

# AstroChemical Newsletter #51

February 2020

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## Abstracts

### Superhydrogenation of pentacene: the reactivity of zigzag-edges

**Dario Campisi, Frederik Doktor S. Simonsen, John D. Thrower, Rijutha Jaganathan, Liv Hornekær, Rocco Martinazzo and Alexander G. G. M. Tielens**

Investigating the hydrogenation of carbonaceous materials is of interest in a wide range of research areas including electronic device development, hydrogen storage, and, in particular, astrocatalytic formation of molecular hydrogen in the universe. Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous in space, locking up close to 15% of the elementary carbon. We have used thermal desorption measurements to study the hydrogenation sequence of pentacene from adding one additional H to the fully hydrogenated pentacene species. The experiments reveal that hydrogenated species with an even number of excess H atoms are highly preferred over hydrogenated species with an odd number of H atoms. In addition, the experiments show that specific hydrogenation states of pentacene with 2, 4, 6, 10, 16 and 22 extra H atoms are preferred over other even numbers. We have investigated the structural stability and activation energy barriers for the superhydrogenation of pentacene using Density Functional Theory. The results reveal a preferential hydrogenation pattern set by the activation energy barriers of the hydrogenation steps. Based on these studies, we formulate simple concepts governing the hydrogenation that apply equally well for different PAHs.

Phys. Chem. Chem. Phys., 2020, Advance Article

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Full-text URL:

<https://pubs.rsc.org/en/content/articlelanding/2020/CP/C9CP05440E#!divAbstract>

### Low-temperature chemistry induced by cosmic rays: positive and negative ions desorption from nitrile-bearing astrophysical ice analogues

**F. de A. Ribeiro, G. C. Almeida, W. Wolff, H. M. Boechat-Roberty, M. L. M. Rocco, E. F. da Silveira**

In cold core of dark molecular clouds, where the UV radiation from external sources is strongly attenuated, cosmic rays can induce chemical reactions on the surface of ice-covered grains promoting the ejection of the processed material to the gas phase. We report the positive and negative secondary ion emission from pure CH<sub>3</sub>CN, C<sub>2</sub>H<sub>3</sub>CN and i-C<sub>3</sub>H<sub>7</sub>CN ices due to the bombardment of heavy ions (<sup>252</sup>Cf fission fragments), simulating the incidence of cosmic rays onto icy surfaces. The secondary ions emitted from each sample were analysed by time-of-flight mass spectrometry (TOF-MS), using

Plasma Desorption Mass Spectrometry (PDMS) technique. Several ionic species were identified, indicating strong fragmentation on the frozen surface. Proton-transfer processes are suggested to play a role for positive ion desorption, as evidenced by the protonated RCNH<sup>+</sup> parent molecules and (RCN)<sub>n</sub>H<sup>+</sup> ionic clusters. The high electron affinity of the cyano radical seems to contribute to the strong emission of CN<sup>-</sup>, as well as anions attributed to the CH<sub>m</sub>CN<sup>-</sup> fragment and (RCN)<sub>n</sub>CN<sup>-</sup> cluster series. Sputtering and desorption of ion clusters (positive and negative) induced by heavy ion bombardment are suggested to constitute a route by which new neutral or ionised molecular species may be delivered to the gas phase where thermal desorption is negligible.

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Full-text URL: <https://arxiv.org/abs/1912.12368>

## The Challenging Detection of Nucleobases from Pre-accretional Astrophysical Ice Analogs

**Alexander Ruf, Justin Lange, Balkis Eddhif, Claude Geffroy, Louis Le Sergeant d'Hendecourt, Pauline Pointot, and Grégoire Danger**

