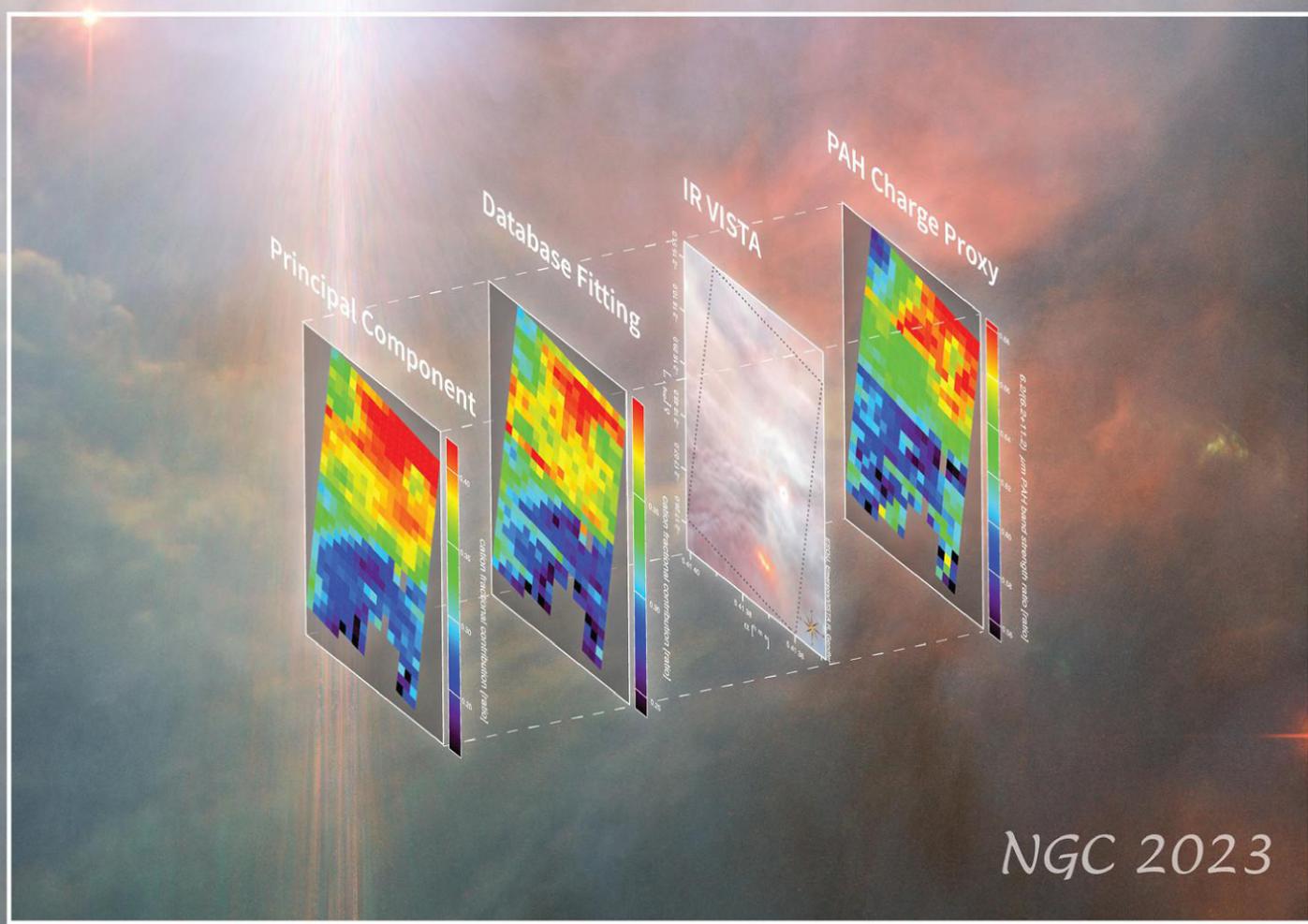


AstropAH

A Newsletter on Astronomical PAHs

Issue 27 | April 2016



Background : ESA/Hubble & NASA

Editorial

Dear Colleagues,

Welcome to the April issue of AstroPAH.

The cover gives a sneak preview of our In Focus. It is a composite picture demonstrating the variations of PAH populations across NGC 2023 obtained by different methods. Dr. Christiaan Boersma has written an *In Focus* on the PAH research of the Astrophysics & Astrochemistry Laboratory at NASA Ames Research Center in view of his recently received distinction. We congratulate Dr. Boersma for his NASA Ames Research Center Space Science & Astrobiology Divisions Outstanding Early Career Space Scientist Award.

Further in this month's release, AstroPAH presents the abstracts of papers on the observation and modelling of PAH population, using data obtained with SOFIA, Spitzer and various archival data. In our meetings section, you can find the third announcement of the international conference on Chemistry and Physics at Low Temperature, in France.

We thank you all for your contributions and please keep them coming. You can send us your contributions anytime. For publication in May, see the deadlines below. Would you like to see your picture as Picture of the Month, your project featured in our In Focus, or distribute your latest paper or upcoming event amongst our community, we encourage you to visit our webpage or contact us (links in the next page).

