

AstropAH

A Newsletter on Astronomical PAHs

Issue 61 • September 2019

A scanning electron micrograph (SEM) showing a large, spherical particle, known as a Borg sphere, surrounded by a field of smaller, irregularly shaped particles. The Borg sphere has a textured surface with many small, flat, crystalline-like structures protruding from it. The background is a dense field of similar but smaller particles.

Borg Sphere



Editorial

Dear Colleagues,

We are extremely pleased to have you back with us after our August break! Science, however, did not take a break and we are thrilled to share this issue with you.

Our In Focus features a very interesting piece by Dr. Martin Cordiner on ionized interstellar buckyballs and their relation to (at least some) diffuse interstellar bands.

We report publications on PAH studies in asteroid environments (also featured on our cover!), PAHs with armchairs, PAH processing, graphene oxide nanoparticles, and other interesting topics.

We have two announcements to share: one about an open postdoctoral research position at the NASA Ames Research Center to work on the PAHdb, the other about the Dissertation Prize of the AAS Laboratory Astrophysics Division. See page 17 for details.

We hope you enjoy this newsletter, and look forward to seeing you again next month!

The Editorial Team

**Next issue: 17 October 2019.
Submission deadline: 4 October 2019.**

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. Alessandra Candian

University of Amsterdam
(The Netherlands)

Dr. David Dubois

NASA Ames Research Center
BAER Institute (USA)

Dr. Elisabetta Micelotta

Department of Physics
University of Helsinki (Finland)

Dr. Ella Sciamma-O'Brien

NASA Ames Research Center (USA)

Dr. Amanda Steber

Deutsches Elektronen-Synchrotron
(Germany)

Contact us:

astropah@strw.leidenuniv.nl

[http://astropah-
news.strw.leidenuniv.nl](http://astropah-news.strw.leidenuniv.nl)

[Click here to Subscribe to AstroPAH](#)

[Click here to Contribute to AstroPAH](#)

Newsletter Design: Isabel Aleman

Background images:

This page: NASA, ESA, and the Hubble Heritage Team (STScI/AURA)

Cover and headers: X-ray by Chandra: NASA/CXC/Univ.Potsdam/L.Oskinova et al; Optical by Hubble: NASA/STScI;
Infrared by Spitzer: NASA/JPL-Caltech

Contents

PAH Picture of the Month	1
Editorial	2
In Focus	4
Recent Papers	11
Announcements	17

PAH Picture of the Month

"Death Star" or "Borg sphere" - Scanning electron microscopy image of aqueous altered fluoranthene crystals from hydrothermal experiments. Fluoranthene molecules form above their melting point in water carbonaceous globules. These carbonaceous globules are similar to nanoglobules found in meteorites. For more details see Giese et al., (2019) in the Abstract Section

Credits: C.C. Giese et al, Meteoritics & Planetary Science, 2019



Ionized Interstellar Buckyballs and the Diffuse Interstellar Bands

by Martin Cordiner

The 'soccer ball' molecule buckminsterfullerene (C_{60}) was first identified by Kroto et al. (1985), during a series of laboratory experiments attempting to synthesise long carbon chain molecules (including cyanopolyynes observed by radio astronomers in carbon-rich astrophysical environments). Using a powerful, pulsed laser to vaporise solid graphite, their experiments (e.g. Kroto et al. 1987; Heath et al. 1987) aimed to simulate the chemistry occurring in the outflows from dying stars such as IRC+10°216. Kroto et al. observed the spontaneous formation of complex molecules in the condensing carbon vapour, including carbon clusters and long chains with more than 20 C atoms. But it was the unusually strong signals at molecular masses corresponding to C_{60} and C_{70} that piqued their interest, ultimately revealing the existence of an entirely new form of carbon: fullerenes.

The extreme elegance and symmetry of the C_{60} structure immediately captured the interest of scientists and the public. The unusual molecular properties of fullerenes, including their size, strength, electrical conductivity and stability make them uniquely attractive for a range of practical uses. For example, the ability to safely house therapeutic agents inside a fullerene cage allows targeted drug delivery within the body, with potential applications for HIV and cancer therapy. Research is also ongoing regarding the use of fullerenes to facilitate long-range electron transport in next-generation solar cells (Song et al. 2018). Through inclusion of a single nitrogen atom inside the C_{60} cage (forming an endohedral fullerene), a nano-scale atomic clock can be produced (Harding et al. 2017). Meanwhile, carbon nanotubes (elongated fullerenes), due to their extremely high tensile strength and light weight, have found applications in advanced sporting equipment such as golf clubs, bicycles and tennis racquets.

The icosahedral symmetry of C_{60} renders its molecular structure extremely stable, and Kroto realised that this stability would allow it to persist in harsh astrophysical environments, including the strongly-irradiated diffuse interstellar medium where less-stable molecules are easily destroyed. This realisation led to the suggestion of C_{60} and, more specifically C_{60}^+ , as possible carriers of (some of) the unidentified diffuse interstellar bands (Kroto 1988). During the 1980's, increasingly detailed observations of the diffuse interstellar band (DIB) spectrum (then comprised of around 50 discrete bands) lead to a shift in thinking away from solid state (dust) carriers, in favour of a molecular origin for many of the bands (e.g. Chlewicki et al. 1986), and large carbon-based molecules in particular, were considered the most attractive candidates (e.g. Leger & d'Hendecourt 1985). Thus, the stage was set for

further investigation of interstellar fullerenes, and their possible role as diffuse interstellar band carriers.

Laboratory measurements of the C_{60}^+ electronic absorption spectrum in noble gas matrices (Kato et al. 1991, Gasyana et al. 1992, Fulara et al. 1993) revealed the presence of two strong bands in the near infrared (around 960 nm), accompanied by two weaker absorptions (near 940 nm). Foing & Ehrenfreund (1994) discovered that the wavelengths of the two strongest C_{60}^+ bands were a close match with two prominent DIBs at 9577 Å and 9632 Å. However, despite this tantalising evidence, matrix perturbations of the laboratory C_{60}^+ spectrum introduced too much uncertainty into the band positions and profiles for a conclusive assignment. The necessary (but difficult) task of obtaining a more accurate, gas-phase near-IR laboratory spectrum of C_{60}^+ was readily accepted by J. P. Maier's group at the University of Basel.

