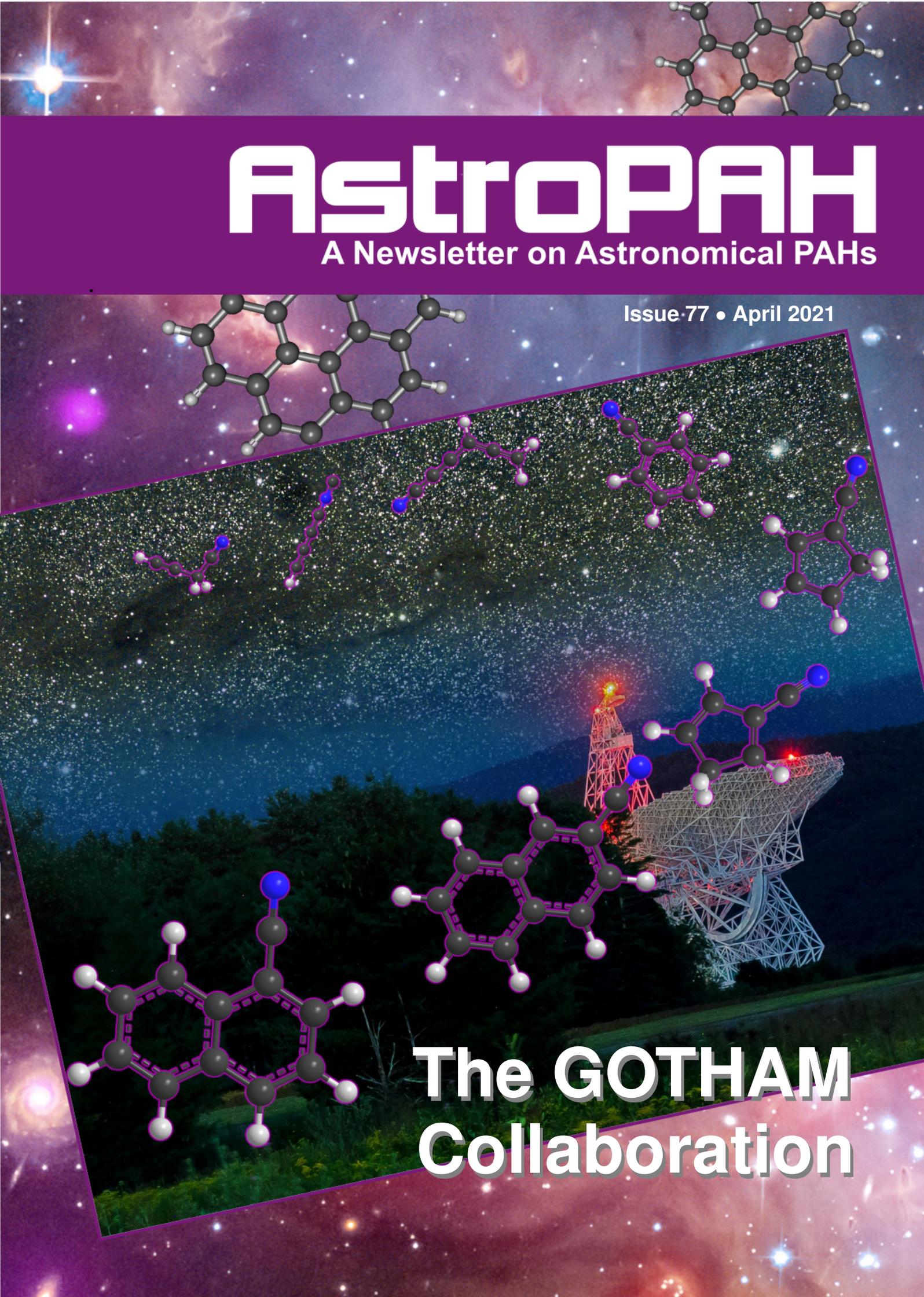


AstropAH

A Newsletter on Astronomical PAHs

Issue 77 • April 2021



The GOTHAM
Collaboration



Editorial

Dear Colleagues,

Welcome to our 77th AstroPAH volume! We hope all of you are healthy and doing well!

The Picture of the Month shows an illustration of the GOTHAM interstellar observation of aromatic and carbon-chain molecules. GOTHAM utilizes the Green Bank Telescope. You can read all about this exciting collaboration in the In Focus. We thank Dr. Brett McGuire for presenting the GOTHAM effort to explore aromatic molecules in the interstellar medium in our In Focus.

Like always, we have many new abstracts to share with you this month. These include cosmic PAH emission reports, soot chemistry as well as the latest publication from GOTHAM on the detection of two interstellar PAHs. Thank you once again for your contributions!

We are also pleased to share two more announcements with you: a PhD opportunity at the Université Côte d'Azur, France on the spectroscopic study of Buckminsterfullerenes (application deadline: 21 May 2021), and the launch of the first version of the online AROMA mass spectrometry database.

You can also go see our new PAH of the Month [on our Instagram page!](#)

We hope you enjoy reading our newsletter, and we thank you for your dedication and interest in AstroPAH! Please continue sending us your contributions, and if you wish to contact us, feel free to use our [email](#).

Enjoy reading our newsletter!

The Editorial Team

**Next issue: 20 May 2021.
Submission deadline: 7 May 2021.**

AstroPAH Newsletter

Editorial Board:

Editor-in-Chief

Prof. Alexander Tielens

Leiden Observatory
(The Netherlands)

Executive Editor

Dr. Isabel Aleman

Institute of Physics and Chemistry,
UNIFEI (Brazil)

Editors

Dr. David Dubois

NASA Ames Research Center (USA)

Dr. Helgi Rafn Hróðmarsson

Leiden Observatory
(The Netherlands)

Dr. Kin Long Kelvin Lee

Massachusetts Institute
of Technology (USA)

Dr. Donatella Loru

Deutsches Elektronen-Synchrotron
(Germany)

Dr. Elisabetta Micelotta

Department of Physics
University of Helsinki (Finland)

Dr. Ella Sciamma-O'Brien

NASA Ames Research Center (USA)

Dr. Sandra Wiersma

Institute de Recherche en
Astrophysique et Planétologie
(France)

Contents

PAH Picture of the Month	1
Editorial	2
In Focus	4
Recent Papers	10
Announcements	19

PAH Picture of the Month

Artistic illustration showing the GOTHAM interstellar observation of aromatic and carbon-chains molecules using spectral matched filtering of radio data from the Green Bank Telescope. More information about the GOTHAM collaboration can be found in the In Focus.

