, Christophe Risacher & Jürgen Stutzki

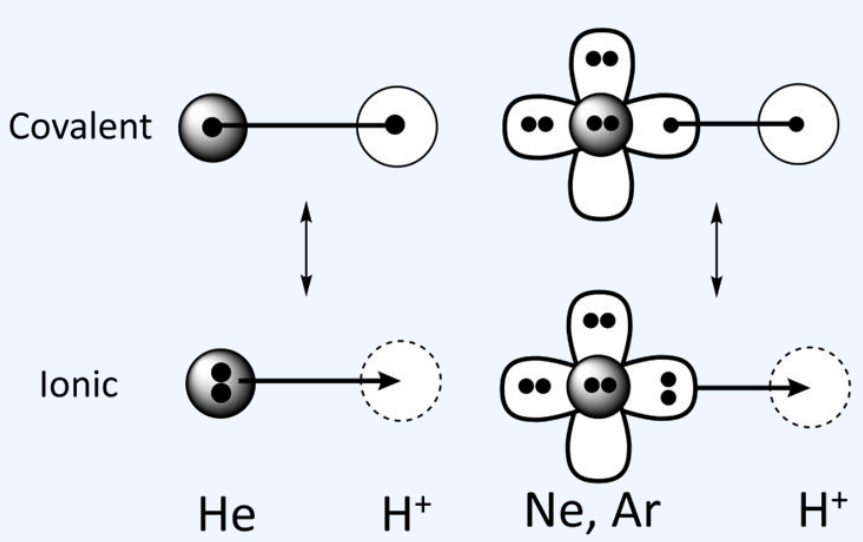
Nature **568**, 357–359 (2019) | Cite this article

Interstellar HeH^+

- What is the **nature** of the **oldest chemical bond** in the Universe? How does it compare with **heavier Ng–H bonds**?







Lucas Araujo

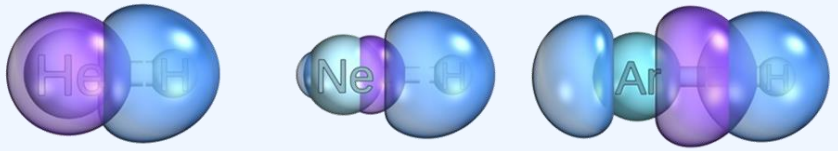
To be submitted to PCCP Early Career Investigator 2024 Issue.

Noble-Gas Molecular Cations

Interstellar HeH^+

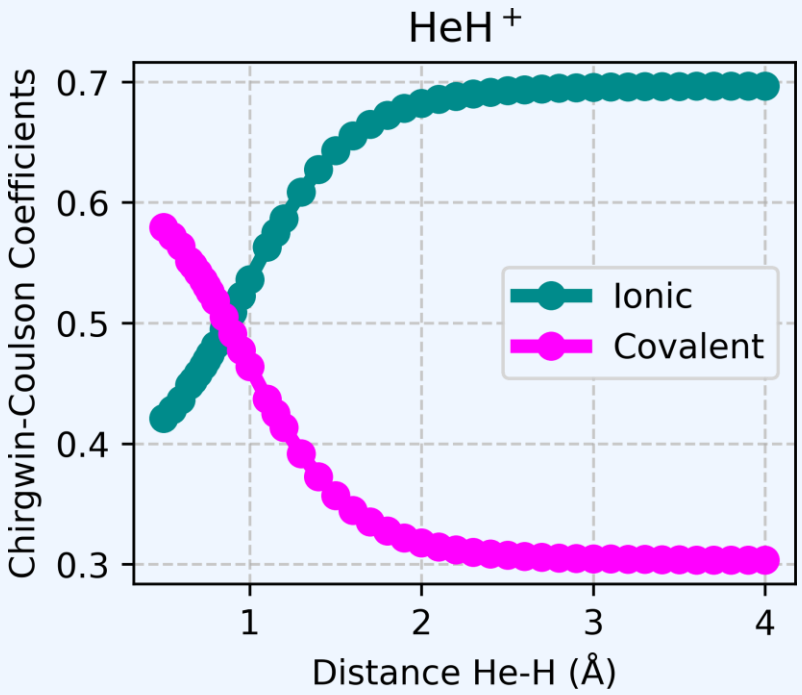
- HeH^+ and ArH^+ dominated by the **covalent configuration.**
- NeH^+ dominated by the **ionic configuration.**
- Oldest bond in the universe is **covalent.**