Work on measuring the C_{60}^+ electronic spectrum was spurred on by the remarkable detection of neutral C_{60} in the Tc 1 planetary nebula (Cami et al. 2010) and in the dense, irradiated interstellar gas of NGC 7023 (Sellgren et al. 2010). These discoveries were based on a match between laboratory infrared emission spectra and observations using the Spitzer Space Telescope, paving the way for a slew of fullerene detections (including C_{60} and C_{70}) in diverse astrophysical environments from young stellar objects, H II regions and PDRs to AGB stars, protoplanetary nebulae and planetary nebulae (see Castellanos et al. 2014 and references therein). A tentative detection of C_{60}^+ in NGC 7023 was also obtained by Berné et al. (2013).

Despite the flurry of activity surrounding fullerenes in space, the existence of C_{60}^+ in the diffuse ISM, and its possible relationship with the diffuse interstellar bands, remained uncertain. It was the breakthrough work of Campbell et al. (2015) that provided the first accurate near-IR spectrum of C_{60}^+ for comparison with the DIBs. Using an ingenious laboratory setup consisting of a 22-pole radio frequency trap to isolate and cool the fullerene ions, the C_{60}^+ spectrum was measured by tagging C_{60}^+ with multiple helium atoms, and the absorption cross sections for C_{60}^+-He were measured using mass spectrometry, as a function of wavelength of a scanned laser. Accounting for a small (0.6 Å) wavelength shift due to the attached helium atoms, a near-perfect match was found between the dominant C_{60}^+ absorption bands and the 9577 Å and 9632 Å diffuse interstellar bands. The match was subsequently confirmed by independent lab experiments involving C_{60}^+ embedded in ultra-cold helium nanodroplets (Kuhn et al. 2016; Spieler et al. 2017).

During the last 100 years, the identity of the diffuse interstellar band carriers has proven to be one of the most difficult problems in astrophysical spectroscopy (Sarre 2006, and references therein). In particular, the DIB research community should be commended for their outstanding ability to prove each other wrong when a new carrier is proposed (as has occurred too many times to count; see Herbig 1995). Of course, the claim of C_{60}^+ as carrier of the 9577 Å and 9632 Å DIBs was met with the same level of skepticism as with previous claims (including from myself). Despite the quality of the match between the laboratory and interstellar C_{60}^+ bands, some doubts remained — in particular, regarding the precise band strength ratios, wavelengths and profiles. Furthermore, the existence in the ISM of the three weaker bands at 9348, 9365 and 9428 Å was called into question (Galazutdinov et al. 2017a,b). Despite the excellent work of Walker et al. (2015, 2016) to confirm the presence of all five C_{60}^+ bands in the ISM, the extreme spectral sensitivity demanded by these observations in a very difficult part of the spectrum, meant that additional, independent confirmation was required to place the assignment of interstellar C_{60}^+ beyond doubt.

Flying Above the Telluric Forest with HST

The extreme difficulty in confirming the presence of all the expected C_{60}^+ bands in the ISM is demonstrated by Figure 1, which shows interstellar spectra of the four strongest C_{60}^+ bands (middle traces; black), compared with the laboratory spectrum of Campbell & Maier (2018) (upper trace; red). The interstellar spectra (towards early-type supergiant stars Cyg OB2 #5 and HD 168625), were observed using the Keck HIRES and CFHT ESPaDOnS high-resolution échelle spectrographs, respectively, both at Mauna Kea — one of the driest observatory sites on Earth — yet, as shown by the bottom (blue) trace, the spectral contamination by telluric water vapor is overwhelming in this part of the spectrum. The $\lambda 9365$ and $\lambda 9428$ bands shown in panels (a) and (b) are overlapped by saturated telluric lines that make reliable measurements of their strengths and profiles impossible. Fringing due to light scattering inside the instrument CCDs is also a problem in this wavelength region, further degrading the spectral quality.

To mitigate these problems, and definitively confirm the presence (or absence) of the weaker C_{60}^+ bands, we initiated a program of near-IR observations from above Earth's atmosphere, using the Hubble Space Telescope (HST) to obtain spectra of multiple, heavily-reddened stars, unhindered by telluric absorption. Navigating the trials of peer review was not the only difficulty in obtaining these data — our sensitivity requirements placed unprecedented demands on the aging HST hardware, and it was necessary to employ a previously untested observing mode to overcome the nominal signal-to-noise ratio limit of 100 for the Space Telescope Imaging Spectrograph (STIS) in the near-IR. Our technique (known as STIS scanning) involved carefully maneuvering the target star along the spectrograph entrance slit, with the STIS shutter held open, so that the starlight was spread evenly across the CCD in the spatial direction, in addition to the usual spectral dispersion.

This unconventional HST observing method had multiple benefits, including: (1) allowing for orders of magnitude increases in the number of counts per science exposure, (2) reducing the impact of individual bad CCD pixels and cosmic ray hits, and (3) improved matching of the CCD illumination characteristics between science and flat-field exposures, thus increasing the overall efficacy of the flat fielding and fringe correction. The resulting spectra yielded an impressive order-of-magnitude improvement in S/N, reaching up to ~ 1000 per summed dispersion pixel.

Further details of the HST observations and data analysis can be found in Cordiner et al. (2017, 2019). Figure 2 shows the mean of five HST spectra observed towards early B-type supergiant stars, with clear detections of the C_{60}^+ $\lambda 9365$, $\lambda 9428$ and $\lambda 9577$ bands. Within the measurement uncertainties, the observed band strength ratios for $\lambda 9365/\lambda 9577$ and $\lambda 9428/\lambda 9577$ matched those measured in the laboratory, and the presence of interstellar C_{60}^+ was thus confirmed.

Fullerenes: Solution to a 100-Year Interstellar Mystery?