Credits: Brett A. McGuire



Contact us:

astropah@strw.leidenuniv.nl

<http://astropah-news.strw.leidenuniv.nl>

[Click here to Subscribe to AstroPAH](#)

[Click here to Contribute to AstroPAH](#)

This newsletter is edited in \LaTeX . Newsletter Design by: Isabel Aleman. Image Credits: Background image in this page: NASA, ESA, and the Hubble Heritage Team (STScI/AURA). Headers background: X-ray and optical image composition. X-ray by Chandra: NASA/CXC/Univ.Potsdam/L.Oskinova et al; Optical by Hubble: NASA/STScI; Infrared by Spitzer: NASA/JPL-Caltech.

Aromatic Explorations into the Interstellar Medium

The GOTHAM collaboration



Overview

PI: Brett McGuire, MIT

The GOTHAM Collaboration can trace its origins back to 2016, when team members Sergei Kalenskii, Anthony Remijan, and I put together a Green Bank Telescope (GBT) proposal to search for benzonitrile ($c\text{-C}_6\text{H}_5\text{CN}$) in TMC-1. Sergei had found some suggestive evidence for the molecule in the publicly available data from Norio Kaifu's earlier survey of the region with the Nobeyama 45-m telescope. Over the course of the next year, it became evident that benzonitrile was not only present in the source, but shockingly abundant (McGuire et al. 2018, *Science* **359**, 202).

The presence of a benzene-ring molecule in this cold, dark, starless core dominated by relatively esoteric long-chain carbon molecules was astonishing. This led us to ask: what else is hiding, both in TMC-1 and sources like it, beyond the reach of the previous generation of telescopes and just waiting for the power of the GBT to uncover?

To answer these questions, a pair of projects on the GBT have been underway since 2018: GOTHAM (GBT Observations of TMC-1: Hunting Aromatic Molecules) and ARKHAM (A Rigorous K-Band Hunt for Aromatic Molecules). GOTHAM is an extremely high-sensitivity,

high-spectral resolution spectral line survey of TMC-1, covering 2–33.5 GHz with a few gaps, while ARKHAM hunts for signatures of aromatic chemistry in other dark clouds.

It quickly became obvious that conducting these observations, analyzing the results, and putting those results in context would take a dedicated, sustained effort from a team of researchers in all areas of astrochemistry. The GOTHAM collaboration was formed shortly after the GBT Large Project of the same name was accepted. GOTHAM (the collaboration) not only conducts and analyzes the GBT observations, but carries out related laboratory spectroscopic and reaction measurement experiments, updates, refines, and expands astrochemical models, and conducts complementary observations on the VLA and other facilities.

In the next few pages, we present overviews of these areas from the Co-PIs who lead each. As an astrochemistry collaboration, our team members naturally contribute to multiple different areas of the work, but can be roughly broken down as follows (in no particular order):

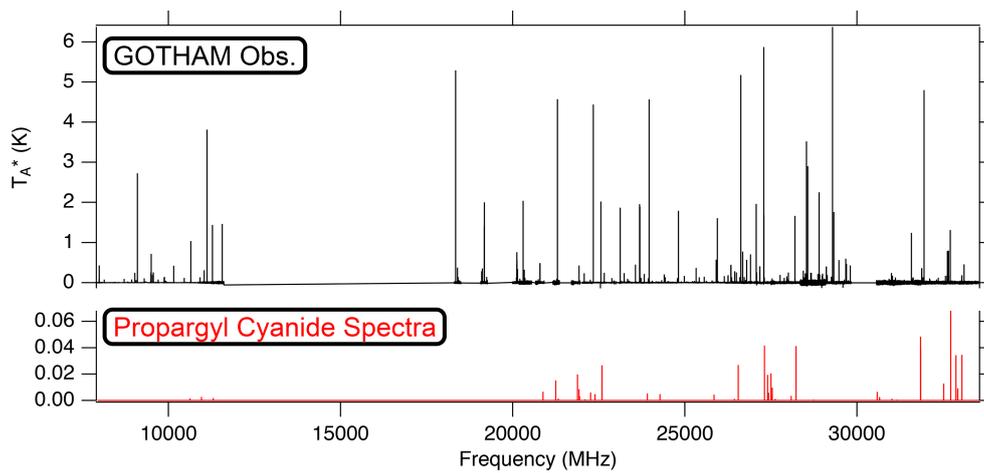
- **Observations** (Co-PI Andrew Burkhardt): Ryan Loomis, Mark Siebert, Anthony Remijan, Sergei Kalenskii, and Maddy Sita.
- **Laboratory** (Co-PI Ilsa Cooke): Kelvin Lee, Bryan Changala, Michael McCarthy, Stefanie Milam, and Haley Scolati
- **Modeling** (Co-PI Ci Xue): Chris Shingledecker, Martin Cordiner, Eric Herbst, and Steve Charnley.

Astronomical Observations

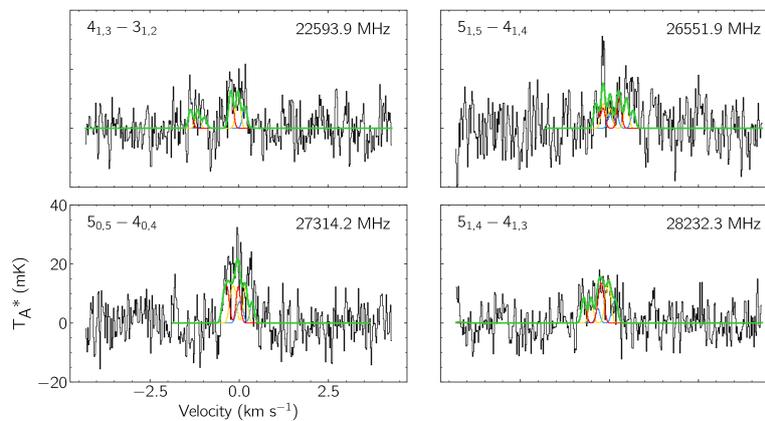
Co-PI: Andrew Burkhardt, CfA

The formation of aromatic molecules has remained poorly constrained for decades due to the inability to detect any specific PAHs within the highly degenerate vibrational features that make up the Unidentified Infrared Bands. In addition, the lack of a permanent electric dipole moment for key aromatic building blocks like benzene (C_6H_6) and naphthalene ($C_{10}H_8$) make them invisible to radio observations; otherwise the main workhorse for molecular astrophysics. As a result, it is not clear whether aromaticity primarily originates from the envelopes of evolved stars (top-down) or from the build-up from small chains in dark clouds (bottom-up). However, polar, functionalized rings with theoretically bright radio transitions do exist and could serve as proxies of these fundamental cyclic species.

