

AstropAH

A Newsletter on Astronomical PAHs

Issue 30 | July 2016



PAH Spectroscopy at the University of Amsterdam

Editorial

Dear Colleagues,

Welcome to our July release of AstroPAH. We have interesting topics for you to keep you warm during the holiday time (on either hemisphere).

On the cover you can enjoy the view of an experimental setup during measurements illuminated only by a blue laser (445 nm). For the non-experimentalists among us, the laboratory lights are turned off to minimise the background noise on the detector that may be induced by ambient light (and admit it, it really looks cool in the dark!).

The In Focus gives you a peek into an exciting (near) future of astronomical PAH research and collaborations with the introduction of the **ITN training network EUROPAH**, which is currently under negotiation.

We have very interesting paper abstracts to present: a model study on the (de)hydrogenation of interstellar PAHs and H₂ formation, an experimental study of the use of C₆₀ as probe for astrophysical conditions, and an experimental study of the breakdown products in the ionisation-induced fragmentation of three PAH species.

We thank you all for your contributions and please keep them coming. You can send us your contributions anytime. **AstroPAH will take a well deserved break in August.** For publication in September, see the deadlines below.

Do you happen to have a picture or photograph that you would like to see featured on our cover? We encourage you to suggest it as Picture of the Month. We would also like to encourage you to send us contributions for the In Focus or upcoming events you wish to distribute amongst our community. Please feel free to inform us of any prizes and funding being awarded, so that we may share these happy moments with our community. Visit our webpage or contact us for more information.

We hope you have great holidays, with time to relax, attend interesting conferences, and/or enjoy your research.

The Editorial Team

**Next issue: 20 September 2016.
Submission deadline: 9 September 2016.**

AstroPAH Newsletter

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PAH Picture of the Month

Photograph of the laser-induced fluorescence (LIF) setup of Prof. W. J. Buma and Dr. A. Petrignani at the University of Amsterdam, The Netherlands. PAH molecules are vaporized via laser desorption and supersonically expanded to produce a cold molecular beam. In this measurement, the molecules are irradiated with blue light to measure their visible absorption spectrum. Subsequent IR-UV double resonance experiments then allow for recording of high-resolution IR absorption spectra.

Credits: Courtesy of A. Petrignani and W. J. Buma.



EUROPAH - A New Multi-disciplinary European Training Network

By Liv Hornekær and the EUROPAH Consortium

EUROPAH is a European Training Network (ETN) aimed at studying the “Extensive and Ubiquitous Role of PAHs in the interstellar medium”, which is presently negotiating a grant agreement with the European Commission under the Horizon 2020 Marie Skłodowska-Curie Action. EUROPAH expects to start in October 2016. The network includes 13 research groups, spread across 10 universities and 3 industrial partners in 6 different countries. The network will train 16 early stage researchers (PhD students) in areas relevant to uncovering the many roles played by Polycyclic Aromatic Hydrocarbons (PAHs) in the ISM.

The network has had a long gestation period, with the first unsuccessful submission under FP7 in 2012. Since then, many new groups have entered the field of “AstroPAH” studies making the field more active than ever. Hence, this is an exciting time to launch a research and training network on PAHs in the ISM.



Figure 1 - EUROPAH nodes.

Scientific Aims

The research and training activities within the network are multi-disciplinary covering experimental and theoretical astrochemistry, surface science, atomic and molecular physics, plasma physics, quantum chemistry, environmental sciences, and science communication. Planned activities span from investigating spectral PAH features potentially related to the Diffuse Interstellar Bands (DIBs) to the effect of PAHs on zebrafish DNA in aqueous environments and the destruction of PAHs in industrial scale plasma systems. The focus of the research and training within the network revolves around five areas presented below.

1) PAH Spectroscopy

This work will be headed by the group of Stephan Schlemmer at University of Cologne but will also involve the groups of Jos Oomens at Radboud University, Harold Linnartz and Xander Tielens at Leiden University, Christine Joblin at Paul Sabatier University and Helmut Zacharias at University of Münster. This will enable PAH spectroscopic measurements for both ionic gas phase PAHs, PAHs on dust grain surface analogues (cf. Fig. 2a for a picture of one of the laser systems to be used), and PAHs embedded in solid water ice matrices. EUROPAH will use action spectroscopic techniques in cryogenic ion traps (cold FTICR, 4 K 22-pole ion trap. cf. Figure 2b for an image of the 4 K 22 pole ion trap at University of Cologne) in combination with tunable visible and UV lasers to obtain electronic spectra of internally cold, mass-selected, gas-phase PAH ions, vibrational IR MPD (infrared multiple-photon dissociation) studies at the free electron laser facility **FELIX**, and solid state IR to VUV spectroscopic absorption studies on functionalized PAHs and PAH clusters on grain surfaces and in icy solids. The aim is to:

