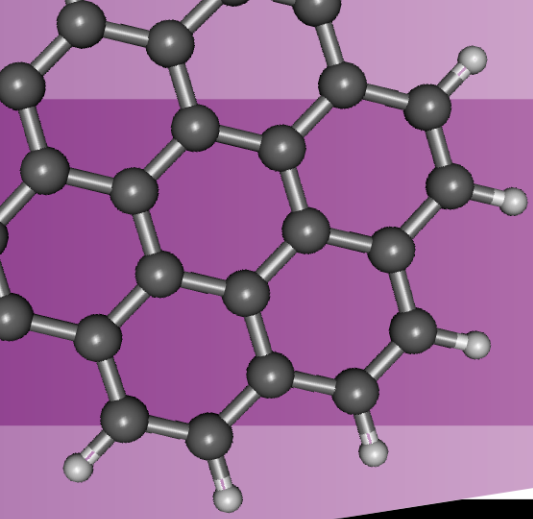
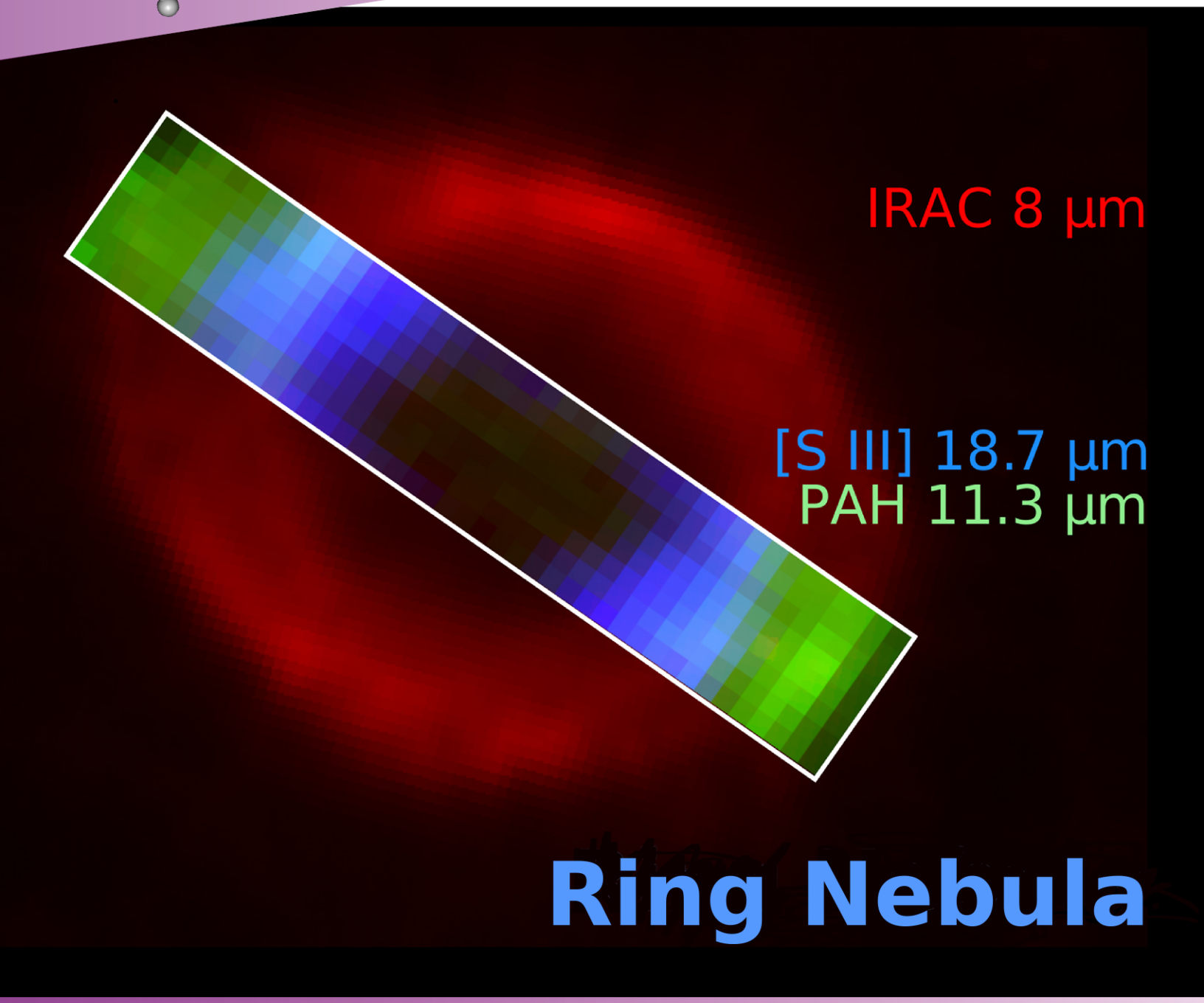


AstroPAH

A Newsletter on Astronomical PAHs

Issue 26 | March 2016



Ring Nebula

Editorial

Dear Colleagues,

Welcome to the March issue of AstroPAH.