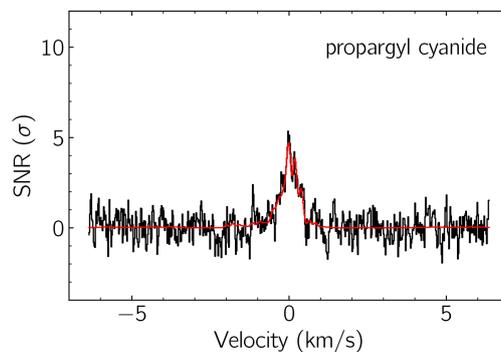
As part of a greater combined observing, modeling, and laboratory effort to critically examine the formation of aromatics at the earliest stages of star formation, the GOTHAM (GBT Observations of TMC-1: Hunting for Aromatic Molecules) survey is a 700+ hour GBT Large Project performing an extremely sensitive spectral survey of the prototypical dark cloud TMC-1, while the companion ARKHAM (A Rigorous K/Ka band Hunt for Aromatic Molecules) is searching for evidence of aromatic chemistry outside of TMC1 through detecting $c-C_6H_5CN$.



MCMC Fitting



Spectral Stack



Matched Filter

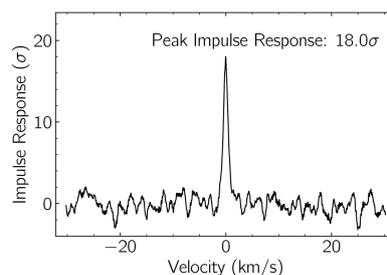


Figure 1. Depiction of the spectral workflow for GOTHAM observations: from the 100 m dish to the matched filter detection of molecules with faint emission.

Utilizing advanced spectral stacking and matched filtering techniques, GOTHAM has resulted in nearly twenty new interstellar molecules and numerous new isotopologues, including the first individually detected aromatic molecule (C_6H_5CN), PAHs (1- & 2- $C_{10}H_7CN$), 5-membered rings (1- & 2- C_5H_5CN), and the longest carbon-chain molecule ($HC_{11}N$). These new detections have opened up an entire new regime of radio-based astrochemistry, showing that aromatic molecules are highly abundant in these cold dense environments. This is surprising as smaller PAHs such as these were thought to be efficiently destroyed prior to dark cloud formation. Similarly, ARKHAM has expanded the horizons for aromaticity, where we have successfully detected $c-C_6H_5CN$ toward all four initial target sources as part of the first data release; the implication is that aromatic chemistry is ubiquitous throughout early star formation. The combined insight from GOTHAM and ARKHAM pushes the limit of what astrochemistry we originally thought is possible, particularly as these discoveries highlight the importance of aromatic species at each stage of stellar evolution.

Chemical Modeling

co-PI: Ceci Xue, UVa

As the primordial stage of star formation, dark clouds set the initial conditions for chemical models of later phases. With carbonaceous molecules probing a significant portion of the overall carbon budget, their discoveries in the dark cloud TMC-1 have important implications on refining both the molecular and elemental carbon content of the earliest stages of star formation. With an emphasis on molecular and elemental content of TMC-1 respectively, two findings that the modeling subgroup of the GOTHAM collaboration reported are highlighted below.

- The GOTHAM studies of aromatic and carbon-chains molecules have provided rigorous constraints on the observed abundances of these species and used them to constrain astrochemical models. As shown in Figure 1, however, the modeled abundances of the aromatic molecules, obtained from a refined gas-grain astrochemical model, are lower by 4–6 orders of magnitudes than the observed abundances. Given that the formation routes of C_6H_5CN and 1- and 2- $C_{10}H_7CN$ from CN radicals with the aromatic hydrocarbons are both barrier-less and exothermic, the inability of the current gas-grain chemical model to reproduce their molecular abundance reveals the insufficient knowledge of the formation of aromatic hydrocarbons under dark cloud conditions.

- C/O ratios have been the center of the controversy for modeling the chemistry under dark cloud conditions. In order to reproduce the observed abundance of the principle carbon-chain molecules (namely cyanopolyynes) in TMC-1, the astrochemical model suggested a higher C/O ratio of 1.1 is needed compared with the C/O ratio of 0.5 observed in diffuse clouds. The enhanced C/O ratio in the cold cloud puts an important constraint not only on modeling the dark cloud chemistry and the chemical process in the late stages of star formation but also on the formation and composition of interstellar grains.

An updated chemical formation network is underdeveloped to account for the other newly detected species and, in turn, to better constrain the elemental ratios under TMC-1 conditions. The detections of aromatic and long carbon-chain molecules in TMC-1 along with the inconsistency of abundances compared with the model results highlight the need for more experimental and theoretical work on their formation and destruction pathways.