- (i) Measure electronic transitions in the near-UV to near-IR range of cold gas-phase PAH cations and cationic fragments in ion trap instruments and in solid water matrices, and search for DIB candidates.
- (ii) Measure the (far-)IR spectra of specific PAHs in order to identify interstellar PAHs but also explore their catalytic role in interstellar chemistry. This includes action-spectroscopy of gas-phase PAHs and their reaction products in different charge and hydrogenation states, as well as the study of specific IR signatures of PAHs present at the surface of grains (including functionalized and super-hydrogenated PAHs), or as part of clusters to obtain insight into the nature of the grain precursors of free PAHs.
- (iii) Explore the signatures of PAHs at higher energy in the UV/far-UV and VUV ranges. The obtained spectroscopic data will be included in appropriate databases connected to the Virtual Observatory (e.g. the Toulouse/Cagliari theoretical database, the Cologne Database for Molecular Spectroscopy).

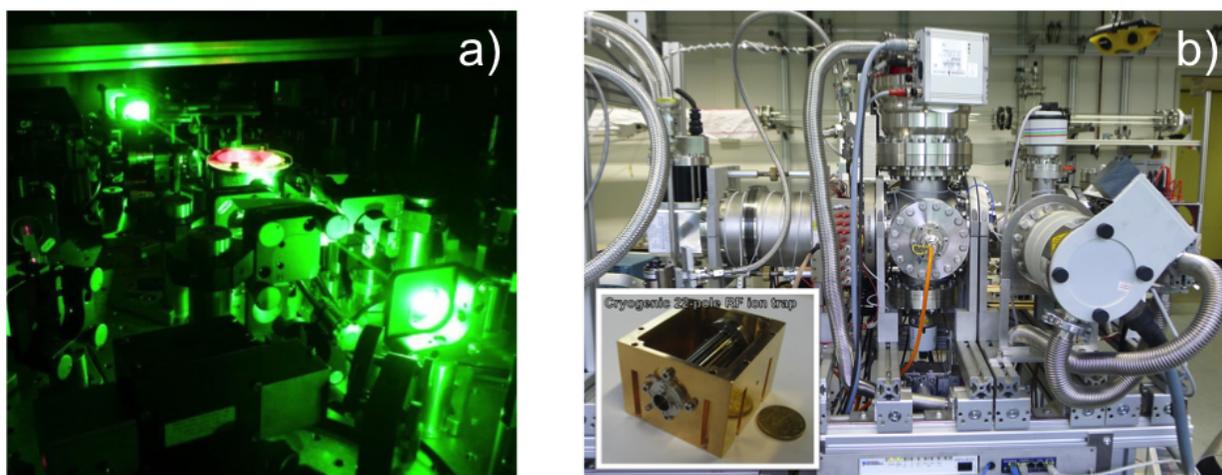


Figure 2 - a) Femtosecond laser set-up at University of Münster for probing ultrafast desorption dynamics. b) Cryogenic 22-pole ion trap setup for vibrational and electronic spectroscopy of PAH ions (University of Cologne).

2) Energetic processing of PAHs and related species in the gas phase

This work will be explored by Xin Tu's group at University of Liverpool in collaboration with Xander Tielens' group at Leiden University, Christine Joblin's group at Paul Sabatier University, and Giacomo Mulas' group at the National Institute of Astrophysics in Rome. Experiments in ion traps and molecular beams will be employed to study the different relaxation channels of energized PAHs as a function of energy and molecular properties: ionisation, fragmentation and/or radiative cooling. Molecule formation through PAH photo-fragmentation will also be investigated. The experimental efforts will be backed by theoretical calculations on relaxation of excited PAH molecules. The processing of PAHs in non-thermal plasmas will be investigated by combined use of gas analysis (FTIR/GC/GCMS), plasma diagnostics including time-resolved emission spectroscopy and ultrafast imaging techniques, and computer-based modelling (cf. Fig. 3 for examples of plasma systems that will be studied). PAH destruction in industrial scale plasma systems will be carried out at the site of industrial partner Unicorn Power Ltd. The obtained data will be used both for astrophysical modelling and for implementation into existing plasma models, as well as for further development of a hybrid technology based on the combination of non-thermal plasma with UV-C for the destruction of PAHs and related species in industrial scale plasma systems.