Amino acids, sugars, and nucleobases are considered as the so-called molecular bricks of life, the major subunits of proteins and genetic materials. All three chemical families have been previously detected in meteorites. In dense molecular cloud ice analogs, the formation of a large set of amino acids and sugars (+derivatives) has been observed. In this contribution, we demonstrate that similar ices (H<sub>2</sub>O:13CH<sub>3</sub>OH:NH<sub>3</sub> ices, 2:1:1) can also lead to the formation of nucleobases. Using combined UPLC-Orbitrap mass spectrometric and UPLC-SRM-triple quadrupole mass spectrometric analyses, we have unambiguously detected cytosine in these primitive, realistic astrophysical ice analogs. Additionally, a huge variety of nucleobase isomers was observed. These results indicate that all central subunits of biochemical materials may have already been present at early stages of chemical evolution of the protosolar nebula, before accretion toward planetesimals. Consequently, the formation of amino acids, sugars, and nucleobases does not necessarily require secondary alteration processes inside meteoritic parent bodies. They might have been supplied from dense molecular cloud ices toward post-accretional objects, such as nonaqueously modified comets, and subsequently delivered onto the early Earth's surface, potentially triggering the emergence of prebiotic chemistry leading to the first living systems.

Alexander Ruf et al 2019 ApJL 887 L31

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## Organosulfur Compounds Formed by Sulfur Ion Bombardment of Astrophysical Ice Analogs: Implications for Moons, Comets, and Kuiper Belt Objects

**Alexander Ruf, Alexis Bouquet, Philippe Boduch, Philippe Schmitt-Kopplin, Vassilissa Vinogradoff, Fabrice Duvernay, Riccardo Giovanni Urso, Rosario Brunetto, Louis Le Sergeant d'Hendecourt, Olivier Mouis**

Carbon, hydrogen, nitrogen, oxygen, and sulfur are the main elements involved in the solid-phase chemistry of various astrophysical environments. Among these elements, sulfur chemistry is probably the least well understood. We investigated whether sulfur ion bombardment within simple astrophysical ice analogs (originating from

H<sub>2</sub>O:CH<sub>3</sub>OH:NH<sub>3</sub>, 2:1:1) could trigger the formation of complex organosulfur molecules. Over 1100 organosulfur (CHNOS) molecular formulas (12% of all assigned signals) were detected in resulting refractory residues within a broad mass range (from 100 to 900 amu, atomic mass unit). This finding indicates a diverse, rich and active sulfur chemistry that could be relevant for Kuiper Belt objects (KBO) ices, triggered by high-energy ion implantation. The putative presence of organosulfur compounds within KBO ices or on other icy bodies might influence our view on the search of habitability and biosignatures.

ApJL (2019 )885 L40

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Full-text URL: <https://iopscience.iop.org/article/10.3847/2041-8213/ab4e9f/meta>

## Data-Driven UPLC-Orbitrap MS Analysis in Astrochemistry

**Alexander Ruf, Pauline Poinot, Claude Geffroy, Louis Le Sergeant d'Hendecourt and Gregoire Danger**

Meteorites have been found to be rich and highly diverse in organic compounds. Next to previous direct infusion high resolution mass spectrometry experiments (DI-HR-MS), we present here data-driven strategies to evaluate UPLC-Orbitrap MS analyses. This allows a comprehensive mining of structural isomers extending the level of information on the molecular diversity in astrochemical materials. As a proof-of-concept study, Murchison and Allende meteorites were analyzed. Both, global organic fingerprint and specific isomer analyses are discussed. Up to 31 different isomers per molecular composition are present in Murchison suggesting the presence of  $\approx 440,000$  different compounds detected therein. By means of this time-resolving high resolution mass spectrometric method, we go one step further toward the characterization of chemical structures within complex extraterrestrial mixtures, enabling a better understanding of organic chemical evolution, from interstellar ices toward small bodies in the Solar System.

Life (2019), 9, 35.