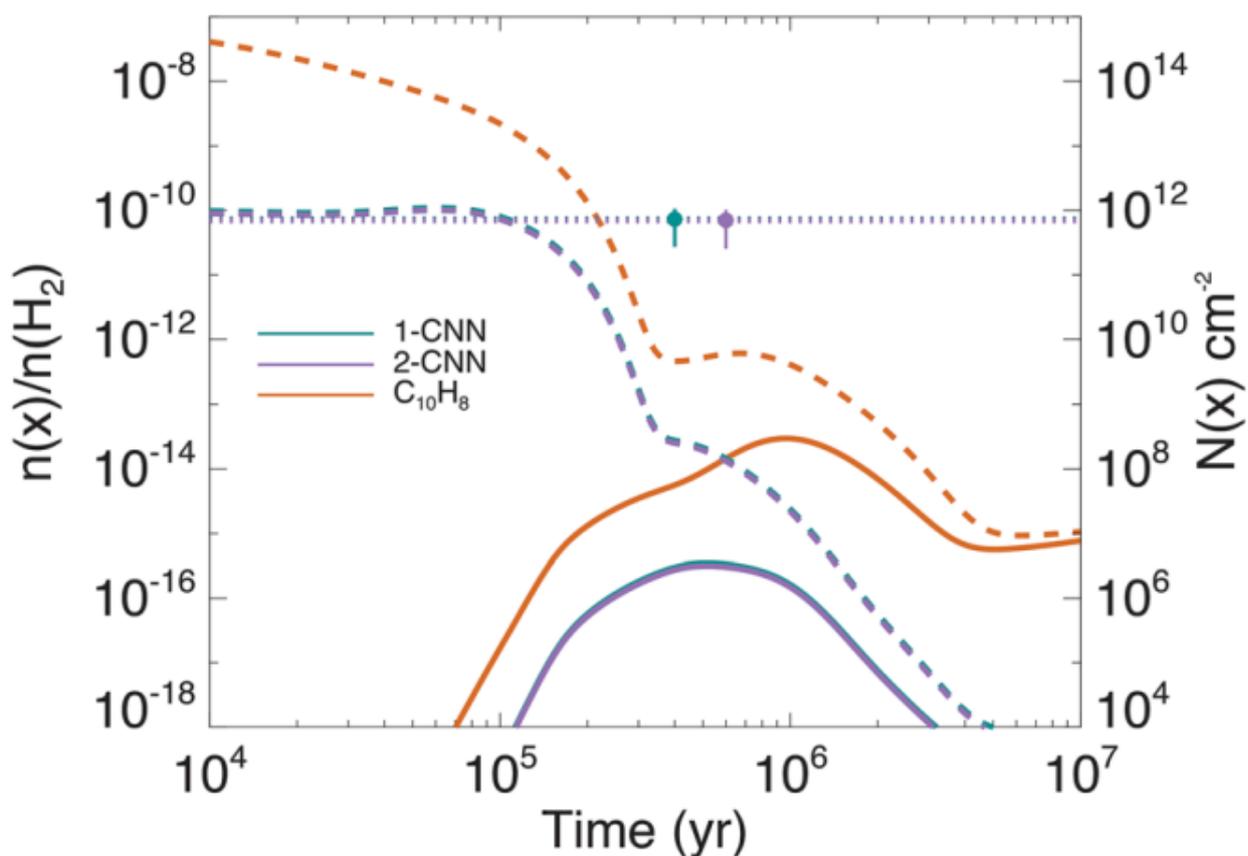


Figure 2. Current state-of-the-art chemical models are unable to reproduce observed quantities of aromatic molecules. See McGuire et al., 2021 DOI: 10.1126/science.abb7535.

Laboratory Spectroscopy

co-PI: Ilsa Cooke, Rennes

Laboratory experiments are key to maximizing the scientific return from the observational data collected in the GOTHAM and ARKHAM surveys. Our laboratory team focuses on three areas of research:

1. High-resolution measurements of rotational spectra,
2. Unbiased reaction studies in discharges coupled to automated and machine learning approaches to identify new species,
3. Low-temperature measurements of kinetic parameters for key reactions.

Some recent highlights from the laboratory include an exhaustive foray into the discharge chemistry of benzene at the Center for Astrophysics — Harvard Smithsonian. In these works, we were successful in the detection and/or refinement of approximately fifty molecules—several of which have eventually led to their discovery in the GOTHAM data; see Figure 3 for a small portion of the laboratory spectrum. This analysis was made possible through combining extremely high throughput broadband rotational spectroscopy and analysis automation with an open-source library for spectroscopic analysis PySpecTools. As part of this work, we had developed a continuous, streamlined workflow from broadband spectra to high precision cavity measurements to rotational Hamiltonians, eventually to the

identification of structures using machine learning and quantum chemistry.

In Rennes, rate constants can be measured for reactions down to around 10 K using the CRESU technique (Cinétique de Réaction en Ecoulement Supersonique Uniforme or Reaction kinetics in uniform supersonic flow). New laboratory techniques are also being developed to measure the products-branching-ratios for neutral-neutral reactions at low temperatures. These critical kinetic data are often lacking from astrochemical models, especially at the low temperatures relevant to TMC-1, where virtually no experimental measurements have been made.

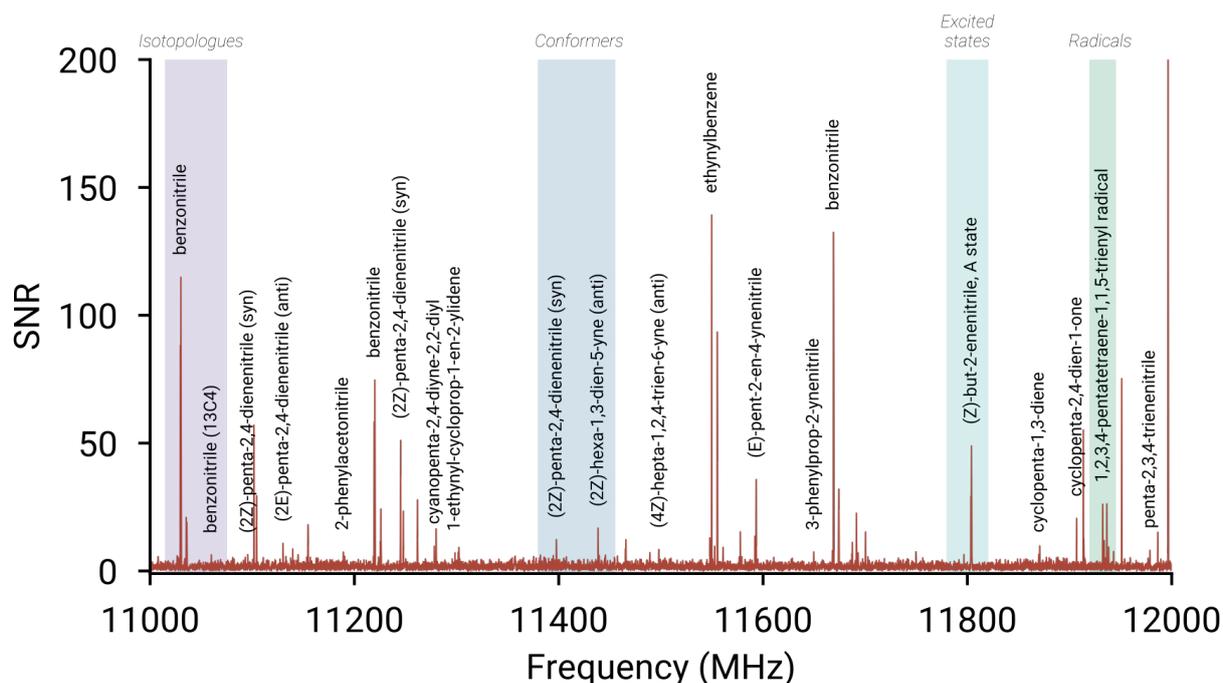


Figure 3. Broadband detection of benzene discharge products with chirped-pulse microwave spectroscopy. With just overnight integration, we can observe a plethora of reaction products; see McCarthy et al. 2020, DOI: 10.1021/acs.jpca.0c02919.