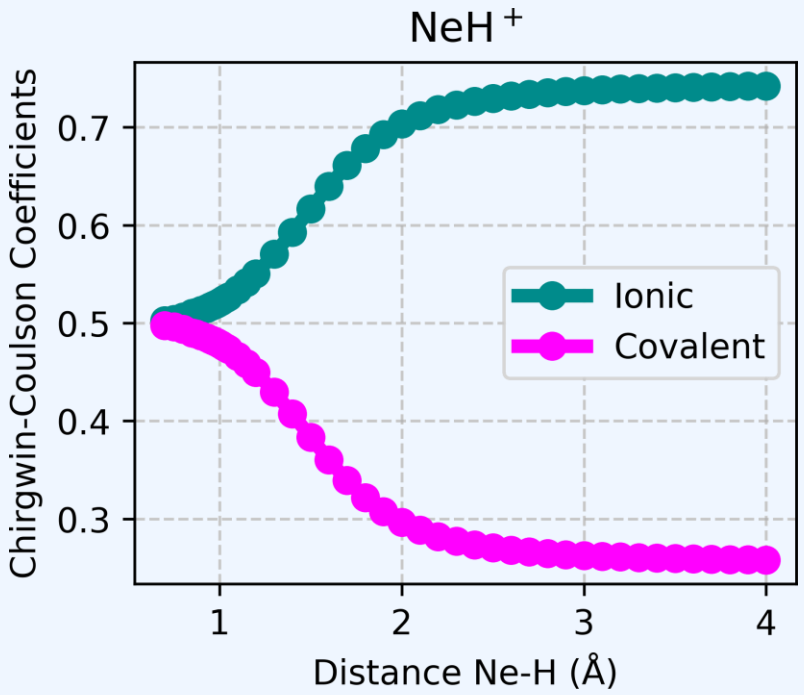
MSVB/aug-cc-pVTZ//CCSD(T)/aug-cc-pVTZ

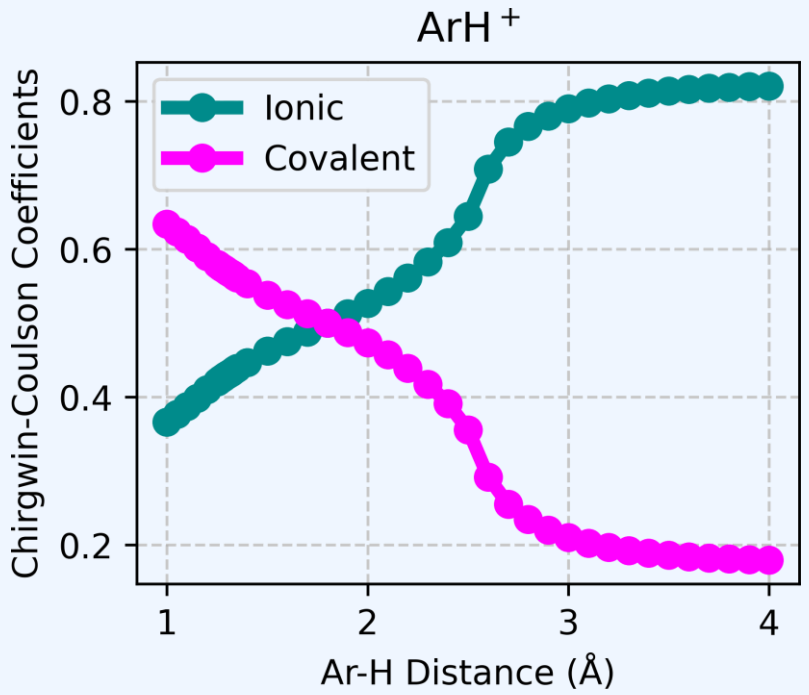


HeH^+	NeH^+	ArH^+
ionic: 0.474	ionic: 0.519	ionic: 0.430
covalent: 0.526	covalent: 0.481	covalent: 0.570

Lucas Araujo

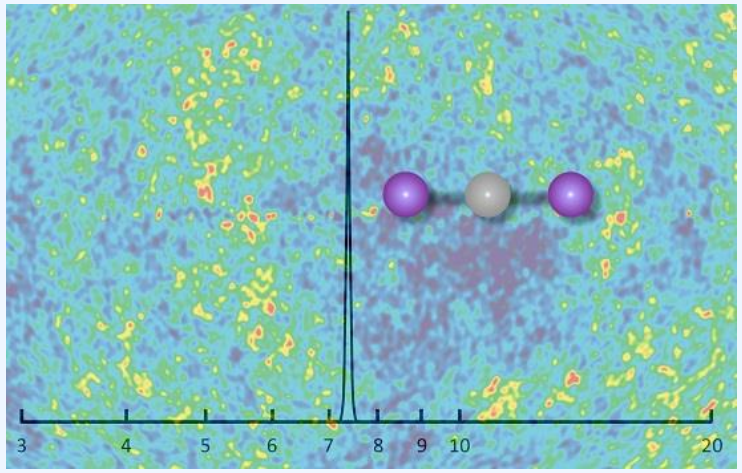






To be submitted to PCCP Early Career Investigator 2024 Issue.