We would like to start by congratulating our fellow editor Alessandra Candian with her newborn daughter. Complimenti e benvenuta!

This month we view PAHs from a different perspective; Health Effects and Safety Issues. John Fetzer, expert in the analysis of PAHs and petroleum-related materials, tells us about their toxicology, handling and storage.

In the abstract section you can find paper abstracts on hydrogenation of PAHs, hydrogenated fullerenes, a possible link between the diffuse interstellar bands and the anomalous microwave emission, and an observational study of a mystery object.

We thank you all for your contributions and please keep them coming. You can send us your contributions anytime. For publication in April, 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: 19 April 2016.
Submission deadline: 8 April 2016.

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

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PAH Picture of the Month

The Ring nebula is a well known planetary nebula where PAH emission has recently been detected with Spitzer-IRS (Cox et al. 2016). In this image the Spitzer IRAC 8 μm image (red) is overlaid by the Spitzer IRS maps of the PAH 11.3 μm emission feature (green) and the [S III] emission line at 18.7 μm (blue). The image shows the stratification of the ionized gas, dust, and PAH emission.

Credits: P. Pilleri & N. Cox (IRAP/CNRS). Figure adapted from Figure 1 of Cox et al. 2016, MNRAS: Letters, 456, L89, "Polycyclic aromatic hydrocarbons and molecular hydrogen in oxygen-rich planetary nebulae: the case of NGC 6720".

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Newsletter Design: Isabel Aleman
Background image: NASA, ESA, and the Hubble Heritage Team (STScI/AURA)

The Polycyclic Aromatic Compounds: Health Effects and Safety Issues

by John Fetzer

Within this short overview, the terms polycyclic aromatic hydrocarbons (PAHs) and polycyclic aromatic compounds (PACs) will be used. The former refers to the fused, multi-cyclic hydrocarbons without substituents or any heteroatoms within the ring structure. The latter is a more inclusive class of both the PAHs and those structures with substituents or heteroatoms within the ring structure.

The Toxicology of PACs

Over 200 years ago, it was observed that chimney sweeps in London had an extremely high rate of scrotal and other skin cancers. Over 100 years later, when chimney soot could be extracted and analyzed, many PAHs were found. So it was suspected that PAHs might cause the cancers that chimney sweeps had. Ninety years ago, coal tar was found to produce skin cancers in laboratory animals.

Anything that causes cancer of any type is called a carcinogen. Anything that damages or causes mutations in DNA or RNA is called a mutagen. Anything that causes tumors is called a teratogen. ***PACs can be all 3.***

Various components in coal tar were isolated, identified, and tested on animals. Increased incidences of skin, lung, bladder, liver, and stomach cancers, as well as injection-site sarcomas were reported in animals. These studies also showed that certain PAHs can affect the hematopoietic and immune systems and can produce reproductive, neurologic, and develop-

mental effects[1−10]. One particular PAH, benzo[a]pyrene, was shown to induce a variety of cancers. The PAHs were found to vary widely in activity, from inactive to as highly active as benzo[a]pyrene. Activity was found to be very specific, based more on the shape than on the number of rings or on the formula. For a set of isomers, ones were found to be highly active, others were found to be varying degrees of less so, and some were found to be totally inactive. This is due to both the shapes of the isomers and to their electron-rich or electron-poor regions, which are where conversion to other molecules by metabolism happens. As far as shape patterns, the idea of bay and fjord regions has been popular (Figure 1 shows examples of the bay and fjord shapes), but is nowhere near an absolute since it is the shape of the metabolites and where the PAH structure adds functional groups that is the real key. It is these metabolites that are the active agents that bind to DNA through hydrogen bonding and acid-base reactions. These metabolites are of a specific spatial geometry to fit into the DNA structure and bind. (Similarly, PAC degradation products can be mutagenic.)

