



Editorial

Dear Colleagues,

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

Our Picture of the Month (on the cover) features a spectacular JWST image of the inner region of the Orion nebula. It shows the well-known Orion Bar photodissociation region, which played a prominent role in early astronomical studies of interstellar PAHs. This image was obtained as part of the James Webb Space Telescope Early Release Science program "Photodissociation Regions for All" (PDRs4All, ID1288). For more information, check the press releases on the [PDRs4All webpage](#).

We are happy to introduce our two new editors: Dr. Amee Sidhu and Dr. Julianna Palotás. You can find their interviews in the In Focus section of this issue! Welcome, Amee and Julianna!

This month, we have yet again a great collection of abstracts for you to discover. As always, they cover a broad range of topics such as the study of cosmic dust analogues, the photodissociation of charged PAHs, and formation mechanisms of large PAH clusters.

We also are happy to share the published thesis by Dr. Pragya Chopra, from the Institute of Physical Chemistry, Christian-Albrechts Universität zu Kiel, on the study of PAHs using pump-probe spectroscopy and Near-edge X-ray absorption fine structure spectroscopy.

If you are on Instagram, be sure to check out our next [PAH of the Month!](#)

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 for a future In Focus or other ideas, feel free to use our [email](#).

The Editorial Team

**Next issue: 20 October 2022.
Submission deadline: 7 October 2022.**

AstroPAH Newsletter

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Contact us:

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PAH Picture of the Month

The inner Orion nebula. This image was obtained with the James Webb Space Telescope (JWST). It is a composite image from several filters and represents emission from ionized gas, hydrocarbons, molecular gas, dust and scattered starlight.

Credits: NASA, ESA, CSA, Data reduction and analysis: PDRs4All ERS Team; image processing S. Fuenmayor. The image is available [here](#).

Interview with Dr. Ameek Sidhu

Postdoctoral Associate at Western University, Canada

Dr. Ameek Sidhu is a postdoctoral associate at Western University Canada. She completed her PhD in Astronomy with a specialisation in planetary science and space exploration under the supervision of Professors Els Peeters and Jan Cami at Western University in 2019. Her research focuses on investigating the emission from large carbonaceous molecules, particularly polycyclic aromatic hydrocarbons (PAHs) and fullerenes in the interstellar medium from an observational and theoretical standpoint.



How did you get into PAH-related research?

I took a special course in Astrophysics in the final year of my Masters in Physics. I was so impressed with the course that I decided to pursue a PhD in astronomy. I also wanted to pursue it outside of my home country, India, to broaden my horizons, so I began applying for PhD positions in Astronomy in Canada. Prof. Els Peeters and Jan Cami offered me a PhD position to study the causes of variations in cosmic PAH emission. I was drawn to the research project and began my PhD under their supervision. During my PhD, I had the opportunity to work with Xander Tielens on theoretical modelling of PAH emission, which introduced me to a different area of PAH research.

What is your current research about?

My current research focuses on investigating the PAH and fullerene emission in various astrophysical environments in order to understand how these carbonaceous molecules respond to changes in the physical conditions, such as gas density, temperature, and radiation field strength, of the regions where they reside. I approach this problem from both an observational and theoretical standpoint.

Observationally, I employ unsupervised machine learning algorithms such as Principal Component Analysis to perform detailed analyses of the fluxes of various PAH and fullerene emission features observed in the interstellar medium. Such analyses are useful in

determining the factors that influence the behaviour of the carbonaceous molecules in space.

On the theoretical front, I develop charge distribution-based emission models of individual molecules using their recently measured or quantum chemically calculated molecular properties. I use these models to calculate the emission of a PAH or fullerene molecule in a specific astrophysical environment and compare the results with the available observations. This comparison between the theory and observations reveals information not only about the characteristics of a molecule in a given environment but also about the physical conditions of that environment.

What are, in your opinion, the present forefronts of PAH research?

PAHs are present almost everywhere in the universe and exhibit spectral variations in response to the changes in the physical conditions of the environments where they reside. This sensitivity on physical conditions combined with their omnipresence makes PAHs an excellent tool for probing the physical conditions of astrophysical regions. However, the necessary empirical relationships between PAH spectral characteristics and physical conditions have not been fully developed yet. One of the most challenging aspects of establishing such relationships is that we do not fully understand the molecular physics behind the PAH emission. A combined effort of observations and theory is required to make progress in this direction. In order to fully understand the physics underlying the PAH emission, I think developing a comprehensive photo-chemical evolution model would be helpful in interpreting the high spectral resolution PAH spectra observed with the James Webb Space Telescope.