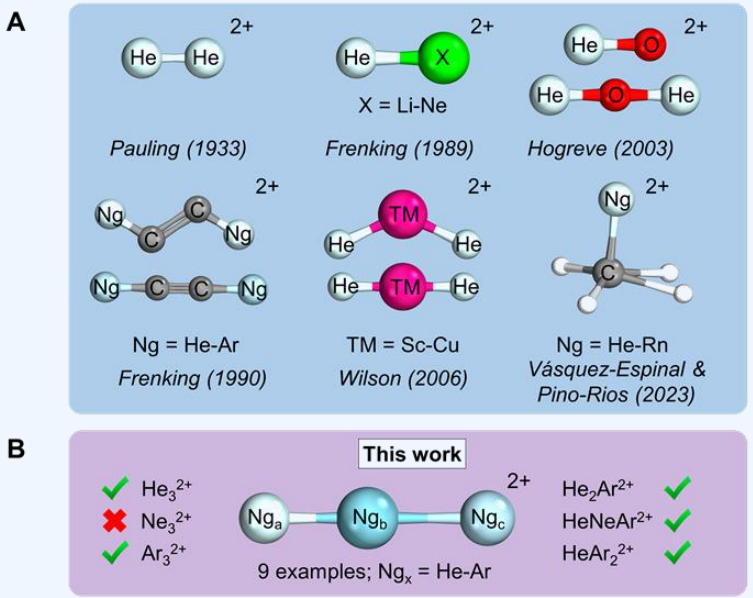
Other proposed He-bonded systems

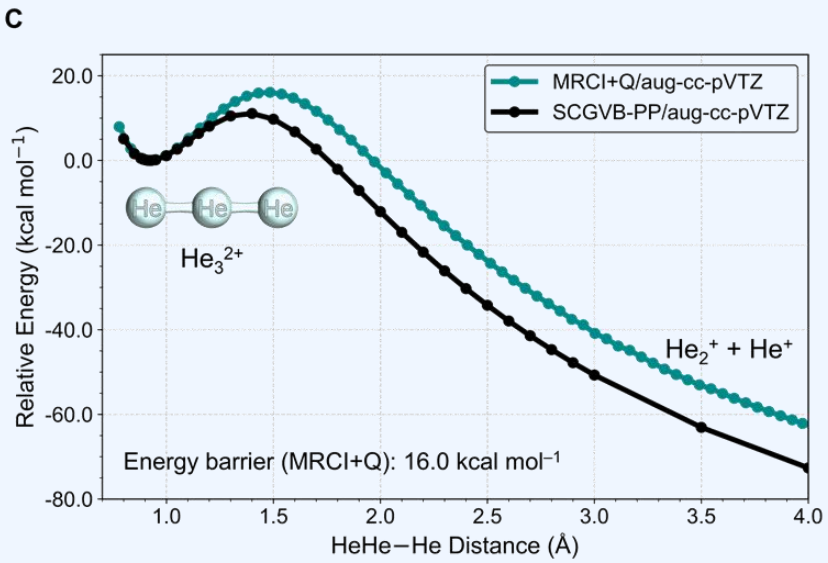


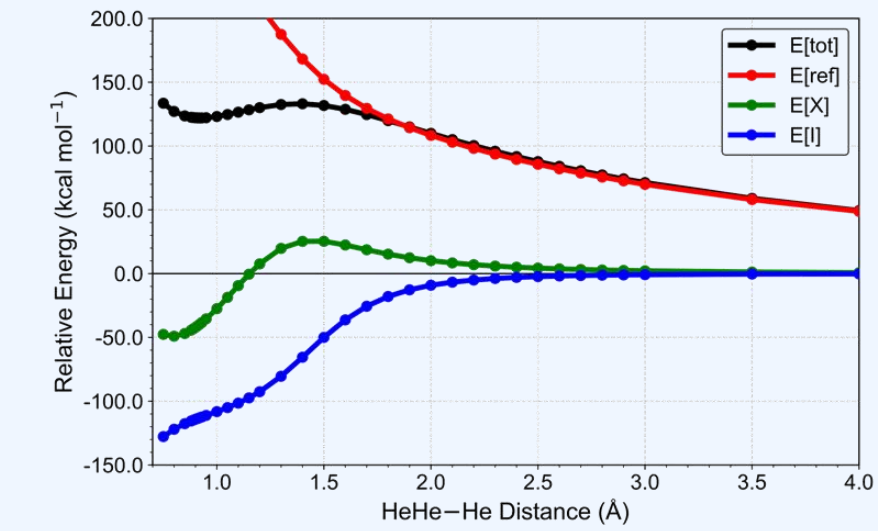
R. C. Fortenberry, L. Wiesenfeld. A Molecular Candle Where Few Molecules Shine: HeHHe$^+$. *Molecules* **2020**, *25*, 2183.

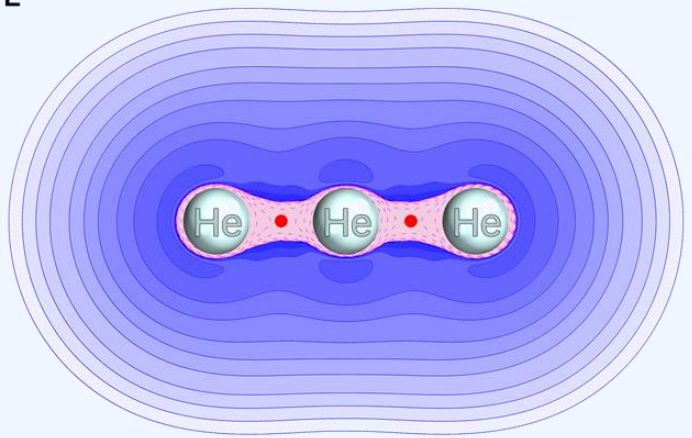
- Systematic investigation of **270 X-Ng-Y molecules**.
- **Chemical aristocracy**: Noble-gas-exclusive covalent compounds.
- **He_3^{2+}** and analogous systems.

L. Araujo, **F. Fantuzzi**, T. M. Cardozo. Submitted to JACS.



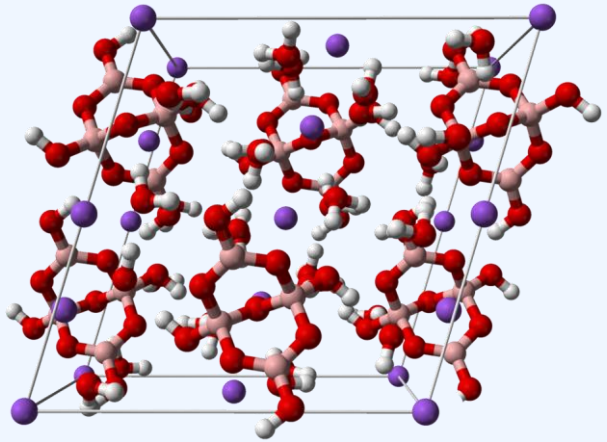






AstroBoron

- Despite its relatively low abundance, **boron** is an intriguing element for **geology** and **astrobiology**.
- On **Earth**: boron is concentrated on **phyllosilicate-bearing sediments** and **evaporite** deposits.
  - Useful for understanding **surface** and **subsurface aqueous** processes (**boron paleosalinity**).
- Boron forms very stable **boron-oxygen minerals**, called **borates** (e.g., borax).