Future Outlooks

PI: Brett McGuire, MIT

GOTHAM is just getting started. Our results so far are just the low-hanging fruit. As we move forward, we will begin to explore more holistic views of both TMC-1 and aromatic chemistry in general, all the while continuing to expand our observational data set and fill in critical gaps in our understanding of these sources (we're looking at you, spatial extent and structure). In the laboratory, we will push on with our reaction screening studies to understand what pockets of chemical space may yield unexpected results, and our modeling subteams will continue to build the foundations of aromatic chemistry into our networks and codes. It's a long road, but we're excited to see where it takes us next.



Abstracts

Detection of two interstellar polycyclic aromatic hydrocarbons via spectral matched filtering

Brett A. McGuire^{1,2,3}, Ryan A. Loomis², Andrew M. Burkhardt³, Kin Long Kelvin Lee^{1,3}, Christopher N. Shingledecker^{4,5,6}, Steven B. Charnley⁷, Ilsa R. Cooke⁸, Martin A. Cordiner^{7,9}, Eric Herbst^{10,11}, Sergei Kalenskii¹², Mark A. Siebert¹¹, Eric R. Willis¹⁰, Ci Xue¹⁰, Anthony J. Remijan² and Michael C. McCarthy³

¹ Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.

² National Radio Astronomy Observatory, Charlottesville, VA 22903, USA.

³ Center for Astrophysics, Harvard & Smithsonian, Cambridge, MA 02138, USA.

⁴ Department of Physics and Astronomy, Benedictine College, Atchison, KS 66002, USA.

⁵ Center for Astrochemical Studies, Max Planck Institute for Extraterrestrial Physics, Garching, Germany.

⁶ Institute for Theoretical Chemistry, University of Stuttgart, Stuttgart, Germany.

⁷ Astrochemistry Laboratory and the Goddard Center for Astrobiology, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA.

⁸ Université de Rennes, Centre National de la Recherche Scientifique, Institut de Physique de Rennes, Unité Mixte de Recherche 6251, F-35000 Rennes, France.

⁹ Institute for Astrophysics and Computational Sciences, Department of Physics, Catholic University of America, Washington, DC 20064, USA.

¹⁰ Department of Chemistry, University of Virginia, Charlottesville, VA 22904, USA.

¹¹ Department of Astronomy, University of Virginia, Charlottesville, VA 22904, USA.

¹² Astro Space Center, Lebedev Physical Institute, Russian Academy of Sciences, Moscow, Russia.

Unidentified infrared emission bands are ubiquitous in many astronomical sources. These bands are widely, if not unanimously, attributed to collective emissions from polycyclic aromatic hydrocarbon (PAH) molecules, yet no single species of this class has been identified in space. Using spectral matched filtering of radio data from the Green Bank Telescope, we detected two nitrile-group-functionalized PAHs, 1- and 2-cyanonaphthalene, in the interstellar medium. Both bicyclic ring molecules were observed in the TMC-1 molecular cloud. In this paper, we discuss potential in situ gas-phase PAH formation pathways from smaller organic precursor molecules.

E-mail: brettmc@mit.edu

Science, Vol. 371, Issue 6535, pp. 1265-1269, (2021)

<https://science.sciencemag.org/content/371/6535/1265.abstract>

Molecular content of nascent soot: Family characterization using two-step laser desorption laser ionization mass spectrometry

Hassan Sabbah¹, Mario Commodo², Francesca Picca³, Gianluigi De Falco³, Patrizi aMinutolo², Andrea D'Anna³ and Christine Joblin¹

¹ Institut de Recherche en Astrophysique et Planétologie (IRAP), Université de Toulouse (UPS), CNRS, CNES, 9 Av. du Colonel Roche, 31028 Toulouse Cedex 4, France

² Istituto di Ricerche sulla Combustione, CNR, P.le Tecchio 80, 80125 Napoli, Italy

³ Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale - Università degli Studi di Napoli Federico II, P.le Tecchio 80, 80125 Napoli, Italy

Molecules constituting nascent soot particles have been analyzed by two-step laser desorption laser ionization mass spectrometry. Three samples have been collected from a slightly sooting ethylene/air premixed flame with the aim to investigate soot composition in the transition from nucleated to just-grown soot particles. Sampling locations have been selected based on the evolution of the particle size distribution along the flame axis. The mass spectrometric results point to a strong evolution of the molecular composition. Just-nucleated soot is rich in polycyclic aromatic hydrocarbons (PAHs) dominated by medium sizes from 18 to 40 carbon atoms but containing sizes as large as 90 carbon atoms. Most abundant PAHs are in the form of *peri*-condensed structures. The presence of a large fraction of odd numbered carbon species shows that pentagonal cycles are a common feature of the detected population. Increasing the distance from the burner outlet, i.e., the particle residence time in flame, leads to an evolution of the chemical composition of this population with a major contribution of carbon clusters including also fullerenes up to about 160 carbon atoms. Our data support a scenario in which large PAHs containing pentagonal rings evolve very efficiently upon thermal processing by a series of dehydrogenation and isomerization processes to form fullerenes. This chemistry happens in the early steps of soot growth showing that carbonization is already active at this stage.

E-mail: anddanna@unina.it, christine.joblin@irap.omp.eu

Proc. Combust. Inst., 38, 1, p1241–1248 (2021)

<https://doi.org/10.1016/j.proci.2020.09.022>

Anharmonic Infrared Spectra of Thermally Excited Pyrene (C₁₆H₁₀): A Combined View of DFT-Based GVPT2 with AnharmonicCaOs, and Approximate DFT Molecular dynamics with DemonNano

Shubhadip Chakraborty¹, Giacomo Mulas^{1,2}, Mathias Rapacioli³, and Christine Joblin¹

¹ Institut de Recherche en Astrophysique et Planétologie, Université de Toulouse (UPS), CNRS, CNES, 9 Av. du Colonel Roche, 31028 Toulouse Cedex 4, France.

² Istituto Nazionale di Astrofisica (INAF), Osservatorio Astronomico di Cagliari, 09047 Selargius (CA), Italy

³ Laboratoire de Chimie et Physique Quantiques (LCPQ/IRSAMC), Université de Toulouse (UPS), CNRS, 118 Route de Narbonne, 31062 Toulouse, France

The study of the Aromatic Infrared Bands (AIBs) in astronomical environments has opened interesting spectroscopic questions on the effect of anharmonicity on the infrared (IR) spectrum of hot polycyclic aromatic hydrocarbons (PAHs) and related species in isolated conditions. The forthcoming James Webb Space Telescope will unveil unprecedented spatial and spectral details in the AIB spectrum; significant advancement is thus necessary *now* to model the infrared emission of PAHs, their presumed carriers, with enough detail to exploit the information content of the AIBs. This requires including anharmonicity in such models, and to do so systematically for all species included, requiring a difficult compromise between accuracy and efficiency.