What was the most important advice somebody gave you?

The famous quote by Abraham Lincoln, "I walk slowly, but I never walk backward", has had the greatest impact on me. This quote gets me going on the days I'm not feeling motivated to work.

What do you do outside of work?

My family and friends are my stress relievers. So, when I'm not working, I spend most of my time with them. I also enjoy painting, reading, and going for hikes.

You just finished your PhD. Can you tell us about your experience going through this milestone? Do you have any advice for students that are preparing to defend?

My PhD journey was a continuous learning experience in research, science communication, networking, and time management. Like any other learning experience, there was a growth curve involved with ups and downs over the course of four years. I persevered and eventually crossed the finish line with a fantastic research experience, some incredible opportunities, and a great network of PAH researchers.

One piece of advice that I can give students is to never be afraid to seek assistance if you are stuck on a problem. I am often guilty of trying to figure everything out on my own. But,

the one thing I learnt along the way was that, when in doubt, ask for help. Others might have figured it out already, and it will save you time.

What does it mean for you to be part of the AstroPAH editorial team?

As a member of the AstroPAH editorial team, I am looking forward to learning more about the work of the broader community of astronomers, theorists, and experimentalists in this field and sharing it with others.

Interview with Dr. Julianna Palotás Postdoctoral Researcher at the University of Maryland, USA



Dr. Julianna Palotás obtained her Bachelor's and Master's degrees in Physics in Budapest, Hungary. After her studies, she moved to the Netherlands to join the group of Prof. Jos Oomens at the FELIX Laboratory under the Horizon2020 Marie Skłodowska-Curie ITN EUROPAH project and as part of the Dutch Astrochemistry Network-II. Currently, she is a postdoctoral researcher in Prof. Leah Dodson's group at the University of Maryland, USA.

How did you get into PAH-related research?

Accidentally! I was looking for interesting PhD positions abroad. A friend of mine drew my attention to an open position at the FELIX Laboratory that aimed to investigate ionised, astrophysically relevant polyaromatic molecules with IR spectroscopy. Previously, I used spectroscopy techniques to study carbon nanotubes, however, I had no astrophysical background or any understanding about PAHs. But I was very much intrigued - Jos was very convincing - and I took the position.

What is your current research about?

I just finished my PhD on ionised fullerenes and large PAHs and recently moved to Maryland and started my first postdoc in the Dodson group! My current research focuses on ion/molecule kinetics and the formation of metal-organic molecules from radiative association reactions.

Which open question in Laboratory Astrophysics would you like to see answered in the near future?

Are there ionized fullerene analogues in space?

Astrochemistry is a very multidisciplinary field. Can you comment on how you collaborate and communicate with different experts and what you like about such interactions?

During my PhD, collaborations were an essential part of the project and networks I was part of. It is interesting to see how other people think about the same topic and questions, and I always feel motivated and inspired after meetings and shared experiments. Also, these collaborations helped me find likeminded people who I had an instant bond with and we became close friends.

What do you do outside of work?

Outside of the lab, I try to stay active and do various sports. I have been practising Brazilian Jiu Jitsu for 6 years, that is something I always make time for.

How do you balance your professional and personal life?

This can be challenging from time to time, requires good time management, planning and clear boundaries. I have my best friends in the same field that I work in, that also helps.

You just finished your PhD. Can you tell us about your experience going through this milestone? Do you have any advice for students that are preparing to defend?

I have an important advice: don't forget to enjoy it. It is a stressful and overwhelming time, but also a great achievement and you should celebrate it. Oh, and pain is temporary but PhD is forever.

What does it mean for you to be part of the AstroPAH editorial team?

Science communication in various forms has always been part of my studies and work. It is something I find important and I am excited to make time for. Being part of the AstroPAH editorial team also means that I am staying close to my favourite molecules and people.