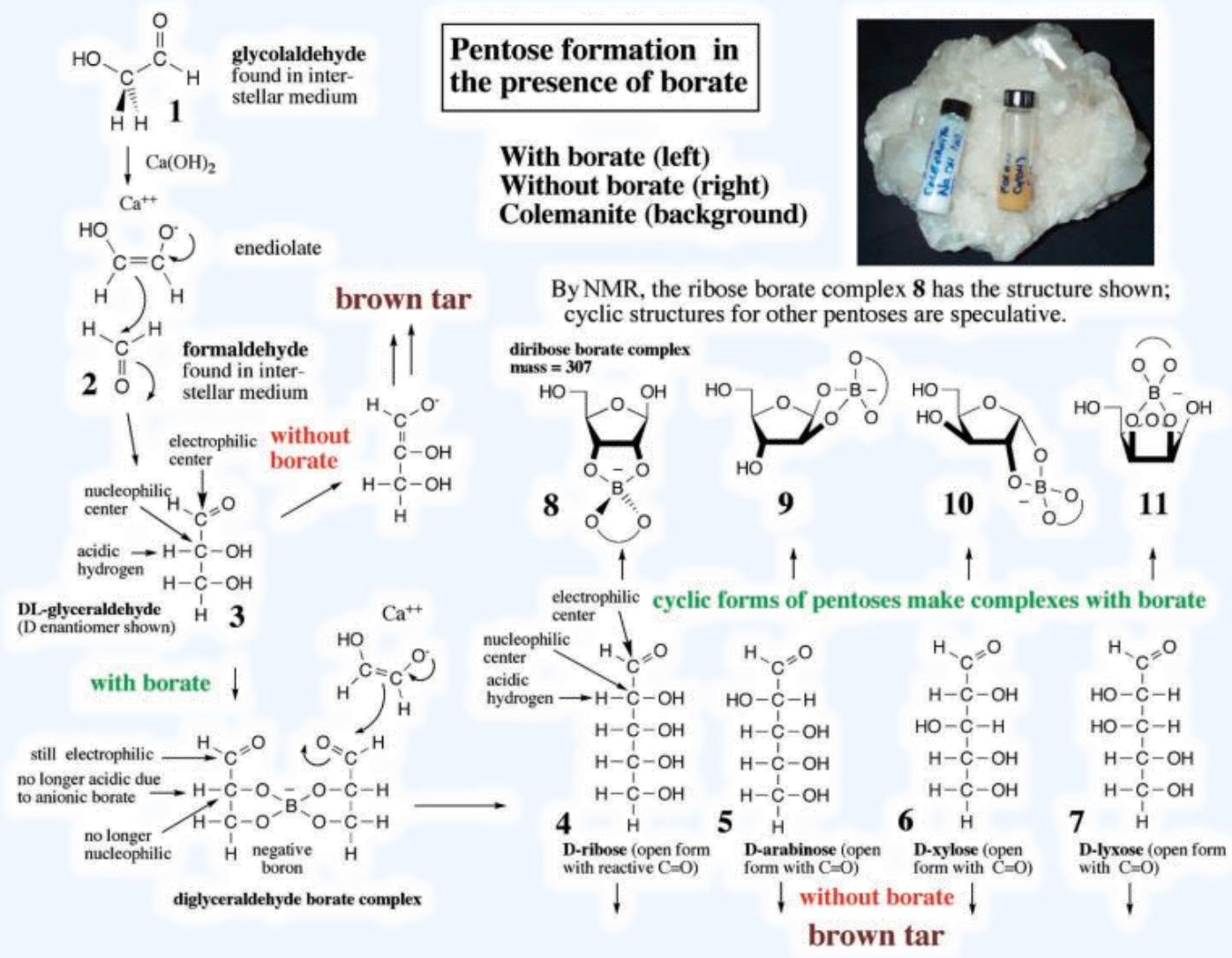


Gasda, P. J. *et al.* In situ detection of boron by ChemCam on Mars. *Geophys. Res. Lett.* **44**(17), 8739–8748 (2017).

University of Kent

AstroBoron

- **Borate anions,** $B(OR)_4^-$, may be necessary for the **origin of life.**
- **Slow** down the **decomposition** of **ribose** in **solution.**
  - Ribose: important **prebiotic compound** and component of **ribonucleic acid** (RNA).
- Mediate **ribose formation** by the **formose reaction.**
  - Formation of **ribose-borate complexes.**



A. Ricardo, M. A. Carrigan, A. N. Olcott, S. A. Benner. Borate Minerals Stabilize Ribose. *Science.* **303**(5655), 196–196 (2004).

Boron in Prebiotic Chemistry & Life

GDCh Minireviews Angewandte Chemie

Prebiotic Chemistry

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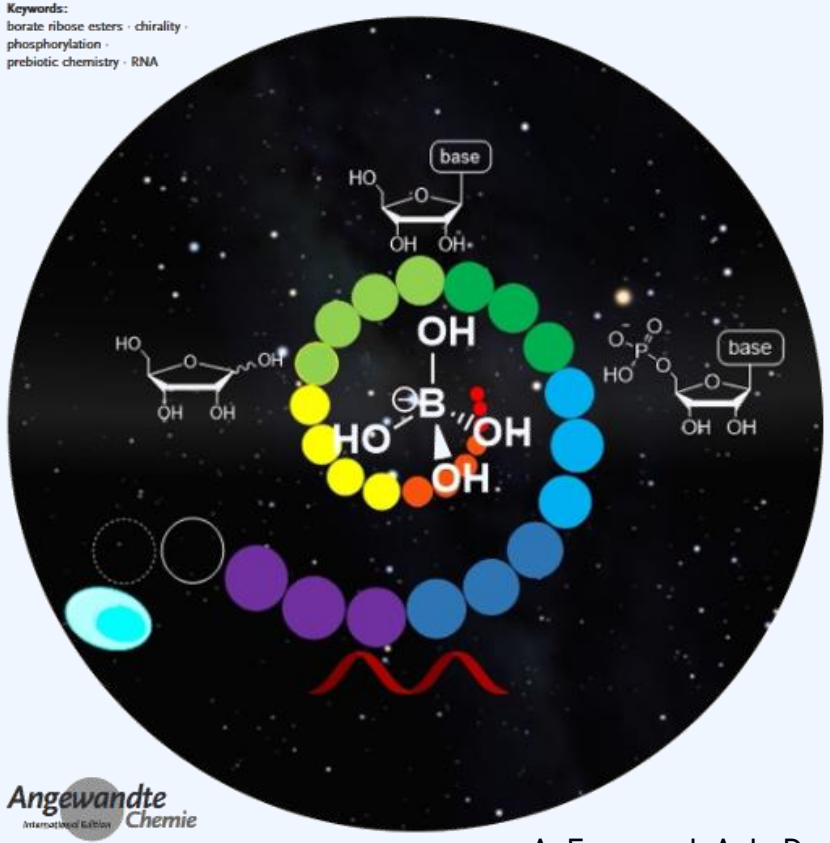
German Edition: doi.org/10.1002/ange.202010616