You can now also connect to our [Facebook page](#). You are welcome to like and share with your colleagues.

The Editorial Team

**Next issue: 17 May 2016.
Submission deadline: 6 May 2016.**

AstroPAH Newsletter

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PAH Picture of the Month

NGC 2023 is a well-known reflection nebula situated below the Horsehead Nebula in Orion. The background shows the Hubble Space Telescope image of part of the nebula. In the foreground, the IR VISTA image shows the region for which Spitzer-IRS spectral map data is available. The other three images compare the variation in PAH charge across the nebula determined in three different ways: 1) using the 6.2/11.2 μm PAH band strength ratio as a qualitative proxy, 2) using a quantitative database fitting approach, and 3) using principal component spectra derived from a different reflection nebula, namely NGC 7023.

Credits: Background ESA/Hubble & NASA. Inset and composition by Christiaan Boersma NASA Ames Research Center/San José State University Research Foundation.

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Newsletter Design: Isabel Aleman
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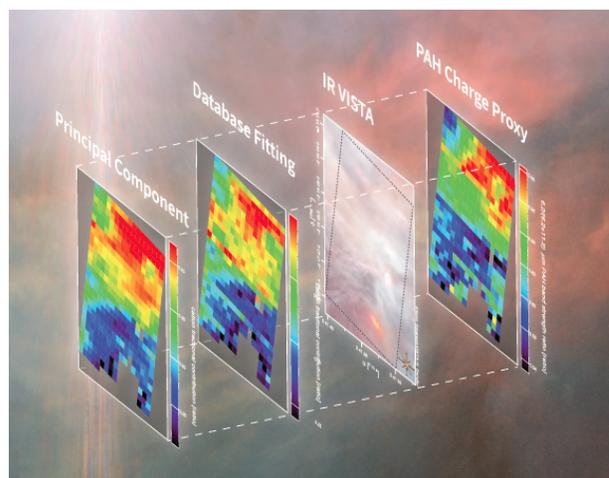
In Focus

A 21st Century Approach to Astronomical PAH Spectroscopy at NASA Ames Research Center: *Mining the Treasure Trove**

by Christiaan Boersma

As the AstroPAH reader is probably well aware, polycyclic aromatic hydrocarbons, PAHs, are ubiquitous in space. However, the general acceptance of the PAH model took some time and, even today, there is still some resistance. Those astronomers embracing the PAH model know very well how PAHs open up a window into the different astronomical environments and processes associated with star and planet formation. From the first discovery of excess infrared emission near 11.2 μm in the late 1960s (Gillett et al. 1967) to the positive identification of the C_{60} -cation as the carrier of the diffuse interstellar bands at 9632 and 9577 \AA just last year (Campbell et al. 2015) illustrates both the scope and progress that has been made with the PAH model.

The launch of the James Webb Space Telescope, JWST, later this decade will usher in a new era of PAH and PAH-related research, as it will provide astronomical observations at unprecedented spatial- and spectral resolutions and with unrivaled sensitivities. In preparation for what JWST will bring and what is already available from other missions like ISO and Spitzer, the Astrophysics & Astrochemistry Laboratory at NASA Ames Research Center is focused on unlocking and mining the treasure trove of information hidden in the astronomical PAH spectrum utilizing data and tools made available through the NASA Ames PAH IR Spectroscopic Database.



See the cover caption for information on this image.

**Based on the Outstanding Early Career Space Scientist Award Lecture given at NASA Ames Research Center on March 8th, 2016*

The Development of the PAH Hypothesis



Figure 1 - The Kuiper Airborne Observatory (KAO) flew out of NASA Ames Research Center from 1975-1995. This highly modified Lockheed C-141A Starlifter jet transport aircraft was capable of carrying out mid- and far-infrared observations up to 45,000 feet (14 km), thereby avoiding nearly all water vapor in the Earth's atmosphere. (Credit: <https://herschel.jpl.nasa.gov/relatedMissions.shtml>)

In the early-mid 1980's the mysterious mid-infrared emission observed towards a variety of astronomical objects compared favorably to the hand-digitized absorption spectra of PAHs in salt pellets. The Kuiper Airborne Observatory (KAO, **Figure 1**) pioneered observations in the 5-10 μm region, including spectra of Orion and NGC 7027. These spectra, complemented with ground-based spectra to cover 2-14 μm , spurred development of the "PAH hypothesis". As with any hypothesis, predictions were made and tested, the number of astronomical observations increased and the case for PAHs in space was assessed.

One of many predictions made in the late 1980's was the presence of two, generally weak, PAH features between 5-6 μm . This was based on the laboratory spectra of PAHs in salt pellets, which consistently showed weak features at 5.25 and 5.7 μm that are due to overtone and combination bands. Again, thanks to the KAO, both features were confirmed in the spectrum of the planetary nebula BD+30°3639.

As the number of astronomical observations increased, additional constraints were placed on the carrier of the mysterious unidentified infrared features. Firstly, since the emission features are observed in regions where the material cannot be emitting thermally, the carrier must be excited through the absorption of a single ultraviolet/visible photon, i.e., the carriers are free, gas-phase, molecule-sized species. Second, the direct correlation between the intensity of the emission features and the amount of available carbon points to the carrier being carbon-rich. Lastly, since the features are observed in extremely harsh environments, the carrier must be highly stable as well. Add to this the growing spectroscopic evidence, the case for PAHs strengthened.