Abstracts

Raman Spectroscopic Study of Pyrene in Cosmic Dust Analogues: Evolution from the Gas to the Solid Phase

Lisseth Gavilan^{1,2}, Claire L. Ricketts^{1,2}, Salma Bejaoui^{1,2}, Christiaan Boersma^{1,3}, Farid Salama¹ and Andrew L. Mattioda¹

¹NASA Ames Research Center, Moffett Field, CA, USA

²Bay Area Environmental Research Institute, Moffett Field, CA, USA

³San Jose State University Research Foundation, San Jose, CA, USA

Raman spectroscopy was employed to characterize pyrene (C₁₆H₁₀), the smallest peri-condensed polycyclic aromatic hydrocarbon (PAH), in microcrystals and in pyrene-derived nanograins. Laboratory spectra in the 200–2000 cm⁻¹ Raman shift region were obtained with a 532 nm laser. The spectrum of microcrystalline pyrene consists of narrow bands (FWHM ~7 cm⁻¹), in good agreement with previous laboratory measurements of single and powder pyrene crystals, and was compared to density functional theory-computed Raman scattering activities of gas phase pyrene monomer and pyrene tetramer clusters, showing that packing in crystals induces shifts in band positions to higher wavenumbers. On the other hand, the spectrum of pyrene-derived nanograins exhibits a broad graphitic G band at 1587 cm⁻¹ (FWHM ~56 cm⁻¹) and multiple disorder D bands, the largest one at 1388 cm⁻¹ (FWHM ~101 cm⁻¹), attributed to defects in the carbonaceous structure. When compared to the D-to-G band strength ratios from the insoluble organic matter (IOM) found in various carbonaceous chondrites, the values found for the pyrene nanograins match those from the highly disordered Allende meteoritic IOM best.

E-mail: Lissethgavilan@gmail.com

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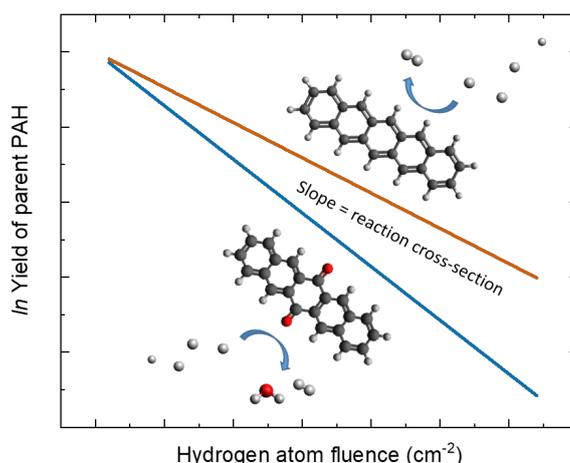
<https://doi.org/10.1021/acsearthspacechem.2c00136>

Enhanced reactivity of oxygen-functionalised PAHs with atomic hydrogen – A route to the formation of small oxygen-carrying molecules

Rijutha Jaganathan¹, Frederik Doktor Skødt Simonsen¹, John D. Thrower¹ and Liv Hornekær^{1,2}

¹Center for Interstellar Catalysis (InterCat), Department of Physics and Astronomy, Aarhus University, Ny Munkegade 120, Aarhus C, Denmark 8000

²Interdisciplinary Nano-Science Centre (iNano), Aarhus University, Gustav Wieds Vej 14, Aarhus C, Denmark 8000



We investigate the interaction of a linear, catacondensed polycyclic aromatic hydrocarbon (PAH), pentacene ($C_{22}H_{14}$), and its oxygen-functionalised form 6, 13 - pentacenequinone ($C_{22}H_{12}O_2$) with atomic hydrogen (H) under interstellar conditions. We compare their reaction cross-sections and reaction products to elucidate the possible role played by oxygen-functionalised PAHs in the formation of small oxygen-carrying molecules in the interstellar medium. We present temperature-programmed desorption measurements in combination with mass spectrometry. The evolution of the mass distribution of the desorbed species with increasing H-atom fluence and their peak desorption temperatures give insight into the reaction products. The experiments reveal reaction cross-sections that are significantly larger for the oxygen-functionalised species compared to pentacene. For both pentacene and 6, 13 - pentacenequinone, hydrogenated species with an even number of excess H-atoms dominate over hydrogenated species with an odd number of H-atoms. The end product, after exposure to large H-fluences, for both pentacene and PQ is fully superhydrogenated pentacene ($C_{22}H_{36}$), with little evidence for any remaining oxygen-containing species. This suggests the release of small molecules OH and/or H_2O by the abstraction of oxygen atoms during hydrogenation, indicating that oxygen functionalised PAHs can act as catalysts for the formation of small oxygen bearing molecules under interstellar conditions.