Boron in Prebiological Evolution

*Ana Franco and José Armando L. da Silva**

Keywords:
borate ribose esters · chirality · phosphorylation · prebiotic chemistry · RNA



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A. Franco, J. A. L. Da Silva. *Angew. Chem. Int. Ed.* **2021**, *50*, 10458-10468.

communications chemistry

ARTICLE

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Boron-assisted abiotic polypeptide synthesis

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Commun. Chem. **2023**, *6*, 89.

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Astrobiology > Vol. 23, No. 5 > Hypothesis Article Full Access

Boron as a Hypothetical Participant in the Prebiological Enantiomeric Enrichment

Ana Franco, Maria Orquídia Neves, and José A.L. da Silva

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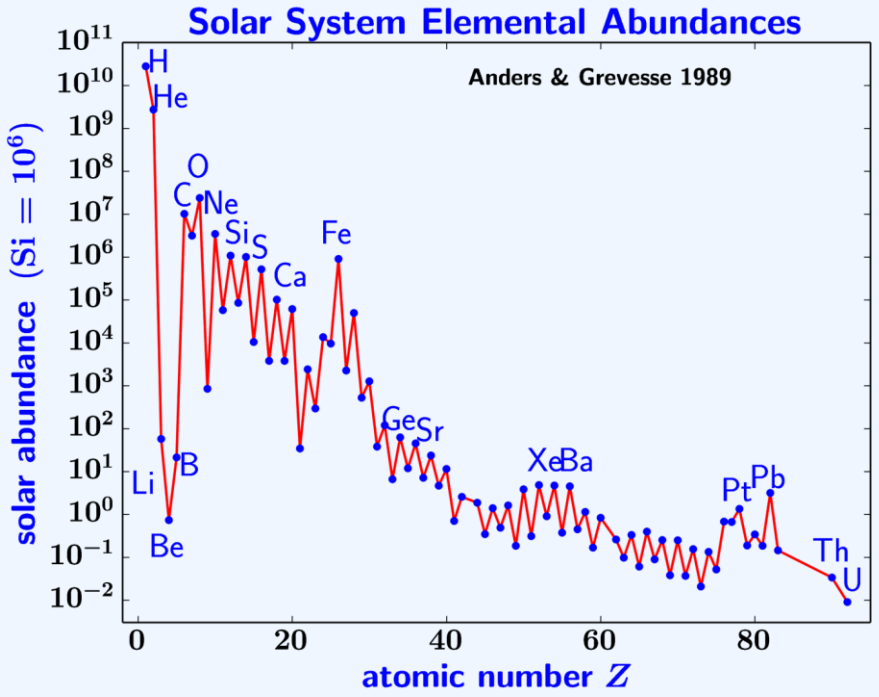
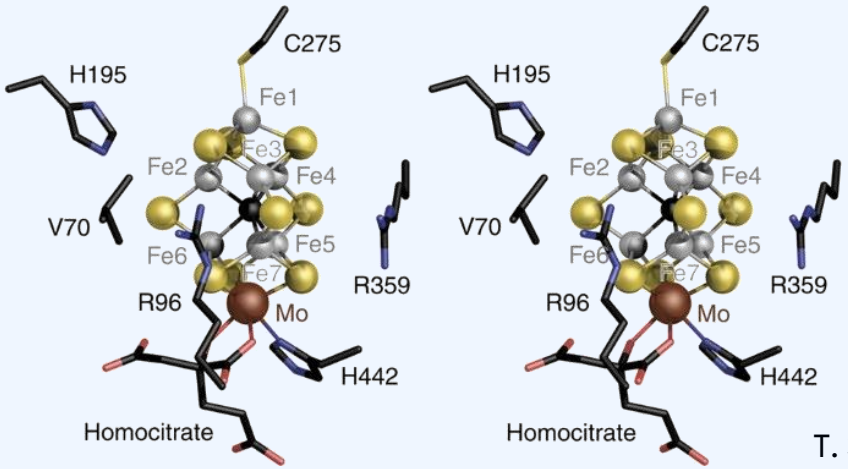
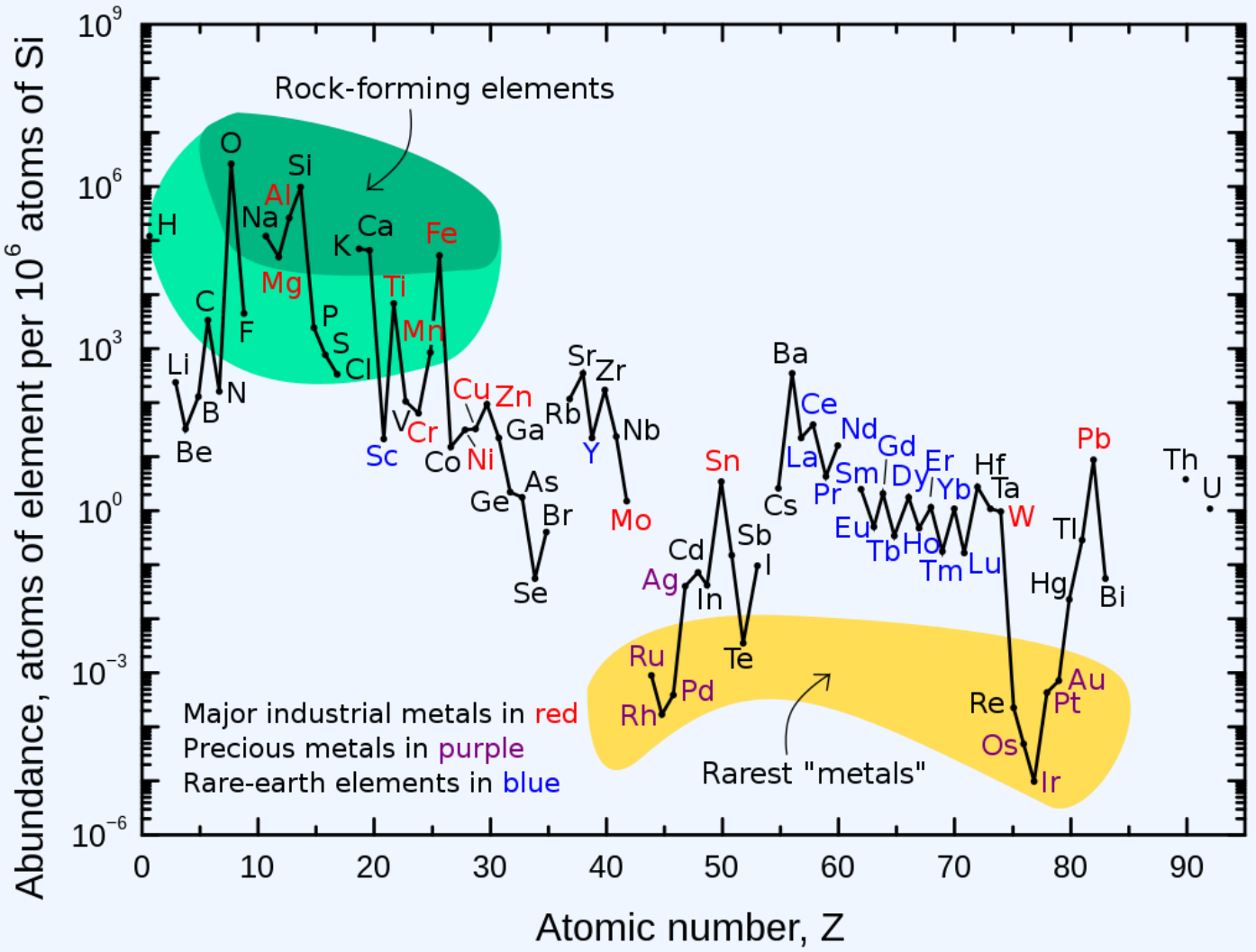
A. Franco, M. O. Neves, J. A. L. Da Silva. *Astrobiology* **2023**, *23*, 605-615.