DOI: [10.3390/life9020035](https://doi.org/10.3390/life9020035)

Full-text URL: <https://www.mdpi.com/2075-1729/9/2/35>

## Constraining Cosmic-Ray Ionization Rates and Chemical Timescales in Massive Hot Cores

**C. J. Barger, R. T. Garrod.**

Several studies have demonstrated that the cosmic-ray ionization rate is highly variable in the interstellar medium. However, constraints of this rate for several regions, including those that contain hot cores, are lacking. Hot cores are appealing sources to study given their rich chemical complexity. The chemistry of these cores can be influenced by both their cosmic-ray ionization rates and their warm-up timescales; however, understanding the chemical response to these parameters requires further investigation. We study these effects using the astrochemical hot-core modeling code MAGICKAL, in which we construct a grid of 81 models using nine ionization rates and nine warmup timescales. We also simulate local thermodynamic equilibrium radiative transfer for these models to obtain results that can be directly compared with observations. We compare molecular emission of these models with observations toward NGC 6334 IRS 1, NGC 7538 IRS 1, W3(H<sub>2</sub>O), and W33A in an effort to constrain their cosmic-ray ionization rates and warm-up timescales. Our best fits to the observations suggest that these sources possess elevated cosmic-ray ionization rates,

compared to the canonical value used in previous modeling studies, and rapid warm-up timescales. We also demonstrate that there exists a strong correlation between the cosmic-ray ionization rate and the total hydrogen column density of a source and a strong correlation between the warm-up timescale and total source mass. Furthermore, these relationships are in good agreement with other theoretical studies.

2020 ApJ, 888, 38

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Full-text URL: <https://iopscience.iop.org/article/10.3847/1538-4357/ab5b0d>

## **Infrared detection of aliphatic organics on a cometary nucleus**

**Raponi, A. ; Ciarniello, M. ; Capaccioni, F. ; Mennella, V. ; Filacchione, G. ; Vinogradoff, V. ; Poch, O. ; Beck, P. ; Quirico, E. ; Sanctis, M. C. De ; Moroz, L. V. ; Kappel, D. ; Erard, S. ; Bockelée-Morvan, D. ; Longobardo, A. ; Tosi, F. ; Palomba, E. ; Combe, J.-P. ; Rousseau, B. ; Arnold, G. ; Carlson, R. W. ; Pommerol, A. ; Pilorget, C. ; Fornasier, S. ; Bellucci, G. ; Barucci, A. ; Mancarella, F. ; Formisano, M. ; Rinaldi, G. ; Istiqomah, I. ; Leyrat, C.**

The European Space Agency's Rosetta mission has acquired unprecedented measurements of the surface of the nucleus of comet 67P/Churyumov-Gerasimenko (hereafter, 67P), the composition of which, as determined by in situ and remote-sensing instruments, including the VIRTIS instrument, seems to be an assemblage of ices, minerals and organic material. We performed a refined analysis of infrared observations of the nucleus of 67P carried out by the VIRTIS-M hyperspectral imager. We find that the overall shape of the infrared spectrum of 67P is similar to that of other carbon-rich outer Solar System objects, suggesting a possible genetic link with them. More importantly, we also confirm the complex spectral structure of the wide 2.8–3.6  $\mu\text{m}$  absorption feature populated by fainter bands. Among these, we unambiguously identify the presence of aliphatic organics by their ubiquitous 3.38  $\mu\text{m}$ , 3.42  $\mu\text{m}$  and 3.47  $\mu\text{m}$  bands. This infrared detection of aliphatic species on a cometary surface has strong implications for the evolutionary history of the primordial Solar System and is evidence that comets provide an evolutionary link between interstellar material and Solar System bodies.

Nature astronomy, 2020, 1-6 p

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Full-text URL: <https://www.nature.com/articles/s41550-019-0992-8>

## **Assessing the viability of silicate nanoclusters as carriers of the anomalous microwave emission: a quantum mechanical study**

**Antoni Macià Escatllar, Stefan T. Bromley**

Nanosized silicate dust is likely to be abundant in many astronomical environments and it is a prime candidate for being the source of the Anomalous Microwave Emission (AME). To assess the viability of silicate nanoclusters as AME carriers, their detailed properties need to be established. Using quantum chemical calculations, we compute the accurate chemical and electronic structures of three families of nanoclusters with astrophysically relevant compositions: Mg-rich olivinic ( $\text{Mg}_2\text{SiO}_4$ )<sub>N</sub>, Mg-rich pyroxenic ( $\text{MgSiO}_3$ )<sub>N</sub>, and silicon monoxide ( $\text{SiO}$ )<sub>N</sub>, all in the  $\leq 1$  nm diameter size regime and for neutral and  $\pm 1$  charge states. From these fundamental data, we directly derive the shapes, ionization potentials, electron affinities, and dipole moments of all nanoclusters. The aspect ratio of the nanoclusters fluctuates significantly with N for small sizes, but