It was pretty quickly realized that given their unique property of having characteristics associated with both molecules and particles, PAHs would not only be witnesses of the conditions in their surroundings but also active participants in the chemistry and astrophysics. Since PAHs are readily photo-ionized, they should, for example, play important roles in regulating the charge balance, temperature and cloud collapse timescales.

However, by the late 1980's there were few infrared spectra of PAHs under astrophysically relevant conditions to refine the PAH hypothesis and develop them into new probes of the cosmos. To address this issue, a program was started at NASA Ames Research Center in 1990 to build a library of PAH spectra. With measuring the PAH spectra at low temperatures and in Argon-matrices, steady progress was made. But, laboratory experiments are severely limited by the size, structure and compositions of the PAHs that are available for study. To overcome this, one turned to theory.

By the late 1990's quantum chemists showed that density functional theory (DFT) methods could be used to accurately compute the vibrational spectra of PAHs, see e.g., **Figure 2**. This was a major breakthrough, as it provided the computed spectra of PAHs relevant to the astrophysical question and development of a robust PAH spectral library.

While great strides were made in the laboratory and with DFT, infrared astronomy had entered the space age. With the launch of the Infrared Space Observatory, ISO, in 1995 it was finally possible to measure the complete mid-infrared PAH emission spectra with a single aperture. The data returned by ISO revealed that PAH

spectra vary spatially within and between objects. These variations reflect changes in the PAH population, e.g., size, charge, structure, etc. In turn, these reflect a changing astrophysical environment and/or a different chemical history. Thanks to its greater sensitivity, the Spitzer Space Telescope, Spitzer, launched in 2003, showed that PAHs are abundant and widespread across the Universe.

Today PAHs are routinely used as probes of the astrophysical environment and, specifically, to track the evolution of carbon through the different stages of the star- and planet formation process. The significance of astronomical PAHs is well established: 1) Up to 30% of the total infrared emission in many sources is carried by PAHs and 10-20% of the cosmic carbon is locked up in emitting PAHs, 2) PAHs play an important role in the energetics and chemical processes in the interstellar medium, 3) PAHs are the largest carbonaceous and most complex molecules known in space and they are more abundant than all other known interstellar polyatomic molecules combined, 4) PAHs are found in meteorites and extraterrestrial interplanetary dust particles, 5) PAHs represent the single largest source of (bio)chemically accessible carbon available in the early solar system (origin of life?), and 6) PAH features can trace the first appearance of carbon in galaxies on cosmological timescales ($z \sim 6$).

Since JWST will capture, for the first time, the full mid-infrared PAH spectrum through a single, large aperture, along the same line of sight and with sufficient spectral and spatial resolution making it possible to fully exploit PAHs as probes of the Universe; one can hardly imagine

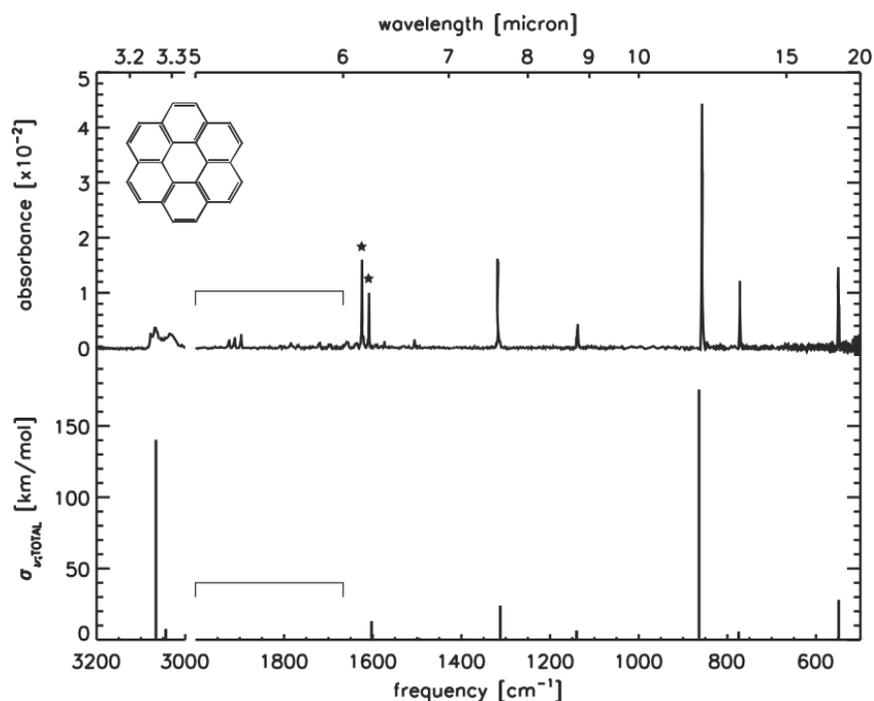


Figure 2 - Computed integrated cross-sections of coronene (bottom) compared to the absorbance spectrum of coronene isolated in an Argon matrix at 15 Kelvin (top). The two horizontal brackets indicate the 5-6 μm region. The PAH features here are due to overtone and combination bands, which are not computed when using the harmonic approximation. The two stars indicate contributions from matrix-isolated water impurities. Figure taken from Bauschlicher et al. (2010).

the impact JWST will have on our understanding of astronomical PAHs and the roles they play in astrophysics across the Universe. See [AstroPAH issue 24](#) for a comprehensive overview of JWST's capabilities and the impact it might have on PAH research to come, by J. Bernard-Salas.