E-mail: liv@phys.au.dk

Astronomy and Astrophysics, **663**, (2022)

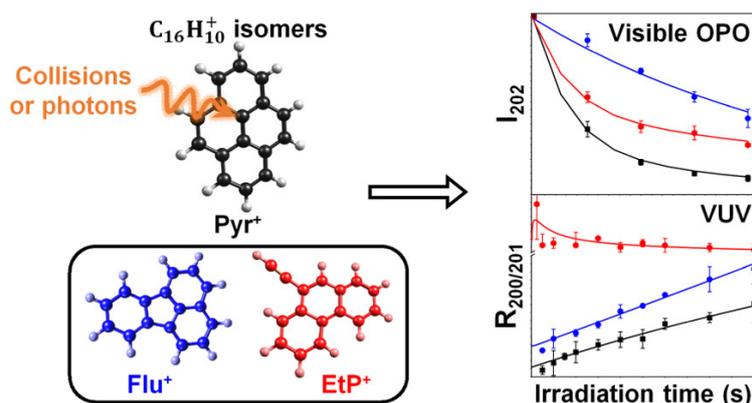
<https://doi.org/10.1051/0004-6361/202243312>

Isomer Differentiation of Trapped $C_{16}H_{10}^+$ Using Low-Energy Collisions and Visible/VUV Photons

M. Viswanathan Vinitha, Venkateswara Rao Mundlapati, Alexandre Marciniak, Mickaël Carlos, Hassan Sabbah, Anthony Bonnamy, Loïc Nogues, David Murat, Odile Coeur-Joly and Christine Joblin

Institut de Recherche en Astrophysique et Planétologie (IRAP), Université Toulouse III - Paul Sabatier, CNRS, CNES, 9 Avenue du Colonel Roche, F-31028 Toulouse, France

Polycyclic aromatic hydrocarbons are major species in astrophysical environments, and this motivates their study in samples of astrochemical interest such as meteorites and laboratory analogues of stardust. Molecular analyses of carbonaceous matter in these samples show a dominant peak at $m/z = 202.078$ corresponding to $C_{16}H_{10}$. Obtaining information on the associated isomeric structures is a challenge for the molecular analysis of samples available in very small quantities (mg or less). Here we show that coupling laser desorption ionization mass spectrometry with ion trapping opens up the possibility of unraveling isomers by activating ion fragmentation via collisions or photon absorption. We report the best criteria for differentiating isomers with comparable dissociation energies, namely pyrene, fluoranthene, and 9-ethynylphenanthrene, on the basis of the parent dissociation curve and the ratio of dehydrogenation channels. Photoabsorption schemes (multiple photon absorption in the visible range and single photon absorption at 10.5 eV) are more effective in differentiating these isomers than activation by low energy collisions. The impact of the activation scheme on the fragmentation kinetics and dehydrogenation pathways is discussed. By analyzing the 10.5 eV photodissociation measurements with a simple kinetic model, we were able to derive a branching ratio for the H and 2H/ H_2 loss channels of the parent ions. The results suggest a role in the formation of H_2 for bay hydrogens that are present in both fluoranthene and 9-ethynylphenanthrene. In addition, we suggest for the latter the presence of a highly competitive 2H loss channel, possibly associated with the formation of a pentagonal ring.



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

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Adsorption of Polycyclic Aromatic Hydrocarbons and C₆₀ onto Forsterite: C–H Bond Activation by the Schottky Vacancy

Dario Campisi^{1,2}, Thanja Lamberts³, Nelson Y. Dzade⁴, Rocco Martinazzo⁵, Inge Loes ten Kate⁶ and Alexander G. G. M. Tielens¹

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

²Department of Chemistry, The University of Chicago, 5735 S Ellis Ave, Chicago, IL 60637, USA

³Leiden Institute of Chemistry, Leiden University, Einsteinweg 55, 2300 RA Leiden, The Netherlands; Leiden Observatory, Leiden University, Niels Bohrweg 2, 2333 CA Leiden, The Netherlands

⁴Cardiff University, Main Building, Park Place, CF10 3AT Cardiff, U.K.; Current Address: John and Willie Leone Family Department of Energy and Mineral Engineering, The Pennsylvania State University, 212 Hosler Building, University Park, PA 16802, USA

⁵Department of Chemistry, Università degli Studi di Milano, Via Golgi 19, 20133 Milan, Italy

⁶Department of Earth Sciences, Faculty of Geosciences, Utrecht University, Princetonlaan 8a, 3584 CB Utrecht, The Netherlands