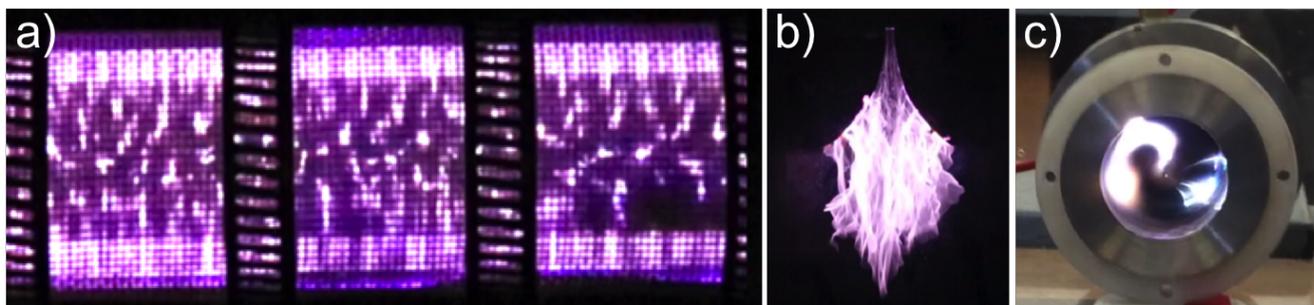


Figure 3 - Different plasma systems at the University of Liverpool (a) dielectric barrier discharge; (b) gliding arc discharge; (c) rotating gliding arc discharge.

3) PAHs in comets and meteorites

The network will also contribute to the investigation of PAHs and the organic inventory of comets and meteorites via activities in the groups of Martin McCoustra and Theodore Henry at Heriot-Watt University, and of Harold Linnartz at Leiden University. Specifically the aim is to:

- (i) Develop a model for the chemical evolution of specific, astrophysically relevant PAH molecules under conditions similar to the asteroidal bodies in the solar system; e.g., temperature history and mineral nanograin content.
- (ii) Evaluate the importance of PAHs for the chemical composition of meteorite parent bodies.
- (iii) Identify the key processes involved in the chemical evolution of PAHs in aqueous settings on meteorite parent bodies and contrast with findings from terrestrial environmental science.

- (iv) Develop a model for the (photo)chemical evolution of specific, astrophysically relevant PAH molecules in interstellar icy grains and comets.
- (v) Identify potential prebiotic molecular markers for the chemical evolution of PAHs in cometary ices.
- (vi) Compare the results with Rosetta's studies on the organic inventory of the comet Churyumov-Gerasimenko.
- (vii) Investigate the influence of nano-scale particles on UV processing of PAHs in aqueous environments of both environmental (using bioanalytical techniques¹) and cometary relevance.
- (viii) Compare and contrast the results of thermal and UV processing in an aqueous setting with that produced by UV photolysis of ices, energetic processing in plasma environments, and UV photolysis of gaseous PAH molecules.

4) PAHs and the astrochemistry of the ISM

This topic will be addressed through activities in the groups of Liv Hornekær and Bjørk Hammer at Aarhus University (cf. Fig. 4 for a picture of one of the experimental setups to be used), as well as those of Helmut Zacharias at University of Münster, Christine Joblin, Didier Lemoine and Bruno Lepetit at Paul Sabatier University, Jos Oomens at Radboud University, Rocco Martinazzo at University of Milan, and Xin Tu at University of Liverpool. With this combination of expertise, chemical reactions involving ionic PAHs in the gas phase under both cold gas and hot plasma conditions, as well as neutral PAHs on dust grain analogue surfaces, can be addressed both experimentally and theoretically.

The aim is to:

- (i) Identify stable chemically functionalised PAHs and their spectral signatures and relate these findings to observations.
- (ii) Map the catalytic activity of PAHs and chemically functionalized PAHs on surfaces and in the gas phase with respect to the formation of simple molecules such as H₂, OH, H₂O and NH₃, as well as the breakdown of PAHs into, e.g., C₂H₂ in chemical reactions.
- (iii) Reveal the photochemical reaction pathways for PAHs and chemically functionalised PAHs. Specifically we will study whether UV irradiation leads to the release of molecular hydrogen from super-hydrogenated PAHs on dust grain surface analogues and in the gas phase, and whether more complex, biologically relevant, molecules can be formed by fragmentation of chemically functionalised PAHs.