Boron: Abundance in Solar System x Earth's Crust







T. Spatzal et al. **Nature Commun.** *2016*, **7**, 10902.

AstroBoron

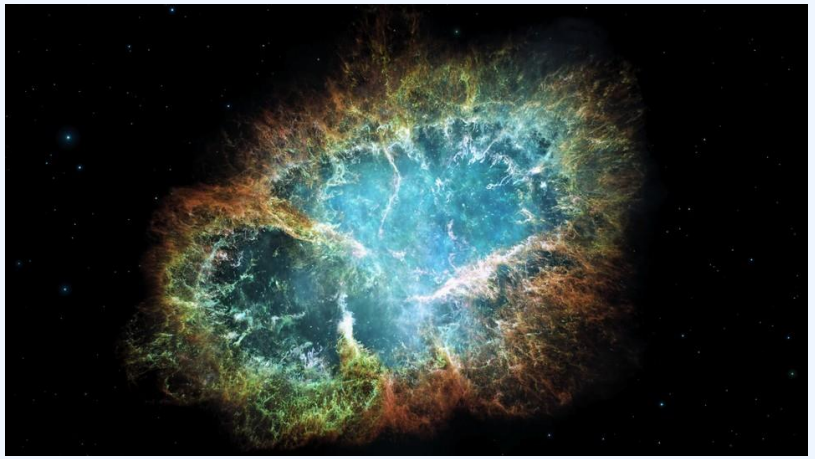
- Boron has been detected in **Martian meteorites** and on **Mars**.
- **Martian meteorites**: concentrations up to 166 ppm (**MIL 090030**).
- **Mars**: calcium-sulphate-filled fractures in the **Gale crater**.
  - Subsurface groundwater conditions could have **supported prebiotic chemical reactions**.
  - Additional support for the **past habitability** of **Gale crater**.