Understanding how to catalytically break the C–H bond of aromatic molecules, such as polycyclic aromatic hydrocarbons (PAHs), is currently a big challenge and a subject of study in catalysis, astrochemistry, and planetary science. In the latter, the study of the breakdown reaction of PAHs on mineral surfaces is important to understand if PAHs are linked to prebiotic molecules in regions of star and planet formation. In this work, we employed a periodic density functional theory along with Grimme's D4 (DFT-D4) approach for studying the adsorption of a sample of PAHs (naphthalene, anthracene, fluoranthene, pyrene, coronene, and benzocoronene) and fullerene on the [010] forsterite surface and its defective surfaces (Fe-doped and Ni-doped surfaces and a MgO-Schottky vacancy) for their implications in catalysis and astrochemistry. On the basis of structural and binding energy analysis, large PAHs and fullerene present stronger adsorption on the pristine, Fe-doped, and Ni-doped forsterite surfaces than small PAHs. On a MgO-Schottky vacancy, parallel adsorption of the PAH leads to the chemisorption process (C–Si and/or C–O bonds), whereas perpendicular orientation of the PAH leads to the catalytic breaking of the aromatic C–H bond via a barrierless reaction. Spin density and charge analysis show that C–H dissociation is promoted by electron donation from the vacancy to the PAH. As a result of the undercoordinated Si and O atoms, the vacancy acts as a Frustrated Lewis Pair (FLP) catalyst. Therefore, a MgO-Schottky vacancy [010] forsterite surface proved to have potential catalytic activity for the activation of C–H bond in aromatic molecules.

E-mail: campisi@strw.leidenuniv.nl

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Comprehensive survey of dissociative photoionization of quinoline by PEPICO experiments

Umesh R. Kadhane¹, M. V. Vinitha^{1,2}, Karthick Ramanathan¹, Arun S.¹, Jordy Bouwman^{3,4,5}, Lorenzo Avaldi⁶, Paola Bolognesi⁶ and Robert Richter⁷

¹Indian Institute of Space Science and Technology, Thiruvananthapuram 695547, Kerala, India

²Institut de Recherche en Astrophysique et Planétologie (IRAP), CNRS, 9 Avenue du Colonel Roche, F-31028 Toulouse, France

³Department of Chemistry, University of Colorado, Boulder, CO 80309, USA

⁴Institute for Modeling Plasma, Atmospheres and Cosmic Dust (IMPACT), NASA/SSERVI, Boulder, CO 80309, USA

⁵Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, CO 80303, USA

⁶CNR-Istituto di Struttura della Materia, Area della Ricerca di Roma 1, Monterotondo, Roma 00015, Italy

⁷Elettra-Sincrotrone Trieste, Strada Statale 14 - km 163,5 in AREA Science Park, Basovizza, TS 34149, Italy

Dissociative photoionisation of quinoline induced by VUV radiation is investigated using photoelectron-photoion coincidence (PEPICO) spectroscopy. Branching ratios of all the detectable fragment ions are measured as a function of internal energy ranging from 2 to 30 eV. A specific generation hierarchy is observed in the breakdown curves of a set of dissociation channels. Moreover, a careful comparison of the breakdown curves of fragments among the successive generations allowed to establish a decay sequence in the fragmentation of quinoline cation. This enabled us to revisit and refine the understanding of the first generation decay and reassign the origin of few of the higher generation decay products of quinoline cation. With the help of the accompanying computational work (reported concurrently) we have demonstrated the dominance of two different HCN elimination pathways over previously interpreted mechanisms. For the first time a specific pathway for acetylene elimination is identified in quinoline⁺ and the role of isomerization in both acetylene as well as hydrogen cyanide loss is also clearly demonstrated. The experiment also established that the acetylene elimination exclusively occurs from the non-nitrogen containing ring of quinoline cation. The formation of a few astronomically important species is also discussed.

E-mail: umeshk@iist.ac.in

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Photodissociation of Quinoline Cation: Mapping the Potential Energy Surface

Karthick Ramanathan¹, Arun S.¹, Jordy Bouwman^{2,3,4}, Lorenzo Avaldi⁵, M. V. Vinita^{1,6}, Paola Bolognesi⁵, Robert Richter⁷ and Umesh R. Kadhane¹

¹Indian Institute of Space Science and Technology, Thiruvananthapuram 695547, Kerala, India.

²Department of Chemistry, University of Colorado, Boulder, CO 80309, USA.

³Institute for Modeling Plasma, Atmospheres and Cosmic Dust (IMPACT), NASA/SSERVI, Boulder, CO 80309, USA.

⁴Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, CO 80303, USA.

⁵CNR-Istituto di Struttura della Materia, Area della Ricerca di Roma 1, Monterotondo, Roma 00015, Italy.

⁶Institut de Recherche en Astrophysique et Planétologie (IRAP), CNRS, 9 Avenue du Colonel Roche, F-31028 Toulouse, France.