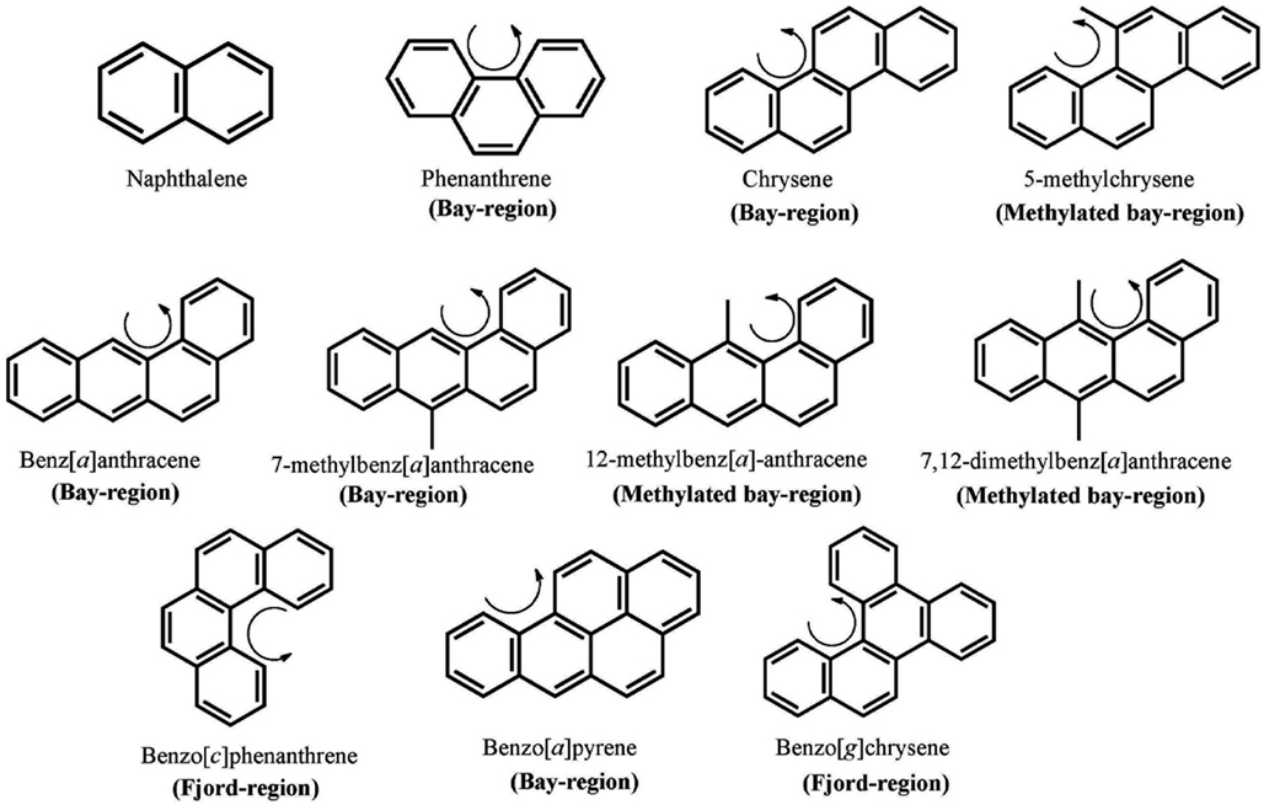

Figure 1 - *Example of PAHs with bay and fjord regions. A bay region is a 3-sided indentation and a fjord region a 4-sided one.*

Therefore, the assessments of health risks were determined to be PAH specific. That is, they were based on the presence and amounts of the total sum of various specific PAHs that have been shown to be biologically active. Analyses, thus, had to also identify the PAHs very specifically down to individual isomer levels. In any studies of PAH biological activity prior to 1985 or so, the ”pure” samples of a PAH very likely had been originally isolated from a coal tar pitch. Only a small number used a PAH sample created through organic-synthesis methods. These

isolations from coal tar used a series of various separation techniques like distillation, sublimation, fractionation by chromatography, and zone refining to get ever-increasing purities. It was very common to find trace impurities of other PAHs within these samples, for even at a purity level of 99.9 % there would be 0.1 % of other PAHs in the sample. The use of these purified fractions could lead to ambiguous or confusing results. A response might be a very weak one of the ”pure” PAH, or a strong one from the sample's very low-concentration impurities. This means assessments prior to 1980 should be considered suspect.