Combining the prior ground-based observations of the $\lambda 9365$, $\lambda 9428$ and $\lambda 9577$ and $\lambda 9632$ bands with our HST observations places the assignment of interstellar C_{60}^+ beyond reasonable doubt. The minor issues raised regarding possible discrepancies in the strength ratios and wavelengths of the $\lambda 9577$ and $\lambda 9632$ bands have been addressed in detail by Walker et al. (2017) and Lallement et al. (2018). Ionised buckminsterfullerene should therefore be considered the first conclusively identified diffuse interstellar band carrier, and

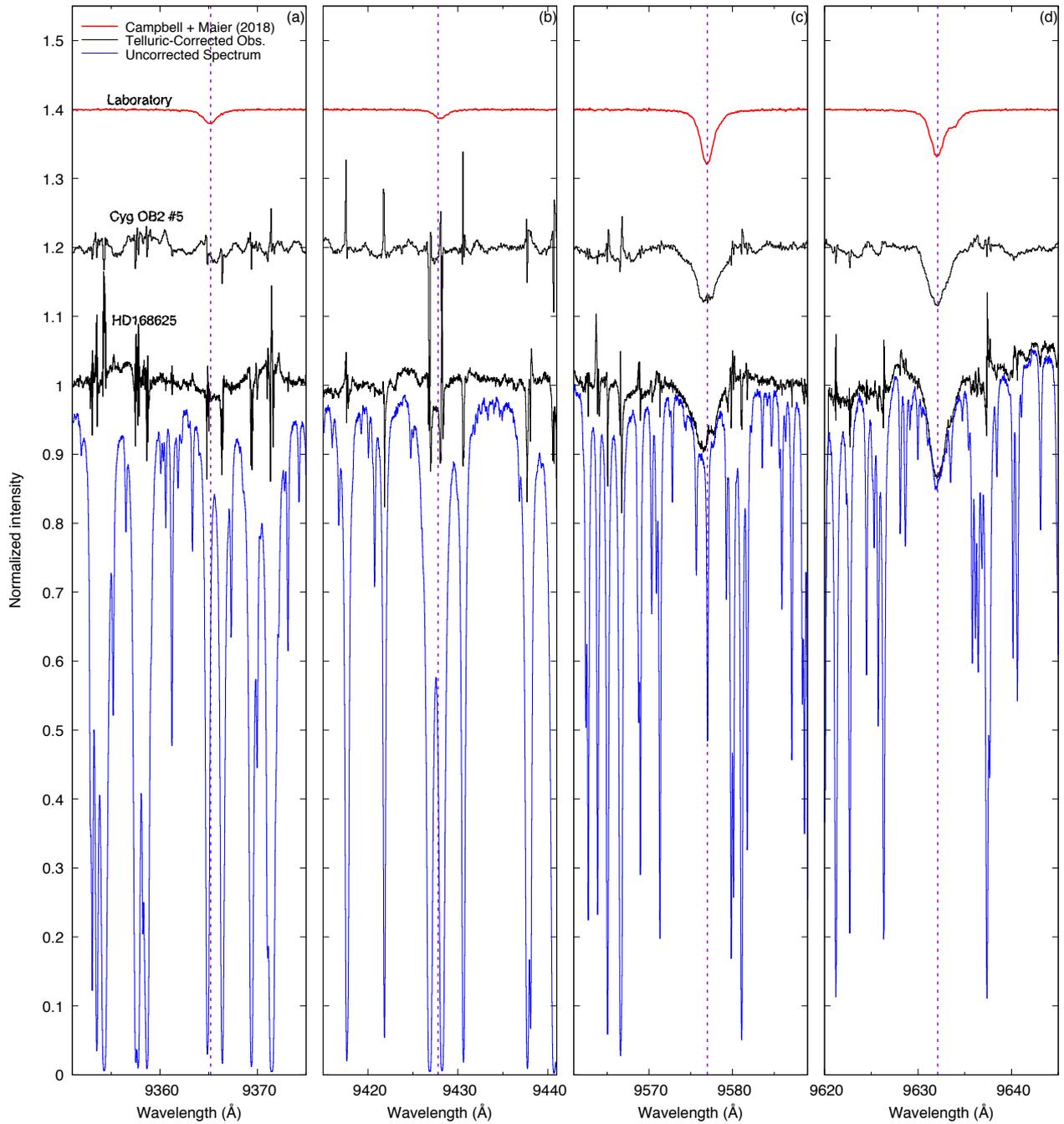


Figure 1: Ground-based échelle spectra (black) of two of the weaker C_{60}^+ bands (panels a and b), and the two stronger bands (panels c and d), towards the heavily-reddened stars Cygnus OB2 #5 and HD 168625. While the stronger $\lambda 9577$ and $\lambda 9632$ bands are readily detected, telluric correction artifacts and fringing (flat-fielding) residuals prevent reliable measurements of the weaker $\lambda 9365$ and $\lambda 9428$ bands. The top (red) trace shows a laboratory comparison spectrum from Campbell & Maier (2018), shifted by -0.6 \AA to correct for the He-atom perturbation, while the bottom (blue) trace shows the spectrum of HD 168625 prior to telluric correction, to highlight severe telluric contamination of this region.