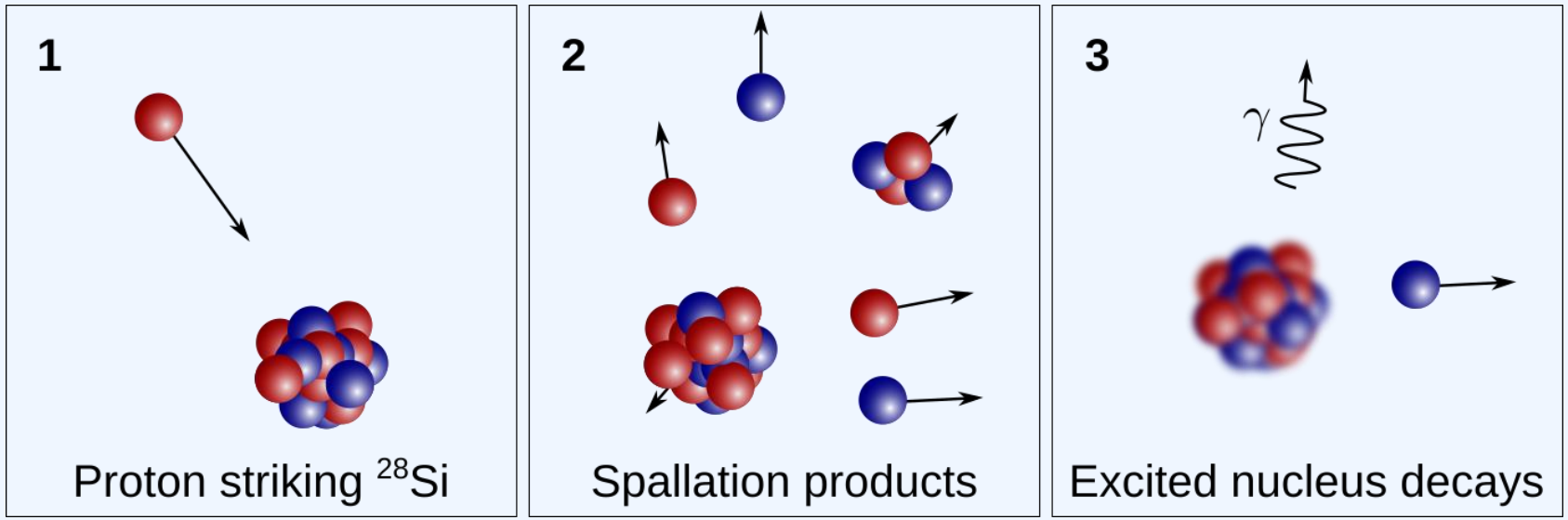
P. J. Gasda *et al.* In situ detection of boron by ChemCam on Mars. *Geophys. Res. Lett.* **44**(17), 8739–8748 (**2017**).

Boron in Space

Where is boron?

- Boron is **not formed** by **stellar nucleosynthesis.**
- Main processes forming boron: **supernovae** and **cosmic ray spallation.**
- So far, **>300 molecules** have been identified in the **interstellar medium.**
  - **No interstellar molecule featuring boron** has been discovered.
- Which **molecules** could be the **interstellar carriers of boron**?





$$^{12}_{6}\mathrm{C} + ^{1}_{1}\mathrm{H} \rightarrow ^{\mathbf{11}}_{\mathbf{5}}\mathbf{B} + 2\,^{1}_{1}\mathrm{H}$$

$$^{12}_{6}\mathrm{C} + ^{1}_{1}\mathrm{H} \rightarrow ^{\mathbf{10}}_{\mathbf{5}}\mathbf{B} + ^{3}_{2}\mathrm{He}$$

$$^{12}_{6}\mathrm{C} + ^{1}_{1}\mathrm{H} \rightarrow ^{9}_{4}\mathrm{B} + ^{3}_{2}\mathrm{He} + ^{1}_{1}\mathrm{H}$$

C. N. Davids, H. Laumer, H., S. M. Austin. Production of the Light Elements Lithium, Beryllium, and Boron by Proton Spallation of ^{12}C. *Phys. Rev. C* **1**, 270 (**1970**).

Boronyl Compounds (B–O) as Interstellar Boron Carriers

University of Kent

Boronyl

- **Boron** is known for its **oxygen affinity**.
- **Boronyl** (BO) is a **monovalent sigma radical** with a robust B≡O triple bond.
- It is **isoelectronic** to the **CN group**, which is ubiquitous in space.
- Hypothesis: **boronyl-containing molecules** are the **carriers** of **interstellar boron**.

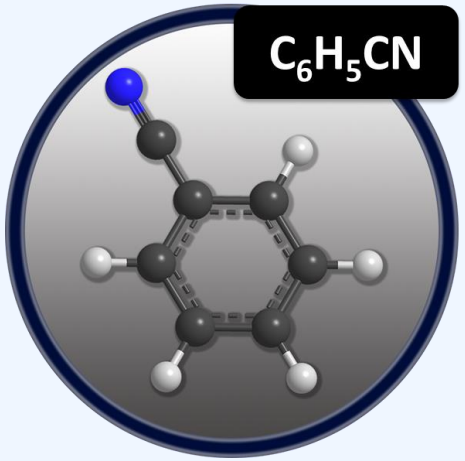
BO^- ($C_{\infty v}$ $^1\Sigma$)

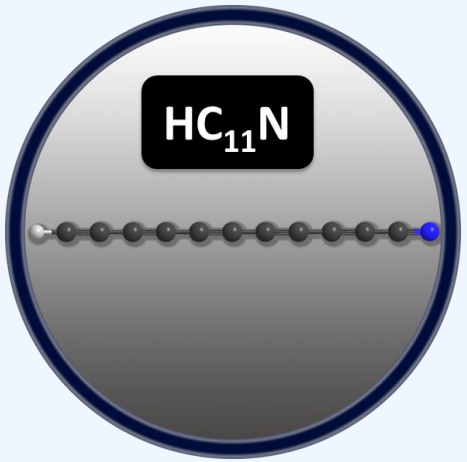
CN ($C_{\infty v}$ $^2\Sigma$)

CO ($C_{\infty v}$ $^1\Sigma$)