The International Agency for Research on Cancer (IARC) is an agency of the World Health Organization. A working group within IARC[11] reviewed all published studies of PAHs and evaluated their validity in determining carcinogenicity. Tables 1 and 2 list the PAHs and NPACs, respectively, that have been defined as ”known”, ”probable-” and ”possible human carcinogens”. **All of them should be assumed to be carcinogenic, mutagenic, and teratogenic when used in the laboratory.**

Safe Handling and Storage of PACs

A fundamental premise when using PAC materials is that they are unsafe. This builds in good habits. At a minimum, gloves should be used at all times. If handling solutions, the glove material must be impervious to the solvent used, as solvents often aggravate the toxic effects of the PAHs. Also many of the light PAHs sublime at normal conditions, so vapors are common. Preferably, sample preparation should be done in a glove box or similar safety set-up.

Solutions of PACs are often light sensitive. This leads to photodegradation and oxidation. The products of these reactions can be very mutagenic. Therefore, **PAC solutions should be kept in amber-colored containers and kept in a dark place** (a refrigerated area also slows down degradation reactions.) If possible, the air space at the top of the container should be flushed with nitrogen after each use.

Access to the PACs that are on the lists given in Tables 1 and 2 should be limited and under-control to ensure that only those well-trained in safe handling procedures are the ones using them. A locked cabinet or cupboard is preferable, with a record book or sample log listing access date and time, user, compounds used (in and out information).

John Fetzer is a recognized expert in the analysis of PAHs and petroleum-related materials. He synthesized, isolated, and discovered about fifty new PAHs. Dr. Fetzer founded Fetzpahs Consulting in 2002 after over twenty years as a research analytical chemist in the petroleum industry.
(http://home.sprintmail.com/~fetzerhaus/fetzpahsconsulting/index.html)
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Table 1: List of PAHs defined as carcinogens

Known human carcinogen	benzo[a]pyrene	$C_{20}H_{12}$	
Probable human carcinogen	cyclopenta[cd]pyrene	$C_{18}H_{10}$	
	dibenz[a,h]anthracene	$C_{22}H_{14}$	
	dibenzo[def,p]chrysene (dibenzo[a,l]pyrene)	$C_{24}H_{14}$	
Possible human carcinogen	benz[j]-aceanthrylene	$C_{20}H_{12}$	
	benz[a]anthracene	$C_{18}H_{12}$	
	benzo[b]fluoranthene	$C_{20}H_{12}$	
	benzo[j]fluoranthene	$C_{20}H_{12}$	
	benzo[k]-fluoranthene	$C_{20}H_{12}$	
	benzo[c]phenanthrene	$C_{18}H_{12}$	
	chrysene	$C_{18}H_{12}$	
	benzo[rst]pentaphene (dibenzo-[a,h]pyrene)	$C_{24}H_{14}$	
	dibenzo[b,def]chrysene (dibenzo[a,i]pyrene)	$C_{24}H_{14}$	
	indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$	
	5-methylchrysene	$C_{19}H_{14}$	

Table 2: List of NPACs defined as carcinogens

Probable or possible human carcinogen	benz[a]acridine	$C_{17}H_{11}N$	
	benz[c]acridine	$C_{17}H_{11}N$	
	dibenz[a,c]acridine	$C_{21}H_{13}N$	
	dibenz[a,h]-acridine	$C_{21}H_{13}N$	
	dibenz[a,i]acridine	$C_{21}H_{13}N$	
	dibenz[a,j]acridine	$C_{21}H_{13}N$	
	7H-dibenzo[c,g]-carbazole	$C_{20}H_{13}N$	
	10-aza-benzo[a]pyrene	$C_{20}H_{13}N$	

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Abstracts

The sequence to hydrogenate coronene cations: A journey guided by magic numbers

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The understanding of hydrogen attachment to carbonaceous surfaces is essential to a wide variety of research fields and technologies such as hydrogen storage for transportation, precise localization of hydrogen in electronic devices and the formation of cosmic H_2. For coronene cations as prototypical Polycyclic Aromatic Hydrocarbon (PAH) molecules, the existence of magic numbers upon hydrogenation was uncovered experimentally. Quantum chemistry calculations show that hydrogenation follows a site-specific sequence leading to the appearance of cations having 5, 11, or 17 hydrogen atoms attached, exactly the magic numbers found in the experiments. For these closed-shell cations, further hydrogenation requires appreciable structural changes associated with a high transition barrier. Controlling specific hydrogenation pathways would provide the possibility to tune the location of hydrogen attachment and the stability of the system. The sequence to hydrogenate PAHs, leading to PAHs with magic numbers of H atoms attached, provides clues to understand that carbon in space is mostly aromatic and partially aliphatic in PAHs. PAH hydrogenation is fundamental to assess the contribution of PAHs to the formation of cosmic H_2.