PAH Spectroscopy

It is the richness of the full astronomical PAH spectrum, shown in **Figure 3**, that makes them the powerful probes they are today. The mid-infrared PAH features can be ascribed to distinct vibrational motions of the chemical sub-groups making up the PAH. For example, the 3.3 μm PAH band is associated with C-H in-plane stretching modes, the 6.2 μm PAH band with C-C in-plane stretching modes, the 8.6 μm PAH band with C-H in-plane bending modes and the emission features between 10-15 μm with C-H out-of-plane bending modes.

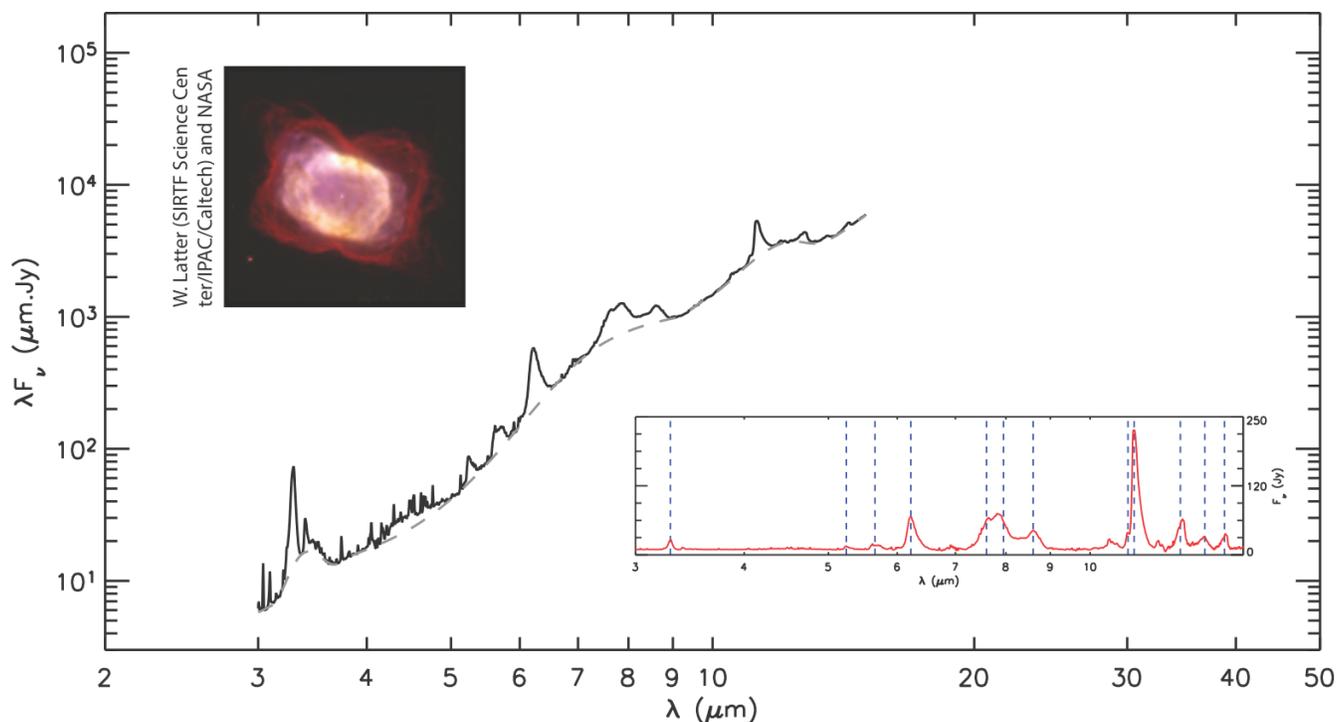


Figure 3 - Mid-infrared ISO spectrum of the planetary nebula NGC 7027. The inset shows the PAH features (red) after subtracting the grey-dashed line from the spectrum. The blue-dashed lines highlight the PAH features at 3.3, 5.25, 5.7, 7.6, 7.8, 8.6, 11.0, 11.2, 12.7, 13.5 and 14.5 μm . Spectrum courtesy of E. Peeters (Peeters et al. 2002).

While the focus here is on the PAH features, keep in mind that mid-infrared astronomical spectra are powerful tracers of many processes, including star formation, the star formation rate, gas heating, metallicity, starburst activity, redshift, strength of the radiation field, geometry of proto-planetary disks, (photo)chemistry, ice composition and chemistry, and cloud charge balance. Two examples of the kind of information contained in the PAH spectra, namely charge state and elemental composition follow.