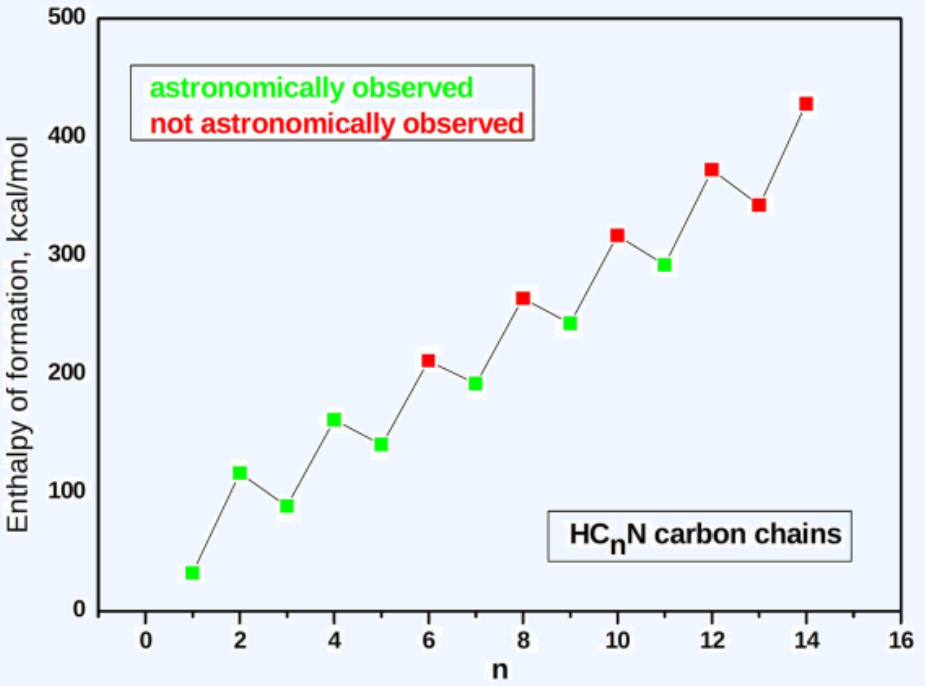
Acc. Chem. Res. 2014, **47**, 2435–2445.

Science **2019**, *359*, 202–205.





Nature Astr. **2021**, 5, 188-196.



H—C≡C—C≡C—C≡C—C≡C—C≡C—C≡N

Can see $HC_{11}N$ chains in space!

… but cannot see $HC_{10}N$ chains?!

Should search **triplet** $HC_{10}N$!

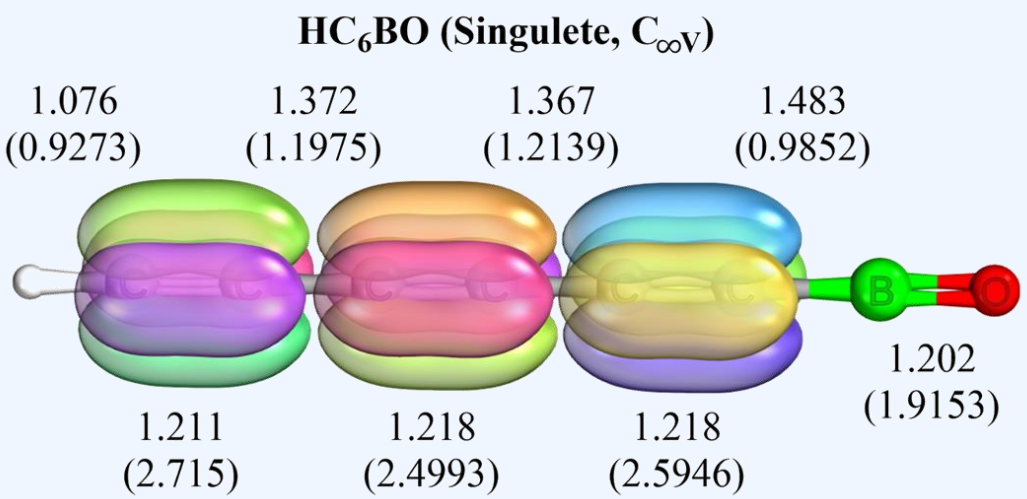
ACS Earth Space Chem. ***2019***, *3, 863–872*

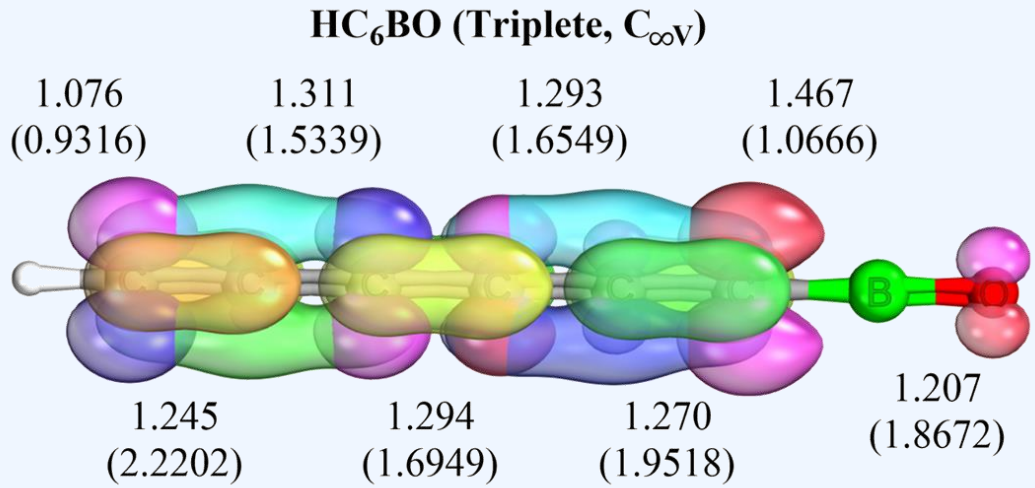
Boronyl Compounds (B–O) as Interstellar Boron Carriers

University of Kent

Boronyl-bearing carbon chains

- **Promising candidates** for **astrophysical detection** and **interstellar boron carriers.**
- Analogous to cyano-bearing carbon chains, but:
  - **Lower energies of formation.**
  - **Larger dipole moments.**
- **Boronyl** carbon chains are **attractive targets** for further astrophysical studies.





Cinthya K. Prieto-García

Unpublished results

Summary

- **Computational** and **theoretical chemistry** can play an important role in **Nuclear Astrochemistry.**

- **Electronic structure, bonding**, and **reactivity** of **astro(phys)(chem)(biolog)ical** atomic and molecular systems.

- **Molecular design**, **spectroscopical** predictions.

- And **many more**.

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etc.