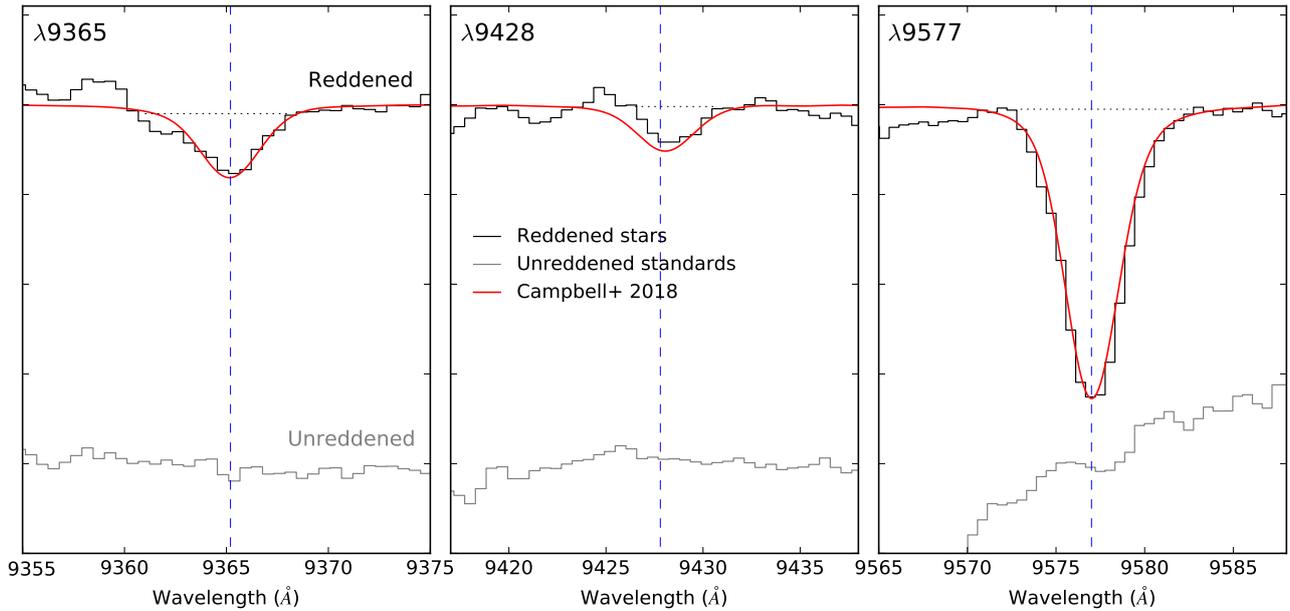


Figure 2: Mean spectra of five heavily reddened early B-type supergiants observed using HST/STIS, with a convolved laboratory C_{60}^+ spectrum overlaid (Campbell & Maier 2018). See Cordiner et al. (2019) for details.

as such, this represents a landmark event in the history of research into the composition of the diffuse ISM.

This discovery naturally leads us to wonder: can fullerenes explain some of the remaining diffuse interstellar bands, the identities of which have eluded astronomers and chemists for over 100 years? The role in interstellar chemistry of fullerene precursors and photo-fragments, or chemically modified fullerenes also remains to be explored. The door is now open, and the potential for new discoveries in this area is great.

While C_{60} and C_{60}^+ are now confirmed to be present in space, hundreds more DIBs remain to be assigned, and it seems that the story of fullerenes and their role in interstellar chemistry is still far from complete. Sir Kroto’s remarkable foresight (and sense of humour), leading to the present moment, is summed up by his closing statement in the 1996 BBC Horizon documentary *Molecules With Sunglasses*: in response to a reporter’s provocation “but others have said that C_{60}^+ is nothing like a match for the diffuse interstellar bands” — Kroto, pausing for thought: “They’re wrong”.

Acknowledgments

The author would like to thank Ewan Campbell for supplying the laboratory C_{60}^+ comparison spectrum, Charles Proffitt for helping develop and refine the HST/STIS scanning strategy, and Rosine Lallement for supplying the telluric-corrected spectrum of HD168625. Additional thanks to Harold Linnartz, Nick Cox, Jan Cami, Paco Najarro, Pascale Ehrenfreund, Bernard Foing, Ted Gull, Peter Sarre and Steve Charnley for their crucial contributions to the HST study.

References

- Berné, O., Mulas, G., Joblin, C., “Interstellar C60+”, *A&A*, 550, L4, 2013
- Castellanos, P., Berné, O., Sheffer, Y., Wolfire, M., Tielens, A. G. G. M., “C60 in photodissociation regions”, *ApJ*, 794, 83, 2014
- Cami, Jan, Bernard-Salas, J., Peeters, E., Malek, S. E., “Detection of C60 and C70 in a Young Planetary Nebula”, *Science*, 329, 1180, 2010
- Campbell, E. K., Holz, M., Gerlich, D., Maier, J. P., “Laboratory confirmation of C60+ as the carrier of two diffuse interstellar bands”, *Nature*, 523, 322, 2015
- Campbell, E. K., Maier, J. P., “Isomeric and Isotopic Effects on the Electronic Spectrum of C₆₀⁺-He: Consequences for Astronomical Observations of C₆₀⁺”, *ApJ*, 858, 36, 2018
- Chlewicki, G., van der Zwet, G. P., van Ijzendoorn, L. J., Greenberg, J. M., Alvarez, P. P., “Shapes and Correlations as Observational Discriminants for the Origin of Diffuse Bands”, *ApJ*, 305, 455, 1986
- Cordiner, M. A., Cox, N. L. J., Lallement, R. et al., “Searching for Interstellar C₆₀⁺ Using a New Method for High Signal-to-noise HST/STIS Spectroscopy”, *ApJL*, 843, L2, 2017
- Cordiner, M. A., Linnartz, H., Cox, N. L. J., “Confirming Interstellar C60 + Using the Hubble Space Telescope”, *ApJL*, 875, L28, 2019
- Herbig, G. H., “The Diffuse Interstellar Bands”, *Annu. Rev. Astrophys.*, 33, 19, 1995
- Foing, B. H. and Ehrenfreund, P., “Detection of two interstellar absorption bands coincident with spectral features of C₆₀⁺” *Nature* 369, 296, 1994
- Fulara, J., Jakobi, M. and Maier, J. P., “Electronic and infrared spectra of C+60 and C60 in neon and argon matrices”, *Chem Phys. Lett.* 211, 227, 1993
- Galazutdinov, G. A., Shimansky, V. V., Bondar, A., Valyavin, G., Krelowski, J., “C60+ — looking for the bucky-ball in interstellar space”, *MNRAS*, 465, 3956, 2017a
- Galazutdinov, G. A., Krelowski, J., “Looking for the Weak Members of the C60+ Family in the Interstellar Medium”, *AcA*, 67, 159, 2017b
- Gasyna, Z., Andrews, L. and Schatz, P. N., “Near-infrared absorption spectra of fullerene (C60) radical cations and anions prepared simultaneously in solid argon”, *J. Phys. Chem.* 96, 1525, 1992
- Harding, R., Zhou, S., Zhou, J. et al., “Spin Resonance Clock Transition of the Endohedral Fullerene ¹⁵N@C₆₀”, *Phys. Rev. Lett.* 119, 140801, 2017
- Heath, J. R., Zhang, Q. S., O’Brien, C., Curl, R. F., Kroto, H. W., Smalley, R. E., “The formation of long carbon chain molecules during laser vaporization of graphite”, *J. Am. Chem. Soc.*, 109, 359, 1987
- Kato, T., Kodama, T., Shida, T. et al., “Electronic absorption spectra of the radical anions and cations of fullerenes: C60 and C70”, *Phys. Lett.* 180, 446, 1991
- Kroto, H. W., Heath, J. R., O'Brien, S. C., Curl, R. F., Smalley, R. E., “C60: Buckminsterfullerene”, *Nature*, 318, 162, 1985
- Kroto, H. W., Heath, J. R., O'Brien, S. C., Curl, R. F., Smalley, R. E., “Long Carbon Chain Molecules in Circumstellar Shells”, *ApJ*, 314, 352, 1987
- Kroto, H. W., “Space, Stars, C60, and Soot”, *Science*, 242, 1139, 1988
- Kuhn, M., Renzler, M., Postler, J. et al., “Atomically resolved phase transition of fullerene cations solvated in helium droplets”, *Nat. Comm.*, 713550, 2016
- Lallement, R., Cox, N. L. J., Cami, J., “The EDIBLES survey II. The detectability of C60+ bands”, *A&A*, 614, 28, 2018