Laboratory spectra of PAHs show that there are striking differences between the neutral and ionized PAH spectrum. Notably, for neutral PAHs the absorption/emission band intensity is mainly concentrated in the C-H in- and out-of-plane modes, i.e., at 3.3 and between 10-15 μm . In contrast, for ionized PAHs the absorption/emission band intensity is mostly concentrated in the C-C in-plane stretching modes, i.e., between roughly 6-9 μm . Therefore, the degree of ionization is proportional to the intensity in the C-C over the C-H modes, for which the 6.2/11.2 μm PAH band strength ratio is a good qualitative proxy.

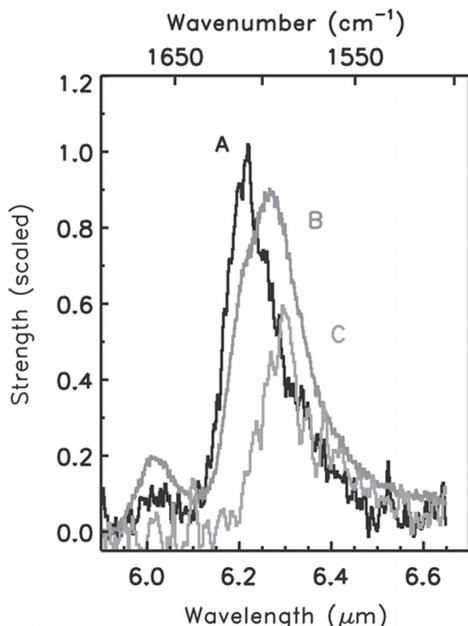


Figure 4 - 6.2 μm PAH band profile classification. (From Peeters et al. 2002)

ISO showed better than ever that the shape of the PAH band profiles varies between and within astronomical objects and, moreover, that these variations could be separated into three classes, designated A-C, where for each subsequent class the peak position of the band falls at longer wavelengths. **Figure 4** shows this classification for the 6.2 μm PAH band. However, it has been difficult to explain the short wavelength peak positions, notably that of class A. To date, the best explanation for this shift seems to be the incorporation of nitrogen into the PAH structure, where substitution of nitrogen for one of the carbon atoms shifts the peak of the 6.2 μm PAH band to shorter wavelengths when compared to its non-nitrogen containing counterpart. If born out, this is an example of how the 6.2 μm band in the PAH spectrum can be used to probe nitrogen chemistry.

Apart from the mid-infrared features, PAHs also have far-infrared bands. Much like the mid-infrared, far-infrared PAH absorption/emission spectroscopy is characterized by vibrational modes covering distinct wavelength regimes. The difference here is that whilst the mid-infrared modes involve molecular vibrations of chemical sub-groups, the far-infrared modes involve the motions of the entire molecule. These vibrations have been classified as the “Jumping-Jack”, “Butterfly” and “Drumhead” modes. Since the lowest frequency of the Drumhead modes scales inversely with the area of the PAH molecule, it could prove to be a good probe for PAH size.

Spectral Reproduction

The goal of spectral reproduction is to reproduce the richness of the astronomical infrared PAH spectrum from-the-ground-up and, through this, gain a deeper understanding of the specific PAH population in a given environment and the astrophysical environment itself. The astronomical spectrum is due to a mixture of PAH and PAH-related species. To reproduce this diversity in PAH carriers, a spectral library which contains computed PAH spectra calibrated from laboratory experiments, is used. The spectra in this library are then combined with astronomical models/simulations to reproduce the observed spectrum. A library, model/simulation framework is provided by the NASA Ames PAH IR Spectroscopic Database (PAHdb hereafter).

PAHdb is comprised of three parts: 1) The PAH spectral library, 2) A website, and 3) A suite of IDL-tools called the AmesPAHdbIDLsuite. Currently the PAH spectral library contains 700 computed PAH spectra, spanning a range in PAH charge, structure and composition. The website, located at www.astrochemistry.org/pahdb, provides a searchable interface to the PAH spectra and associated molecular data. In addition, it is the place from which the database can be downloaded as well as the AmesPAHdbIDLsuite. The website also offers several tools to be used online that allow for the inter-comparison of PAH spectra and comparison with astronomical spectra. The AmesPAHdbIDLsuite is a collection of object classes written in the Interactive Data Language (IDL) that allows one to work with the spectral data offline. Furthermore, it has a variety of tools that make working with the spectral data and comparing it to astronomical data straightforward. An analogue to the AmesPAHdbIDLsuite written in Python is under development.