We performed a benchmark study to compare the performances of two methods in calculating anharmonic spectra, comparing them to available experimental data. One is a full quantum method, AnharmoniCaOs, relying on an *ab initio* potential, and the other relies on Molecular Dynamics simulations using a Density Functional based Tight Binding potential.

The first one is found to be very accurate and detailed, but it becomes computationally very expensive for increasing temperature; the second is faster and can be used for arbitrarily high temperatures, but is less accurate. Still, its results can be used to model the evolution with temperature of isolated bands.

We propose a new recipe to model anharmonic AIB emission using minimal assumptions on the general behaviour of band positions and widths with temperature, which can be defined by a small number of empirical parameters. Modelling accuracy will depend critically on these empirical parameters, allowing for an incremental improvement in model results, as better estimates become gradually available.

E-mail: giacomo.mulas@inaf.it

accepted for publication in J. Mol. Spec. (2021)

<https://arxiv.org/abs/2102.06582>

A spectroscopic view on cosmic PAH emission

Els Peeters^{1,2}, Cameron Mackie³, Alessandra Candian^{4,5} and Alexander G. G. M. Tielens⁵

¹ Department of Physics & Astronomy and Institute for Earth and Space Exploration, University of Western Ontario, London, Canada

² SETI Institute, 189 Bernardo Avenue, Suite 100, Mountain View, CA 94043, USA

³ Lawrence Berkeley National Laboratory, University of California, Berkeley, USA

⁴ van 't Hoff Institute for Molecular Sciences, University of Amsterdam, the Netherlands

⁵ Leiden Observatory, Leiden University, the Netherlands

Polycyclic Aromatic Hydrocarbon molecules (PAHs) are ubiquitously present at high abundances in the Universe. They are detected through their infrared (IR) fluorescence UV pumped by nearby massive stars. Hence, their infrared emission is used to determine the star formation rate in galaxies, one of the key indicators for understanding the evolution of galaxies. Together with fullerenes, PAHs are the largest molecules found in space. They significantly partake in a variety of physical and chemical processes in space, influencing star and planet formation as well as galaxy evolution.

Since the IR features from PAHs originate from chemical bonds involving only nearest neighbor atoms, they have only a weak dependence on the size and structure of the molecule, and it is therefore not possible to identify the individual PAH molecules that make up the cosmic PAH family. This strongly hampers the interpretation of their astronomical fingerprints. Despite the lack of identification, constraints can be set on the characteristics of the cosmic PAH family thanks to a joint effort of astronomers, physicists, and chemists.

This account presents the spectroscopic properties of the cosmic PAH emission as well as the intrinsic spectroscopic properties of PAHs and astronomical modeling of the PAH evolution required for the interpretation of the cosmic PAH characteristics. We discuss the observed spectral signatures tracing PAH properties such as charge, size, and structure and highlight the related challenges. We discuss the recent success of anharmonic calculations of PAH infrared absorption and emission spectra and outline the path forward. Finally, we illustrate the importance of models on PAH processing for the interpretation of the astronomical data in terms of the charge balance and PAH destruction.

Throughout the paper, we emphasize that huge progress is on the horizon on the astronomical front. Indeed, the world is eagerly awaiting the launch of the James Webb Space Telescope (JWST). With its incredible improvement in spatial resolution, combined with its complete spectral coverage of the PAH infrared emission bands at medium spectral resolution and superb sensitivity, JWST will revolutionize PAH research. Previous observations could only present spectra averaged over regions with vastly different properties, thus greatly confusing their interpretation. The amazing spatial resolution of JWST will disentangle these different regions. This will allow us to quantify precisely how PAHs are modified by the physical conditions of their host environment and thus trace how PAHs evolve across space. However, this will only be achieved when the necessary (and still missing) fundamental properties of PAHs, outlined in this paper, are known. We strongly encourage you to join this effort.

E-mail: epeeters@uwo.ca

Acc. Chem. Res. (2021)

<https://doi.org/10.1021/acs.accounts.0c00747>

Interaction of Aromatic Molecules with Forsterite: Accuracy of the Periodic DFT-D4 Method

Dario Campisi¹, Thanja Lamberts^{1,2}, Nelson Y. Dzade³, Rocco Martinazzo⁴, Inge Loes ten Kate⁵ and Alexander G. G. M. Tielens¹

¹ Leiden Observatory, Leiden University, Niels Bohrweg 2, 2333 CA Leiden, The Netherlands

² Leiden Institute of Chemistry, Leiden University, Einsteinweg 55, 2300 RA Leiden, The Netherlands

³ Cardiff University, Main Building, Park Place, CF10 3AT Cardiff, U.K.

⁴ Department of Chemistry, Università degli Studi di Milano, Via Golgi 19, 20133 Milan, Italy

⁵ Department of Earth Sciences, Faculty of Geosciences, Utrecht University, Princetonlaan

Density functional theory (DFT) has provided deep atomic-level insights into the adsorption behavior of aromatic molecules on solid surfaces. However, modeling the surface phenomena of large molecules on mineral surfaces with accurate plane wave methods (PW) can be orders of magnitude more computationally expensive than localized atomic orbitals (LCAO) methods. In the present work, we propose a less costly approach based on the DFT-D4 method (PBE-D4), using LCAO, to study the interactions of aromatic molecules with the 010 forsterite (Mg_2SiO_4) surface for their relevance in astrochemistry. We studied the interaction of benzene with the pristine 010 forsterite surface and with transition-metal cations (Fe_2^+ and Ni_2^+) using PBE-D4 and a vdW-inclusive density functional (Dion, Rydberg, Schröder, Langreth, and Lundqvist (DRSLL)) with LCAO methods. PBE-D4 shows good agreement with coupled-cluster methods (CCSD(T)) for the binding energy trend of cation complexes and with PW methods for the binding energy of benzene on the forsterite surface with a difference of about 0.03 eV. The basis set superposition error (BSSE) correction is shown to be essential to ensure a correct estimation of the binding energies even when large basis sets are employed for single-point calculations of the optimized structures with smaller basis sets. We also studied the interaction of naphthalene and benzocoronene on pristine and transition-metal-doped 010 forsterite surfaces as a test case for PBE-D4. Yielding results that are in good agreement with the plane wave methods with a difference of about 0.02–0.17 eV, the PBE-D4 method is demonstrated to be effective in unraveling the binding structures and the energetic trends of aromatic molecules on pristine and transition-metal-doped forsterite mineral surfaces. Furthermore, PBE-D4 results are in good agreement with its predecessor PBE-D3(BJM) and with the vdW-inclusive density functionals, as long as transition metals are not involved. Hence, PBE-D4/CP-DZP has been proven to be a robust theory level to study the interaction of aromatic molecules on mineral surfaces.