especially for the olivinic and pyroxenic nanoclusters, it tends to stabilize towards  $\sim 1.3$  for the largest sizes considered. These latter two nanocluster families tend to have mass distributions consistent with approximately prolate ellipsoidal shapes. Our calculations reveal that the dipole moment of all our nanoclusters can be substantially affected by changes in chemical structure (i.e. different isomers for a fixed N), ionisation, and substitution of Mg by Fe. Although all these factors are important, the dipole moment of our Mg-rich silicate nanoclusters is always found to be large enough to account for the observed AME. However, (SiO)<sub>N</sub> nanoclusters are only likely to be potential AME contributors when they are both charged and their chemical structures are anisotropically segregated. We also model the emissivity per H of a representative (Mg<sub>2</sub>SiO<sub>4</sub>)<sub>3</sub> nanocluster by directly calculating the quantum mechanical rotational energy levels and assuming a distribution of occupied levels in accordance with equilibrium Boltzmann statistics. We compare our bottom-up results with previously published classical models and show that a population of silicate nanoclusters containing only 1% of the total Si budget can reproduce the AME emissivity.

A&A, Forthcoming article

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Full-text URL: <https://www.aanda.org/articles/aa/pdf/forth/aa36419-19.pdf>

## Amino acetaldehyde conformers: structure and spectroscopic properties

**P. Redondo, M. Sanz-Novo, A. Largo and C. Barrientos**

We present a computational study of the different conformers of amino acetaldehyde. This molecule is a precursor of glycine and also an isomer of the detected molecules acetaldehyde and methylformamide. In addition, a previous theoretical result shows that amino acetaldehyde could be formed from the gas phase reaction of formamide with CH<sub>5</sub><sup>+</sup>. Different computational approaches, going from density functional theory (DFT) to coupled cluster (CC) calculations, are employed for the characterization of the amino acetaldehyde conformers. We locate four low-lying conformation on the singlet potential energy surface (PES), two with a synperiplanar arrangement of the carboxylic oxygen atom and the NH<sub>2</sub> group, and the other two conformers with an anticlinal disposition. All levels of theory predict the conformer with a synperiplanar arrangement and the H atoms of the NH<sub>2</sub> group pointing in the direction of the oxygen, denoted as in-sp-amino acetaldehyde, as the most stable. The viability of the interconversion processes between the four conformers in space is analysed. Relevant spectroscopic parameters to rotational spectroscopy with ‘spectroscopic’ accuracy at the composite level are reported. Vibrational frequencies and infrared intensities are also computed at the CC with single and double excitations (CCSD) level including anharmonic corrections. This information could help in the experimental characterization of amino acetaldehyde that could be considered as a good candidate molecule to be searched for in space.

2020, MNRAS, 492, 1827.

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Full-text URL: <https://academic.oup.com/mnras/article-abstract/492/2/1827/5681404?redirectedFrom=fulltext>

## First detection of the 448 GHz ortho-H<sub>2</sub>O line at high redshift: probing the structure of a starburst nucleus at $z = 3.63$