- Leger, A., D'Hendecourt, L., "Are polycyclic aromatic hydrocarbons the carriers of the diffuse interstellar bands in the visible?", *A&A*, 146, 81, 1985
- Sarre, P. J., "The diffuse interstellar bands: A major problem in astronomical spectroscopy", *J. Mol. Spec.*, 238, 1, 2006
- Sellgren, K., Werner, M. W., Ingalls, J. G., Smith, J. D. T., Carleton, T. M., Joblin, C., "C60 in Reflection Nebulae", *ApJL*, 722, L54, 2010
- Song, S., Hill, R., Choi, K. et al., "Surface modified fullerene electron transport layers for stable and reproducible flexible perovskite solar cells", *Nano Energy*, 49, 324, 2018
- Spieler, S., Kuhn, M., Postler, J., "C₆₀⁺ and the Diffuse Interstellar Bands: An Independent Laboratory Check", *ApJ*, 846, 168, 2017
- Walker, G. A. H., Bohlender, D. A., Maier, J. P., Campbell, E. K., "Identification of More Interstellar C60+ Bands", *ApJL*, 812, L8, 2015
- Walker, G. A. H., Campbell, E. K., Maier, J. P., Bohlender, D., Malo, L., "Gas-phase Absorptions of C60+: A New Comparison with Astronomical Measurements", *ApJ*, 831, 130, 2016
- Walker, G. A. H., Campbell, E. K., Maier, J. P., Bohlender, D., "The 9577 and 9632 Diffuse Interstellar Bands: C₆₀⁺ as Carrier", *ApJ*, 843, 56, 2017



Dr. Martin Cordiner is a principal investigator in astrochemistry and astrobiology in the Department of Physics, Catholic University of America. He works full-time as a researcher at the NASA Goddard Space Flight Center in Greenbelt, Maryland, where he aims to understand the organic inventory and chemical evolution of astrophysical environments including solar system bodies, interstellar clouds and circumstellar envelopes. This work is accomplished through multi-wavelength ground- and space-based spectroscopic observations, combined with radiative transfer and chemical-kinetic computer simulations. Dr. Cordiner first became interested in interstellar fullerenes and PAHs during his PhD work on the diffuse interstellar band problem, and continues to study the physics and chemistry of the diffuse ISM using the Hubble Space Telescope.

Email: martin.cordiner@nasa.gov



Abstracts

The evolution of polycyclic aromatic hydrocarbons under simulated inner asteroid conditions

Claudia-Corina Giese^{1,2}, Inge Loes Ten Kate², Oliver Plümper², Helen E. King², Christoph Lenting³, Yang Liu^{2,4,5}, and Alexander G. G. M. Tielens¹

¹ Leiden Observatory, Faculty of Science, Leiden University, 2300 RA Leiden, the Netherlands

² Department of Earth Sciences, Faculty of Geosciences, Utrecht University, 3584 CD Utrecht, the Netherlands

³ Steinmann-Institut for Geology, Mineralogy und Palaeontology, University of Bonn, 53115 Bonn, Germany

⁴ Soft Condensed Matter, Debye Institute for Nanomaterials Science, Utrecht University, 3584 CC Utrecht, the Netherlands

⁵ Plymouth Electron Microscopy Centre, University of Plymouth, Devon, PL4 8AA Plymouth, UK

Large polycyclic aromatic hydrocarbons (PAHs) are an important component of the interstellar medium. PAHs have been identified in the soluble and insoluble matter of carbonaceous chondrites (CCs). Here, we study the evolution of PAHs under conditions relevant to the interiors of asteroids and compare our results to PAHs observed in CCs. We have performed long-term and short-term hydrothermal experiments, in which we exposed PAH-mineral mixture analogs of meteorites to temperature conditions representative of those predicted for asteroids interiors. Our results show that small PAHs with melting points within the aqueous alteration temperature of CCs form carbonaceous spherules in the presence of water. In this work, we describe the microstructure and morphology of these spherules. We discuss the similarities and differences compared to globules isolated from CCs.

E-mail: c.c.giese@uu.nl

Meteoritics & Planetary Science, 54, 1930-1950 (2019)

<https://onlinelibrary.wiley.com/doi/full/10.1111/maps.13359>

Polycyclic Aromatic Hydrocarbons with Armchair Edges: Potential Emitters in Class B Sources

Alessandra Ricca^{1,2}, Joseph E. Roser^{1,2}, Els Peeters^{1,3}, Christiaan Boersma²

¹ Carl Sagan Center, SETI Institute, 189 Bernardo Ave., Mountain View, CA 94043, USA

² NASA Ames Research Center, Mail Stop 245-6, Moffett Field, CA 94035-001, USA

³ Department of Physics and Astronomy, University of Western Ontario, London, ON N6A 3K7, Canada

We have systematically investigated a series of polycyclic aromatic hydrocarbons (PAHs) with armchair edges that maximize the aromaticity, denoted as Clar PAHs, using density functional theory. Their structures fall into three major categories: branched, intermediate, and armchair. Branched PAHs contain up to 60 carbons, they are eroded and the least stable, and their spectra are the most complex. Armchair PAHs are the most stable and

their spectra differ from the nominal PAH spectra by lacking a 11.2 μm band and having their 7.8 μm and 8.2 μm bands coalesce as their size increases. Only intermediate and armchair PAHs have 12.7/13.5 μm PAH band intensity ratios that are consistent with observations. The fitting results show that Clar PAH spectra are more consistent with class B than class A sources, with only a few small Clar PAHs contributing to the fit of the class A source IRAS 23133+6050 and large Clar PAHs contributing to the fit of the class B source IRAS 173473139, and NGC 7027. Overall, our study suggests that large Clar PAHs are potential emitters in class B sources.