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doi:10.1038/srep19835
http://www.nature.com/articles/srep19835#close

CK Vul: a smorgasbord of hydrocarbons rules out a 1670 nova (and much else besides)

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We present observations of CK Vul obtained with the *Spitzer Space Telescope*. The infrared spectrum reveals a warm dust continuum with nebular, molecular hydrogen and HCN lines superimposed, together with the "Unidentified Infrared" (UIR) features. The nebular lines are consistent with emission by a low density gas. We conclude that the *Spitzer* data, combined with other information, are incompatible with CK Vul being a classical nova remnant in "hibernation" after the event of 1670, a "Very Late Thermal Pulse", a "Luminous Red Variable" such as V838 Mon, or a "Diffusion-induced nova". The true nature of CK Vul remains a mystery.

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MNRAS, 457, 2871, 2016

http://mnras.oxfordjournals.org/content/457/3/2871

A search for hydrogenated fullerenes in fullerene-containing planetary nebulae

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Detections of C_{60} and C_{70} fullerenes in planetary nebulae (PNe) of the Magellanic Clouds and of our own Galaxy have raised the idea that other forms of carbon such as hydrogenated fullerenes (fulleranes like $C_{60}H_{36}$ and $C_{60}H_{18}$), buckyonions, and carbon nanotubes, may be widespread in the Universe. Here we present VLT/ISAAC spectra (R$\sim$600) in the 2.9-4.1 μm spectral region for the Galactic PNe Tc 1 and M 1-20, which have been used to search for fullerene-based molecules in their fullerene-rich circumstellar environments. We report the non-detection of the most intense infrared bands of several fulleranes around $\sim$3.4-3.6 μm in both PNe. We conclude that if fulleranes are present in the fullerene-containing circum-

stellar environments of these PNe, then they seem to be by far less abundant than C_{60} and C_{70}. Our non-detections together with the (tentative) fulleranes detection in the proto-PN IRAS 01005+7910 suggest that fulleranes may be formed in the short transition phase between AGB stars and PNe but they are quickly destroyed by the UV radiation field from the central star.

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http://xxx.unizar.es/abs/1602.07481

http://www.iac.es/preprints/?c=view&pre_id=16015

The Diffuse Interstellar Bands and Anomalous Microwave Emission May Originate from the Same Carriers

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We argue that the observed spectroscopic and statistical properties of the diffuse interstellar band (DIB) carriers are those that are needed to produce the anomalous microwave emission (AME). We explore this idea using a carrier-impartial model for AME based on the observed DIB statistical properties. We show that an observed distribution of profile widths for narrow DIBs can be mapped into an AME spectrum. The mapping model is applied to width distributions observed for HD 204827 and HD 183143, selected because their spectroscopic and statistical properties bracket those for most other sight lines. The predicted AME spectra for these sight lines agree well with the range of spectral shapes, and peak frequencies, $\sim$23-31 GHZ, typically observed for AME. We use the AME spectral profiles to derive a strong constraint between the average carrier size and its rotational temperature. The constraint is applied to a variety of postulated molecular carrier classes, including polycyclic aromatic hydrocarbons, fulleranes, hydrocarbon chains, and amorphous hydrocarbon clusters. The constraint favors small, cold carriers with average sizes of $\sim$8-15 carbon atoms, and average rotational temperatures of $\sim$3-10 K, depending on carrier type. We suggest new observations, analyses, and modeling efforts to help resolve the ambiguities with regard to carrier size and class, and to further clarify the DIB-AME relationship.

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ApJ, 2015, 813, 122

http://dx.doi.org/10.1088/0004-637X/813/2/122

2016 Annual Laboratory Astrophysics Division of the AAS Meeting

San Diego, CA
June 13-16, 2016

Science Organizing Committee:
Farid Salama, Randall Smith, Steven Federman, Paul Drake, Daniel Wolf Savin, John Black, Nancy Janet Chanover, Gianfranco Vidali, Karin Öberg, Edward Brown, Jan Cami, Oswald Siegmund.