**C. Yang, E. González-Alfonso, A. Omont, M. Pereira-Santaella, J. Fischer, A. Beelen, R. Gavazzi**

Submillimeter rotational lines of H<sub>2</sub>O are a powerful probe in warm gas regions of the ISM, tracing scales and structures ranging from kpc disks to the most compact and dust-obscured regions of galactic nuclei. The ortho-H<sub>2</sub>O(423-330) line at 448 GHz, which was recently detected in a local luminous infrared galaxy (Pereira-Santaella et al. 2017), offers a unique constraint on the excitation conditions and ISM properties in deeply buried galaxy nuclei since the line requires high far-IR optical depths to be excited. In this letter, we report the first high-redshift detection of the 448 GHz H<sub>2</sub>O(423-330) line using ALMA, in a strongly lensed submillimeter galaxy (SMG) at  $z=3.63$ . After correcting for magnification, the luminosity of the 448 GHz H<sub>2</sub>O line is  $\sim 10^6 L_{\odot}$ . In combination with three other previously detected H<sub>2</sub>O lines, we build a model that "resolves" the dusty ISM structure of the SMG, and find that it is composed of a  $\sim 1$  kpc optically thin (optical depth at  $100\mu\text{m}$   $\tau_{100} \sim 0.3$ ) disk component with dust temperature  $T_{\text{dust}} \sim 50$  K emitting a total infrared power of  $5e12 L_{\text{sun}}$  with surface density  $\Sigma_{\text{IR}} = 4e11 L_{\text{sun}} \text{ kpc}^{-2}$ , and a very compact (0.1 kpc) heavily dust-obscured ( $\tau_{100} > \sim 1$ ) nuclear core with very warm dust (100 K) and  $\Sigma_{\text{IR}} = 8e12 L_{\text{sun}} \text{ kpc}^{-2}$ . The H<sub>2</sub>O abundance in the core component,  $X[\text{H}_2\text{O}] \sim (0.3-5) \times 10^{-5}$ , is at least one order of magnitude higher than in the disk component. The optically thick core has the characteristic properties of an Eddington-limited starburst, providing evidence that radiation pressure on dust is capable of supporting the ISM in buried nuclei at high redshifts. The multi-component ISM structure revealed by our models illustrates that dust and molecules such as H<sub>2</sub>O are present in regions characterized by highly differing conditions and scales, extending from the nucleus to more extended regions of SMGs.

A&A Letter Accepted

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Full-text URL: <https://arxiv.org/pdf/2001.06589>

## Exploring the formation pathways of formamide Near young O-type stars

**V. Allen, F. F. S. van der Tak, A. López-Sepulcre, Á. Sánchez-Monge, V. M. Rivilla, and R. Cesaroni**

**Context.** As a building block for amino acids, formamide (NH<sub>2</sub>CHO) is an important molecule in astrobiology and astrochemistry, but its formation path in the interstellar medium is not understood well. **Aims.** We aim to find empirical evidence to support the chemical relationships of formamide to HNCO and H<sub>2</sub>CO. **Methods.** We examine high angular resolution ( $\sim 0.2''$ ) Atacama Large Millimeter/submillimeter Array (ALMA) maps of six sources in three high-mass star-forming regions and compare the spatial extent, integrated emission peak position, and velocity structure of HNCO and H<sub>2</sub>CO line emission with that of NH<sub>2</sub>CHO by using moment maps. Through spectral modeling, we compare the abundances of these three species. **Results.** In these sources, the emission peak separation and velocity dispersion of formamide emission is most often similar to HNCO emission, while the velocity structure is generally just as similar to H<sub>2</sub>CO and HNCO (within errors). From the spectral modeling, we see that the abundances between all three of our focus species are correlated, and the relationship between NH<sub>2</sub>CHO and HNCO reproduces the previously demonstrated abundance relationship. **Conclusions.** In this first interferometric study, which compares two potential parent species to NH<sub>2</sub>CHO, we find that all moment maps for HNCO are more similar to NH<sub>2</sub>CHO than H<sub>2</sub>CO in one of our six sources (G24 A1). For the other five sources, the relationship between NH<sub>2</sub>CHO, HNCO, and H<sub>2</sub>CO is unclear as the different moment maps for each source are not consistently more similar to one

species as opposed to the other.

A&A, Forthcoming article

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## Announcements

### **Symposium on the lifecycle of cosmic PAHs**

Registration is now open for the "The lifecycle of cosmic PAHs" symposium, at Aarhus University, Denmark from 15th-19th June, 2020.

Abstract submission for contributed talks and posters closes on 20th February, 2020.