E-mail: Alessandra.Ricca-1@nasa.gov

Alessandra Ricca et al 2019 ApJ 882 56

<https://doi.org/10.3847/1538-4357/ab3124>

PAH Products and Processing by Different Energy Sources

Gustavo A. Cruz-Diaz^{1,2}, S. E. Erickson³, E. F. da Silveira⁴, A. Ricca^{2,5}, A. L. F. de Barros^{2,6}, C. A. P. da Costa⁴, R. C. Pereira⁶, and A. L. Mattioda²

¹ Bay Area Environmental Research Institute, Moffett Field, Mountain View, CA 94035, USA

² NASA Ames Research Center, Moffett Field, Mountain View, CA 94035, USA

³ University of Minnesota, Twin Cities, Minneapolis, MN, USA

⁴ Departamento de Física, Pontifícia Universidade Católica do Rio de Janeiro (PUC-Rio), Rua Marques de São Vicente, 225, 22453-900, Rio de Janeiro, Brazil

⁵ Carl Sagan Center, SETI Institute, 189 Bernardo Avenue, CA 94043, USA

⁶ Departamento de Física, Centro Federal de Educação Tecnológica Celso Suckow da Fonseca (CEFET-RJ), Av. Maracanã, 229, 20271-110, Rio de Janeiro, RJ, Brazil

Isoviolanthrene ($\text{C}_{34}\text{H}_{18}$), a polycyclic aromatic hydrocarbon (PAH) molecule, was studied via matrix isolation in argon and water at 20 K. Infrared spectroscopy was performed in situ where samples were irradiated using ultraviolet light. Experimental spectra were compared to theoretical spectra for vibrational band assignment, determination of the corresponding A-values, and photoproduct identification. Isoviolanthrene was also deposited as a thin film and irradiated with different energy sources: ultraviolet photons (10.2 eV), soft electrons (1.5 keV), protons (1.5 MeV), and He^+ particles (1.5 MeV), to understand the effects of different energy sources on a PAH. Anions and cations of isoviolanthrene were produced as a result of UV photolysis in an argon matrix. Hydrogen- and oxygen-rich aromatic photoproducts were produced by ultraviolet photons when isoviolanthrene was isolated in a water matrix. The irradiated PAH thin films results were dependent on the energy source. Irradiation with ultraviolet photons yielded a broad underlying feature centered at 9.6 μm , while bombardment with soft electrons gave a broad feature centered at 7.7 μm . In the case of proton bombardment, no broad feature was detected, in contrast with He^+ bombardment that destroyed most of the isoviolanthrene and produced broad features in the C-Hoop and CH stretching regions. A comparison of astronomical IR emission observations with our experimental results in the mid-infrared range has revealed a similarity between the observed plateaus and the broad features produced by our experiments.

E-mail: gustavo.a.cruzdiaz@nasa.gov

G. A. Cruz-Diaz et al 2019 ApJ 882 44

<https://doi.org/10.3847/1538-4357/ab311f>

Storage time dependent photodissociation action spectroscopy of polycyclic aromatic hydrocarbon cations in the cryogenic electrostatic storage ring DESIREE

Mark H. Stockett, Mikael Björkhage, Henrik Cederquist, Henning T. Schmidt, Henning Zettergren

Department of Physics, Stockholm University, Stockholm, Sweden

The multi-photon photodissociation action spectrum of the coronene cation ($C_{24}H_{12}^+$) has been measured in the cryogenic electrostatic storage ring DESIREE (Double ElectroStatic Ion Ring ExpEriment) as a function of storage time. These measurements reveal not only the intrinsic absorption profile of isolated coronene cations, but also the rate at which hot-band absorptions are quenched by radiative cooling. Just after injection, the action spectrum is severely reddened by hot-band absorptions. These hot bands fade with a time constant of 200 ms, which is consistent with radiative cooling via infrared emission from vibrational transitions. The comparison of the present results to those obtained in cryogenic ion trap experiments is discussed at length.

E-mail: Mark.Stockett@fysik.su.se

Faraday Discuss. 217 126, 2019

<http://dx.doi.org/10.1039/C8FD00161H>

The Photolysis of Aromatic Hydrocarbons Adsorbed on the Surfaces of Cosmic Dust Grains

M. S. Murga^{1, 2}, V. N. Varakin², A. V. Stolyarov² and D. S. Wiebe¹

¹ Institute of Astronomy, Russian Academy of Sciences

² Lomonosov Moscow State University, Moscow, Russia

The results of laboratory mass-spectrometer studies of the laser-induced dissociation of molecules of simple aromatic hydrocarbons adsorbed on a quartz substrate under the conditions of deep vacuum and low temperatures are adapted to the physical and chemical conditions in regions of active star formation in molecular clouds. The main properties of the photolysis of physically adsorbed molecules compared to the photodissociation of isolated molecules in the gas phase are identified. The relevance of molecular photolytic desorption to the real conditions in the interstellar medium is analyzed, in particular, to the conditions in photodissociation regions. It is shown that the photodissociation of adsorbed benzene occurs along other channels and with appreciably lower efficiency than does the corresponding process in the gas phase. The photodissociation of aromatic hydrocarbons adsorbed on the surfaces of interstellar grains cannot make a large contribution to the abundance of hydrocarbons with small numbers of atoms observed in the interstellar medium.

E-mail: murga@inasan.ru

Astronomy Reports, Volume 63, Issue 8, pp.633-641 (2019)

<https://ui.adsabs.harvard.edu/abs/2019ARep...63..633M/abstract>

Graphene Oxide Nanoparticles in the Interstellar Medium

Peter J. Sarre¹

¹ School of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom

Dust particles play a major role in the formation, evolution and chemistry of interstellar clouds, stars and planetary systems. Commonly identified forms include amorphous and crystalline carbon-rich particles and silicates. Also present in many astrophysical environments are polycyclic aromatic hydrocarbons (PAHs), detected through their infrared emission, and which are essentially small flakes of graphene. Astronomical observations over the past four decades have revealed a widespread unassigned 'Extended Red Emission' (ERE) feature which is attributed to luminescence of dust grains. Numerous potential carriers for ERE have been proposed but none has gained general acceptance. In this Letter it is shown that there is a strong similarity between laboratory optical emission spectra of graphene oxide and ERE, leading to this proposal that emission from graphene oxide nanoparticles is the origin of ERE and that these are a significant component of interstellar dust. The proposal is supported by infrared emission features detected by the *Infrared Space Observatory (ISO)* and the *Spitzer Space Telescope*.