¹This is where the zebrafish get involved!

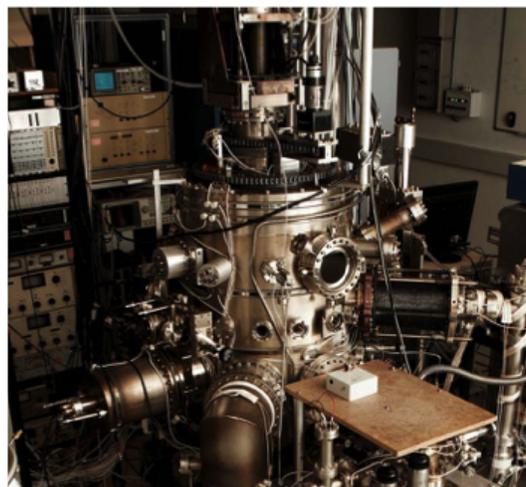


Figure 4 - Experimental setup at Aarhus University used for studies of PAH reactivity.

5) The interaction of and connection between PAHs and nano-scale carbonaceous and silicate grains

The network will contribute to this work via research activities carried out in Martin McCoustra's group at Heriot-Watt University and in the groups of Liv Hornekær and Bjørk Hammer at Aarhus University, Christine Joblin at Paul Sabatier University, and Jos Oomens at Radboud University. The work will focus both on experimental and theoretical studies of PAH clusters in the gas phase and on the interaction of PAHs with dust grain analogue surfaces. Specifically, the aim is to:

- (i) Investigate the formation and dissociation of PAH clusters in the gas phase and the interaction of PAHs with relevant model surfaces to probe binding between PAHs and model grain surfaces and formation of PAH agglomerates (cf. Fig. 5 for an image of the experimental setup to be used at Heriot-Watt University).
- (ii) Identify specific features of clustered and surface agglomerated PAHs across the IR, VIS and UV, including ring heterogeneity (hetero-atoms and side chains).
- (iii) Describe the mechanism of formation of interstellar dust grains from their initial condensation to grain aggregate formation via grain-grain collisions and relate these findings to observations. We will study the rates and mechanisms of clustering and agglomeration, relating them to the nature of the fundamental interactions and to observations on relevant astronomical objects.



Figure 5 - The dual atomic beam UHV system for studies of solid state and surface processes in astrophysical environments at Heriot-Watt University.

The network will be coordinated by Aarhus University in Denmark, with Liv Hornekær as coordinator and Andrew Cassidy as project manager. More information can be found on the EUROPAH website at www.europah.eu.

EUROPAH Recruitment

EUROPAH will recruit 16 early-stage researchers (ESRs) across the network. Each ESR will be enrolled in a PhD program and complete a specially designed training schedule in tandem with performing research and innovation projects at their host organisation. The training in this highly multidisciplinary network will combine astronomy, molecular physics, molecular spectroscopy, environmental science, quantum chemistry, surface sciences, plasma physics and scientific communication.

Who can apply?

Details on the 16 individual positions are provided on the EUROPAH website at www.europah.eu.

To qualify as an ESR in the EUROPAH network you must:

- be in the first four years² of your research career, since, e.g., completion of your masters degree,
- not already possess a doctorate degree,
- be willing to move to a country within the network³ in which you have not lived for more than 12 months over the last 3 years,
- be proficient in both written and spoken English.

What do I do now?

Check out the project descriptions at www.europah.eu and then forward a 2-page CV and 1-page cover letter, listing your favoured projects in order of preference, to

recruitment@europah.eu

by the deadline: September 15th 2016.

² Full-time equivalent research experience.

³ You must also be eligible for a working permit for this country.