⁷Elettra-Sincrotrone Trieste, Strada Statale 14 - km 163,5 in AREA Science Park, Basovizza, TS 34149, Italy.

A detailed exploration of the potential energy surface of quinoline cation ($C_9H_7N^{*+}$) is carried out to extend the present understanding of its fragmentation mechanisms. DFT calculations have been performed to explore new fragmentation schemes giving special attention to previously unexplored pathways such as isomerisation and elimination of HNC. The isomerization mechanisms producing 5–7 membered ring intermediates have been described and are found to be a dominant channel both energetically and kinetically. Energetically competing pathways have been established for the astrochemically important HNC-loss channel, which has hitherto never been considered in the context of the loss of a 27 amu fragment from the parent ions. Elimination of acetylene was also studied in great detail. Overall computational results are found to complement the experimental observations from the concurrently conducted PEPICO investigation. These could potentially open the doors for rich and interesting VUV radiation driven chemistry on the planetary atmospheres, meteorites and comets.

E-mail: umeshk@iist.ac.in

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Theoretical study of the formation of large, astronomically relevant PAH-organic molecule clusters

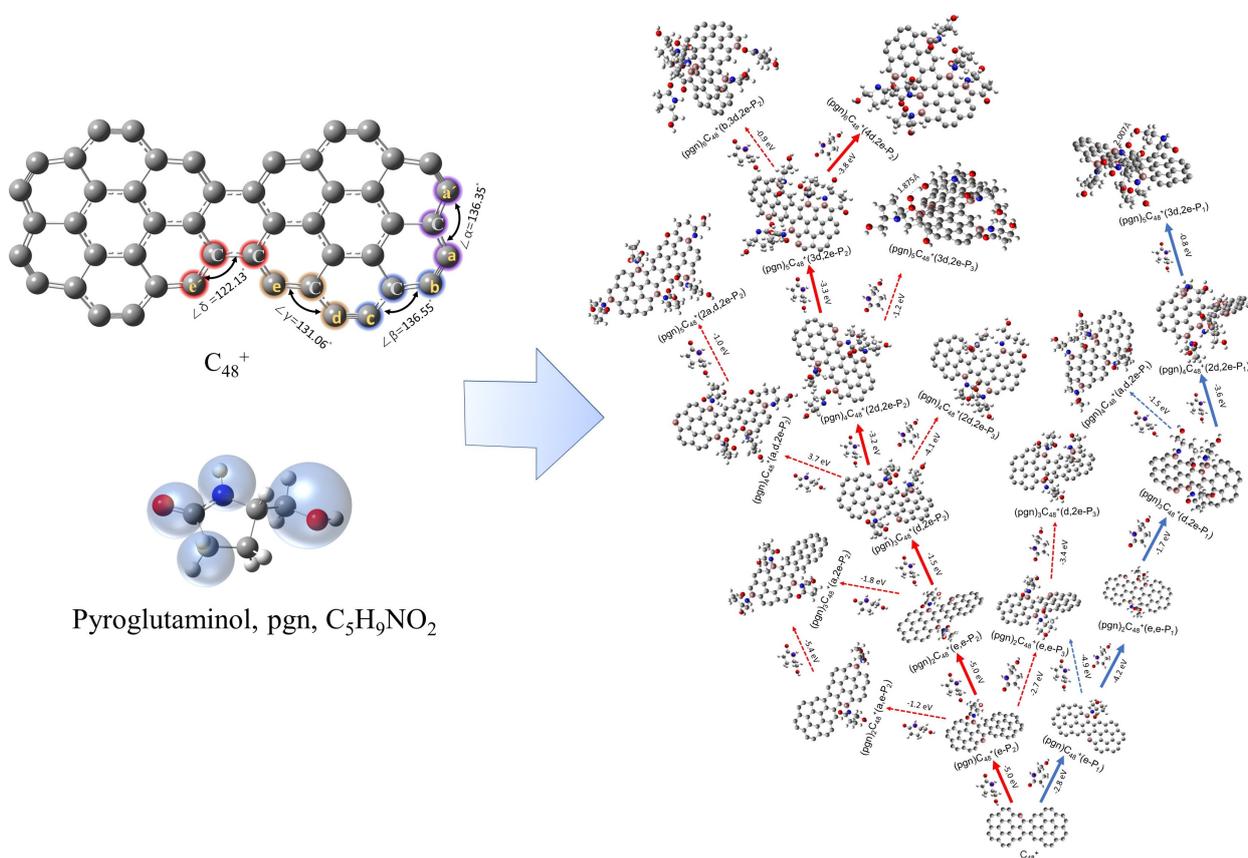
Yuanyuan Yang^{1,2,3}, Xiaoyi Hu^{1,2,3}, Congcong Zhang^{1,2,4}, Yang Chen³, Junfeng Zhen^{1,2,4} and Liping Qin^{1,2}