E-mail: peter.sarre@nottingham.ac.uk

Accepted for publication in MNRAS

<https://arxiv.org/abs/1908.07787>

<https://doi.org/10.1093/mnras/slz131>

The Performance of Explicitly Correlated Wavefunctions [CCSD(T)-F12b] in the Computation of Anharmonic Vibrational Frequencies

Donatus Agbaglo^{1,2} and Ryan C. Fortenberry³

¹ Georgia Southern University, Department of Chemistry & Biochemistry, Statesboro, GA 30460, U.S.A.

² University of Memphis, Department of Chemistry, Memphis, TN 38152, U.S.A.

³ Department of Chemistry & Biochemistry, University of Mississippi, University, MS 38655-1848, U.S.A.

CCSD(T)-F12b/cc-pVTZ-F12 anharmonic vibrational frequencies match experiment or higher-level theory to within an average of 10.3 cm^{-1} for a sample set of 11 molecules. This is further reduced below 7.0 cm^{-1} when extreme differences are removed from the data set. CCSD(T)-F12b/cc-pVTZ-F12 and CCSD(T)-F12b/cc-pVDZ-F12 frequencies differ on average by 4.8 cm^{-1} . The CCSD(T)-F12b frequencies require orders of magnitude less computer time than higher-order theory and cc-pVDZ-F12 less than cc-pVTZ-F12, especially as the number of atoms increases. Hence, utilization of these levels of theory may provide accurate vibrational frequencies for larger molecules like PAHs, provided that the core-electron correlation is not significant.

E-mail: r410@olemiss.edu

Chem. Phys. Lett. 136720 (2019), *in press*

<https://doi.org/10.1016/j.cplett.2019.136720>

Photodetachment and Photoreactions of Substituted Naphthalene Anions in a Tandem Ion Mobility Spectrometer

James N. Bull,¹ Jack T. Buntine,¹ Michael S. Scholz,¹ Eduardo Carrascosa,¹ Linda Giacomozzi,² Mark H. Stockett,² and Evan J. Bieske¹

¹ School of Chemistry, University of Melbourne, Melbourne, Australia

² Department of Physics, Stockholm University, Stockholm, Sweden

Substituted naphthalene anions (deprotonated 2-naphthol and 6-hydroxy-2-naphthoic acid) are spectroscopically probed in a tandem drift tube ion mobility spectrometer (IMS). Target anions are selected according to their drift speed through nitrogen buffer gas in the first IMS stage before being exposed to a pulse of tunable light that induces either photodissociation or electron photodetachment, which is conveniently monitored by scavenging the detached electrons with trace SF₆ in the buffer gas. The photodetachment action spectrum of the 2-naphtholate anion exhibits a band system spanning 380-460 nm with a prominent series of peaks spaced by 440 cm⁻¹, commencing at 458.5 nm, and a set of weaker peaks near the electron detachment threshold corresponding to transitions to dipole-bound states. The two deprotomers of 6-hydroxy-2-naphthoic acid are separated and spectroscopically probed independently. The molecular anion formed from deprotonation of the hydroxy group possesses a photodetachment action spectrum similar to that of the 2-naphtholate anion with an onset at 470 nm and a maximum at 420 nm. Near threshold, photoreaction with SF₆ is observed with displacement of an OH group by an F atom. In contrast, the anion formed from deprotonation of the carboxylic acid group features a photodissociation action spectrum, recorded on the CO₂ loss channel, lying to much shorter wavelength with an onset at 360 nm and maximum photoresponse at 325 nm.

E-mail: evanjb@unimelb.edu.au

Faraday Discuss., 217 34, 2019

<http://dx.doi.org/10.1039/C8FD00217G>

Cavity ring down spectroscopy of cold neutral phenanthrene and phenanthridine in supersonic jets

Salma Bejaoui^{1,2} and Farid Salama¹

¹ NASA-Ames Research Center, Space Science & Astrobiology Division, Mail Stop 245-6, Moffett Field, California 94035-1000, USA

² NPP, Universities Space Research Association, 615 National Ave, Mountain View, California 94043, USA

Here we study the effect of nitrogen insertion on the electronic spectra of polycyclic aromatic hydrocarbon (PAH) molecules measured under laboratory conditions that are relevant for comparison with astronomical data. We examine the case of the substitution of carbon atoms by nitrogen atoms in the benzenoid skeleton of phenanthrene (C₁₄H₁₀), a prototype non-compact PAH. The vibronic transitions of the $2^1A_1(S_1) \leftarrow X^1A_1(S_0)$ electronic absorption band system of neutral phenanthrene (C₁₄H₁₀) and phenanthridine (C₁₃H₉N) molecules seeded in a supersonic free jet expansion of argon gas are measured

in the 315-345 nm region using the cavity ring down spectroscopy (CRDS) technique. Additional measurements of the absorption spectra of the phenanthrene, phenanthridine and 1,10-phenanthroline ($C_{12}H_8N_2$) molecules isolated in 10-K solid argon matrices are also presented. The results obtained confirm that laboratory spectra of cold, isolated molecules obtained under astrophysically relevant conditions are required for a direct, unambiguous comparison with astronomical observations as well as for the understanding of the physical evolution of the interstellar medium.

E-mail: salma.bejaoui@nasa.gov

S. Bejaoui and F. Salama, AIP Advances 9:8, 085021 (2019)

<https://doi.org/10.1063/1.5100152>

Infrared spectrum of hydrogenated corannulene *rim*- $HC_{20}H_{10}$ isolated in solid para-hydrogen

Pavithraa Sundararajan¹, Masashi Tsuge^{1,2}, Masaaki Baba³ and Yuan-Pern Lee^{1,4,5}

¹ Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan

² Institute of Low Temperature Science, Hokkaido University, Sapporo 060-0819, Japan

³ Division of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan

⁴ Center for Emergent Functional Matter Science, National Chiao Tung University, Hsinchu 30010, Taiwan