E-mail: campisi@strw.leidenuniv.nl

accepted for publication in J. Phys. Chem. A (2021)

<https://doi.org/10.1021/acs.jpca.1c02326>

Rapid soot inception via α -alkynyl substitution of polycyclic aromatic hydrocarbons

Peng Liu¹, Hanfeng Jin¹, Jiuzhong Yang², Zepeng Li^{1,3}, Anthony Bennett¹, Amir Farooq¹, S. Mani Sarathy¹ and William L. Roberts¹

¹ King Abdullah University of Science and Technology (KAUST), Clean Combustion Research Center, Thuwal 23955-6900, Saudi Arabia.

² National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, An-hui 230029, China.

³ State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China.

Soot particles alter global climate and dominate the origin and evolution of carbonaceous interstellar material. Convincing experimental evidence has linked polycyclic aromatic hydrocarbons (PAH) to soot inception under low-temperature astrochemistry and high-temperature combustion conditions. However, significant gaps still remain in the knowledge of PAH and soot formation mechanisms. Here, we report theoretical and experimental evidence for a soot inception and growth pathway driven by peri-condensed aromatic hydrocarbons (PCAH) with an alkynyl substitution. Initially, free radicals attack the α -alkynyl substitution of PCAHs to form covalently bound compounds yielding resonantly stabilized radicals (RSRs), which promote further clustering through repeated addition reactions with negligible energy barriers. The proposed pathway is shown to be competitive at temperatures relevant to astrochemistry, engine exhaust manifold and flames because it does not require H-abstraction reactions, the requisite reaction precursors are in abundance, and the reaction rate is high. Such addition reactions of PCAHs with α -alkyne substituents create covalently bound clusters from moderate-size PAHs that may otherwise be too small to coagulate.

E-mail: peng.liu.1@kaust.edu.sa; hanfeng.jin@kaust.edu.sa

Fuel, Vol 295, 120580 (2021)

<https://www.sciencedirect.com/science/article/pii/S0016236121004567>

Gas-phase synthesis of corannulene — a molecular building block of fullerenes

L. Zhao¹, S. Doddipatla¹, R. I. Kaiser¹, W. Lu², O. Kostko², M. Ahmed², L. B. Tuli³, A. N. Morozov³, A. H. Howlader³, S. F. Wnuk³, A. M. Mebel³, V. N. Azyazov^{4,5}, R. K. Mohamed⁶ and F. R. Fischer^{6,7,8}

¹ Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii, USA

² Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, USA

³ Department of Chemistry and Biochemistry, Florida International University, Miami, Florida, USA

⁴ Samara National Research University, Samara 443086, Russian Federation

⁵ Lebedev Physical Institute, Samara, Russian Federation

⁶ Department of Chemistry, University of California, Berkeley, CA 94720, USA

⁷ Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

⁸ Kavli Energy Nano Sciences Institute at the University of California Berkeley and the Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

Fullerenes (C_{60} , C_{70}) detected in planetary nebulae and carbonaceous chondrites have been implicated to play a key role in the astrochemical evolution of the interstellar medium. However, the formation mechanism of even their simplest molecular building block — the corannulene molecule ($C_{20}H_{10}$) — has remained elusive. Here we demonstrate via a combined molecular beams and *ab initio* investigation that corannulene can be synthesized in the gas phase through the reactions of 7-fluoranthenyl ($C_{16}H_9$) and benzo[ghi]fluoranthen-5-yl ($C_{18}H_9$) radicals with acetylene (C_2H_2) mimicking conditions in carbon-rich circumstellar envelopes. This reaction sequence reveals a reaction class in which a polycyclic aromatic hydrocarbon (PAH) radical undergoes ring expansion while simultaneously forming an out-of-plane carbon backbone central to 3D nanostructures such as buckybowl and buckyball. These fundamental reaction mechanisms are critical in facilitating an intimate understanding of the origin and evolution of the molecular universe and, in particular, of carbon in our galaxy.

E-mail: ralfk@hawaii.edu

Phys. Chem. Chem. Phys., 23, 5740-5749 (2021)

<https://doi.org/10.1039/D0CP06537D>

Impact of Metals on (Star)Dust Chemistry: A Laboratory Astrophysics Approach

Rémi Bérard^{1,2}, Kremena Makasheva², Karine Demyk¹, Aude Simon³, Dianailys Nuñez Reyes¹, Fabrizio Mastrorocco¹, Hassan Sabbah^{1,4} and Christine Joblin¹

¹ IRAP, CNRS, UPS, CNES, Université de Toulouse, Toulouse, France,

² LAPLACE, CNRS, UPS, INPT, Université de Toulouse, Toulouse, France

³ LCPQ-IRSAMC, UPS, CNRS, Université de Toulouse, Toulouse, France

⁴ LCAR-IRSAMC, UPS, CNRS, Université de Toulouse, Toulouse, France

Laboratory experiments are essential in exploring the mechanisms involved in stardust formation. One key question is how a metal is incorporated into dust for an environment rich in elements involved in stardust formation (C, H, O, Si). To address experimentally this question we have used a radiofrequency cold plasma reactor in which cyclic organosilicon dust formation is observed. Metallic (silver) atoms were injected in the plasma during the dust nucleation phase to study their incorporation in the dust. The experiments show formation of silver nanoparticles (~ 15 nm) under conditions in which organosilicon dust of size 200 nm or less is grown. The presence of AgSiO bonds, revealed by infrared spectroscopy, suggests the presence of junctions between the metallic nanoparticles and the organosilicon dust. Even after annealing we could not conclude on the formation of silver silicates, emphasizing that most of silver is included in the metallic nanoparticles. The molecular analysis performed by laser mass spectrometry exhibits a complex chemistry leading to a variety of molecules including large hydrocarbons and organometallic species. In order to gain insights into the involved chemical molecular pathways, the reactivity of silver atoms/ions with acetylene was studied in a laser vaporization source. Key organometallic species, $\text{Ag}_n\text{C}_2\text{H}_m$ ($n = 1-3$; $m = 0-2$), were identified and their structures and energetic data computed using density functional theory. This allows us to propose that molecular Ag–C seeds promote the formation of Ag clusters but also catalyze hydrocarbon growth. Throughout the article, we show how the developed methodology can be used to characterize the incorporation of metal atoms both in the molecular and dust phases. The presence of silver species in the plasma was motivated by objectives finding their application in other research fields than astrochemistry. Still, the reported methodology is a demonstration laying down the ground for future studies on metals of astrophysical interest, such as iron.