For more information please visit the symposium webpage

<https://conferences.au.dk/cosmicpah2020/>

Agenda:

Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous in space where they play a key role in the heating of interstellar gas via the photoelectric effect, in setting the ionization balance of the interstellar medium (ISM) and potentially also as catalysts for formation of interstellar molecular complexity and as a component of interstellar organic material and dust. PAHs are identified as carriers of the aromatic infrared bands (AIBs) and are observed in a diverse range of interstellar environments. Yet, their lifecycle in interstellar space is still not well understood. The aim of this symposium is to bring observational astronomers, theorists and experimentalists working on PAH observations, formation, fragmentation, photo-physics, spectroscopy, surface science and chemistry together to shed light on the lifecycle of cosmic PAHs and to explore the future opportunities for PAH research provided by novel theoretical and experimental methods and future observational missions with focus on JWST and ELT. This is the third installment in a series of meetings on interstellar polycyclic aromatic hydrocarbons (PAHs) with previous meetings held in Toulouse in 2010 and in Noordwijk in 2016.

Invited speakers include:

Kathryn Altwegg, Bern University; Jeremy Chastenet, University of California San Diego; Christine Joblin, Universite Paul Sabatier Toulouse 3; Christiaan Boersma, NASA Ames research center; Sandra Brünken, Radboud University; Francois Dulieu, L'université de Cergy-Pontoise ; Giacomo Mulas, INAF; Jan Cami, Universtiy of Western Ontario; Melanie Schnell, Christian-Albrechts-Universität zu Kiel; Henning Zettergren, Stockholm University; Wybren Jan Buma, Universiteit van Amsterdam; José Ángel Martín Gago, Instituto de Ciencia de Materiales de Madrid - CSIC; Ewen K. Campbell, University of Edinburgh; Michael Duncan, University of Georgia; Partha P. Bera, NASA Ames research center; Javier R. Goicoechea, Consejo Superior de Investigaciones Científicas - CSIC; M. Samy El-Shall, Virginia Commonwealth University; Jordy Bouwman, Leiden University; Stefanie N. Milam, NASA Goddard Space Flight Center; Jos Oomens, Radboud University.

Scientific Organising Committee: Liv Hornekær; Els Peeters; Alessandra Candian; Olivier Berné; Xander Tielens; Annemieke Petrignani.

Local Organising Committee: Andrew Cassidy; John Thrower; Frederik Simonsen; Rijutha Jaganathan; Georgios Pantazidis; Karin Vittrup; Liv Hornekær.

### **FROM CLOUDS TO PLANETS II: THE ASTROCHEMICAL LINK**

Harnack Haus, Berlin (28.09-02.10, 2020;

<https://events.mpe.mpg.de/event/12/overview>)

In 2015, we gathered at the Harnack Haus in Berlin to discuss about star and planet formation and the crucial role played by Astrochemistry in our understanding of the various steps that transform an interstellar cloud in stellar systems like our own. It is now time to meet again and present the exciting results that have been achieved in recent years, thanks to ALMA, IRAM, JVLA, GBT, APEX, SOFIA and other facilities, as well as thanks to coordinated efforts in the laboratory and theory (in particular, quantum chemistry and chemical-dynamical models of evolving clouds and disks). This will be important to cast a fresh look into the future, which we already know is going to be bright, thanks to revolutionary telescopes coming up in the next few years (such as JWST and ELT) and next decades (SKA and ngVLA).

During the conference, we will make a journey through space and time, starting from interstellar clouds and then moving to cloud filaments and dense cores on the verge of star formation, to protostars and their embedded disks, to planet-forming disks to exoplanet and finally landing in our Solar System, while delving into laboratory facilities and theoretical calculations and simulations. Each evening, before dinner, there will be a general talk on each topic of the conference (the “aperitive talk”), to allow all communities to understand better the “big picture” and to facilitate finding links across disciplines, which always provide fertile ground in our journey towards understanding our astrochemical origins.

Students and young researchers are encouraged to attend and interact with all participants, to present their work and broaden their horizons. Some financial help will be available for them upon request.

The total number of participants is limited to less than or equal to 120.

If you are interested in attending and present an oral contribution or poster, the deadline for the abstract submission is the 31th May. Please follow instructions at <https://events.mpe.mpg.de/event/12/abstracts/>