EUROPAH related activities at Aarhus University

Liv Hornekær: In my group at Aarhus University, we study the catalytic activity and the functionalization of PAHs on surfaces under interstellar conditions. Our activities have traditionally focused on reactions with atomic hydrogen and the catalysis of molecular hydrogen. Under EUROPAH, we plan to extend these activities to include other atomic species and the catalytic formation of more complex molecules, as well as the interaction of functionalized PAHs with dust grain analogue surfaces. The techniques we use are state-of-the-art surface science techniques, including temperature programmed desorption (TPD) (see Fig. 4 for a photo of the experimental setup) and

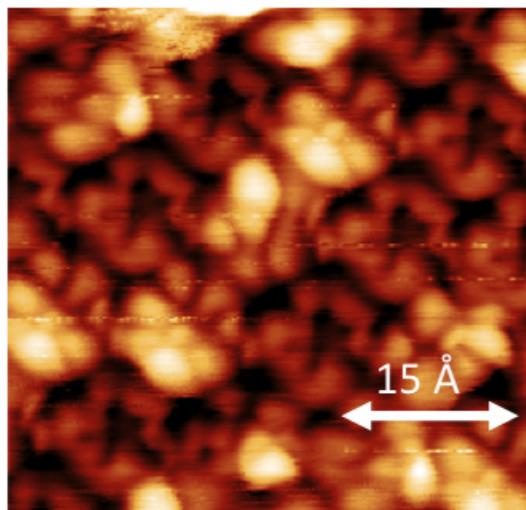


Figure 6 - STM image of super-hydrogenated coronene molecules on graphite.

helium cryogenic Low Temperature Scanning Tunnelling Microscopy (LT-STM). Using LT-STM, we are able to image distinct PAH molecules on dust grain analogue surfaces with sub-molecular resolution. An example of such an image is displayed in Fig. 6. In this case, the STM image is of a layer of coronene molecules (brown outlines) on graphite exposed to an atomic H atom beam. Bright molecular lobes characterize the super-hydrogenated molecules. In the interpretation of our results, we collaborate closely with theoreticians such as EUROPAH participants Bjørk Hammer at Aarhus University and Rocco Martinazzo at University of Milan.



Liv Hornekær is an associate professor in the Department of Physics and Astronomy and the Interdisciplinary Nanoscience Center of Aarhus University, in Denmark.

Email: liv@phys.au.dk

Announcements

Nature Astronomy is now open for submissions

Nature Astronomy is a truly multidisciplinary journal launching in January 2017. It will represent – and foster closer interaction between – all of the key astronomy-relevant disciplines. As a Nature Research journal, it will publish the most significant research, review and comment at the cutting edge of astronomy, astrophysics, cosmology and planetary science.

Nature Astronomy will offer a range of content types – including original research, Review Articles, Perspectives, Commentaries, News & Views and Research Highlights – to explore topical issues as well as showcasing significant advances in the field.

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Hydrogenation and dehydrogenation of interstellar PAHs: Spectral characteristics and H₂ formation

H. Andrews¹, A. Candian¹ and A.G.G.M. Tielens¹

¹ Leiden Observatory, Leiden University, P.O. Box 9513, 2300 RA Leiden, The Netherlands

Context. We have modelled the abundance distribution and IR emission of the first 3 members of the coronene family in the north-west photodissociation region of the well-studied reflection nebulae NGC 7023.

Aims. Our aim was 3-fold: i) analyze the distribution of abundances; ii) examine the spectral footprints from the hydrogenation state of PAHs; and iii) assess the role of PAHs in the formation of H₂ in photodissociation regions.

Methods. To model the physical conditions inside the cloud, we used the Meudon PDR Code, and we gave this as input to our kinetic model. We used specific molecular properties for each PAH, based on the latest data available at the present time. We considered the loss of an H atom or an H₂ molecule as multiphoton processes, and we worked under the premise that PAHs with extra H atoms can form H₂ through an Eley-Rideal abstraction mechanism.

Results. In terms of abundances, we can distinguish clear differences with PAH size. The smallest PAH, coronene (C₂₄H₁₂), is found to be easily destroyed down to the complete loss of all of its H atoms. The largest species circumcircumcoronene (C₉₆H₂₄), is found in its normal hydrogenated state. The intermediate size molecule, circumcoronene (C₅₄H₁₈), shows an intermediate behaviour with respect to the other two, where partial dehydrogenation is observed inside the cloud. Regarding spectral variations, we find that the emission spectra in NGC 7023 are dominated by the variation in the ionization of the dominant hydrogenation state of each species at each point inside the cloud. It is difficult to catch the effect of dehydrogenation in the emitted PAH spectra since, for any conditions, only PAHs within a narrow size range will be susceptible to dehydrogenation, being quickly stripped off of all H atoms (and may isomerize to cages or fullerenes). The 3 μm region is the most sensitive one towards the hydrogenation level of PAHs.