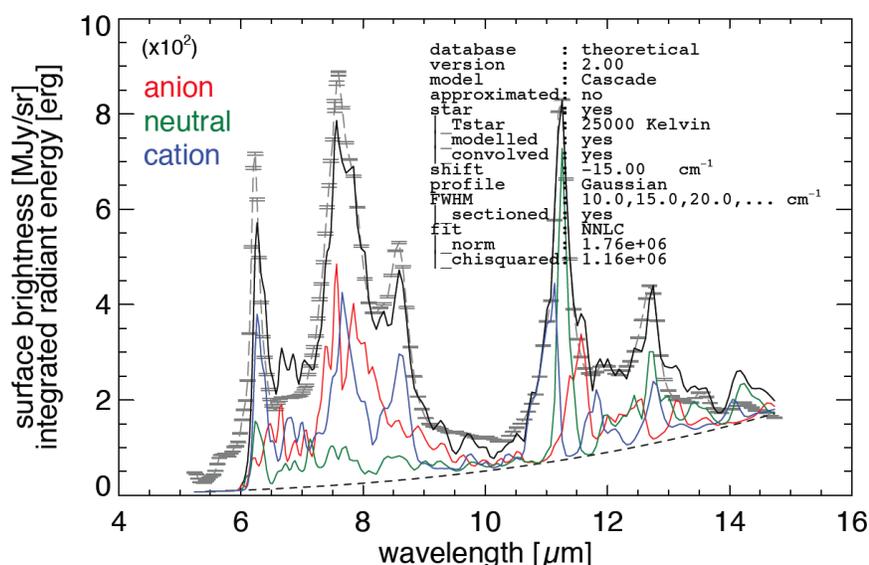


Figure 5 - Spectroscopic fit to a Spitzer-IRS spectrum of a position in the reflection nebula NGC 2023 using the data and tools made available through the NASA Ames PAH IR Spectroscopic Database. Figure adapted from Boersma et al. 2016.

Spectral fitting is chosen as the “from-the-ground-up” approach to reproduce the astronomical spectrum, since spectroscopic assignments are based on spectra of actual aromatic molecules in specific charge states, structures, sizes and so on. This allows the analysis of the spectra without the need of an ad-hoc interpretation of the state of the PAH population since the average synthesized spectra can be traced back to the fully characterized individual PAH molecules.

Required for spectroscopic fitting are: a PAH spectral library, a PAH emission model and a fitting algorithm. PAHdb provides all these. The AmesPAHdbIDLsuite is used for modelling and fitting. The PAH emission model is used to transform the integrated absorption cross-sections from the spectral library into PAH emission cross-sections. The PAH emission model describes each PAH’s excitation-emission process. The first step is PAH excitation, for which a radiation field and a description of the PAH’s UV/VIS absorption cross-section is provided. In the second step the PAH molecular physics describes how the absorbed energy is transformed into the PAH emission bands. See [AstroPAH issue 25](#) for a comprehensive overview of modelling PAH features in space by G. Mulas+.

With all requirements met, **Figure 5** demonstrates the result of a spectroscopic fit of a Spitzer-IRS spectrum from one position in the reflection nebula NGC 2023. The quality of the fit is good and it illustrates the power of the fitting approach as it shows how the spectrum can be broken down into the contributions from specific PAH charge states. Compared to the traditional

approach of measuring PAH band strength and associating them with a specific charge state, e.g., the 11.2 μm PAH band exclusively with neutral PAHs and the 6.2 μm PAH band with exclusively charged PAHs, the figure shows that all PAH band have contributions from different PAH charge states. With the fitting approach this band overlap and subclass confusion is removed.

Mining the Treasure Trove

The database fitting technique was applied to Spitzer-IRS spectral map data on 6 reflection nebulae, covering 10 large fields. For each of these fields the spectral map data was first reduced and analyzed using the traditional approach of PAH band strength determination. A map of the 6.2/11.2 μm PAH band strength ratio, labeled “PAH Charge Proxy”, can be seen on the cover image for the reflection nebula NGC 2023. Morphologically, the image compares well with the infrared image obtained by VISTA, labeled “IR VISTA”, for the same field. The result for the charge breakdown using the database fitting approach is shown in the image labeled “Database Fitting”. Again, morphologically speaking, the image compares well with that of the VISTA-image, with the database fitting approach revealing subtle details, such as, the bar-like structure visible in the VISTA-image halfway across the image.

The next step is to calibrate the qualitative 6.2/11.2 μm PAH charge proxy by comparing it with the quantitative PAH ionized fraction. This is presented in **Figure 6** for all 10 reflection nebula fields.

Having a quantitative measure for the PAH ionized fraction provides a direct link to physical parameters describing the local astrophysical environment through the PAH ionization parameter. The PAH ionization parameter relates the PAH ionization fraction to the strength of the radiation field, the electron density and the gas temperature.

The database fitting approach also allows for the determination of principal PAH emission components in terms of PAH subclasses. Considering such principal components determined for charge on the reflection nebula NGC 7023, the cover image also includes a “Principal Component” representation of the PAH ionized fraction in NGC 2023. Again, the morphological similarity is good, indicating that the principle component spectral analysis approach is a promising new diagnostic tool that is readily adaptable to different astronomical objects and environments.