¹CAS Key Laboratory of Crust-Mantle Materials and Environment, University of Science and Technology of China, Hefei 230026, China

²CAS Center for Excellence in Comparative Planetology, University of Science and Technology of China, Hefei 230026, China

³CAS Center for Excellence in Quantum Information and Quantum Physics, Hefei National Laboratory for Physical Sciences at the Microscale, and Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China

⁴CAS Key Laboratory for Research in Galaxies and Cosmology, Department of Astronomy, University of Science and Technology of China, 96 Jinzhai RD., Hefei, Anhui 230026, China



Expanded tree (in building block pathways) shows the trunk and branches of these various formation pathways for these clusters, $((C_5H_9NO_2)_n C_{48}^+$, n from 0 to 6 (based on the -NH functional groups of pyroglutaminol).

Context: Polycyclic aromatic hydrocarbon (PAH) molecules play an essential role in the prebiotic compound evolution network in the interstellar medium (ISM). A recent experimental study revealed that large, astronomically relevant PAH-organic molecule clusters are gradually formed through the ion-molecule collision reaction pathway in the presence of a strong radiation field.

Aims: We present a theoretical survey for the formation processes of PAH-organic molecule clusters (e.g., such as the graphene carbon cluster (C_{48}^+) organic molecule (Pyroglutaminol, pgn, $(C_5H_9NO_2)_n$) cluster cations, $(pgn)_n C_{48}^+$, $n=[1,6]$), to illustrate the building block mechanism for the formation of large prebiotic compounds.

Methods: To investigate the stability and the building block formation mechanisms of PAH-organic molecule clusters in the ion-molecule collision reaction process, we carried out theoretical calculations with DFT, including the hybrid density functional B3LYP, as implemented in the Gaussian 16 program. The basis set of the 6-311++G** and 6-31+G** was selected and used for different cluster systems.

Results: We investigated the structure of newly formed species and the energy for these reaction pathways. The ion-molecule reaction between $((C_5H_9NO_2)_n C_{48}^+$, $n=[0,5]$) with $(C_5H_9NO_2)_n$ readily occur, resulting in a very large number of reaction pathways and very complex newly formed molecular clusters. An expanded tree (in building block pathways) shows the trunk and branches of these various formation pathways. These clusters (e.g., the graphene carbon cluster and its organic molecules) provide a possible formation and chemical-evolution route for the large complex prebiotic compounds in bottom-up and energy allowed processes in the ISM.

Conclusion: The gas-phase reactions between large PAH species and organic molecules occur relatively easily, resulting in a very large number of reaction pathways and very complex newly formed molecular clusters. These PAH-organic molecule clusters will lead to large organic molecules, which may contain some of the critical molecular configurations that can characterize living material.

E-mail: jfzhen@ustc.edu.cn

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Gas-phase reaction of fullerene monocations with 2,3-benzofluorene indicates the importance of charge exchanges

Congcong Zhang^{1,2,4}, Xiaoyi Hu^{1,2,3}, Yuanyuan Yang^{1,2,3}, Yang Chen³, Junfeng Zhen^{1,2,4} and Liping Qin^{1,2}

¹CAS Key Laboratory of Crust-Mantle Materials and Environment, University of Science and Technology of China, Hefei 230026, China

²CAS Center for Excellence in Comparative Planetology, University of Science and Technology of China, Hefei 230026, China

³CAS Center for Excellence in Quantum Information and Quantum Physics, Hefei National Laboratory for Physical Sciences at the Microscale, and Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China

⁴CAS Key Laboratory for Research in Galaxies and Cosmology, Department of Astronomy, University of Science and Technology of China, 96 Jinzhai RD., Hefei, Anhui 230026, China