Conclusions. Based on our results, we conclude that PAHs with extra H atoms are not the carriers of the 3.4 μm band observed in NGC 7023, since these species are only found in very benign environments. Finally, concerning the role of PAHs in the formation of H₂ in photodissociation regions, we find that H₂ abstraction from PAHs with extra H atoms is an inefficient process compared to grains. Instead, we propose that photodissociation of PAHs of small-to-

intermediate sizes could contribute to H₂ formation in PDR surfaces, but they cannot account by themselves for the inferred high H₂ formation rates in these regions.

E-mail: heandrew@strw.leidenuniv.nl

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C₆₀ as a probe for astrophysical environments

Abel C. Brieva¹, Roland Gredel², Cornelia Jäger¹, Friedrich Huisken¹ and Thomas Henning²

¹ Laboratory Astrophysics Group of the Max Planck Institute for Astronomy at the Friedrich Schiller University Jena, Institute of Solid State Physics, Helmholtzweg 3, 07743 Jena, Germany

² Max Planck Institute for Astronomy (MPIA), Königstuhl 17, 69117 Heidelberg, Germany

The C₆₀ molecule has been recently detected in a wide range of astrophysical environments through its four active intramolecular vibrational modes (T1u) near 18.9 μm, 17.4 μm, 8.5 μm, and 7.0 μm. The strengths of the mid-infrared emission bands have been used to infer astrophysical conditions in the fullerene-rich regions. Widely varying values of the relative intrinsic strengths (RIS) of these four bands are reported in laboratory and theoretical papers, which impedes the derivation of the excitation mechanism of C₆₀ in the astrophysical sources. The spectroscopic analysis of the C₆₀ samples produced with our method delivers highly reproducible RIS values of 100, 25 ± 1, 26 ± 1 and 40 ± 4. A comparison of the inferred C₆₀ emission band strengths with the astrophysical data shows that the observed strengths cannot be explained in terms of fluorescent or thermal emission alone. The large range in the observed 17.4 μm/18.9 μm emission ratios indicates that either the emission bands contain significant contributions from emitters other than C₆₀, or that the population distribution among the C₆₀ vibrational modes is affected by physical processes other than thermal or UV excitation, such as chemo-luminescence from nascent C₆₀ or possibly, Poincaré fluorescence resulting from an inverse internal energy conversion. We have carefully analyzed the effect of the weakly-active fundamental modes and second order modes in the mid-infrared spectrum of C₆₀ and propose that neutral C₆₀ is the carrier of the unidentified emission band at 6.49 μm which has been observed in fullerene-rich environments.

E-mail: abelcbrieva@gmail.com

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Breakdown Products of Gaseous Polycyclic Aromatic Hydrocarbons Investigated with Infrared Ion Spectroscopy

Annemieke Petrignani^{1,2,4}, Martin Vala³, John R. Eyler³, A.G.G.M. Tielens¹, Giel Berden², A.F.G. van der Meer², Britta Redlich² and Jos Oomens²

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

² Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7c, NL-6525 ED Nijmegen, The Netherlands

³ Department of Chemistry and Center for Chemical Physics, University of Florida, Gainesville, FL 32611-7200, USA

⁴ Current affiliation: University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

We report on a common fragment ion formed during the electron-ionization-induced fragmentation of three different three-ring polycyclic aromatic hydrocarbons (PAHs), fluorene ($C_{13}H_{10}$), 9,10-dihydrophenanthrene ($C_{14}H_{12}$), and 9,10-dihydroanthracene ($C_{14}H_{12}$). The infrared spectra of the mass-isolated product ions with $m/z = 165$ were obtained in a Fourier transform ion cyclotron resonance mass spectrometer whose cell was placed inside the optical cavity of an infrared free-electron laser, thus providing the high photon fluence required for efficient infrared multiple-photon dissociation. The infrared spectra of the $m/z = 165$ species generated from the three different precursors were found to be similar, suggesting the formation of a single $C_{13}H_9^+$ isomer. Theoretical calculations using density functional theory (DFT) revealed the fragment's identity as the closed-shell fluorenyl cation. Decomposition pathways from each parent precursor to the fluorenyl ion are proposed on the basis of DFT calculations. The identification of a single fragmentation product from three different PAHs supports the notion of the existence of common decomposition pathways of PAHs in general and can aid in understanding the fragmentation chemistry of astronomical PAH species.

E-mail: a.petrignani@science.ru.nl

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