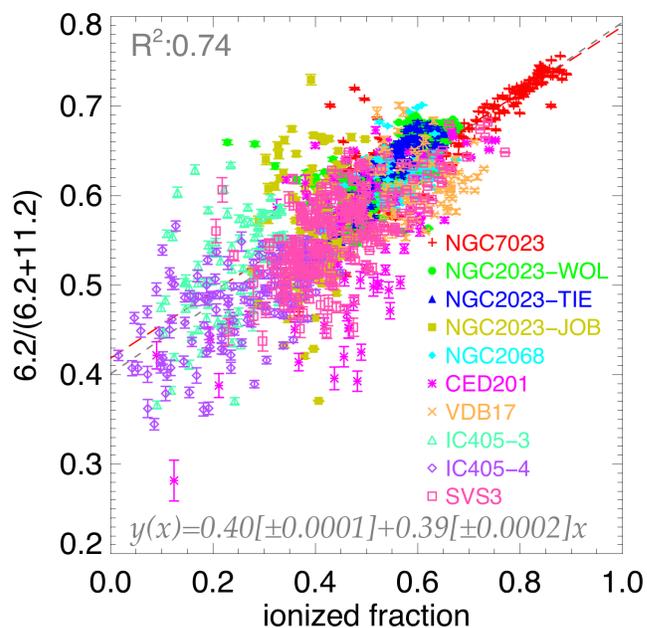


Figure 6 - The 6.2/11.2 μm PAH band strength ratio, in terms of an ionized fraction, as a qualitative charge proxy calibrated against the database fitting determined quantitative ionized fraction. Indicated are the linear squared linear correlation coefficient (R^2), the best straight line fit equation (short-dashed line) and the best straight line fit through the data on NGC 7023 alone (long-dashed line). Figure adapted from Boersma et al. 2016.

Scheduled for launch later this decade, JWST will again revolutionize the PAH field and it is my hope that the tools developed here, and those currently under development, make mining the treasures in the PAH spectrum accessible to PAH- and non-PAH experts alike.

Acknowledgments

Dr. Louis J. Allamandola / NASA Ames Research Center
Dr. Jesse D. Bregman / NASA Ames Research Center



Christiaan Boersma is a research associate and astronomer at NASA Ames Research Center. His research focuses on the role of PAHs in a multitude of astronomical environments. The NASA Ames PAH IR Spectroscopic Database (PAHdb) plays an important part in that research. Email: Christiaan.Boersma@nasa.gov

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(For more information or additional references, please contact the author)

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Abstracts

Mapping PAH sizes in NGC 7023 with SOFIA

B.A. Croiset¹, A. Candian¹, O. Berné^{2,3}, and A. G. G. M. Tielens¹

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

² Université de Toulouse, UPS-OMP, IRAP, Toulouse, France

³ CNRS, IRAP, 9 Av. colonel Roche, BP 44346, 31028 Toulouse Cedex

NGC 7023 is a well-studied reflection nebula, which shows strong emission from polycyclic aromatic hydrocarbon (PAH) molecules in the form of aromatic infrared bands (AIBs). The spectral variations of the AIBs in this region are connected to the chemical evolution of the PAH molecules which, in turn, depends on the local physical conditions. We use the capabilities of SOFIA to observe a 3.2' x 3.4' region of NGC 7023 at wavelengths that we observe with high spatial resolution (2.7'') at 3.3 and 11.2 μm . We compare the SOFIA images with existing images of the PAH emission at 8.0 μm (Spitzer), emission from evaporating very small grains (eVSG) extracted from Spitzer-IRS spectral cubes, the ERE (HST and CFHT), and H₂ (2.12 μm). We create maps of the 11.2/3.3 μm ratio to probe the morphology of the PAH size distribution and the 8.0/11.2 μm ratio to probe the PAH ionization. We make use of an emission model and of vibrational spectra from the NASA Ames PAHdb to translate the 11.2/3.3 μm ratio to PAH sizes. The 11.2/3.3 μm map shows the smallest PAH concentrate on the PDR surface (H₂ and extended red emission) in the NW and South PDR. We estimated that PAHs in the NW PDR bear, on average, a number of carbon atoms (N_C) of ~ 70 in the PDR cavity and ~ 50 at the PDR surface. In the entire nebula, the results reveal a factor of 2 variation in the size of the PAH. We relate these size variations to several models for the evolution of the PAH families when they traverse from the molecular cloud to the PDR. The PAH size map enables us to follow the photochemical evolution of PAHs in NGC 7023. Small PAHs result from the photo-evaporation of VSGs as they reach the PDR surface. Inside the PDR cavity, the PAH abundance drops as the smallest PAH are broken down. The average PAH size increases in the cavity where only the largest species survive or are converted into C₆₀ by photochemical processing.

E-mail: croiset@strw.leidenuniv.nl

Accepted for publication in A&A

<http://arxiv.org/abs/1603.02577>

Dust and Polycyclic Aromatic Hydrocarbon in the Pre-Transitional Disk around HD 169142

Ji Yeon Seok and Aigen Li

Department of Physics and Astronomy, University of Missouri, Columbia, MO 65211, USA

The pre-transitional disk around the Herbig Ae star HD 169142 shows a complex structure of possible ongoing planet formation in dust thermal emission from the near infrared (IR) to millimeter wavelength range. Also, a distinct set of broad emission features at 3.3, 6.2, 7.7, 8.6, 11.3, and 12.7 μm , commonly attributed to polycyclic aromatic hydrocarbons (PAHs), are detected prominently in the HD 169142 disk. We model the spectral energy distribution (SED) as well as the PAH emission features of the HD 169142 disk simultaneously with porous dust and astronomical PAHs taking into account the spatially resolved disk structure. Our porous dust model consisting of three distinct components that are primarily concentrated in the inner ring, middle ring, and outer disk, respectively, provides an excellent fit to the entire SED, and the PAH model closely reproduces the observed PAH features. The accretion of ice mantles onto porous dust aggregates occurs between ~ 16 AU and 60 AU, which overlaps with the spatial extent (~ 50 AU) of the observed PAH emission features. Finally, we discuss the role of PAHs in the formation of planets possibly taking place in the HD 169142 system.