Rationale: The 2016 LAD meeting will be devoted to the interplay between laboratory astrophysics and other fields in astronomy, planetary science and related sciences. The meeting will be held jointly with the 228th Meeting of the AAS, and feature the inaugural 2015 Laboratory Astrophysics Prize talk by Lou Allamandola, a talk by the 2016 Laboratory Astrophysics Prize winner Peter Beiersdorfer, and a talk by the inaugural LAD Early Career Prize Winner François Lique. The sessions will cover the full range of LAD topics, with special focus on interplay with observatories such as ALMA, Hitomi (née Astro-H – now launched!), and NuSTAR.

The session titles and invited speakers are listed below; each session has room for contributed talks. A parallel 4-day long poster session, with all posters up the entire time, is also planned. We encourage you to submit.

Key dates:
Regular Registration: February 23 through April 14, 2016
Late Registration: April 15 through May 16, 2016
Late Abstract: April 19, 2016, 9:00 pm ET

E-mail for contact: lad.vchair@aas.org
Webpage: http://lad.aas.org/meetings/lad2016

Sessions:
Bridging Laboratory & Astrophysics: Dust & Ices with ALMA & Hitomi
Monday, 13 June 2016: 10:00 am-11:30 am
Laboratory astrophysics is the Rosetta Stone that enables astronomers to understand and interpret the cosmos. This session will focus on the interplay between astrophysics with theoretical and experimental studies into the underlying dust and ice processes, which drive our Universe, focusing on connections to ALMA or Hitomi observations.
Confirmed Speakers:

- Lou Allamandola, NASA/Ames Research Center [Inaugural Laboratory Astrophysics Prize Talk]
- Lia Corrales, MIT

Bridging Laboratory and Astrophysics: Molecules seen with ALMA I
Monday, 13 June 2016: 2:00 pm-3:30 pm
Laboratory astrophysics is the Rosetta Stone that enables astronomers to understand and interpret the cosmos. This session will focus on the interplay between astrophysics with theoretical and experimental studies into the underlying molecular processes, which drive our Universe, with special attention to connections with ALMA observations.
Confirmed Speakers:

- Viviana Guzman, Harvard
- Paola Caselli, MPE

Bridging Laboratory and Astrophysics: Molecules seen with ALMA II
Tuesday, 14 June 2016: 10:00 am-11:30 am
Laboratory astrophysics is the Rosetta Stone that enables astronomers to understand and interpret the cosmos. This session will focus on the interplay between astrophysics with theoretical and experimental studies into the underlying molecular processes, which drive our Universe, with special attention to connections with ALMA observations.
Confirmed Speakers:

- François Lique, University Le Havre [Inaugural LAD Early Career Prize Talk]
- Lucy Ziurys, University of Arizona

Bridging Laboratory and Astrophysics: Planetary Physics seen with ALMA and Hitomi
Tuesday, 14 June 2016: 2:00pm-3:30 pm
Laboratory astrophysics is the Rosetta Stone that enables astronomers to understand and interpret the cosmos. This session will focus on the interplay between astrophysics with theoretical and experimental studies into the underlying planetary science processes, which drive our Universe, with special attention to observations done with ALMA and Hitomi.
Confirmed Speakers:

- Martin Cordiner, NASA/Goddard Space Flight Center
- Geoff Blake, CalTech

Bridging Laboratory and Astrophysics: Atomic Physics seen with Hitomi
Wednesday, 15 June 2016: 10:00 am-11:30 am
Laboratory astrophysics is the Rosetta Stone that enables astronomers to understand and interpret the cosmos. This session will focus on the interplay between astrophysics with theoretical and experimental studies into the underlying atomic processes, which drive our Universe, with special attention to observations done with Hitomi.
Confirmed Speakers:

- Peter Beiersdorfer, Lawrence Livermore National Lab [2016 Laboratory Astrophysics Prize Talk]
- Renata Cumbee, University of Georgia

Bridging Laboratory and Astrophysics: Atomic, Nuclear, & Particles Physics with Hitomi and NuSTAR
Wednesday, 15 June 2016: 2:00pm-3:30 pm
Laboratory astrophysics is the Rosetta Stone that enables astronomers to understand and interpret the cosmos. This session will focus on the interplay between astrophysics with theoretical and experimental studies into the underlying nuclear processes, which drive our Universe, with special attention to observations done with Hitomi and NuSTAR.
Confirmed Speakers:

- Javier Garcia, Harvard-Smithsonian Center for Astrophysics
- Steven Boggs, UC-Berkeley

AstroPAH Newsletter

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