E-mail: christine.joblin@irap.omp.eu

Front. Astron. Space Sci. 8:654879 (2021)

<https://doi.org/10.3389/fspas.2021.654879>

The Interstellar Medium toward the Galactic Center Source 2MASS J17470898–2829561

T. R. Geballe¹, Y. Pendleton², J. Chiar³, and A. G. G. M. Tielens⁴

¹ Gemini Observatory/NSF's NOIRLab, Hilo, Hawai'i, USA

² NASA Ames Research Center, Moffett Field, California, USA

³ Diablo Valley College, Pleasant Hill, CA, USA

⁴ Leiden University, Leiden, The Netherlands

We describe and discuss remarkable infrared spectra, covering key portions of the 2 – 5 μm wavelength interval, of the probable OH/IR supergiant 2MASS J17470898–2829561 (2M1747), located in direction of the Sgr B molecular cloud complex within the Central Molecular Zone (CMZ) of the Galaxy. This star was originally singled out for examination based on its suitability for spectroscopy of lines of H_3^+ in the CMZ. Analysis of the spectra shows that 2M1747 is deeply embedded within Sgr B1, with $A_V \gtrsim 100$ mag, making it the only star within Sgr B for which infrared spectra have been obtained at present, and thereby a unique infrared probe of the dense interstellar medium within the CMZ. Despite the high extinction, spectra of 2M1747 reveal a veiled photosphere in the K band and circumstellar gas in the M band, giving clues as to its nature. Its 3.5 – 4.0 μm spectrum contains the strongest absorption lines of H_3^+ observed toward any object to date. The 4.5 – 4.8 μm spectrum has impressively deep and wide absorption lines of interstellar CO, most of which arise in dense gas within Sgr B1. The 3 – 5 μm spectrum also contains several solid state absorption features, which are characteristic of both dense and diffuse clouds, and which raise questions about the identifications of some of these features. We discuss the nature of the star, the extinction to it, the extinction law for dust in the CMZ, and the identifications of the various solid-state features and where they are produced along this complex line of sight.

E-mail: tom.geballe@noirlab.edu

accepted for publication in *Astrophys. J.* (2021)

<https://arxiv.org/abs/2103.06514>



Announcements

PhD proposal:

In silico spectroscopic studies of the Buckminsterfullerene C₆₀ in view of the interpretation of experimental studies and astrophysical observations

Université Côte d'Azur, France

Advertised by Patrick Cassam-Chenai

Buckminsterfullerene, C₆₀, is an icosahedral molecule constituted of 60 carbon atoms. Its unique physical properties are the object of active researches. It has been detected in a great variety of circumstellar and interstellar environments, including protoplanetary nebulae^[1], thanks to its infrared (IR) spectra, which results from transitions between its vibrational energy levels. Furthermore, a recent high-resolution spectroscopic experiment on isolated molecules has produced data lists of unprecedented quality^[2], whose interpretation remains incomplete. This is why a theoretical study of the rotation-vibration spectrum of C₆₀ is of paramount interest.

In our laboratory, we have developed a computer code, CONVIV, that solves the Schrödinger equation for molecular rotation-vibration degrees of freedom with state-of-the-art accuracy^[3].

It can be used to perform calculations of the infrared spectrum of molecules of arbitrary sizes, including C₆₀ which has 174 internal degrees of freedom. It has enabled us to test the force fields available in the literature for this system^[4]. These tests have revealed that the description of C₆₀ anharmonicity by these force fields is not satisfactory, which is not surprising, because it is only arising from the transformation from internal coordinates (internuclear lengths and angles) into Cartesian coordinates.

The PhD work will first consist in constructing a potential energy surface for C₆₀ able to really capture the anharmonicity of this system. Then, in introducing the use of non-Abelian symmetries in the CONVIV code, to fully exploit the high, icosahedral symmetry of C₆₀ when calculating its rotation-vibration spectrum with this code. Finally, the obtained results will be confronted to the experimental and observational data, in order to extract as much information as possible from the latter.

References

- [1] Y. Zhang, S. Kwok, *Astrophys. J.* **730**, 126 (2011).
- [2] P. B. Changala, M. L. Weichman, K. F. Lee, M. E. Fermann, J. Ye, *Science* **363**, 49 (2019).
- [3] P. Cassam-Chenaï, J. Liévin, *J. Computational Chemistry* **27**, 627-640 (2006).
- [4] D. A. Jelski, L. Nemes, S. Broughton, *J. Cluster Science* **16**, 1 (2005).

E-mail for contact: cassam@unice.fr

Webpage: <https://math.unice.fr/~cassam/>

Deadline for Application: 21 May 2021

Mass Spectrometry Database

Launch of the first version of the AROMA Database

Institut de Recherche en Astrophysique et Planétologie (IRAP), Université de Toulouse (UPS), CNRS, CNES, 9 Av. du Colonel Roche, 31028 Toulouse Cedex 4, France

Advertised by Hassan Sabbah

We announce the launch of the first version of the AROMA database at <https://aroma.irap.omp.eu>. AROMA DB provides information on the molecular content of dust samples recorded with the AROMA (Astrochemistry Research of Organics with Molecular Analyzer) setup developed in the framework of the Nanocosmos ERC synergy project (<https://nanocosmos.iff.csic.es>). The dust samples are cosmic dust analogues that are produced in various reactors (Stardust machine, flames, dusty plasmas, laser vaporization sources. . .) or come from natural samples such as meteorites. Targeted molecules include polycyclic aromatic hydrocarbons (PAHs), carbon clusters, fullerenes, and various hydrocarbons as well as metallic species labelled elements. AROMA DB is developed at IRAP in the framework of the OVGSO (<https://ov-gso.irap.omp.eu/doku.php>), with the objective to share data and tools in mass spectrometry. Your feedback is very welcome to improve the functionalities and the use of the database.

E-mail for contact: Hassan.Sabbah@irap.omp.eu

AstroPAH Newsletter

<http://astropah-news.strw.leidenuniv.nl>

astropah@strw.leidenuniv.nl

Next issue: 20 May 2021

Submission deadline: 7 May 2021