⁵ Institute of Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan

Hydrogenated polycyclic aromatic hydrocarbons have been proposed to be carriers of the interstellar unidentified infrared (UIR) emission bands and the catalysts for formation of H_2 ; spectral characterizations of these species are hence important. We report the infrared (IR) spectrum of mono-hydrogenated corannulene ($HC_{20}H_{10}$) in solid para-hydrogen ($p\text{-}H_2$). In experiments of electron bombardment of a mixture of corannulene and $p\text{-}H_2$ during deposition of a matrix at 3.2 K, two groups of spectral lines increased with time during maintenance of the matrix in darkness after deposition. Lines in one group were assigned to the most stable isomer of hydrogenated corannulene, *rim*- $HC_{20}H_{10}$, according to the expected chemistry and a comparison with scaled harmonic vibrational wavenumbers and IR intensities predicted with the B3PW91/6-311++G(2d,2p) method. The lines in the other group do not agree with predicted spectra of other $HC_{20}H_{10}$ isomers and remain unassigned. Alternative hydrogenation was achieved with H atoms produced photochemically in the infrared-induced reaction $Cl + H_2 (v = 1) \rightarrow H + HCl$ in a $Cl_2/C_{20}H_{10}/p\text{-}H_2$ matrix. With this method, only lines attributable to *rim*- $HC_{20}H_{10}$ were observed, indicating that hydrogenation via a quantum-mechanical tunneling mechanism produces preferably the least-energy *rim*- $HC_{20}H_{10}$ regardless of similar barrier heights and widths for the formation of *rim*- $HC_{20}H_{10}$ and *rub*- $HC_{20}H_{10}$. The mechanisms of formation in both experiments are discussed. The bands near 3.3 and 3.4 μm of *rim*- $HC_{20}H_{10}$ agree with the UIR emission bands in position and relative intensity, but other bands do not match satisfactorily with the UIR bands.

E-mail: pavi.nctu@gmail.com, yplee@nctu.edu.tw

J. Chem. Phys. 151, 044304 (2019)

<https://aip.scitation.org/doi/10.1063/1.5111169#suppl>



Announcements

CALL FOR NOMINATION

Laboratory Astrophysics Division (LAD) Dissertation Prize

Dear all,

The **Laboratory Astrophysics Division (LAD)** of the American Astronomical Society (AAS) invites nominations for the LAD Dissertation Prize. The field of laboratory astrophysics encompasses all fundamental theoretical and experimental research into the underlying processes that drive the cosmos.

The Dissertation Prize is presented, normally on an annual basis, to recognize an outstanding theoretical or experimental doctoral dissertation (or equivalent) in laboratory astrophysics. The prize is awarded to an individual who has completed their PhD or equivalent degree in any of the three calendar years immediately preceding the award year. The prize includes a cash award, a citation, and an invited lecture by the recipient at a meeting of the Division.

The recipients for each year will be announced typically in January/February of that year, and their presentations will be made at the annual LAD meeting. In 2020, the LAD meeting will be held jointly with the AAS Summer Meeting, 30 May - 4 June 2020, in Madison, WI. Any nominee not selected will be automatically considered in the next two consecutive years, or as long as the nominee is eligible, whichever is less.

The Nomination Package for the Dissertation Prize must include:

1. A nomination letter, including a one-sentence proposed citation. Only one signator allowed.
2. Two letters of support. Additional letters will not be considered. Only one signator per letter allowed.
3. A summary of the thesis (not to exceed 5 pages including figures and bibliography).
4. A statement from the nominee's university (Ph.D. or equivalent degree has been awarded).
5. A curriculum vitae.
6. A publication list.

Additional material (such as reprints, etc.) will not be considered. Nominators, letter writers, and candidates need not be AAS or LAD members. Self-nominations are allowed and encouraged. The deadline for receipt of the nomination package and supporting letters for the Dissertation Prize is **by 11:59:59 pm EST on December 31st 2019**.

Attracting and serving a diverse and inclusive membership worldwide is a primary goal for LAD. In calling for nominations, we wish to remind you how important it is to give full consideration to qualified women, members of underrepresented minority groups, and scientists from outside the United States. All nomination material should be sent by the deadline directly to the LAD Secretary (lad.secretary@nasa.gov).

Please don't hesitate to email any questions you may have.

Sincerely,

Rachel Smith
LAD Secretary

Postdoctoral research position

The NASA Ames PAH IR Spectroscopic Database

Advertised by: The NASA Ames PAH IR Spectroscopic Database Team

Deadline for Application: November 1st, 2019

The NASA Ames PAH IR Spectroscopic Database (PAHdb) Team is offering a 1-2 year postdoctoral research position. The PAHdb Team is part of the [Astrophysics & Astrochemistry Laboratory](#) group at NASA Ames Research Center (ARC), in the [Space Science and Astrobiology Division](#). Located in the heart of Silicon Valley, ARC lies at the southern tip of the San Francisco Bay, bordering the city of Mountain View. This highly interdisciplinary research group consists of chemists, physicists, and astronomers.

The successful applicant is expected to work on applying the data and tools that are part of PAHdb to analyze and interpret the emission attributed to polycyclic aromatic hydrocarbons in astronomical observations, as well as further develop and expand the (software) tools in preparation for the *James Webb Space Telescope* (JWST). JWST will measure the PAH features with spectral coverage and sensitivity that far exceeds earlier observations and with a reach that is far deeper than previously possible. Work is expected to be published in peer-reviewed journals and there is strong encouragement to present your research at (international) conferences, both oral and in posters. Some recent relevant publications (DOIs) are given below and the development of the (software) tools is done on [GitHub](#).

- [10.3847/1538-4357/aaf562](https://doi.org/10.3847/1538-4357/aaf562)
- [10.3847/1538-4365/aaa019](https://doi.org/10.3847/1538-4365/aaa019)
- [10.3847/1538-4357/aabcbe](https://doi.org/10.3847/1538-4357/aabcbe)
- [10.25080/majora-4af1f417-00f](https://doi.org/10.25080/majora-4af1f417-00f)

Applicants must be highly qualified, self-motivated, fluent in English, have a solid background in infrared astronomy, and knowledgeable with infrared spectroscopy. Being able to use Python is a must. Some exposure to IDL and experience with software development would be highly beneficial. The application package should be sent to Christiaan.Boersma@nasa.gov and include:

1. Cover letter
2. CV/Résumé
3. List of publications
4. Statement of qualifications relevant to the position (e.g., coding experience/examples)
5. Research interests
6. Names and contact information of two references

E-mail contact: Christiaan.Boersma@nasa.gov

AstroPAH Newsletter

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

Next issue: 17 October 2019
Submission deadline: 4 October 2019