Fullerene and polycyclic aromatic hydrocarbon (PAH) molecules, as well as their cations and clusters, are of great interest in astrochemistry. In this work, the ion-molecule collision reaction between fullerene (e.g. a C_{54/56/58} and C₆₀ system or a C_{64/66/68} and C₇₀ system) monocations and neutral PAHs (e.g. 2,3-benzofluorene, C₁₇H₁₂) is studied in the gas phase to determine the importance of charge exchanges and to illustrate the competition between charge transfer and molecular adduct formation channels. The experimental results show that the charge transfer channel is the dominant channel (i.e. charge exchange) in the reaction between fullerene (C₆₀ and C₇₀) monocations and 2,3-benzofluorene, while the molecular adduct formation channels are the dominant channels in the reaction between fullerene (C_{54/56/58} and C_{64/66/68}) monocations and 2,3-benzofluorene. The observed reaction behaviours are investigated with quantum calculations, and the CH₂ unit binding effect of 2,3-benzofluorene is determined to be the main reason for the results. Our findings on the ion-molecule collision reaction between fullerene monocations and 2,3-benzofluorene provide a good model for understanding the physical-chemical processes of the charge transfer channel and the cluster adduct formation channels. Neutral fullerenes (C₆₀ and C₇₀) increase the abundance of their monocations through collision reactions with coexisting neutral molecules in the interstellar medium.

E-mail: jfzhen@ustc.edu.cn

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THESIS

Astrochemically Relevant Polycyclic Aromatic Hydrocarbons Investigated using Ultrafast Pump-probe Spectroscopy and Near-edge X-ray Absorption Fine Structure Spectroscopy

Pragya Chopra

Institution: Institute of Physical Chemistry, Christian-Albrechts-Universität zu Kiel, Kiel, Germany and Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany

Advisor: Prof. Dr. Melanie Schnell (Institute of Physical Chemistry, Christian-Albrechts-Universität zu Kiel, Kiel, Germany and Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany)

The chemical complexity of the interstellar medium has been a subject of great interest to researchers for decades. A significant contender in this chemical make-up, constituting ~10% of the total carbon in the universe, is a set of molecules called polycyclic aromatic hydrocarbons (PAHs). These molecules, widely-considered as key contributors to the Unidentified Infrared Bands, may be integral in elucidating the physical environments surrounding them, thereby adding to our understanding of the interstellar medium.

Several important photochemical and photophysical reactions involving PAHs form the basis of this work. Under the powerful radiation of the interstellar environment, PAHs undergo ionisation relatively easily. They can also fragment with the loss of H, H₂ and small hydrocarbons in different charged states, and are even known to isomerise. The fundamental aspects of the dominant chemical processes related to PAHs can be studied and quantified within a laboratory framework. Further, incorporation of the requisite environmental conditions of interstellar space in the experimental set-ups is essential in producing useful results.

This work integrates three spectroscopic techniques in order to shed light on the relevant photochemical processes involving PAHs. Using ultrafast pump-probe spectroscopy, we studied the relaxation and fragmentation dynamics of three PAHs, namely, fluorene, phenanthrene, and pyrene. The molecules were pumped using ~90 fs long XUV pulses with 30.3 nm photon energy from the Free-electron Laser, FLASH and they were probed using IR pulses at 810 nm with ~60 fs pulse durations. We were able to determine the lifetimes of the excited states of these PAHs in different charged states. We could also elucidate the fragmentation patterns of these molecules having multiple competing fragmentation channels. Another set of pump-probe experiments with a 810 nm pump and 405 nm probe pulse allowed us to study the relaxation and fragmentation dynamics of fluorene. It was seen that both the XUV and IR as pump pulses result in qualitatively similar fragmentation patterns. Slightly longer relaxation times of the electronically excited, singly charged fluorene were seen in the latter set of experiments due to the higher energy of the 405 nm probe pulse.

The electronic structure of doubly charged phenanthrene and doubly-dehydrogenated phenanthrene cations was studied using near-edge X-ray absorption fine structure

(NEXAFS) spectroscopy. The electronic transitions from the C K-edge to unoccupied molecular orbitals were measured using photons in the region of 275-305 eV at PETRA III. The NEXAFS spectra thus obtained were compared with theoretical X-ray spectra. All the different possible doubly-dehydrogenated structures of phenanthrene were considered for this analysis. Finally, to account for the high temperatures of the experimental source used, the X-ray spectra were averaged for the vibrationally displaced ensembles.

This work also describes the set-up of a nearly completed IR-UV ion dip spectrometer to study higher-order clusters of polycyclic aromatic hydrocarbons. The resonance-enhanced multiphoton ionisation scheme, which allows the ion dip spectra to be measured, was tested for two previously studied molecules, indole and acenaphthene. The spectra are presented in this work.

Through this multi-spectroscopic approach, we investigate fundamental properties and processes involving PAHs, which can be relevant in the context of the interstellar medium.

E-mail: pragyachopra73@gmail.com

Website: https://macau.uni-kiel.de/receive/macau_mods_00002871

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astropah@strw.leidenuniv.nl

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