E-mail: seokji@missouri.edu, lia@missouri.edu

Accepted for publication in ApJ

<http://arxiv.org/abs/1512.04992>

Polycyclic Aromatic Hydrocarbon emission in *Spitzer*/IRS maps I: Catalog and simple diagnostics

D. J. Stock¹, W. D.-Y. Choi¹, L. G. V. Moya¹, J. N. Otaguro¹, S. Sorkhou¹, L. J. Allamandola², A. G. G. M. Tielens³, E. Peeters^{1,4}

¹ Department of Physics and Astronomy, University of Western Ontario, London, ON, N6A 3K7, Canada

² NASA Ames Research Center, MS 245-6, Moffett Field, CA 94035-0001, USA

³ Leiden Observatory, Leiden University, PO Box 9513, 2300 RA, The Netherlands

⁴ SETI Institute, 189 Bernardo Avenue, Suite 100, Mountain View, CA 94043, USA

We present a sample of resolved galactic H II regions and photodissociation regions (PDRs) observed with the *Spitzer* infrared spectrograph (IRS) in spectral mapping mode between the wavelengths of 5–15 μm . For each object we have spectral maps at a spatial resolution of $\sim 4''$ in which we have measured all of the mid-infrared emission and absorption features. These include the PAH emission bands, primarily at 6.2, 7.7, 8.6, 11.2 and 12.7 μm , as well as the spectral emission lines of neon and sulfur and the absorption band caused by silicate dust at around 9.8 μm . In this work we describe the data in detail, including the data reduction and measurement strategies, and subsequently present the PAH emission band intensity correlations for each of the objects and the sample as a whole. We find that there are distinct differences between the sources in the sample, with two main groups, the first comprising the

H II regions and the second the reflection nebulae (RNe). Three sources, the reflection nebula NGC 7023, the Horsehead nebula PDR (an interface between the H II region IC 434 and the Orion B molecular cloud) and M 17, resist this categorization, with the Horsehead PDR points mimicking the RNe and the NGC 7023 fluxes displaying unique bifurcated appearance in our correlation plots. These discrepancies seem to be due to the very low radiation field experienced by the Horsehead PDR and the very clean separation between the PDR environment and a diffuse environment in the NGC 7023 observations.

E-mail: dstock84@gmail.com

ApJ, 819, 65 (2016)

<http://adsabs.harvard.edu/abs/2016ApJ...819...65S>

Meetings

THIRD ANNOUNCEMENT CPLT 2016: Chemistry and Physics at Low Temperature *REGISTRATION AND CALL FOR POSTERS*

**Biarritz, France
3 - 8 July 2016**

Dear Colleagues,

This is the third announcement of the international conference on Chemistry and Physics at Low Temperature, to be held in the beautiful city of Biarritz, France, from the 3rd to the 8th of July 2016.

CPLT2016 will address new developments and current state-of-the-art in the following areas: structure, dynamics and reactivity in cryogenic solids and aggregates, including systems of biological, interstellar or atmospheric interest. There will be seven sessions:

- cryogenic matrices and quantum hosts,
- reaction intermediates and unstable species,
- spectroscopy and dynamics at low temperature,
- astrophysics, astrochemistry and atmospheric science,
- biological systems,
- cryocrystals and clathrates,
- new techniques and applications.

The meeting consists of invited lectures, invited and contributed talks, posters and many opportunities for discussions. It covers issues at the interface of physics and chemistry at very low temperature and brings together colleagues from all over the world. The meeting runs from Sunday, 3rd July afternoon until Friday 8th July after lunch. The speakers are senior and young promising researchers in many areas of modern low temperature chemical physics who will give an overview of some of the most exciting areas of research and help define the future of our field. A list of confirmed speakers and the preliminary program are available on the conference

website. There will be a best poster prize and reduced fees for students and post-docs.

Registration is open until May 15, 2016.

The deadline for poster presentations is May 3rd, 2016.

There is limited space, so apply soon!

More information on the conference (registration, poster submission, program, list of speakers, accommodation, city of Biarritz) can be found at: www.cplt16.com. Note that the conference fees cover full board accommodation and registration fees.

Additional information can be obtained via email to: info@cplt16.com.

We are looking forward to an exciting meeting and hope to welcome you in Biarritz in July!

The local organizing committee:

Joëlle Mascetti (University of Bordeaux, chair)

Claudine Crépin-Gilbert (University of Paris-Sud, co-chair)

Stéphane Coussan (Aix-Marseille University, co-chair)

AstroPAH Newsletter

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

Next issue: 17 May 2016
Submission deadline: 6 May 2016